

# Agricultural chemicals in rural, private water wells in Illinois: recommendations for a statewide survey

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## **EXECUTIVE SUMMARY**

The Illinois State Geological Survey and the Illinois State Water Survey have developed recommendations for the design of a statewide survey to assess the level of occurrence of agricultural chemicals (pesticides and nitrates) in rural private wells. The project is a response to the mandate of the Illinois Groundwater Protection Act to evaluate the impact of pesticides on groundwater, particularly in rural areas where pesticides are used most intensively. This evaluation is part of an ongoing program of basic and applied groundwater research conducted by the Illinois Department of Energy and Natural Resources.

Within the last decade, groundwater contamination by agricultural chemicals has been documented throughout the United States (USEPA, 1987a). The widespread occurrence of pesticides and nitrates in groundwater together with the toxicity of many of these chemicals, even at low concentrations, have caused concern over the potential for adverse health effects from chronic exposure to pesticides and nitrates from groundwater sources of drinking water.

In Illinois, the concern over the potential for agricultural chemical contamination of groundwater is based on these facts:

- Agricultural chemicals are extensively used: two out of three acres of rural Illinois are treated with pesticides and each year Illinois farmers apply approximately 1 million tons of nitrogen fertilizer (IDOA, 1987) and more than 60 million pounds of pesticides (Pike, 1985).
- Groundwater is the only source of drinking water in many rural areas. In 1980, 97 percent of the rural population used groundwater for drinking water (Withers, Piskin, and Student, 1981).
- Aquifers occur at shallow depths throughout the state: approximately 40 percent of the rural land is underlain by aquifers within 50 feet of the surface.
- Pesticide contamination of groundwater has been found in other midwestern states. In Iowa, pesticides have been detected in a third of the wells sampled and in 39 percent of the total number of samples (Kelley, 1987).

Our knowledge of the extent of agricultural chemical contamination of groundwater in Illinois remains limited. Previous sampling programs by the Illinois Environmental Protection Agency (IEPA), the Illinois Department of Public Health (IDPH), and the State Geological Survey (ISGS) have analyzed for relatively few compounds and only sampled public water supply wells or wells thought to be highly vulnerable to contamination. Several statewide groundwater monitoring plans have been developed over the past 5 years (O'Hearn and Schock, 1985; Shafer et al., 1985), and components of each have been incorporated into sampling programs conducted by the IEPA. However, none of these monitoring plans was designed to assess the occurrence of agricultural chemicals in groundwater. A national pesticide survey (NPS), currently being conducted by the U.S. Environmental Protection Agency (USEPA), will also sample wells in Illinois; but data appropriate for describing conditions at the state level will not be generated.

We recommend that an initial effort to assess the extent of agricultural chemical contamination of groundwater be focused on private water wells in rural areas of the state. The experimental design proposed in this document will maximize the acquisition of data on the potential exposure of the rural population of Illinois to agricultural chemicals in drinking water. By sampling existing wells, this approach will minimize sample collection costs.

The key elements of the experimental design are

- sample population defined as drilled, rural, private water-supply wells;
- recommended analytes based on use in Illinois and potential to contaminate groundwater;
- stratified random sampling design using the potential for contamination of shallow aquifers as the stratification variable;
- sampling plan for randomly selecting wells to sample within each of the strata;
- characterization of well sites and identification of potential contamination sources;

- well-sampling schedule that addresses the potential for temporal variability in the occurrence of agricultural chemicals;
- protocols for sample collection, transport, and storage to ensure that the samples are representative;
- use of USEPA NPS analytical methods;
- quality assurance/quality control procedures to ensure collection of high quality data;
- recommendations for project organization and management;
- recommendations for data management, statistical analysis, and interpretation of survey results.

The definition of the sample population excludes large-diameter dug or bored wells, which are highly susceptible to surface or near-surface sources of contamination because of their design and generally shallow depth. Inclusion of these wells might bias the assessment of the validity of using depth-to-aquifer as a predictor of contamination potential. Thus we recommend that dug and bored wells be sampled in a special study.

The groundwater samples should be analyzed for agricultural chemicals that have a high potential to contaminate groundwater and have been extensively used in Illinois. USEPA-NPS analytical methods permit analysis of a wide variety of chemical compounds and are recommended for use in the statewide survey. Nitrate-nitrogen should also be a priority analyte.

The use of statistical sampling is recommended as the most cost-effective approach to estimate the statewide occurrence of agricultural chemicals in rural, private wells. The most appropriate statistical sampling technique for this survey is stratified random sampling, which involves the division of the population into nonoverlapping subpopulations called strata. The use of stratified random sampling is recommended because the potential for contamination of aquifers or water wells by agricultural chemicals varies across the state. The rural areas of the state were classified into one of four contamination-potential strata on the basis of depth to the uppermost aquifer.

This sampling design will allow statistically valid inferences to be made regarding the frequency of occurrence of agricultural chemicals in groundwater samples from rural, private water wells in Illinois and in each of the four strata. It will also determine the significance of the differences between the strata in the occurrence of agricultural chemicals. A minimum of 384 samples will be collected from each stratum. This sample size will allow valid inferences on the occurrence of agricultural chemicals in rural private wells to be made with a high level of confidence (95 percent) and at an acceptable level of precision ( $\pm 5$  percent). Consequently, the results of the statewide survey could be used to target educational and monitoring programs to areas where contamination is likely to occur.

After all wells have been sampled, a re-stratification of the wells based on other variables, such as well depth, depth of screened intervals, and source aquifer will allow for estimates, at a lower level of confidence, of the significance of these factors in the occurrence of agricultural chemicals in the sampled wells. Seasonal differences in the frequency of occurrence of agricultural chemicals in wells within the various strata also may be statistically verifiable.

The survey design dictates that candidate wells for sampling be identified using a two-step process. First, points would be randomly selected within areas of the state delineated on the basis of depth to the uppermost aquifer (the stratification variable) using the Geographic Information System (GIS). Then these selected sampling points would be located in the field; and the well closest to the sampling point would be sampled. Ideally, only one well would be closest to the sampling point. If two or more wells are equidistant to the sampling point, the well to be sampled should be randomly selected.

The sampling schedule addresses the potential for temporal variability in the occurrence of agricultural chemicals; the samples should be collected weekly over a 1-year period from a constant, equal number of locations in each stratum. To expedite sampling, two or three sampling teams would be formed and the wells sampled during one period would be grouped by geographic region.

A detailed plan for implementation of a statewide survey includes (1) protocols for sample collection, transport, storage, and analysis; (2) forms for recording the chain-of-custody, reporting sample analyses, interviewing well users, and describing well sites; (3) detailed quality assurance-quality control program for field and laboratory activities; and (4) recommendations for data management, statistical analysis, and data interpretation.

We recommend that the statewide survey be conducted jointly by the Illinois Department of Agriculture (IDOA), the Illinois Department of Public Health (IDPH), and the Illinois Department of Energy and Natural Resources (IDENR). The Illinois State Water Survey (ISWS) and the Illinois State Geological Survey (ISGS), divisions of IDENR, should be primarily responsible for implementation of a pilot study, modifications to the experimental design on the basis of results of the pilot study, GIS-related aspects of well selection, and maintenance of the overall database. The Surveys should also assist in analysis and interpretation of the results of the statewide study. The IDOA and IDPH should be responsible for on-the-ground identification of the well sites, well-user interviews and well-site inventories, collection and chemical analyses of water samples, quality assurance/quality control procedures, notification of well users, and report preparation.

The estimated total cost for completion of the statewide survey is \$2.3 million for a 2-year period. This estimate is based on the experimental design proposed in this study and assumes new staff and equipment would be required by each of the agencies to implement the statewide survey. The estimate also assumes that space for laboratories and offices is available and that no funds for space or basic support services are needed.

The Illinois State Geological and State Water Surveys have received funding to conduct a pilot study in cooperation with the Illinois Department of Agriculture (IDOA) to field test and evaluate the various components of the experimental design proposed in this study. The pilot study will provide a preliminary assessment of the occurrence of agricultural chemicals in rural, private wells in representative hydrogeologic settings in the state. The pilot study will include developing the analytical methods, field testing of the specific procedures for selecting and characterizing wells sites and collecting well samples, and training of IDOA and IDPH personnel. The results of the pilot study should allow for more accurate estimates of the probability of occurrence of agricultural chemicals in rural, private wells in the four contamination-potential strata proposed in this study. Using these results, it may be possible to reduce the number of samples to be collected and analyzed in the statewide survey.

The Illinois Groundwater Protection Act mandates comprehensive, long-term monitoring of groundwater. We recommend that an integral component of a monitoring program be an assessment of groundwater contamination by agricultural chemicals. Program elements would include

- continued monitoring of rural private wells by the IDPH and IDOA as warranted by the results of the statewide survey,
- monitoring of large-diameter dug and bored wells, and private wells in suburban areas,
- expansion of the current monitoring of public water-supply wells by the IEPA,
- research monitoring by the ISGS and ISWS,
- database management to assess trends and evaluate programs.



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## INTRODUCTION

Within the last decade, routine monitoring of public water supplies and an increasing number of small-scale retrospective investigations conducted throughout the United States have documented groundwater contamination by agricultural chemicals (nitrogen fertilizers and pesticides). By 1985, at least 17 different pesticides had been found in the groundwater of 23 states (Cohen, Eiden, and Lorber, 1986). In 1987, the U.S. Environmental Protection Agency (USEPA) reported that a total of 20 pesticides had been detected in the groundwater of 24 states (USEPA, 1987a). Reports from some states include instances of pesticides being detected in a few wells in a small area; whereas in other studies, hundreds of detections have been reported in many wells over large areas. Other studies have shown that increased nitrate levels in groundwater in susceptible hydrogeologic settings have paralleled increased use of nitrogen fertilizers (Hallberg, 1986).

In most cases, known pesticide contamination of groundwater because of agricultural applications at label rates has been at very low concentrations. Typically, concentrations in most samples have been too low to be considered a health concern. Concentrations have ranged from less than 1 part per billion (ppb) to greater than 10 ppb. Nevertheless, concern is widespread that chronic exposure to pesticides, even at low levels, in drinking water may cause cancer, mutagenesis, teratogenesis, or immunologic-related disorders (Evans, 1987). Health concerns over excessive nitrate levels in drinking water have focused on methemoglobinemia in infants. Other reports, which have been disputed, have correlated high levels of nitrates in groundwater to gastric cancer, nervous system impairment, and birth defects (Kovan, 1988).

To date, federal and state drinking water standards have only been established for nitrates (10 mg/L  $\text{NO}_3\text{-N}$ ) and 12 pesticides. The maximum allowable concentrations for these pesticides for which finished drinking water standards have been established range from 0.1 to 100 ug/L. Recently, the USEPA released health guidance advisories for an additional 50 pesticides. Although these standards or advisories provide some reference point against which to evaluate the results of groundwater quality monitoring, the health effects of combinations of pesticides or of pesticides and nitrates are largely unknown. The extent of human exposure to agricultural chemicals from groundwater sources of drinking water is also unknown.

In September 1987, the Illinois Groundwater Protection Act (P.A. 85-863) became law. One part of this act mandates the Illinois Department of Energy and Natural Resources (DENR) to 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."

The project discussed in this report was proposed in June 1987 in anticipation of the need to define more accurately the extent of agricultural chemical contamination of groundwater resources within rural areas of Illinois. Illinois ranks first among states in usage of nitrogen fertilizer (Detroy, Hunt, and Holub, 1988) and is second in usage of pesticides (Hallberg, 1987). Two out of three acres in rural Illinois are treated with pesticides. In 1980, 97 percent of the rural population relied upon groundwater for drinking water (Withers, Piskin, and Student, 1981).

Reports of pesticide contamination of groundwater from surrounding states, particularly Iowa and Minnesota, have provided additional impetus to state and local officials to monitor agricultural chemicals in groundwater in Illinois. The climate, soils, geology, and agricultural practices of these two states are comparable to those of Illinois. In Iowa, pesticides were detected in one third of the 356 wells sampled and in 39 percent of 548 samples (Kelley, 1987). An estimated 27 percent of the population of Iowa has been exposed to pesticides in drinking water (USEPA, 1987a). In Minnesota, 51 of 100 shallow observation wells and private water wells, and 28.5 percent of 400 public water wells sampled had detectable levels of pesticides (Klaseus, Buzicky, and Schneider, 1988).

This report presents recommendations for the design of a statewide survey that would address one aspect of the agricultural chemicals in groundwater issue--the level of occurrence of agricultural chemicals in rural private wells. In four parts, the report discusses

1. the potential for agricultural chemicals to contaminate groundwater in Illinois;
2. the previous research in Illinois, and state and federal groundwater monitoring plans;
3. a recommended experimental design for a statewide survey of agricultural chemical contamination of rural private wells;
4. recommendations for implementation of the survey and development of a comprehensive monitoring program.

## POTENTIAL FOR CONTAMINATION OF ILLINOIS GROUNDWATER BY AGRICULTURAL CHEMICALS

The potential for contaminants such as pesticides or nitrates to occur in groundwater at any particular place and time depends upon many factors: (1) contaminant mass and chemical properties (such as solubility and persistence); (2) the retardation capacity of the soils and geologic materials; (3) the timing and intensity of infiltration/recharge events; and (4) properties of the groundwater flow system. Consequently, a statewide assessment of the potential for agricultural chemicals to contaminate aquifers should be based on patterns of agricultural chemical use, soil properties, climate, and hydrogeologic conditions. An evaluation of the potential for groundwater contamination is limited by the availability of information on these factors for the state and, perhaps more significantly, by our understanding of the interactions between the various parameters known to affect pesticide movement to groundwater.

In Illinois, approximately 98 percent of corn and soybean acreage is treated with herbicides, and 44 percent of corn acreage is treated with insecticides (Pike, 1985). But distribution of cropland varies across the state: less than 20 percent of Pope and Hardin Counties is cropland, compared to nearly 95 percent of Piatt County. In addition, Illinois has approximately 430 different soil types, and their properties, which affect pesticide movement, vary considerably. Distribution of groundwater resources also varies across the state, from areas such as Mason County where an aquifer occurs within a few feet of the land surface, to counties where aquifers lie hundreds of feet below the surface and are protected by overlying materials of low permeability.

### Agricultural Chemical Usage in Illinois

Farmland comprises 28 million of the 38 million acres of land in Illinois (IDOA, 1987). In 1986, more than 22 million acres of field crops were harvested, including 10.56 million acres of corn and 9.15 million acres of soybeans. Nearly 3 million acres were planted in wheat and other small grains. Corn is produced primarily in northern and central Illinois. Most of the soybeans are grown in the central and south-central parts of the state. The major wheat-growing areas are in the southern part of the state. Soybeans and corn are the major crops to which herbicides are applied. Corn and wheat are the primary crops to which nitrogen fertilizers are applied.

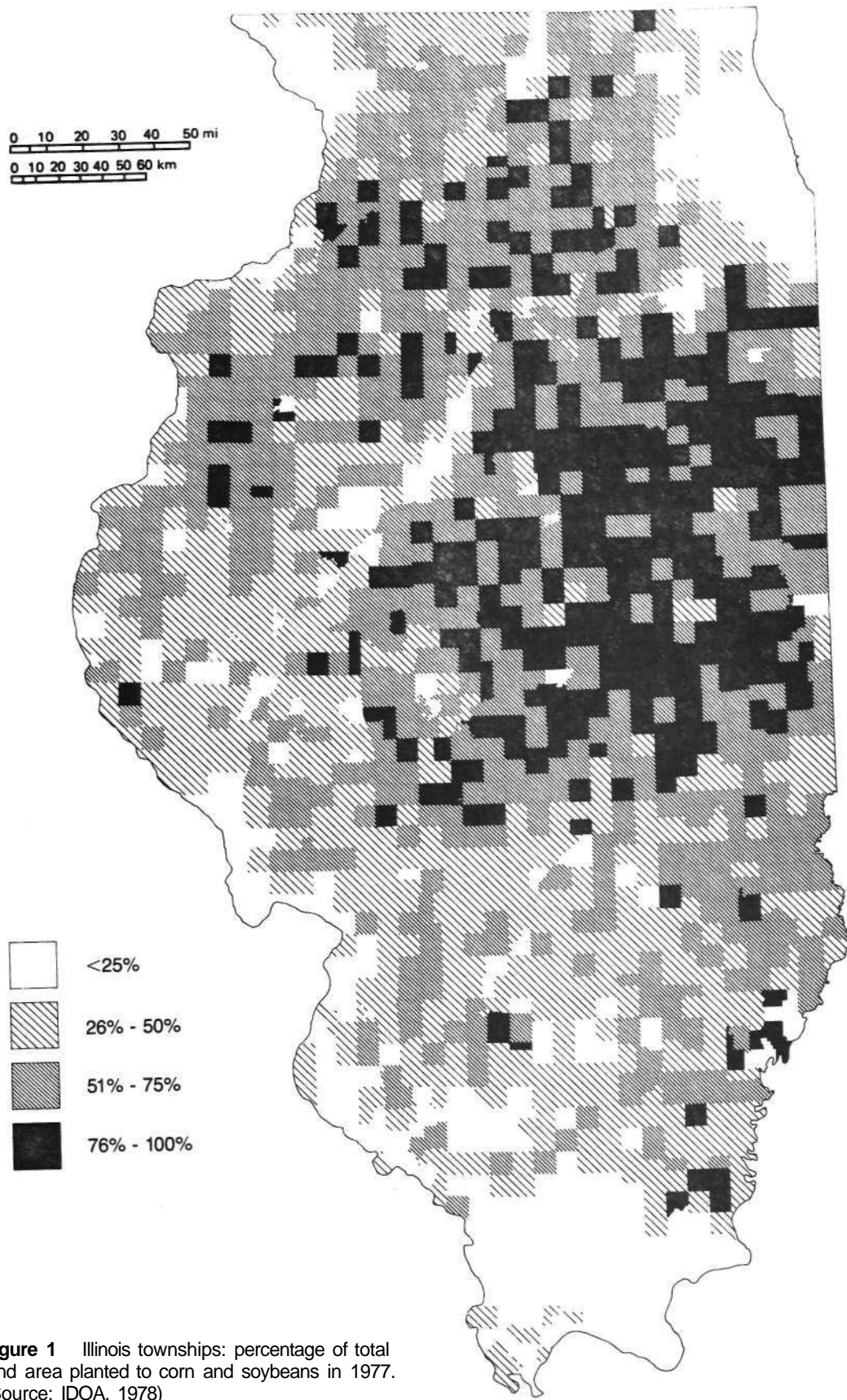
In 1985, an estimated 59.8 million pounds of herbicides and 5.39 million pounds of insecticides were applied to the 20.7 million acres of corn and soybeans in Illinois (Pike, 1985). Herbicides were applied to 99 percent of the corn and 97 percent of the soybean acreage; insecticides were applied to 44 percent of the corn and 1 percent of the soybeans. Only a small percentage of the small grain and hay or pasture acres received pesticide applications (table 1).

Application rates for herbicides are specified on the product label and vary according to the time of application, soil texture and organic matter content, and the type and severity of the weed problem. Typical application rates for the most commonly used corn and soybean herbicides

**Table 1** Pest control practices in Illinois in 1985 (Pike, 1985)

Crop	Total acres planted	Farms with crop (%)	Acres treated with herbicide (%)	Acres treated with insecticide (%)
Corn	11,700,000	96	99	44
Soybeans	9,000,000	89	97	<1
Small grains*	1,950,000	43	7	<1
Hay	1,200,000	43	3	4
Pasture	1,700,000	41	1	<1

\* Small grains include oats, wheat, rye and sorghum.



**Figure 1** Illinois townships: percentage of total land area planted to corn and soybeans in 1977. (Source: IDOA, 1978)

**Table 2** Changes since 1978 in total pounds of herbicides and insecticides (active ingredient) applied in Illinois (Good and Taylor, 1987)

	Herbicides (million lbs AI)	Decrease (%)	Insecticides (million lbs AI)	Decrease (%)
1978	78.6	---	9.3	---
1982	65.4	16.8	7.3	21.5
1985	59.8	23.9	5.8	37.6

range from 0.3 to 5.0 pounds per acre. In 1985, the average application rate for corn herbicides was 3.7 pounds per acre, and for soybeans, 1.83 pounds per acre (Pike, 1985). From 1978 to 1985, the total volume of herbicides applied (table 2) decreased by 23.9 percent. This decrease may be attributed to the decrease in corn and soybean acreage since 1978, to the development of new compounds with more concentrated formulations, and to the greater use of herbicides in combinations, which generally reduces total rates of application.

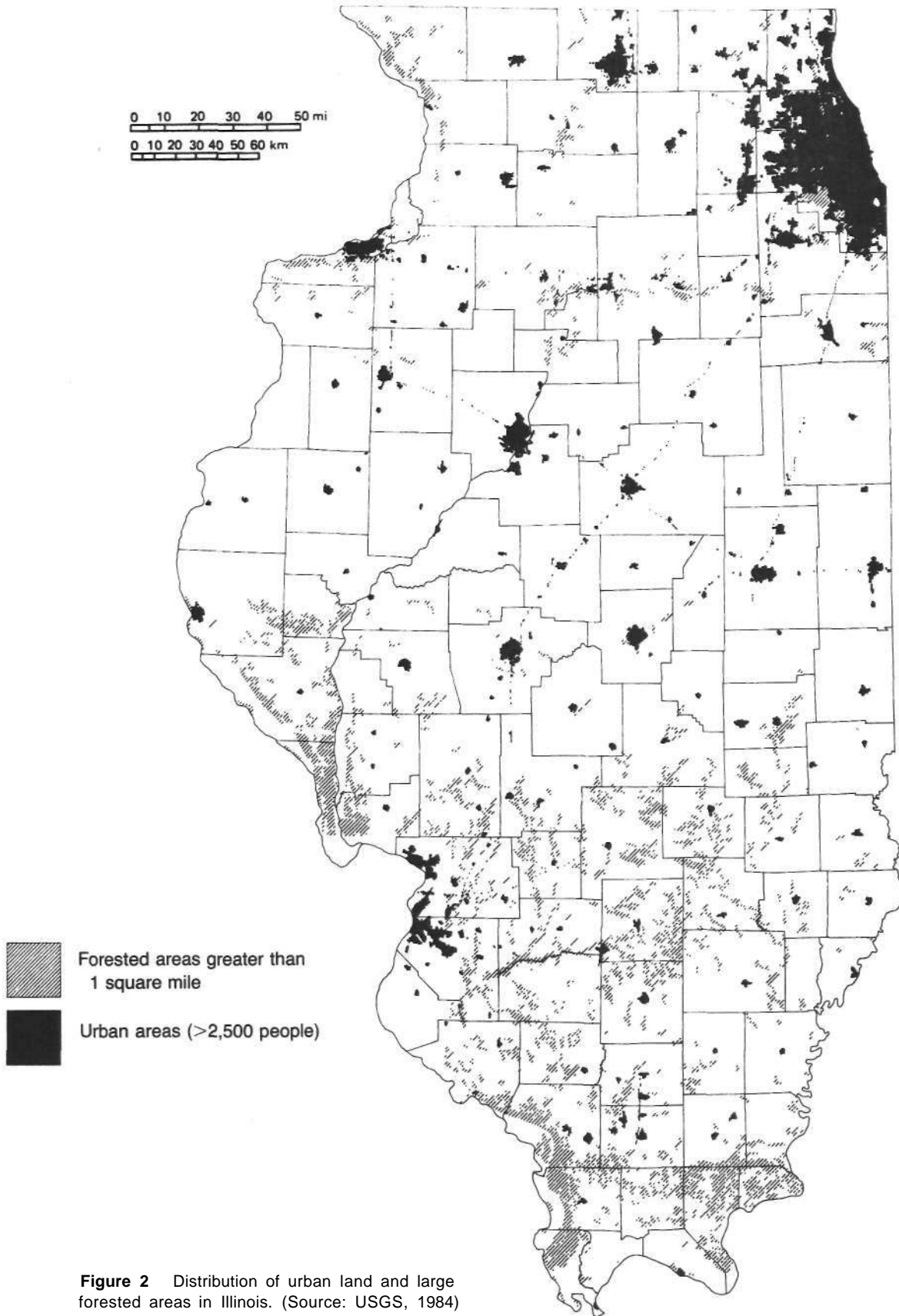
In Illinois, most insecticides are applied to corn (table 1) to control northern and western corn rootworm. In 1985, approximately 97 percent of the total acreage of corn planted after corn (34 percent of the total corn acreage) was treated with an insecticide (Pike, 1985); 13 percent of the total acreage of corn after soybeans was treated. Application rates, which are also specified on the product label, vary on the basis of the target insect and the crop grown. Application rates for corn rootworm control are typically 1.0 to 1.4 pounds of active ingredient per acre.

The total amount of insecticides applied in Illinois also decreased between 1978 and 1985 (table 2). This reflects a drop in the total acres of corn treated from 65 percent in 1978 to 44 percent in 1985 (Pike, 1985). It may also be due to more widespread use of integrated pest management (IPM) practices (Good and Taylor, 1987) and/or the use of synthetic pyrethroid compounds that are effective at rates of 0.1 to 0.2 pounds per acre (Dover, 1986).

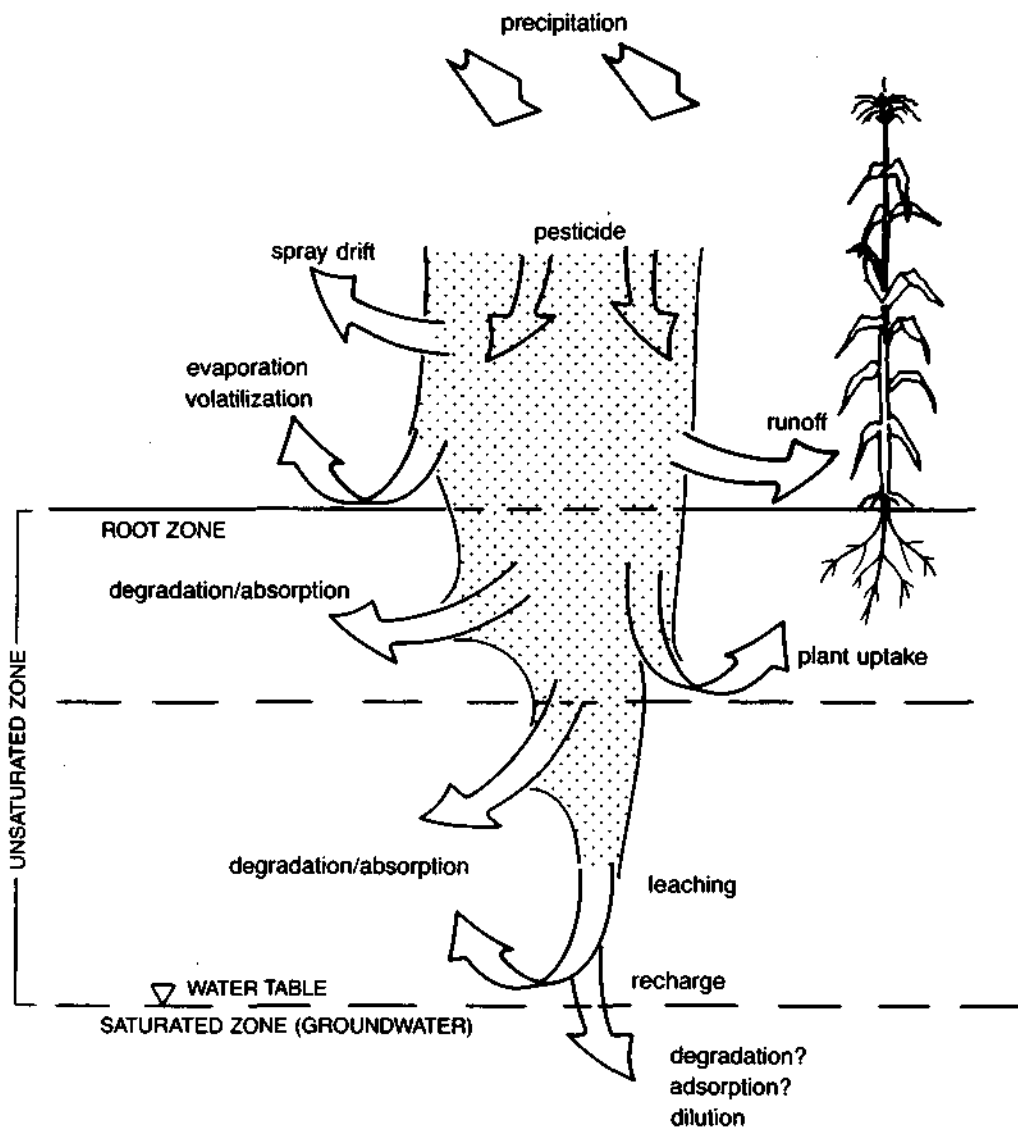
Each year, Illinois farmers apply approximately 1 million tons of nitrogen fertilizer. Almost all corn acres receive applications of nitrogen: the average application rate is 156 pounds per acre (IDOA, 1987). Nitrogen is also applied to most of the wheat in the state, but application rates are much lower (table 3). Less than 10 percent of the soybean acreage receives nitrogen, and where applied, rates are usually less than 20 pounds per acre.

Recommended nitrogen application rates for corn are based on yield goals determined primarily by the productivity of the soil and agronomic management practices. Recommended rates under a high level of management range from 80 pounds per acre for the light-colored claypan soils of southern Illinois to 205 pounds per acre for the highly productive, deep loess, prairie soils of central and northern Illinois (Cooperative Extension Service, 1987). Average nitrogen application rates have remained constant over the last 5 years (IDOA, 1987).

In more than 80 percent of the townships in Illinois, more than 50 percent of the total land area is devoted to corn and soybeans (fig. 1). On average, two of every three acres of land in rural areas of the state are treated with pesticides. This pattern of land use suggests that shallow groundwater is always in close to a potential source of contamination (corn or soybean field). All of rural Illinois could be affected by agricultural chemicals. Furthermore, regional flow of groundwater could potentially transport agricultural chemicals to adjacent noncropped areas. Consequently, only large noncropped areas, such as forested and urban land, can be considered to have a minimal potential for contamination of shallow aquifers from agricultural chemicals. Urban areas with a population greater than 2500 and forested areas larger than 1 square mile are shown in figure 2.



**Figure 2** Distribution of urban land and large forested areas in Illinois. (Source: USGS, 1984)



**Figure 3** Potential pathways of pesticide loss and transport (modified from Severn, 1987).

### Soil Properties

A pesticide applied to the soil surface is subject to several processes that affect the potential for movement to groundwater: (1) volatilization to the atmosphere, (2) chemical or microbial degradation, (3) adsorption by the soil, and (4) transport by water (fig. 3).

The rates of volatilization at the soil surface are influenced by pesticide concentration, soil-water content, and temperature but primarily controlled by the vapor pressure of the pesticide (McEwen and Stephenson, 1979). Pesticide degradation is primarily the result of biochemical processes carried out by microorganisms, although nonbiological degradation and pesticide uptake by plants and subsequent decomposition by plant enzymes also occur. The rate of microbiological breakdown depends on the chemical structure of a pesticide and many environmental factors that affect the growth of the microorganisms: pesticide concentration in the soil, moisture content, temperature and pH, the availability of nutrients, and the presence or absence of free oxygen (Ashton, 1982). Because microbiological activity is limited in subsoil environments, pesticides are usually more persistent at depth than in surface horizons.



The retention of organic pesticides by soil (adsorption) decreases the concentration of pesticides in the soil water and their availability for transport to groundwater. Adsorption is dependent on both pesticide chemistry and soil properties. Positively charged pesticides are retained on cation exchange sites associated with organic matter or various clay minerals. Most pesticides are nonpolar, however, and adsorption primarily depends on the organic carbon content of the soil.

Soil properties play a major role in controlling the rate and nature of downward movement of chemicals through the soil. The primary mode of transport is mass flow in which dissolved pesticides move with percolating water. In the unsaturated zone, mass flux of a chemical is directly related to the hydraulic conductivity of the soil and indirectly to the texture, water content, bulk density or porosity, and pore size distribution of the soil.

The soil properties that most directly affect potential leaching of reactive compounds such as pesticides are organic carbon content and hydraulic conductivity. Nitrate, a nonreactive anion, is highly water soluble and not subject to adsorption to organic matter or clays. Consequently, the rate of nitrate movement is controlled by the rate at which the soil water moves. Under certain conditions, however, nitrate may undergo denitrification and subsequent volatilization.

Although soil properties are recognized as an extremely important factor in estimating the potential for agricultural chemical contamination of groundwater, the existing information on soil properties is not in a form that can be easily used in a statewide assessment. There are two primary sources of data on Illinois soils: the General Soil Map of Illinois and accompanying text (Fehrenbacher et al., 1984) and county soil survey reports prepared by the USDA Soil Conservation Service in cooperation with the Illinois Agricultural Experiment Station.

The General Soil Map of Illinois has been published at a scale of 1:500,000. The soil associations shown on that map were delineated on the basis of similarities in parent material and surface-soil color. Within a soil association, even the major soils differ in several important properties, such as organic carbon content and permeability, that affect the potential for leaching of agricultural chemicals. Consequently, the soil association map is not suitable for evaluating leaching potential on a statewide scale.

A much higher degree of accuracy in mapping and characterization of soil properties is available in published county soil survey reports. These reports include detailed soil maps at a scale of 1:15,840 and data on the bulk density, clay content, organic matter content, and permeability for the various horizons of each of the soils mapped. Unfortunately, these maps have not been digitized for computer-aided mapping. Maps of the entire state will probably not be completed until the mid-1990s. With digitization of the soil survey maps and anticipated improvement in models to predict leaching of pesticides, it may be possible in the future to develop computer-generated maps indicating leaching potential at the state, county, and farm level.

### **Environmental and Agronomic Management Factors**

The amount of water available to move dissolved chemicals through the unsaturated zone to the water table (recharge) depends on a large number of factors, including agronomic management practices and climate. Management factors affecting the potential for groundwater contamination by pesticides include pesticide selection, application rates and timing, incorporation methods, tillage practices, and crop rotations. In addition, water management practices, including irrigation, drainage, and conservation measures, influence water infiltration and runoff and consequently the movement of pesticides.

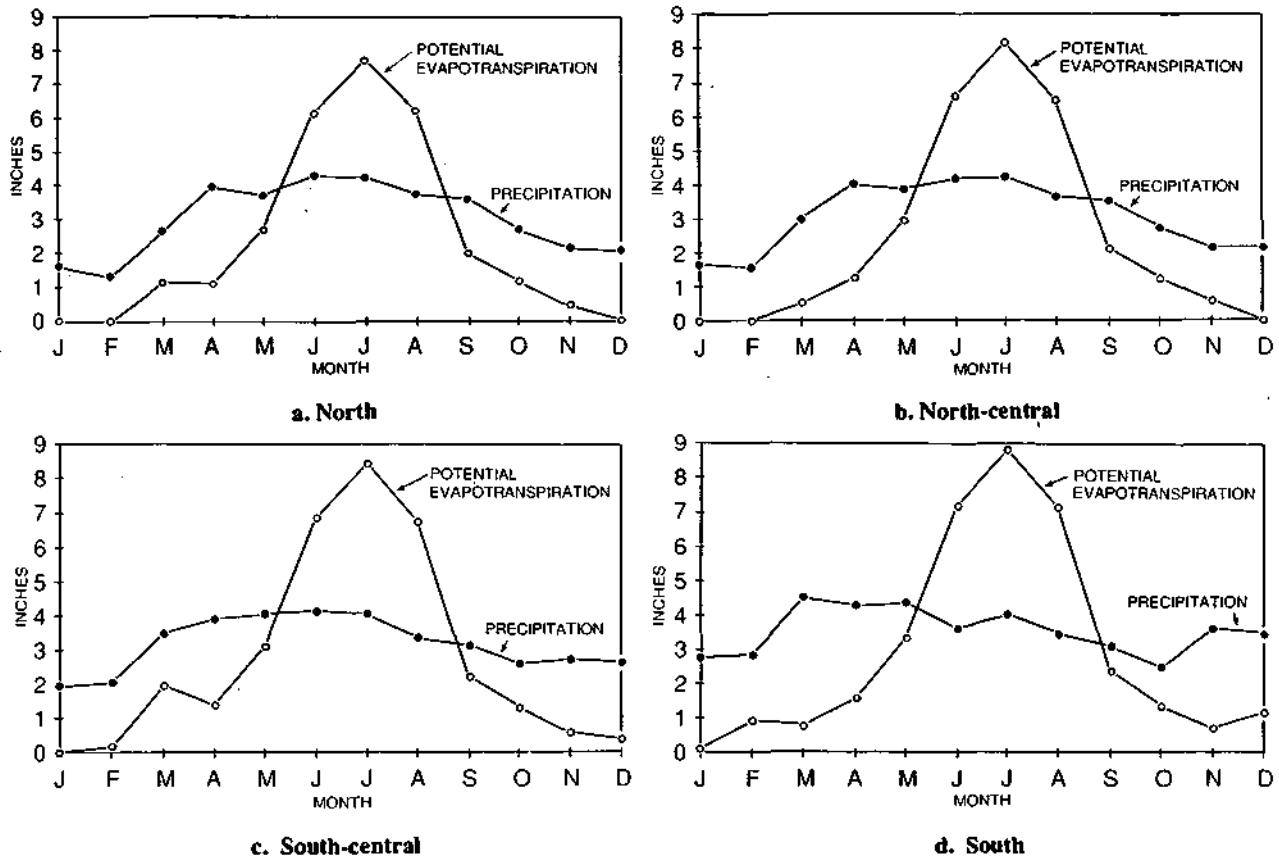
The intensity and distribution of rainfall and the extent of evapotranspiration determine the amount of water leaching through the crop root zone and the mass flux of dissolved chemicals. Average total precipitation varies across the state from 32 inches in the north to 46 inches in the south. However, higher temperatures in the south create higher potential evapotranspiration rates and higher potential water deficits during the growing season (fig. 4).

### Hydrogeologic Conditions

Considering the hydrogeologic conditions that affect the potential for groundwater contamination requires a clear understanding of the terms used. In the Illinois Groundwater Protection Act (IGPA), groundwater is defined as "underground water that occurs within the saturated zone and geologic materials where the fluid pressure in the pore space is equal to or greater than atmospheric pressure" (IGPA, 1987). Aquifer refers to "water-saturated soils and geologic materials that are sufficiently permeable to readily yield economically useful quantities of water to wells, springs, or streams under ordinary hydraulic gradients" (IGPA, 1987). Above the water table (top of the zone of saturation), pore spaces in the earth materials contain both water and air. The water flowing from agricultural drainage tile is groundwater. Making the distinction between an aquifer and groundwater is important when establishing compliance points for regulatory monitoring.

With current agricultural practices and technology, the leaching of agricultural chemicals, particularly fertilizer nitrogen, into groundwater (the saturated zone) may be impossible to prevent because more than a third of the soils in the state have seasonally high water tables within 5 feet of the surface (Drablos and Moe, 1984). Through most of Illinois, groundwater may occur within 5 to 20 feet of land surface; however, aquifers are deeply buried in many areas: agricultural chemicals may be found in groundwater, but the aquifer would probably be unaffected.

Once contaminants such as pesticides or nitrates reach the water table, their rate of movement to an aquifer depends upon the hydraulic gradient and conductivity, effective porosity, and attenuating capacity of the materials overlying the aquifer. In general, the rate of movement of a



**Figure 4** Annual precipitation and potential evapotranspiration distribution for four east-west bands across Illinois (Bowman and Collins, 1987).

**Table 3** Summary of collective pesticide monitoring data in Iowa by hydrogeologic setting (modified from Kelley et al., 1987)

Total wells	Wells with detections (%)	Total samples	Samples with detections (%)
<i>Alluvial aquifers (sand and gravel near the surface)</i>			
148	39	181	42
<i>Pleistocene aquifers (buried sand and gravel)</i>			
90	14	92	16
<i>Shallow bedrock (&lt;50 ft) and karst</i>			
71	62	211	54
<i>Deep bedrock (&gt;50 ft)</i>			
47	4	64	9

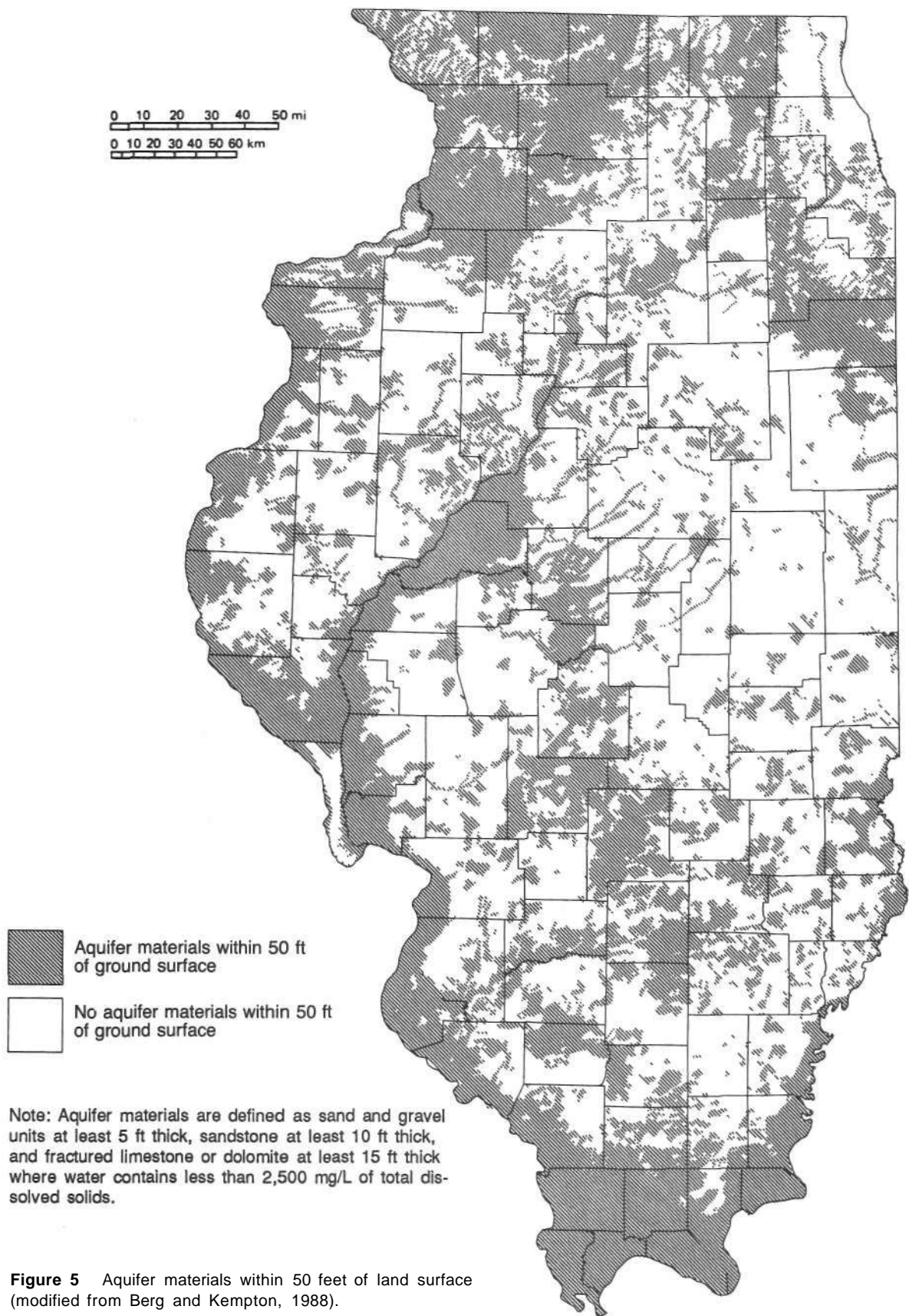
contaminant is controlled by the linear velocity of the groundwater. However, mechanical dispersion causes some contaminant molecules to move faster and others to move slower than the average linear velocity of the groundwater. These processes also cause the contaminant plume to spread in directions transverse to the groundwater flow path (Freeze and Cherry, 1979).

Reactive contaminants, such as dissolved pesticides, are potentially subject to adsorption by the aquifer matrix and chemical and microbial degradation. As a result, the movement of the contaminant is slowed and its concentration in solution is reduced. If the adsorption reaction between the contaminant and aquifer material is reversible, the adsorbed compound may desorb and re-enter the liquid phase (groundwater). A net transfer of contaminant via desorption into the liquid phase is possible if the concentration of the contaminant in solution decreases due to dispersion, dilution, and/or the cessation of contaminant input.

Distance to an aquifer is extremely important for predicting aquifer contamination from surface-applied agricultural chemicals. The time it takes a contaminant to reach an aquifer is affected not only by rate of movement, but also by distance to the aquifer. (Travel time equals distance divided by rate of movement.) Since most organic pesticides were developed after World War II and not used extensively until the 1960s, there probably has not been sufficient time for these compounds to reach deep aquifers.

Since 1980, state and federal agencies in Iowa have documented the extent of groundwater contamination by agricultural chemicals in that state (Hallberg and Hoyer, 1982; Hallberg et al., 1983, 1984; Hallberg, 1986; Libra et al., 1984; Kelley et al., 1986; Detroy, 1986; Thompson, Libra, and Hallberg, 1986). These studies have contributed to understanding the mechanisms by which agricultural chemicals are transported to groundwater and identified hydrogeologic settings susceptible to contamination (Hallberg, 1987). The studies summarized by Kelley et al. (1986), indicated significant differences in the occurrence of pesticides in different hydrogeologic settings (table 3). A much higher percentage of wells withdrawing water from aquifers within 50 feet of the surface had detectable levels of pesticides than wells finished in deeper aquifers. Similar results have been reported in Minnesota (Klaseus, Buzicky, and Schneider, 1988) where pesticides were most commonly found in karst areas and in shallow sand and gravel aquifers. Hallberg (1987) reported similar results for nitrate in groundwater, and on the basis of limited sampling, noted significant concentrations of nitrates in wells 150 to 200 feet deep in shallow bedrock areas.

Our present understanding of pesticide persistence and movement, coupled with the results of the Iowa studies, suggests that an intensively cultivated area with an aquifer within 50 feet of land surface is most susceptible to contamination. Shallow aquifers occur throughout Illinois but are most prevalent in the northern and southern parts of the state and adjacent to the major stream valleys (fig. 5).



**Figure 5** Aquifer materials within 50 feet of land surface (modified from Berg and Kempton, 1988).

## **GROUNDWATER MONITORING**

### **Previous Studies to Monitor for Agricultural Chemicals in Groundwater**

To date, Illinois has had no coordinated monitoring program to determine the presence of agricultural chemicals in groundwater. The limited sampling programs that have been conducted in the last 5 years have varied in scale and purpose, number of analytes and levels of detection, and degree of hydrogeologic characterization of the area(s) from which samples were collected. As a result, although probably more than 1000 analyses have been performed to determine the presence of pesticides, knowledge of the extent of agricultural chemical contamination of groundwater in Illinois is still very limited.

The first attempt to address the issue of groundwater contamination by pesticides was conducted jointly by the Illinois Department of Agriculture (IDOA), the Illinois Department of Public Health (IDPH), and the Illinois Natural History Survey (INHS). In this study (Felsot and Mack, 1984), 25 private wells were sampled in five "susceptible" regions across the state. Samples were collected in June 1983 and analyzed for a wide variety of pesticides. Characteristics of susceptible areas were well-drained or sandy soils with low organic matter content and shallow, unconfined aquifers. None of the samples contained pesticides above the 1.0 ug/L detection limit.

The Illinois Environmental Protection Agency (IEPA) conducts compliance monitoring for those compounds and elements specified under state and federal drinking water regulations. Until 1986, the compliance monitoring was primarily concerned with inorganic chemicals, those covered in the Safe Drinking Water Act. In the IEPA program, most public water supply systems are sampled every 3 to 5 years. If the water supplies are not in compliance with the regulations, local officials are notified of the problem and further testing is conducted. If repeated sampling indicates that a problem exists, corrective actions are initiated.

In 1984, the IEPA initiated a pilot program to monitor community water supply wells for pesticides. During 1985, samples were collected from 92 public water supply wells consisting of 68 wells withdrawing water from sand and gravel aquifers, 15 wells finished in Silurian dolomite, and 9 wells in the Ironton-Galesville sandstone. No pesticides were detected in this sampling program (Clark and Sinnott, 1988).

During fall 1985 and spring 1986, the IEPA collected samples from an additional 195 public water supply wells finished in sand and gravel aquifers. Most of these wells were a purposefully selected subset of a groundwater monitoring network proposed by O'Hearn and Schock (1985) to assess regional ambient (background) groundwater quality in the state's principal aquifers. (A principal aquifer is identified by O'Hearn and Schock [1985] as one with a potential yield of at least 100,000 gallons per day per square mile and an area of at least 50 square miles.) In addition, 78 wells located outside the "principal aquifer boundaries" were sampled. Analyses for 34 pesticides (chlorinated hydrocarbon and organophosphate insecticides and six currently used herbicides) found none above detection limits (Clark and Sinnott, 1988).

With these results, the IEPA shifted its monitoring program to a site-specific approach that selects wells for sampling on the basis of hydrogeologic factors and the proximity of potential point sources, such as agricultural chemical distributors. To date, this approach has identified three public water supply wells with trace levels of currently used herbicides (Clark and Sinnott, 1988). These detections have been attributed by IEPA to point sources located within 50 to 700 feet of the wellhead.

The IDPH is currently conducting a sampling program to determine the extent of contamination of wells serving agrichemical mixing and loading facilities (Long, 1988). Wells were randomly selected for sampling from a list of more than 1500 facilities licensed by the IDOA. To date, 77 percent of the 50 well samples analyzed have had detectable levels of at least one pesticide. The most frequently detected compounds were the commonly used corn and soybean herbicides.

Although most compounds were detected at low parts per billion (ppb) levels, concentrations greater than 1000 ppb were found in some wells. More than 60 percent of the wells tested exceeded the drinking water standard of 10 parts per million (ppm) nitrate-nitrogen (NO<sub>3</sub>-N). Nitrate concentrations ranged from 1.2 to 1288 ppm. The median concentration was 25.0 ppm.

Long (1988) also reported on two joint IDPH/IEPA investigations of water quality in private or noncommunity wells close to agrichemical facilities. The neighboring wells generally had pesticide concentrations ranging from less than 0.1 ppb to 5 ppb; however, in several samples, pesticides were detected at concentrations greater than 50 ppb. The IDPH plans to continue this survey of agrichemical facilities and will expand the program to include repeat sampling of wells, characterization of well construction and site conditions, and testing of nearby private wells (Long, 1988).

For many years, the IDPH and county health departments have conducted routine analyses of well water samples for nitrates, bacterial contamination, and various inorganic parameters. In most cases these analyses have been conducted at the request of the well owner who suspected contamination or was concerned about exposing an infant to nitrates. As a consequence of this biased approach to selecting wells for sampling and the frequent lack of adequate locational information, data from this testing program cannot be used to assess, in a statistically valid manner, the extent of nitrate contamination of water supply wells.

The Illinois State Geological Survey (ISGS) has recently completed a study to determine spatial and temporal variability in the occurrence of agricultural chemicals in groundwater in a part of Mason County (McKenna et al., 1988). Preliminary results indicate that the upper part of the aquifer has been significantly contaminated by nitrogen fertilizers. Nitrate-nitrogen levels in the groundwater samples exceeded the drinking water standard (10 mg/L) in 58 percent of the samples from monitoring wells (10 to 30 feet deep) and 49 percent of the samples from private wells (25 to 40 feet deep).

Trace levels of pesticides are reaching shallow groundwater; however, pesticide concentrations exceeded the drinking water standards in only a few samples. Analyses of 15 samples from irrigation wells, 75 to 120 feet deep, indicate that the lower part of the aquifer is still relatively unaffected by pesticides and nitrates. Although the overall frequency of detection of agricultural chemicals in the shallow monitoring and private wells was high, there was extreme variability over time in the occurrence of agricultural chemicals in any particular well.

In 1987, limited sampling of rural private wells in two counties of southern Illinois was initiated by local water-quality committees cooperating with the University of Illinois Cooperative Extension Service, the Illinois Department of Public Health, and the Illinois Department of Agriculture. In Washington County, five of seven "shallow" wells sampled and four of 13 "deep" wells had trace levels of pesticides. Atrazine, a corn herbicide, and DDE, a degradation product of the banned insecticide DDT, were most frequently detected (Kolweier et al, 1988). In Crawford County, ten samples were collected; six were from dug or bored wells. Atrazine was detected in two samples at concentrations of 3.8 and 5.7 ppb (University of Illinois et al., 1988). Clark and De Kalb Counties have started sampling programs and several other counties have expressed interest in conducting similar water-quality surveys (Bicki, personal communication, 1988).

In addition to these studies that assess the areal extent of agricultural chemical contamination of groundwater, several ongoing studies within the state are focused on topics related to pesticides and groundwater. Bicki and Felsot (1988) are investigating the effects of tillage practices and irrigation scheduling on pesticide and nitrate leaching on a sandy soil in Mason County. Bicki, Keefer, and McKenna (1987) are investigating the effects of tile drainage systems on movement of pesticides to shallow groundwater. Bicki, McKenna, and Berg (1987) are attempting to develop a methodology to assess the potential for groundwater contamination from agricultural chemicals for individual farms. McKenna, Chou, and Miller (1986) are studying the persistence and mobility of selected pesticides in loessial soils of Illinois.

### **Groundwater Monitoring Plans**

Several statewide groundwater monitoring plans have been developed over the past 5 years, and parts of each have been incorporated into monitoring programs conducted by the IEPA. Each of these plans included sampling of public water-supply wells in order to characterize ambient water quality in principal aquifers. However, none of these monitoring plans was designed to determine the occurrence of agricultural chemicals in groundwater. None of the plans targeted those wells most at risk from agricultural chemicals-rural, private wells.

A national pesticide monitoring program is currently being conducted by the USEPA. Their primary objective is to gather information at the national level, therefore, only a few wells will be sampled in Illinois. Thus, no data appropriate for describing local conditions will be generated.

**Ambient groundwater quality monitoring plans** In 1984, the Illinois State Water Survey (ISWS) developed a plan for monitoring the ambient groundwater quality of the state (O'Hearn and Schock, 1985). The purpose of the plan was to provide reliable information on the quality of groundwater in aquifers throughout the state for management, research, and planning. The proposed monitoring program would establish a baseline for groundwater quality values against which comparisons could be made. The plan recommended use of existing public water supply wells and prioritization of aquifers for monitoring. This approach was intended to maximize the ability of the proposed monitoring network to document changes in groundwater quality while avoiding the cost of the installation of new, dedicated monitoring wells. The overall plan could be used in any set of circumstances, at any time, and still be responsive to the particular needs of the state.

The monitoring strategy recommended three interdependent levels of monitoring activity. The first level was an ongoing, fixed station monitoring of selected wells in cycles of 3 to 5 years. The results of the analyses from this level of monitoring were to be reviewed annually by the scientific staff of the Illinois Department of Energy and Natural Resources (ENR) in order to detect trends or problems. The second level called for intensive surveys to be carried out in 2- to 5-year cycles in areas of the state underlain by principal aquifers. At the third level of monitoring, special studies would be initiated when information from either of the other two levels of monitoring indicated that contamination might be occurring. Although this plan has not been implemented, the IEPA used the list of selected wells as a guide in its public water supply monitoring program.

**Monitoring hazardous wastes** In 1985, the Illinois State Water Survey responded to the mandates of Public Act 83-1268 by investigating activities related to hazardous wastes in Illinois (Shafer et al., 1985). The primary goals of this study were to (1) identify the locations and types of activities; (2) evaluate available information about hazardous waste contamination of groundwater; and (3) make recommendations for a statewide groundwater monitoring plan based on groundwater use, aquifer yield, hazardous-substance-related activities, and aquifer susceptibility.

The factor distinguishing this monitoring plan from others was that sampled wells would be located in areas where contamination from hazardous materials was most likely to occur. The overall recommendations for monitoring followed the same three levels of activity suggested in the O'Hearn and Schock plan (1984) for monitoring ambient groundwater quality. The first level was a continued program of compliance monitoring throughout the state with the addition of scanning for organic compounds. At the second level, the principal aquifers would be intensively monitored over a relatively short period of time on a cyclic basis to determine spatial and temporal variations in water quality in the aquifer. The third level, special studies, would be initiated in response to potential or developing problems identified in the first two levels. This monitoring program has not been implemented.

**National Pesticide Survey** The federal government has demonstrated its awareness of the potential problem of pesticides in groundwater supplies of drinking water. The U.S. Environmental Protection Agency (Mason et al, 1987), through its Offices of Pesticide Programs and Drinking Water, has initiated a multiyear, nationwide survey of pesticide contamination in domestic and community water wells. The National Pesticide Survey (NPS) is a multiphase project consisting of a planning phase to characterize the United States in terms of pesticide use and groundwater vulnerability and to select sampling points; a pilot study to test the concepts of the plan; sample collection; and analysis of the data and information resulting from the survey. The two goals of the survey are to (1) characterize pesticide contamination of drinking water wells, and (2) determine how pesticide concentrations in drinking water wells correlate with patterns of pesticide use and with groundwater vulnerability.

During the planning phase of the NPS, all 3137 counties of the United States were stratified by a scheme that placed each county into one cell of a 3 by 4 matrix. The matrix consisted of three categories of groundwater vulnerability and four categories of pesticide use. The selection of public wells was made from a USEPA database that contains the vulnerability and usage information. The private wells to be sampled are located in a subset of 90 counties. These counties were selected using a stratified, random design. Counties evaluated as vulnerable with high pesticide usage were overselected in comparison to medium and low counties. Areas within each of the counties were evaluated once again on an intra-county basis in terms of cropping and vulnerability. Finally, wells were selected, also oversampling those in subcounty areas evaluated as cropped and vulnerable.

Four of the 90 counties randomly selected for private well sampling in the NPS are in Illinois --Kane, McHenry, Peoria, and Warren counties. Sampling will begin in August 1988 in Kane County and continue through December 1989, finishing in Peoria County.

Although the NPS will collect samples at the county level, its intent is to acquire information at the national scale. The results of the NPS will not provide sufficient detail for planning and program development within a state.



## EXPERIMENTAL DESIGN

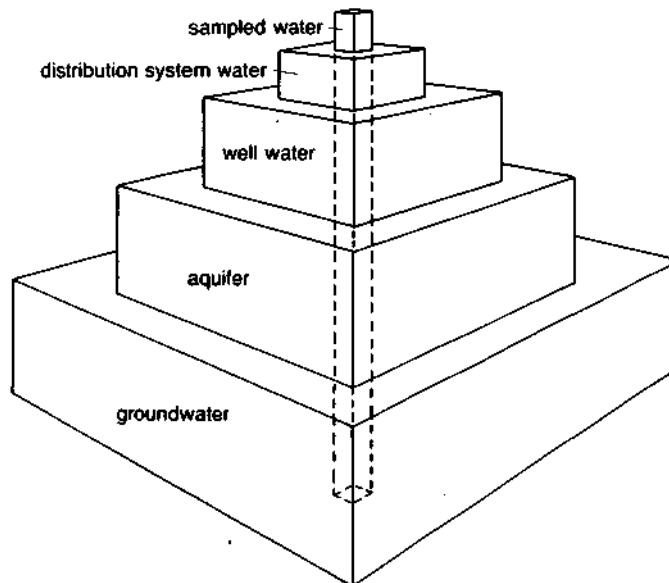
Environmental sampling involves the collection of samples in space and time with the intent that the samples will represent, at some significance level, actual field conditions. By collecting a number of samples in an area, we attempt to account for the potential spatial variability of the measured parameter. Repetitive sampling over time at one point in space or distributing sampling points over both space and time is intended to allow the data analyst to recognize the effects of temporal variability on the measured parameter.

A sampling program may provide a one-time assessment (survey) of water quality, or it may be part of a continual, possibly long-term, monitoring program. The initial step in designing a groundwater-quality sampling program is to develop a clear statement of objectives and to precisely define the population to be sampled. Cartwright and Shafer (1986) described several reasons for conducting a sampling program:

- assess background (ambient) water quality in aquifers;
- assess the present status of water quality in aquifers;
- use detection monitoring to determine suitability for the present usage;
- predict future groundwater-quality trends;
- determine the impact of certain land-use practices on local groundwater quality through special purpose monitoring;
- monitor for research purposes;
- monitor for cosmetic purposes.

In most cases, a sampling program will only be able to meet one of these objectives.

Another important step in designing a sampling program is to specify what is to be sampled. As noted previously, the technical definitions of groundwater and aquifer are not synonymous, although in common usage the terms are used interchangeably. In addition, groundwater withdrawn through a well may not necessarily represent the water within the aquifer. Physical and chemical properties such as temperature, pH, dissolved oxygen, and total dissolved solids can change due to mixing of aquifer waters during pumping or to contact with the components of the water delivery system (pump, well material, and pipe). Figure 6 schematically presents the relationship between the various populations available for "groundwater" sampling.



**Figure 6** Relationship between various groundwater subpopulations available for sampling.

## Target Population and Study Objectives

The initial effort to assess the extent of agricultural chemical contamination of Illinois groundwater should be focused on rural, private wells. This approach will maximize acquisition of data on the potential exposure of the rural population of Illinois to agricultural chemicals through drinking water and minimize sample collection costs. However, inferences made on the basis of data acquired in this proposed survey will thus be limited to the target population (rural, private wells) and cannot be extrapolated to other populations such as public wells or aquifers. Moreover, this survey is not intended to directly address issues related to the transport of agricultural chemicals to and in the groundwater system.

The recommended target population of this proposed assessment is defined as follows:

*rural*: outside the boundaries of an incorporated area with a population greater than 2,500 and outside of a forested or other natural area greater than 1 square mile;

*private water wells*: both private and semiprivate water systems as defined in the Illinois Groundwater Protection Act (P.A. 85-863);

*water wells*: drilled or driven wells, not including large-diameter dug or bored wells. Because of their shallow depth or construction, dug wells are particularly sensitive to contamination from surface application of chemicals. (Dug and bored wells are discussed in the *Recommendations* section.)

In this survey the term agricultural chemicals refers to both pesticides and nitrates. The term pesticides, which includes insecticides, herbicides, and fungicides, is defined in the Illinois Pesticide Act of 1979 as "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest or any substance or mixture of substances intended as a plant regulator, defoliant or desiccant." The phrase, "occurrence of a pesticide" is defined as the presence above the analytical detection limit of one or more of the specific pesticides being analyzed. For purposes of statistical analysis, the occurrence of nitrates is defined as presence in groundwater samples above a predetermined concentration; for example, 10 mg/L nitrate-nitrogen (NO<sub>3</sub>-N), the drinking water standard, or 1 mg/L, which is often cited as a background concentration in groundwater.

The sampling design proposed in the next section of this document (*Sampling Plan*) is intended to allow

*statistically valid inferences at specified levels of confidence and precision regarding*

- the overall level of occurrence of agricultural chemicals in groundwater samples collected from rural, private water-supply wells in Illinois;
- the occurrence of agricultural chemicals in samples from various subsets (strata) of rural, private wells. The stratification of wells into the subpopulations is based on a mapped assessment of the contamination potential of shallow aquifers. This assessment is used to estimate the potential for agricultural chemicals to contaminate private wells.
- the significance of the differences between the levels of occurrence in the strata.

*estimates at lower levels of confidence and/or precision regarding*

- the occurrence of agricultural chemicals in samples from wells stratified by other characteristics, such as well depth, depth of screened interval, or source aquifer;
- the significance of the differences between those strata in the level of occurrence;
- seasonal differences in the frequency of occurrence in the various strata.

## Recommended Analytes

Because of the large number of pesticides used in Illinois and the high cost of analyses, only chemicals with high usage or high potential to cause groundwater contamination should be

**Table 4** Priority analytes for which USEPA NPS analytical methods are available

<i>Chemical Name</i>	<i>Type<sup>1</sup></i>	<i>Method<sup>2</sup></i>	<i>Chemical name</i>	<i>Type</i>	<i>Method</i>
2,4-D	H	3	disulfoton	I	1
2,4-DB	H	3	disulfoton sulfone	D	1
acifluorfen	H	3	disulfoton sulfoxide	D	1
alachlor	H	1	endrin	I	2
aldrin	I	2	endrin aldehyde	D	2
atrazine	H	1	EPTC	H	1
atrazine dealkylated	D	4	ethoprop	I	1
bentazon	H	3	heptachlor	I	2
butylate	H	1	heptachlor epoxide	D	2
carbaryl	I	5	linuron	H	4
carbofuran	I	5	metolachlor	H	1
carbofuran phenol	D	4	metribuzin	H	1
carboxin	F	1	metribuzin DA	D	4
chloramben	H	3	metribuzin DADK	D	4
chlordane	I	2	metribuzin DK	D	4
chlorpropham	H	1	nitrate-nitrogen	-	9
cyanazine	H	4	picloram	H	3
DDT	I	2	propachlor	H	2
diazinon	I	1	simazine	H	1
dicamba	H	3	terbufos	I	1
dieldrin	I	2	trifluralin	H	2
dinoseb	H	3	vernolate	H	1

<sup>1</sup> H = herbicide, I = insecticide, F = fungicide, D = degradation product

<sup>2</sup> Method number indicates USEPA NPS recommended analytical method.

selected as priority analytes for the Illinois survey. The USEPA National Pesticide Survey (NPS) analytical methods are recommended because they permit analysis of a wide variety of chemical compounds. The availability of an NPS method for analyzing a pesticide was a criterion for analyte selection.

Initially, 253 pesticides were listed as potential candidates for the survey. From this list, compounds were selected for further evaluation on the basis of past and present usage in Illinois, their designation as a priority analyte in the USEPA NPS, and/or detection in monitoring programs in other midwestern states. Twenty-six compounds from the initial compilation were selected for the base list of priority analytes. Additional compounds were selected for further review.

Information about all initial and potential analytes was compiled in a database that includes information on usage in Illinois, chemical properties, and possible methods of analysis. On the basis of these data, additional compounds with available USEPA NPS methods were selected as priority analytes (table 4). An additional 18 compounds were recommended as analytes, contingent upon the availability of analytical methods (table 5). Information on analytical methods for these compounds has been requested from the manufacturers. Chemical properties, crop usage, and health information for the compounds listed in tables 4 and 5 appear in Appendix A.

Nitrate-nitrogen was selected as a priority analyte, along with the pesticides, because nitrogen fertilizers are also used in large quantities in Illinois and can be a source of groundwater contamination.

The complete list of priority analytes was reviewed by University of Illinois researchers and state agency personnel involved in pesticide research or regulation. Additions and deletions were made on the basis of their recommendations.

**Table 5** Additional analytes dependent upon availability of analytical methods

<i>Chemical Compound</i>	<i>Type<sup>1</sup></i>	<i>Chemical compound</i>	<i>Type<sup>1</sup></i>
bromoxynil	H	metalaxyl	F
CDAA	H	methyl parathion	I
chlorpyrifos	I	pendimethalin	H
ethalfuralin	H	phorate	I
fluazifop-butyl	H	phorate sulfone	D
clomozone	H	phorate sulfoxide	D
fonofos	I	sethoxydim	H
glyphosate	H	terbufos degradation products	D
imazaquin	H	trimethacarb	I

<sup>1</sup> H = herbicide, I = insecticide, F = fungicide, D = degradation product

### Sampling Design

Since sampling all units within a population is frequently impractical, sampling theory is used to select a specific segment of the population (subpopulation). Proper sampling, incorporating statistical theory, allows inferences to be made about the population on the basis of data from the sampled subpopulation.

Three sampling techniques, purposive, random, and geostatistical, were considered for this study. Purposive sampling is a nonprobabilistic technique by which an investigator selects a small sample of "typical" units from the sample population. This technique is convenient and often economical; however, statistical inferences about the sample population cannot be made on the basis of this type of sampling. Because the purpose of the proposed survey is to define the extent of the occurrence of agricultural chemicals on a statewide basis, use of purposive sampling is not appropriate. In random sampling, the sample population is generally assumed to approximate a normal distribution; this assumption is generally valid for sample populations larger than 100. Geostatistical sampling assumes that the sample population is spatially correlated. In general, the occurrence of agricultural chemicals in private wells may be spatially correlated on a local scale; but, on a statewide scale, the occurrence probably will not be strongly correlated in space. Thus random sampling, rather than geostatistical sampling, is used in this survey.

**Types of random sampling** For this study, five types of random sampling were considered: simple, systematic, cluster, stratified random, and double sampling. The following descriptions are summarized from Cochran (1963).

Simple random sampling is a method of selecting  $n$  units (the sample size) from all  $N$  units in the population. Each  $n$ th unit has the same probability of being selected. An advantage of this technique is its simplicity-sampling of units is random, no judgment is involved. It can be used to make statistical inferences about the sample population, but cannot be used to make inferences concerning the effect of one or more variables on the sample population. The use of simple random sampling is not recommended.

Systematic sampling involves dividing all  $N$  units into  $k$  subpopulations. In the first  $k$ th subpopulation, a unit is selected randomly, and that unit is selected in each of the other  $k-1$  subpopulations. For example, assume that each subpopulation contains 15 units, and the 7th unit is randomly selected. Then the 7th unit is also selected from each of the other  $k-1$  subpopulations. In terms of the overall population, units 7, 22, 37, 52...are selected. There are two possible advantages to using systematic sampling instead of simple random sampling. First, selecting a sample is easier and less subject to error. In addition, systematic sampling may be more precise than simple random sampling. The improvement in precision depends on the nature of the population being sampled. Systematic sampling cannot be recommended for this survey because a complete list of wells in the sample population is not available.

Cluster sampling involves dividing all population units into groups of units or clusters. Clusters for sampling are randomly selected from the list of total clusters. All units within each cluster are then sampled. Cluster sampling is a useful technique if a comprehensive list of units is not available. This technique can be used to make statistical inferences about the sample population, but it cannot be used to make inferences concerning the effect of one or more variables on the sample population. Thus, it is not recommended.

Stratified random sampling involves dividing the population into nonoverlapping subpopulations, called strata. A simple random selection process is used to choose samples within each of the strata. Stratification is based on scientific judgment and can increase the precision of the estimates of the entire population, if the entire heterogeneous population is composed of homogeneous subpopulations.

Double sampling is similar to stratified random sampling; however, the distribution of the stratification variable is not known prior to sampling. Thus, double sampling, also known as two-phase sampling, involves taking a relatively large preliminary sample to determine the mean or frequency distribution of the variable  $x$ . Then a smaller sample of the variable of interest,  $y$ , may be taken. This technique is useful when it is relatively inexpensive to sample for  $x$  compared to  $y$ .

The most appropriate technique for this survey is stratified random sampling. This technique can be used to statistically define the extent of the occurrence of agricultural chemicals in the sample population wells and to obtain insight into the importance of one or more stratification variables, such as the potential for contamination of shallow aquifers, to the occurrence of agricultural chemicals in rural, private wells.

Double sampling should be used to analyze the results from the initial stratified random sampling. The sampled wells would be stratified on the basis of information obtained from a well site survey, such as well depth and well characteristics. This analysis would yield a preliminary indication of the significance of these variables to the occurrence of agricultural chemicals in the sampled wells.

**Stratification variables** The purpose of stratified random sampling is to divide the sampling population so that the variance of the subpopulations is less than the variance of the sample population. Several variables that are important for estimating the potential for contamination of private wells were considered for use as stratification variables in this project: pesticide use, well depth, source aquifer, and potential for groundwater contamination of shallow aquifers. (See section on *Potential for Contamination of Illinois Groundwater by Agricultural Chemicals*.)

Stratification by two variables, pesticide use and potential for contamination of shallow wells, was also considered. (Stratification by two variables would form a matrix of strata.) Because pesticides are applied to two out of three acres of all rural areas in Illinois, stratification by pesticide use would not be cost effective: the sample size would have to be doubled, but the information would increase only marginally.

Well depth, a crude measure of contamination potential, was also considered and eliminated as a stratification variable because a complete and verified list of the depths of private wells is not available in ISGS or ISWS files. Furthermore, many well owners probably cannot provide reliable information on the depth of their wells, and the depth of an operating well cannot be readily measured. Because a complete list of wells with depth data is not available, well depth cannot be used as a basis to randomly select wells for sampling.

Source aquifer, the aquifer that supplies water to the private well, could not be used as a variable because of a lack of verified data. The ISGS has not yet mapped all the aquifers used for private water supplies.

Potential for contamination of shallow aquifers from agricultural chemicals was selected as the stratification variable for this survey. The Stack-Unit Map of Illinois (Berg and Kempton, 1988), which provided data on geological materials to a depth of 50 feet, was interpreted to identify four sets of geological sequences-each rated for susceptibility of shallow aquifers to contamination from agricultural chemicals. Land-use data supplied by the U.S. Geological Survey (1985) were used to identify nonrural areas. (As defined earlier in this report, nonrural indicates urban areas with population greater than 2500 and forested areas larger than 1 square mile.) These land-use and geologic maps were combined to form a map depicting the potential for shallow aquifer contamination from agricultural chemicals in rural areas of Illinois (fig. 7).

The mapping of the contamination potential sequences was based primarily on depth from land surface to highly permeable aquifer materials:

- top of aquifer materials within 5 feet;
- top of aquifer materials between 5 and 20 feet;
- top of aquifer materials between 20 and 50 feet;
- no aquifer materials within 50 feet.

Depth to the uppermost aquifer is currently considered to be the most appropriate, mappable criteria for statewide assessment of the potential for agricultural chemical contamination of rural, private wells. This approach is further justified by the fact that private water wells are usually completed within the uppermost aquifer. The mapped contamination potential of the area surrounding a well is assumed to be correct and will not be field checked. Conventions used in generating the contamination potential map are discussed in Appendix B.

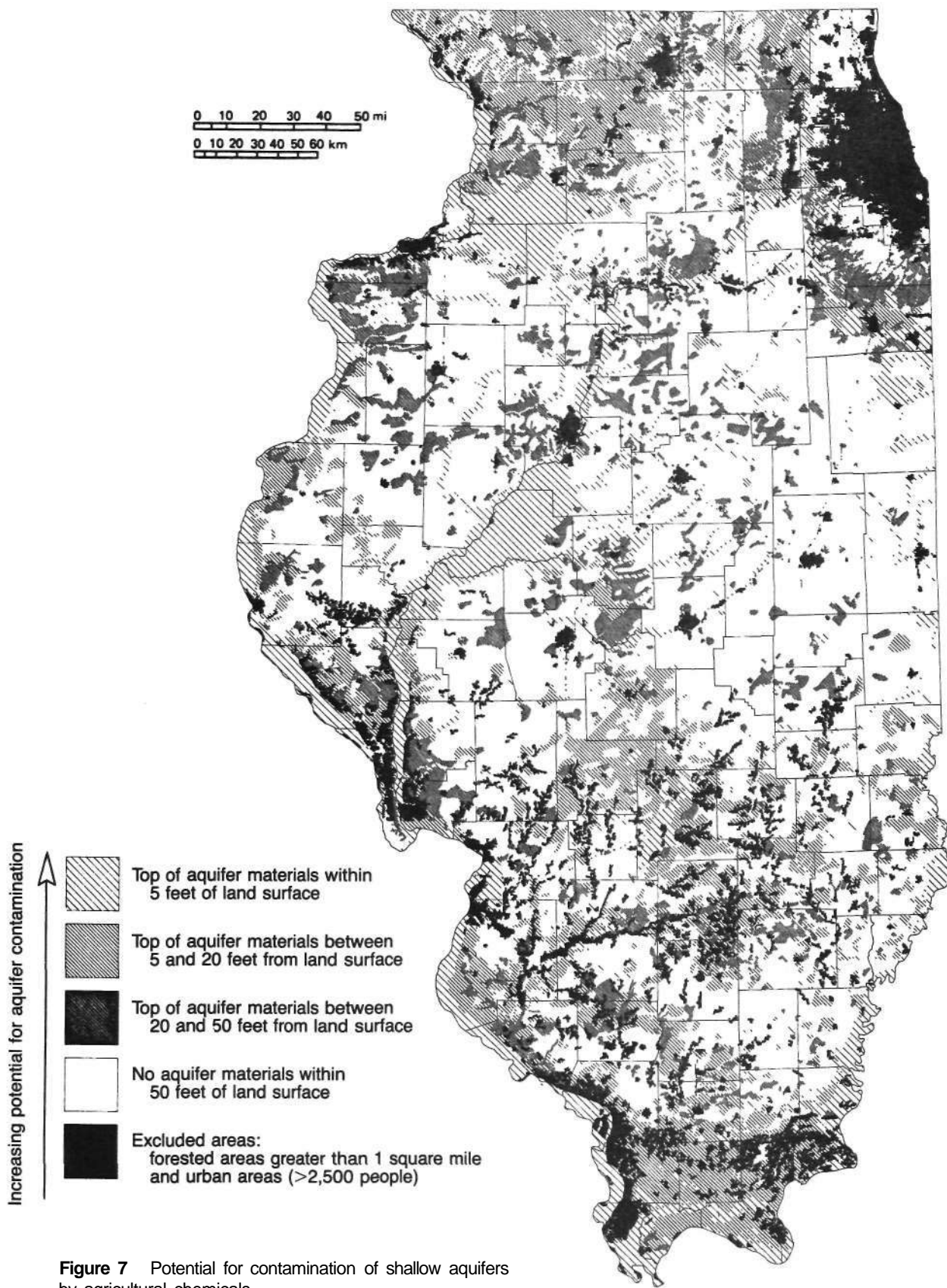
**Selection of sample size** To determine the sample size for a survey, we assume the sample population is normally distributed. The following parameters must be known or estimated: the acceptable confidence interval, anticipated probability of occurrence, acceptable precision of estimates, estimated population size, and test statistics. The cost of conducting the survey will affect which confidence interval and precision of estimates are achievable.

Table 6 shows the effect of confidence level on sample size. The number of samples collected must be increased considerably to increase the level of confidence. Level of confidence can best be illustrated with an example: given a 95 percent level of confidence, the confidence interval of the sample estimate for 95 of 100 repeated samples from the same population would contain the population estimate. The confidence interval may be defined as a range of values with limits determined by the sample standard deviation and confidence coefficient. The confidence coefficient increases as the level of confidence increases.

**Table 6** Effect of confidence level and probability of occurrence (P) on sample size\*

P	confidence level (%)			
	80	90	95	99
0.10	59	98	139	239
0.30	138	227	322	554
0.50	164	270	383	659

\* assumes sample population, (N) = 100,000 and precision,  $p = \pm 0.05$



**Figure 7** Potential for contamination of shallow aquifers by agricultural chemicals.

Selection of the appropriate level of confidence depends upon the anticipated use of the survey results and the economic impact of that use. The results of this proposed survey might be used to determine areas in which to focus educational programs explaining optimum methods for use of pesticides. Since the cost of an educational program would be relatively low, an 80-percent level of confidence would probably be satisfactory. Table 6 indicates that 164 samples are needed for each stratum if (1) the population of the largest stratum is 100,000 wells, (2) an 80-percent level of confidence is acceptable, and (3) the probability of occurrence equals 0.50.

Another use of the survey results might be to determine where to conduct comprehensive groundwater-contamination investigations, which would cost more. A 95-percent level of confidence might be appropriate for this situation; thus, 383 samples per stratum must be collected. A third use of the survey results might be to determine areas in which use of agricultural chemicals should be curtailed or even banned. Because a reduction or ban of agricultural chemical usage would have a significant impact on the economy of the state, a 99-percent level of confidence would be appropriate. In this situation, 659 samples per stratum would be required. These examples illustrate the effect of the potential uses of the survey results on the sample size and indicate clearly that use of the survey results must be anticipated during the design of the survey.

Table 7 shows the relationship between probability of occurrence and sample size. Note that the maximum sample size is required when the probability of occurrence is 0.50 and that the sample size is symmetric about 0.50. As table 8 shows, the sample size is 322 for both  $p = 0.30$  and  $p = 0.70$ . No prior information is available regarding the occurrence of agricultural chemicals within the various sampling strata; thus, a conservative approach is recommended. The most conservative approach would be to assume a probability of occurrence of 0.50.

The relationship between sample size ( $n$ ) and precision ( $p$ ) is shown in table 8. As the precision value (margin of error in sample estimate) decreases, the sample size increases. For example, if the population size were 20,000 wells, probability of occurrence 0.50, and the confidence level 95 percent, then one would need 6489 samples for a precision of  $\pm 0.01$  ( $0.50 \pm 0.01$ ), or 377 samples for a precision of  $\pm 0.05$  ( $0.50 \pm 0.05$ ).

The relationship between sample size ( $n$ ), population size ( $N$ ), probability of occurrence ( $P$ ), and precision ( $p$ ) is shown in table 9. As population size increases, sample size increases slightly.

**Table 7** Effect of probability of occurrence ( $P$ ) on sample size ( $n$ )

$P^*$	$n$
0.02	31
0.05	73
0.10	139
0.20	246
0.30	322
0.50	383
0.70	322
0.90	139
0.95	73
0.98	31

\*95-percent confidence level;  
 $N = 100,000$  and  $p = \pm 0.05$

**Table 8** Effect of precision ( $p$ ) on sample size ( $n$ )

Population size	Sample size		
	$p=0.01$	0.03	0.05
20,000	6489	1014	377
40,000	7745	1040	381
60,000	8279	1049	382
80,000	8575	1054	383
100,000	8763	1056	383
200,000	9164	1062	384

All values for 95-percent confidence level and  $P=0.50$ .



**Table 9** Effect of population size (N), probability (P), and precision (p) on sample size (n)

<i>N</i>	<i>n1</i>	<i>n2</i>	<i>n3</i>
20,000	377	318	377
40,000	381	321	381
60,000	382	321	382
80,000	383	322	383
100,000	383	322	383
200,000	384	323	384

All cases are for 95-percent confidence levels.

n1: P = 0.50 and p = ±0.05

n2: P = 0.30 and p = ±0.05

n3: P = 0.10 and p = ±0.03

**Table 10** Effect of test statistic on sample size (n)

<i>P1</i>	<i>P2</i>	<i>n<sub>min</sub></i>
0.50	0.49	19,204
0.50	0.47	2,130
0.50	0.45	765
0.50	0.43	389
0.50	0.40	189
0.40	0.39	18,359
0.40	0.37	2,020
0.40	0.35	719
0.40	0.33	362
0.40	0.30	173
0.10	0.09	6,604
0.10	0.08	1,572
0.10	0.07	663
0.10	0.06	352
0.10	0.05	212

Assumes a 95-percent confidence level.

$$n_{min} = \frac{(1.96)^2 (P1 \cdot Q1 + P2 \cdot Q2)}{(P1 - P2)^2} \quad \text{where } Q1 = 1 - P1$$

As the estimates become more precise (±0.05 to ±0.03) a larger sample size is required. This increase can be offset, however, by the decrease due to the probability of occurrence: compare the first column of data (P = 0.50 and p = ±0.05) with the third column (P = 0.10 and p = ±0.03).

The relationship between sample size and the test statistic (table 10) is used to determine whether the difference between two estimated proportions is statistically significant. Table 10 shows values for two estimated proportions (P1 and P2) and minimum sample size, *n<sub>min</sub>*: if the proportion in one stratum is 0.40 while the proportion in another stratum equals 0.37, 2,020 samples will be needed to indicate that the difference in the proportions is statistically significant. The number of samples to make such a distinction is reduced to 362 if the two proportions equal 0.40 and 0.33. Basically, *n<sub>min</sub>* decreases as the difference between P1 and P2 increases.

**Table 11** Drilled wells in rural Illinois by contamination potential strata (calculations based on NWWA data)

Strata class	Wells	Rural wells Rural land	
	total no.	%	area %
<5 ft	54,354	20.0	14.7
>5 to <20 ft	37,708	13.8	13.1
>20 to <50 ft	34,614	13.8	10.7
>50 ft	142,694	52.3	61.5

If the goal of stratified sampling is to optimize the comparison between strata (by minimizing variance of the estimates for each stratum), then the best strategy is to take an equal number of samples from each strata class. Sudman (1976) indicates that a sample proportional to the strata population in the overall population is required to optimize the overall estimates. Optimizing for strata comparison results in greater variance in the overall estimates than if sample size were optimized for overall estimates. Data regarding the number of wells within various strata (table 11) are needed to determine the ramifications of the optimization strategy. These calculations were based on data from the National Water Well Association (NWWA), U.S. Census Bureau. (Appendix B presents additional discussion on estimating the number of wells in each stratum.)

Although each stratum does not contain the same number of wells (table 11), we recommend collecting an equal number of samples from each stratum. The increased variance of the overall estimates seems less important than an increase in the variance of the strata values.

In summary, stratified random sampling is the recommended approach. The samples should be stratified on the basis of the estimated potential for well contamination by agricultural chemicals. Sampling should be optimized for comparison of strata estimates; thus, an equal number of samples should be selected for each stratum. In addition, a 95 percent level of confidence, 50 percent probability of occurrence, and a  $\pm 0.05$  precision level should be used. As indicated in the preceding discussion, a minimum of 384 samples must be collected from each stratum. In addition, this large sample size will improve the results of doubling sampling by increasing the number of available samples.

### Nonresponse

Another consideration for the sampling plan is nonresponse, defined as the inability to obtain a well water sample from a sampling location (e.g. cannot locate a well, or owner refuses to cooperate). According to the sampling literature, the nonresponse population usually differs from the response population. Thus, nonresponse introduces bias into the sample. Cochran (1963) indicates that due to the nonresponse bias, the number of samples taken must be significantly increased to preserve the level of survey precision.

The NPS (Mason et al., 1987) uses an inflation factor to account for nonresponse. The inflated sample size is simply the original sample size divided by the anticipated response rate. The sample size is determined according to the criteria discussed previously. The number of samples to be collected in the field is this value divided by the product of various rates, such as anticipated response rate (R1) or eligibility rates (R2) (equation 1). Equation 1 is used to determine the field sample size—that is the number of field samples one must attempt to collect in order to obtain the minimum number of samples needed for the statistical analysis:

$$\text{number of field samples} = \frac{\text{samples needed for statistical analysis}}{(R1) (R2) \dots (Rn)} \quad [1]$$

With little previous experience to guide selection of these parameters, we estimate that the response rate would equal 0.90 and the eligibility rate equal 0.99. Multiple attempts should be made to sample all wells to obtain a response rate of 90 percent or greater. Thus, the field sample size would equal 431 for 95 percent level of confidence, 50 percent probability of occurrence, and  $\pm 0.05$  precision level.

### **Sampling Plan**

The sampling plan has two components: the selection of wells to be sampled and a schedule for sampling of these wells.

**Well selection** Random sampling requires that wells be selected so that no bias exists (i.e., all wells have a non-zero chance of being selected). Ideally, one would randomly select wells for sampling from a comprehensive list of wells. As previously noted, such a list does not exist. The most complete lists of wells and well locations are available from the ISGS and ISWS. Comparison of the number of wells on these lists with 1980 Census data (number of homes with wells) indicates that a combined, two-Survey list would be approximately 65 percent complete. (The Census data cannot be used for well selection because its locational data are inadequate.) Use of the Surveys' lists might and probably would introduce bias into the sampling plan. For example, wells in a geologically sensitive area (where sand and gravel occur at or within 5 feet of ground surface) are likely to be under-reported in the Surveys' lists. In these areas, wells are more likely to be installed by the homeowner, rather than by a professional well driller. The homeowner is less likely than a professional well driller to file the appropriate forms for the new well with the Surveys.

Sample bias is not an insurmountable obstacle if it can be quantified. However, quantifying the bias in the Surveys' incomplete lists of wells may be a more time-consuming task than adopting another well selection scheme.

For this survey, candidate wells for sampling should be identified in a two-step process. First, random points would be selected. Then wells would be selected near these randomly distributed points. The Geographic Information System (GIS) should be used to delineate the four strata and to select sampling locations. A grid of sufficient density (50 by 50 feet) should be overlaid on all rural areas in Illinois. The grid nodes are assigned sequential numbers. Randomly selecting from these node numbers would allow the random selection of sampling locations for each strata throughout rural areas of the state.

Once the sampling locations are randomly selected, they must be identifiable in the field. This would be accomplished by plotting a portion of the grid containing the sampling location and another coverage, such as townships. The township coverage contains information regarding the location of township, range, and section lines. This composite map at the scale of 1:24,000 could be used as an overlay on USGS 7.5-minute quadrangle maps. One possible drawback to this scheme would be the need to produce approximately 2,000 maps for the state.

The randomly selected x,y coordinates are sampling locations, not specific wells to be sampled. The premise behind this well selection protocol is to select the closest well to the sampling location. Ideally, there should be a single well close to the sampling location. If two or more wells are equidistant to the sampling location, the well to be sampled should be randomly selected.

**Scheduling of well sampling** The occurrence of agricultural chemicals in well water is expected to vary through time (McKenna et al., 1988; Hallberg, 1986). However, the available data do not allow for predictions regarding the temporal variability in occurrence of agricultural chemicals in various hydrogeologic settings. There are three options for developing a sampling schedule to address temporal variability—one that does not account for any possible variation over time in the occurrence of agricultural chemicals in well water, and two that attempt to account for this possible variability.

One option is to ignore temporal variability. If no temporal correlation is assumed, scheduling of well sampling does not have to proceed according to some statistically rigorous scheme; rather, it is only a matter of logistics. Well sampling may begin at any time and be completed on a schedule based on factors (such as convenience) other than random sampling. For this survey, however, ignoring temporal variability is unacceptable because the survey results may be biased and not represent the true occurrence of agricultural chemicals in private wells. The wells must be sampled for a specified time, according to a statistically valid scheme.

A second option for obtaining data on temporal variability would involve the systematic sampling of an additional small number (three to five) of wells from each of the strata. Although most of the wells would be sampled without regard to a statistically rigid schedule, the additional three to five wells in each stratum would be sampled on a regular basis (every 2 weeks). Because of the small number of wells to be systematically sampled, these wells should be selected from wells in which agricultural chemicals have been found. If this option is selected, it is recommended that these wells be sampled for a minimum of 2 years, an approach that would increase the number of samples to be analyzed and require the cooperation of a number of well owners.

A third option is to select a constant number of wells to be sampled each week during a 1-year period. The number of wells (approximately eight wells per stratum) is determined by dividing the total number of wells to be sampled by the number of sampling periods (50 one-week periods) during the project. To expedite sampling, the wells sampled during one sampling period would be grouped by geographic region. The time to sample wells from these geographic regions should be randomly selected.

Although the information generated from either option that accounts for temporal variability would not be definitive, it would be quite useful for planning a more focused study concerning the temporal distribution of agricultural chemicals in private wells. For this reason, either option that incorporates, rather than ignores, temporal variability is preferred.

The confidence level of the second option (taking a subsample of three to five wells every 2 weeks) may be higher because the temporal distribution data all come from the same wells, rather than from different wells within the same stratum, as in the third option. However, the second option would require 156 to 258 additional samples per stratum during a 2-year study. This increase in the number of samples would be cost prohibitive. Thus, the third option, which does not require any additional samples, is recommended, although it requires more careful management to maintain statistical validity.

### **Analysis of Sample Data**

Data collected during the proposed survey on the occurrence of agricultural chemicals in rural, private water wells should be statistically analyzed in order that inferences can be made about all rural, private water wells on the basis of data collected from the sample population. These results should not be used to make inferences regarding the occurrence of agricultural chemicals in water from other types of wells or in aquifers. In addition, the proposed survey has not been designed to provide statistically valid data regarding the concentration of the various agricultural chemicals found in the sample population of wells. However, concentration data will be analyzed on a compound by compound basis, although at lower levels of confidence than the occurrence data.

The estimates of number of wells per stratum (table 11) will be field checked. Accurate estimates of number of wells in each stratum are essential for accurate statistical analysis. Details of field checking are discussed in Appendix B. Every effort should be made to verify and supplement the data concerning the sampled wells not obtained during the well-user interview and site observation. This information should be gathered from records on file at the ISWS and ISGS.

The statistical analysis should proceed as follows:

- compute the proportion of wells with occurrences of agricultural chemicals in each stratum;

- determine the validity of the estimates of stratum proportions by computing the variance and confidence interval for the stratum proportions;
- compute the proportion of occurrence, variance, and confidence interval for the overall sample population;
- calculate the test statistic to determine whether the stratum proportions are significantly different.

The equations to calculate these values are presented in Appendix C.

Double sampling should follow this statistical analysis and would aid in evaluating the significance of factors controlling the occurrence of agricultural chemicals in the wells. Double sampling involves two-phases: Sampled wells would originally be stratified on the basis of contamination potential. After well-site characterization, they would be stratified on the basis of a variable such as well depth. The occurrence of agricultural chemicals in wells from all strata would be determined as a function of well depth or other stratification variable. Because of the sampling technique employed, the variance of these estimates would be larger than the variances of the estimates based on stratification by shallow-aquifer susceptibility. Again, the statistical inferences are only valid for rural private wells in Illinois, not for public water wells or aquifers.

Finally, the data on occurrence should be analyzed for time-dependent trends using time series analysis as described by Pandit and Wu (1983). This is a powerful technique for identifying simple to complex temporal trends in equally spaced data.

### **Sample Tracking and Laboratory Coordination**

**Sample tracking** A sample tracking system, based on a unique, four-digit identification number for each well, should be established before wells are selected for sampling. This randomly assigned number would be combined with other digits and letters to identify specific samples from a well. Use of the four-digit base number would allow analytical results to be related to information gathered during the well-user interview and the well-site characterization (Appendixes E and F). Data entered into portable computers in the field should be transferred to the office computerized data management system. This information would be readily accessible to field, laboratory, and project staff for scheduling and tracking the project; cross-referencing, integrating, and analyzing data; conducting statistical analyses; and reporting results. The final configuration of the data management system would depend on the level of funding, the length of field trips, number of laboratories, and compatibility of computers.

Each sample containers issued to a sample collector would be assigned a seven-character identification number, such as 3647-02-A:

- 3647 four-digit base number associated with all samples from a well;
- 02 two digits indicating the type of sample to be collected or the quality assurance/quality control component;
- A one-letter code designating the number of times the wells was sampled.

For example, samples in bottles labeled 3647-01-A and 3647-13-B were collected from the same well on two separate occasions: the A and B refer to different sampling events; numbers 02 and 13 (center digits) indicate the type of sample collected at this well during one sampling event. The two digits identifying sample type should be randomly assigned by the QA officer. Using this procedure prevents the analytical staff from knowing what type of sample ( e.g. field spike or duplicate) is being analyzed. For two different sites, the same two center digits in the identification number could indicate different types of samples. The analytical results could be linked to the sample type during data interpretation.

A maximum of 30 samples could be collected at any one site during one sampling event. This many samples would rarely be taken, since 30 represents the number of samples needed for all analytical methods and all possible QA/QC samples that can be associated with one sampling event at a well. The number is derived from the total possible samples:

<i>Component</i>	<i>Total Bottles</i>
1 field sample per method per sampling	= 6
QA/QC samples	
Duplicates (1 per method per sampling) (collected at 10 percent of the sites)	= 6 (maximum)
Trip Blanks (1 per method per sampling) (collected at 5 percent of the sites)	= 6 (maximum)
Field Spikes (1 per method per sampling) (collected at 5 percent of the sites)	= 6 (maximum)
Blinds (1 per method per sampling) (submitted at the discretion of the QA officer)	= 6 (maximum)
Maximum Possible Collections	30

A color-coded label should be applied to the bottles for the QA/QC components of any sample set. Duplicates, trip blanks, field spikes, and blind samples would be labeled with separate colors to distinguish them from field samples and help prevent errors in sample collection. The sample collector would be supplied with a field instruction sheet, including a list of the samples to collect, their identification numbers, color codes, and instructions for handling each type of sample. Before leaving the well site, the sample collector should check the list, verify that all samples have been properly collected and handled, then remove the color-coded stickers (to ensure the integrity of the samples). The field instruction sheet would not be sent to the laboratory; it would be returned to the staff member who assigned the numbers. Thus, the samples sent to the laboratory would have no indication of which are well samples and which are QA/QC samples. The staff member responsible for assigning the numbers would still be able to relate the results to the well sampled because the base number would be written on the field-site survey form.

The next step would be to develop procedures for tracking the chain-of-custody of each set of sample containers and field questionnaires. Chain-of-custody forms (fig. 8) should be used to record distribution of sample bottles, collection and storage of samples, transport of samples from the field to the laboratory, and analysis in the laboratory. By checking the chain-of-custody forms, the laboratory or project manager would know where the sample set had been, what had been done to it, and who had handled it.

Chain-of-custody forms would be issued with each set of labeled sample bottles. The laboratory staff member who releases the sampling equipment and materials to the field staff would list those items on the form and sign it (fig. 8). In turn, the sample collector would check the list against the materials received and sign the form. The sample custody forms should always be kept with the samples. If the samples are transported to the laboratories by someone other than the sample collector, the change in custody of those samples and materials would be indicated by the signatures and dates on the form. Upon transfer of the samples and any remaining materials to the laboratory personnel, the sample custody forms should be signed and dated acknowledging receipt of the samples at the laboratory. Any comments about the condition of the samples upon receipt should be included on these forms.

When the samples are received at the laboratory, any numbers or identification codes assigned to the samples in the lab should be added to the sample custody form and checked against the field site survey form so that samples are properly associated with analytical results.

**Kit preparation** Collecting samples from each well site for both the individual analytical methods and the associated QA/QC procedures requires handling a large volume of sample bottles. For easy handling, bottles should be organized into kits in the laboratory. Kit preparation would include labeling bottles, assigning identification numbers, preparing individual chain-of-custody

**CHAIN OF CUSTODY**

IDENTIFICATION NUMBER \_\_\_\_\_

For the transfer to the collectors:

Materials released: By \_\_\_\_\_  
Containers \_\_\_\_\_  
Chemical preservatives \_\_\_\_\_  
Equipment \_\_\_\_\_  
Materials received:  
Receiver \_\_\_\_\_  
Date \_\_\_\_\_ Time \_\_\_\_\_

For the samplers, storers, and transporters:

Transfer of materials to \_\_\_\_\_  
Reason for transfer \_\_\_\_\_  
Receiver \_\_\_\_\_ Date \_\_\_\_\_  
Comment on condition of materials or samples:

Transfer of materials to \_\_\_\_\_  
Reason for transfer \_\_\_\_\_  
Receiver \_\_\_\_\_ Date \_\_\_\_\_  
Comment on condition of materials or samples:

Transfer of materials to \_\_\_\_\_  
Reason for transfer \_\_\_\_\_  
Receiver \_\_\_\_\_ Date \_\_\_\_\_  
Comment on condition of materials or samples:

Transfer of materials to \_\_\_\_\_  
Reason for transfer \_\_\_\_\_  
Receiver \_\_\_\_\_ Date \_\_\_\_\_  
Comment on condition of materials or samples:

For the laboratory:

Receipt of samples at laboratory:  
Receiver \_\_\_\_\_ Date \_\_\_\_\_  
Time of receipt \_\_\_\_\_  
Condition of samples \_\_\_\_\_

**Please add additional laboratory identification numbers to be used with this sample** \_\_\_\_\_

**Please write the Identification number for each sample on your lab analysis forms.** \_\_\_\_\_

Figure 8 Sample chain-of-custody form.

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## Illinois Statewide Agricultural Chemical Survey

IDENTIFICATION NUMBER 3647-04-A

Well owner John Q. Public

Well location Sec. 12, T48N, R63

Sample collector James L. Sampler

Sampling date 10/23/90 Sampling time 15:55

1 L of water preserved with mercuric chloride for Method 1  
Store immediately in cooler;  
Return within 96 hours to laboratory

---

**Figure 9** Sample bottle label.

forms, preparing bottles, and assembling kits. The following recommendations for kit preparation follow closely those developed for the USEPA NPS Pilot Survey (Mason et al., 1987).

Attached to each sample bottle and QA/QC bottle should be a sample label containing the identification number, well location and user's name, sample collector's name, and sampling date and time (fig. 9). General instructions for storage and preservation of samples as prescribed by the specific analytical method should also be provided on the labels.

Separate bottles (one for each analytical method) should be prepared for each type of sample. The type of samples to be obtained at each well site should be determined before collection, and in general, consist of field samples, duplicate samples, trip blanks, and field spikes.

The recommended bottle types, sizes, and preservatives are those used in the USEPA NPS methods required for the recommended analytes (see section, *Experimental Design-Analytical Methods*). If other methods are required to analyze additional compounds, bottle type and preservative requirements for those methods may differ (table 6, section *Experimental Design-Recommended Analytes*). Preservatives should be added to the bottles before kits are assembled. Bottle and preservative requirements for these methods are given in table 12. Clean, labeled bottles containing preservative should then be organized into a kit for each well site.

**Table 12** Preparation of sample collection bottles (Mason et al., 1987)

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Method	Preservative <sup>1</sup>	Sample volume	Bottle <sup>2</sup> type	Preservative volume (mL)
NPS-1	mercuric chloride	1 L	A	10
NPS-2	mercuric chloride	1 L	A	10
NPS-3	mercuric chloride	1 L	A	10
NPS-4	mercuric chloride	1 L	A	10
NPS-5	pH buffer	250 mL	B	2.5
NPS-9	sulfuric acid	125 mL	C	0.25

---

<sup>1</sup> mercuric chloride: dissolve 1 g reagent grade HgCl<sub>2</sub> crystal in 1 L of deionized water.

pH buffer: 100 mL of 1 M potassium acetate solution plus 156 mL of 1 M chloroacetic acid solution.

sulfuric acid: use reagent-grade concentrated H<sub>2</sub>SO<sub>4</sub>.

<sup>2</sup> A 1 L graduated borosilicate glass bottles

B 250 mL amber glass bottles

C 125 mL clear plastic bottles

Teflon-lined caps should be used with bottle types A & B.



The chain-of-custody forms should also be organized at this time and placed with the kits. Each kit should be labeled on the outside with the well identification number and location. The sample bottles should be packed in styrofoam or wrapped in bubble paper to minimize breakage.

**Laboratory management** A coordinated management program should be developed by the laboratory managers, under the guidance of the project supervisor. The laboratory managers would determine sample container storage and transport procedures, oversee analytical scheduling, and supervise the computerization of analytical results. They would also oversee the calibration of field instrumentation and the recording of QA/QC information for the laboratory.

Laboratory results should be reported on paper forms (fig. 10) and filed for a minimum of 5 years. Data should also be entered into a computerized data management system (see section, *Sample Tracking*). The system should be compatible with existing systems at each laboratory and allow easy retrieval by staff conducting the statistical analysis and scientific interpretation.

**Figure 10** Sample form.

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**Laboratory Analysis Results Report**

Identification no. \_\_\_\_\_ Laboratory no. (if different) \_\_\_\_\_

List all other laboratory numbers associated with this sample set: \_\_\_\_\_

---

**Attach all sheets associated with the same sample set for data entry, reporting, filing:**

Well owner \_\_\_\_\_

Location of well from which samples were taken \_\_\_\_\_

Sampling date \_\_\_\_\_ Date of Receipt at Laboratory \_\_\_\_\_

Delivered by \_\_\_\_\_

Received by \_\_\_\_\_

Extraction date \_\_\_\_\_ Analyst \_\_\_\_\_

Analysis date: Begin \_\_\_\_\_ Analyst \_\_\_\_\_

End \_\_\_\_\_

Comments:

Analytical Method No.   4  

Internal standard added \_\_\_\_\_ Surrogate standard added \_\_\_\_\_

Associated laboratory QA/QC sample nos. \_\_\_\_\_

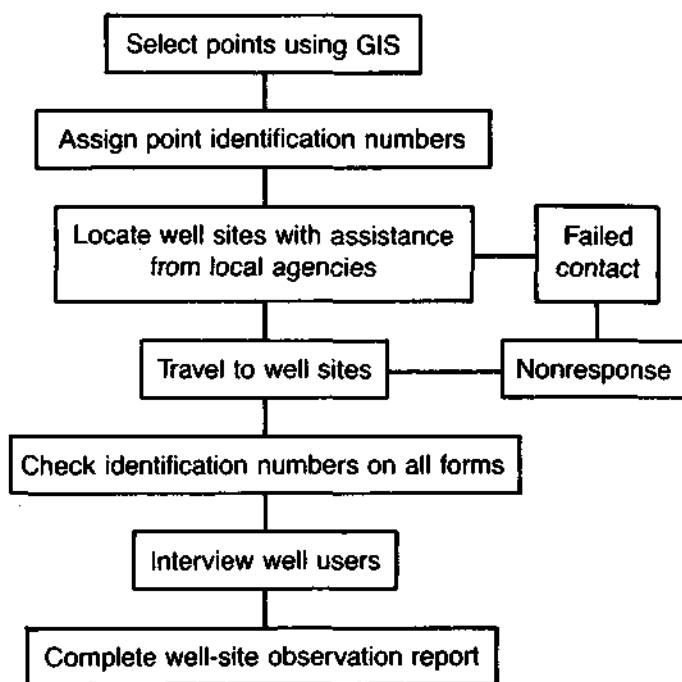
<i>Compound</i>	<i>Units</i>	<i>Analytical Results</i>
<small>(For each method, the compounds to be analyzed will be listed on the form)</small>		
internal standard	_____	_____
surrogate standard	_____	_____
atrazine dealkylated	_____	_____
carbofuran phenol	_____	_____
cyanazine	_____	_____
linuron	_____	_____
metribuzin DA	_____	_____
metribuzin DADK	_____	_____
metribuzin DK	_____	_____

## Field Procedures

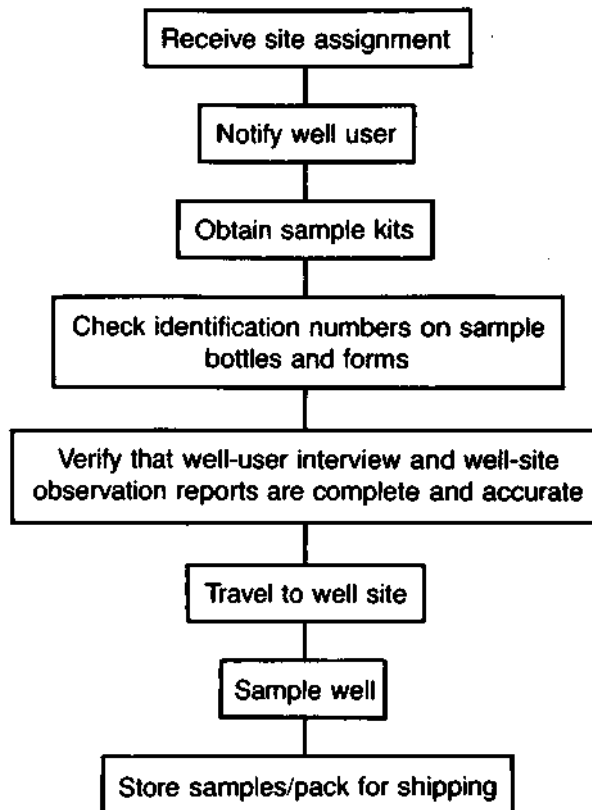
In general, field procedures would consist of two phases: (1) locating well sites, interviewing well users, and recording site characteristics; and (2) collecting samples. Detailed protocols should be developed, not only for training of personnel but also for documenting procedures. Thorough training of all personnel (field, laboratory, and management) should be completed before collection of any field samples.

**Well-site location and interview procedure** (fig. 11) As discussed in the section, *Sampling Plans-Well Selection*, the Geographic Information System (GIS) should be used to generate a list of points from which the actual well sites should be located. The maximum allowable distance of a well site from the GIS point will depend upon the final polygon size and should be established before the well selection begins; the maximum distance rule will prevent the selection of wells outside the boundary of the polygon. The field team should sample the well closest to the GIS point. If two well locations are equidistant from the GIS point, the team should randomly pick one well to sample and contact the well user. If contact cannot be made after a reasonable effort, the team should treat that well as a nonresponse.

Determination of well locations is followed by assignment of identification numbers (see section, *Sample Custody, Tracking, Laboratory Coordination-Sample Tracking Scheme*). After receiving the list of points (each with distinct locational information), the field teams should contact the Soil and Water Conservation Districts, Soil Conservation Service, County Cooperative Extension Service, Agricultural Stabilization and Conservation Service, Farm Bureau, and other local agencies for assistance in locating wells closest to the GIS-generated point. The field team should then set up appointments and travel to the well site to complete the well-site observation report (Appendix E) and to conduct the well-user interview (Appendix F). In addition to the well-user's name, address, and telephone number, the well-user interview is designed to collect information concerning the well site, location, well construction, use of the area surrounding the well, and pesticide use. The well-site observation report is intended to compile information about the physical surroundings of the well.



**Figure 11** Flow chart of recommended well-site location and interview process.



**Figure 12** Flow chart of recommended sampling process.

The success of this plan depends on gaining the cooperation of private well users. At the interview, the field team should describe the program and assure the well user that the results from the analysis of samples from their wells will be reported to them within a reasonable time. A handout describing the statewide survey should be given to each well user. If the well user is someone other than the well owner, a copy of the results will also be sent to both persons.

Researchers conducting the interviews should also explain that a field team will return at a later date to collect samples. For this reason, they must obtain information regarding the tap from which the sample will be collected—whether it is closed during winter, has a nonstandard fitting, or if the water is chemically treated. They must also clearly explain to the well user how long they may have to pump the well to collect a representative sample.

After well selection, the next phase would be the sample collection (fig. 12). The field teams should receive the well-site assignments, notify the well-user of the sampling date, then obtain their sample kits and travel to the well location. Also, they should check the identification numbers on all forms and bottles and verify that the user-interview and well-site observation report has been completed. Sample collection, which is described in the following section, should then proceed.

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### Illinois Statewide Agricultural Chemical Survey

Identification no. (base no.) 3647  
Well user John Q. Public  
Well location Sec. 12, T48N, R3E  
Sample collector James L. Sampler  
Sampling date 10/23/90 Sampling time 15:55  
pH 7.4 Temperature (°C) 12

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**Figure 13** Sample field measurements form.

**Sample collection** Collection bottles and preservatives for samples, replicates, spikes, and blanks should be prepared and assembled into kits in the laboratory, as described in the *Kit Preparation* section. Since individual samples for each analytical method will be collected at each site, individual sample identification numbers should be assigned and carried through the entire analytical process.

To allow for constant monitoring of the pH, electrical conductivity (EC) and temperature of the well water, we recommend using a flow-through cell (for example, that designed by Garske and Schock [1986]). Suggested modifications to the cell include the deletion of redox (Eh) electrodes and the addition of closed glass tubes to allow for pH electrode calibration at the sample temperature. Teflon tubing should be used to transport the water from the water source to the flow-through cell. The Teflon tubing should be covered with foam pipe insulation to minimize temperature fluctuations due to ambient conditions.

Water should be run from the sampling outlet for approximately 15 minutes at a rate of 6 to 12 gallons per minute through the Teflon tubing before the flow-through cell is connected. The flow-through cell should then be connected and the water allowed to flow through the cell. EC and temperature should be monitored at this time. Since the electrical conductivity measurements will be used only to monitor sample stabilization, temperature compensation and checks against standards need not be performed. However, the EC meter should be checked in the laboratory before and after each sampling trip, and the results kept in a log book. After the sample temperature has stabilized, the pH electrodes should be calibrated using buffers equilibrated to the sample temperature in the closed glass tubes. After calibration, the pH measurement should be taken and the electrodes re-calibrated for a second measurement. Measurements of temperature and pH should then be recorded on a field measurements form (fig. 13).

Water samples should then be collected using a valve system to bypass the flow-through cell (Barcelona, 1983). The tubing and flowthrough cell should be flushed with sample water for a minimum of 15 minutes before samples are collected. The valve system should also have a Teflon T-splitter (divider) for simultaneous collection of duplicate samples.

When the field teams return to the laboratory, the Teflon tubing should be cleaned by flushing with deionized water for a minimum of 10 minutes. Also, the tubing and the flowthrough cell should be inspected at that time for cracks, residues, or any other flaws.

**Sample storage and handling** After collection, the water samples must be stored at 4° C in refrigerators or on ice in coolers, and the temperature of the storage container recorded in the field log book. If stored on ice, the bottles should be sealed in plastic bags to eliminate potential leakage into or from the sample bottles. The laboratory manager should check 10 percent of the samples received to ensure that the bags are still completely sealed. The manager should also check to determine that the temperature of the samples is still acceptable.

When the samples arrive at the laboratory for organic-compound determinations, they should be logged in and stored away from light at 4° C until extraction. Samples must be extracted within 14 days of sample collection, unless shorter storage times are indicated by time-storage studies. Each laboratory should conduct time-storage studies for all compounds, unless data are available from the USEPA NPS Pilot Survey or other sources. Sample extracts should also be stored at 4° C away from light in explosion-proof refrigerators until analysis. Analyses should be performed within 14 days of extraction.

Samples for nitrate-nitrogen analysis should be logged in and stored at 4° C; these samples should be analyzed within 30 days of collection.

Dates of collection, laboratory receipt, extraction, and analysis should be recorded for each sample on the chain-of-custody form and the sample analysis forms. The sample collection and receipt dates should be recorded in a log book at the time the sample is received in the laboratory or before delivery to the laboratory by the field team or the laboratory staff. Verification that the appropriate tasks were performed within the specified time intervals will then be possible.

QA/QC requirements are summarized in figure 14. At least 10 percent of the sample wells should be randomly selected for collection of duplicate samples. Trip blanks, which are samples of laboratory water exposed to field and sampling conditions, should be included at a minimum of 5 percent of the sample sites. Field spikes, consisting of collected samples spiked with known concentrations of analytes, should also be included at a minimum of 5 percent of the sample sites. Spiked concentrations should be one to five times greater than the estimated detection limit for that compound (Mason et al., 1987).

During the analytical process, samples for organic analysis and method blanks should be spiked with surrogate and internal standards as described by the USEPA (Mason et al., 1987). A minimum of 10 percent of the samples should be analyzed in replicate for both the inorganic and organic analyses. Ten percent of the analyzed samples should also be spiked with known concentrations of analyte(s) as a quantification check (Mason et al., 1987).

It is also recommended that a minimum of 10 percent of the positive identifications of pesticides be confirmed by gas chromatography/mass spectroscopy (GC/MS). Three percent of the samples should be sent for complete analysis by GC/MS.

### **Analytical Methods**

Methods developed for the USEPA NPS are recommended for use in this survey. Method summaries are presented here (Mason et al., 1987). Specific conditions for detection of the analytes are given in the USEPA's full descriptions of methods (1987c).

**NPS 1: determination of nitrogen- and phosphorus-containing pesticides** A measured volume of sample (approximately 1 L) is solvent-extracted with methylene chloride by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried, and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chromatographic conditions permit the separation and measurement of the analytes in the extract by gas chromatography (GC) with a nitrogen-phosphorus detector (NPD). Priority analytes detected with this method include

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

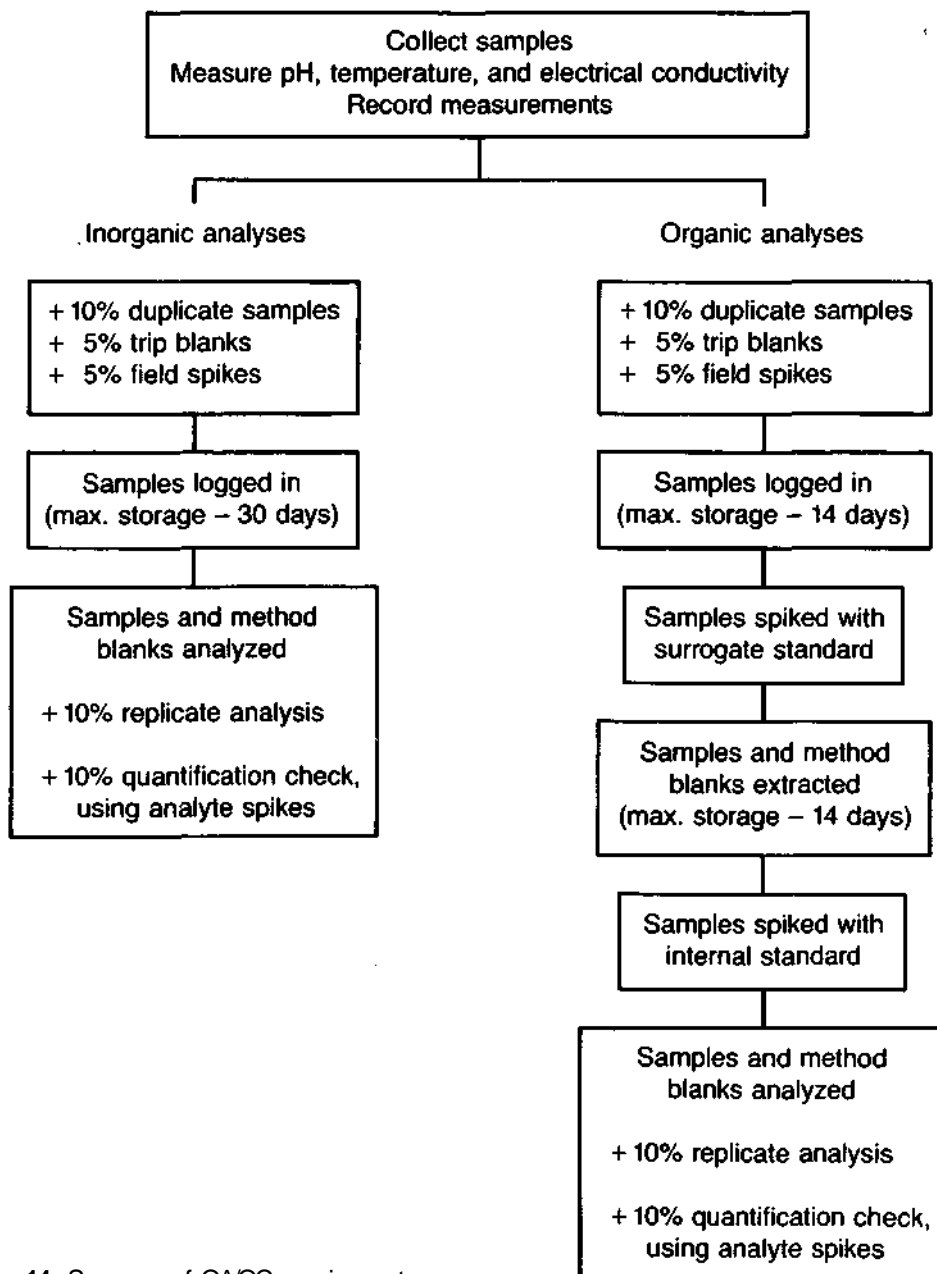


Figure 14 Summary of QA/QC requirements.

**NPS 2: determination of chlorinated pesticides** A measured volume of sample (approximately 1 L) is solvent-extracted with methylene chloride by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried, and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by gas chromatography (GC) with an electron capture detector (ECD). Priority analytes detected by this method include

aldrin	endrin	heptachlor epoxide
chlordane	endrin aldehyde	propachlor
DDT	heptachlor	trifluralin
dieldrin		

**NPS 3: determination of chlorinated acids** A measured volume of sample (approximately 1 L) is adjusted to pH 12 with 6 N sodium hydroxide and shaken for 1 hour to hydrolyze derivatives. Extraneous organic material is removed by a solvent wash. The sample is acidified, and the chlorinated acids are extracted with ethyl ether by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The acids are converted to their methyl esters using diazomethane as the derivatizing agent. Excess derivatizing reagent is removed, and the esters are determined by gas chromatography (GC) using an electron capture detector (ECD). The method provides a Florisil cleanup procedure to aid in the elimination of interferences that may be encountered. Priority analytes detected with this method include

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

**NPS 4: determination of pesticides in groundwater by high-performance liquid chromatography with an ultraviolet detector** A measured volume of sample (approximately 1 L) is solvent-extracted with methylene chloride by mechanical shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried, and concentrated to a volume of 5 mL after solvent substitution with methanol. Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector. Priority analytes detected with this method include

atrazine dealkylated	linuron	metribuzin DADK
carbofuran phenol	metribuzin DA	metribuzin DK
cyanazine		

**NPS 5: measurement of N-methylcarbamoyloximes and N-methylcarbamates** The water sample is filtered and a 400  $\mu$ L aliquot is injected into a reverse phase HPLC column. Separation of the analytes is achieved using gradient elution chromatography. After elution from the HPLC column, the analytes are hydrolyzed with 0.05 N sodium hydroxide (NaOH) at 95° C. The methyl amine formed during hydrolysis is reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent derivative that is detected by a fluorescence detector. Priority analytes detected with this method include

carbaryl	carbofuran
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**NPS 9: measurement of nitrate-nitrogen by cadmium reduction** A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (the original content plus the reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure both with and without the Cu-Cd reduction step.

#### Quality Assurance/Quality Control Procedures

Before beginning a full-scale survey, a formal QA/QC plan should be developed and submitted to the funding agency for review. (Appendix D contains detailed guidelines.) The objective is to ensure that the data obtained are of known, high quality and meet specified requirements of accuracy and precision. The plan should document and verify the procedures under which the data are obtained, formalize quality assurance functions, assign responsibilities, and provide information for project managers. The QA/QC plan should cover the following areas:

- introduction
- project description: objectives, experimental design, schedule, and project organization
- quality assurance objectives
- sampling and analytical procedures (including QA/QC procedures)

- acceptance criteria for precision, bias, representativeness, completeness, and comparability
- sample custody and management
- data reduction and validation
- system and performance audits
- preventative maintenance procedures
- corrective action

**Project Organization and Responsibilities**

The *project manager* would be responsible for the overall operation of the proposed project (fig. 15), including planning, management, cost control, and reporting. He would also supervise the use of the GIS to select random points for locating wells to sample, and assign the well-site base identification numbers. Another important task would be the assignment of specific responsibilities to other staff. Through regular staff meetings, the project manager would ensure open communication between the field, laboratory, quality control, and management teams.

The *quality assurance (QA) officer* would implement and monitor all QC measures to ensure that the data meet the standards for accuracy, precision, and completeness as specified in the formal QA/QC plan. He should also work with the project manager on the random selection of sites for QA/QC samples.

The *laboratory managers* would train the technical staff and ensure that correct procedures are followed. They would determine specific sample-container storage and transport procedures, oversee analytical scheduling, and supervise the recording and computerization of analytical results. They would also supervise the regular calibration of field instrumentation as well as the recording of QA/QC information for the laboratory.

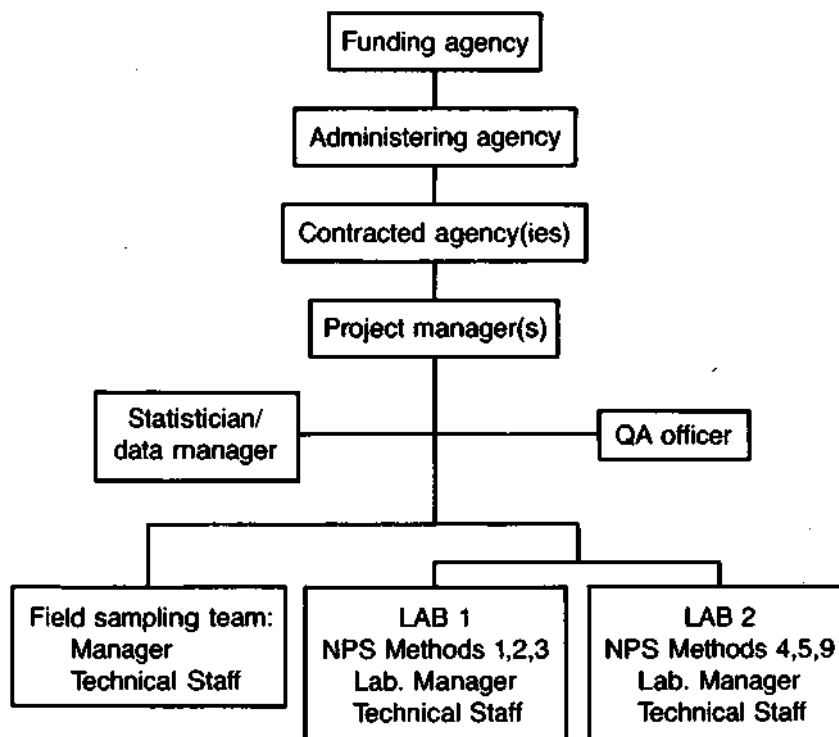


Figure 15 Recommended project organization.



The field team manager would train field sampling personnel to locate the closest well to the GIS-selected sample point, administer questionnaires, maintain chain-of-custody, and to collect, store, and transport samples. The field manager and the QA officer would work together to ensure that correct procedures are followed and representative samples collected.

The project statistician or data manager, together with the project manager and QA officer, would be responsible for the implementation of a computerized, integrated sample tracking and data management program. Each well sampled would have many associated attributes, including results of analyses for pesticides, responses to well-user interviews, and locational data. A relational database compatible with or transferable to GIS should be developed to allow for statistical analysis of water-quality data, and the generation of maps for display and interpretation. The statistician would also be responsible for the statistical analysis of data as described in the *Experimental Design-Analysis of Data* section of this report.

### **Report of Results to Well Users**

The report would contain a list of the compounds for which analyses were performed, and any positive results measured, as well as any results that exceed any regulatory or recommended levels. If problems are evident (i.e. results exceed regulatory levels), recommendations as to whom to contact would be given to the well-user and/or well-owner. The notification report would also contain the general background information collected about the well from the interview, the observation of the well site, and the Surveys' records search. This part of the notification can serve as a further check on the well site information, especially if the report is accompanied by a pre-paid post card that will be returned by the user to verify that he has received the report and to indicate whether there are any errors in the information on the report form, whether he is willing to have further samples taken if needed, whether he has any questions about the results, and if he has any comments about the conduct of the project staff.

### **Estimated Costs**

The estimated total cost of the statewide survey of the occurrence of agricultural chemicals in rural, private, water wells is \$2.3 million for a 2-year period. This estimate is based on the experimental design proposed in this study and the assumption that new staff and equipment would be required by each of the agencies in order to implement the statewide survey. These estimates also assume that laboratory and office space are presently available and that there will be no costs for space or basic support services; however, this assumption may not be correct. Information from the pilot study (see *Recommendations* section) should permit more accurate estimates of the costs of implementing the various phases of this experimental design.

The total cost per well sampled would be approximately \$1440. By comparison, the estimated total cost per well sampled in the National Pesticide Survey is \$7000 (Kotas, personal communication, 1988). Approximately one-half of the per-sample cost is for the purchase of necessary equipment, project management, and QA/QC.

An initial estimate of the costs associated with locating, characterizing, and sampling the approximately 1600 wells in the four strata is \$600,000. This estimate is based on the anticipated costs for implementing the specific procedures recommended in this experimental design. The estimated costs for analyzing 1600 well samples (plus necessary QA/QC samples) with the six NPS methods is \$1.2 million. If additional analytes that could not be analyzed with the NPS methods were included, laboratory costs would be substantially higher.

The estimated project management cost is \$500,000 over a 24-month period. These costs include computers and software for tracking and analysis of data, report preparation, and general management of the project. Recommended project staff include the project manager and assistant, a statistician, a data-entry-data-reduction technician, a secretary, and a quality assurance officer.

## RECOMMENDATIONS

### Implementation of a Statewide Survey

For the initial statewide survey of the occurrence of agricultural chemicals in groundwater, we recommend this experimental design including the following key elements:

- sample population defined as rural, private water wells,
- analytes recommended on the basis of their usage in Illinois and their potential to contaminate groundwater,
- stratified random sampling with the potential for contamination of shallow aquifers as the stratification variable,
- sampling plan for random selection of wells within each of the strata,
- well-sampling schedule that addresses the potential for temporal variability in the occurrence of agricultural chemicals,
- procedures for locating and characterizing well sites,
- protocols for sample collection, transport, storage, and analysis,
- procedures for quality assurance/quality control,
- recommendations for project organization and management,
- recommendations for data management, statistical analysis, and interpretation.

We also recommend that the statewide survey be conducted jointly by the Illinois Department of Agriculture (IDOA), the Illinois Department of Public Health (IDPH), and the Illinois Department of Energy and Natural Resources (DENR). The IDOA has regulatory authority over the marketing and use of pesticides in Illinois. The IDPH has regulatory authority over private water wells and routinely samples private wells for nitrates and bacterial contamination. The State Water Survey and State Geological Survey Divisions of DENR are mandated to conduct basic and applied research related to groundwater protection.

The State Surveys should be primarily responsible for implementing a pilot study, including development of the analytical methods, field testing of the procedures for the experimental design proposed in this report, and training of IDOA and IDPH personnel in procedures for characterizing well sites and collecting samples.

For the statewide survey, the IDOA and IDPH should be responsible for on-the-ground identification of the well sites, well-user interviews and well-site inventories, collection and chemical analyses of water samples, quality assurance/quality control procedures, notification of well users, and report preparation. The State Surveys' role in implementation of the statewide survey should include modifications to the experimental design on the basis of pilot study results, mapping of the contamination-potential strata, GIS-related aspects of well selection, and verification of well information. The Surveys should also assist in analyzing and interpreting the results of the statewide survey, maintain the overall database, and undertake research regarding the fate of agricultural chemicals in the environment.

If the funding level for this project should be substantially lower than necessary to implement the experimental design, we would recommend reductions in

- *analytical methods*--for example, eliminating NPS methods 4 and 5 would result in substantial savings on analytical equipment and personnel; however, costs of project administration and sample collection would not be reduced, and information on the presence of nine pesticides and degradation products would not be available (see section, *Analytical Methods*).
- *the number of subpopulations (strata)*--resulting, of course, in a proportional decrease in the number of samples to be collected and analyzed. However, field and laboratory costs would not be proportionally less. Project administration costs would not be reduced significantly. If this alternative were to be pursued, we would recommend that the subpopulations not be combined. Elimination of one or both of the middle strata would be preferable.

Another option, which is not recommended, is to reduce the sample size in each stratum. As discussed previously, a reduction in the number of samples collected from each stratum would significantly affect the confidence level or precision of the estimates made, and consequently, the ability to make valid inferences regarding the occurrence of agricultural chemicals in rural, private wells.

### **Pilot Study**

The Illinois State Geological Survey and the Illinois State Water Survey have received funding to conduct a pilot study in cooperation with the Illinois Department of Agriculture (IDOA). Specific objectives of the pilot study are to

- evaluate the validity of using the proposed contamination potential ratings as a strata criteria by assessing the occurrence of agricultural chemicals in rural private wells in representative hydrogeologic settings in the state;
- implement the National Pesticide Survey (NPS) analytical methods and establish quality assurance/quality control procedures;
- field test the well selection procedures;
- field test procedures to inventory well sites, conduct well-user interviews, and collect water samples (including use of sampling equipment, documentation of sample custody, and proper storage and transportation of samples);
- train IDOA and IDPH sampling teams in these procedures;
- establish information management techniques, including database development for sample custody and tracking, laboratory management, compilation of analytical results, and report generation.

With these results providing estimates of the probability of agricultural chemicals occurring in the four contamination potential strata proposed in this study, we may be able to propose reductions in the number of samples to be collected and analyzed, yet maintain the same levels of confidence and precision. For example, if the results of the pilot study indicate the highest estimated level of occurrence in any stratum to be 30 percent, compared to the conservative estimate of 50 percent used in this experimental design, the required number of samples for each stratum could be reduced to 322 from 384; and the required number of samples for all four subpopulations (strata) could be reduced by nearly 250 samples. If the highest level of occurrence is 20 percent, a total of 552 fewer samples would be required (see *Selection of Sample Size* section). Any substantial reduction in sample size would result in significant cost savings.

A tentative initial schedule for completion of the pilot study and the statewide survey is shown in table 13. The actual scheduling and timing of the statewide survey would depend upon an evaluation of the procedures and results of the pilot study, which would help identify difficulties and alternative procedures. Proper scheduling and coordination among the three agencies is essential to ensure completion of the statewide survey.

### **Long-Term Monitoring and Research Needs**

The experimental design proposed in this study is intended to determine in a statistically valid manner the extent and magnitude of the occurrence of agricultural chemicals in rural, drilled, private water-supply wells. Study results will be limited to the sample population and to the year in which samples are collected. This statewide survey will not provide data on the extent of agricultural chemical contamination of other types of wells, such as public water-supply wells, nor will it assess the water quality in aquifers.

**Table 13** Tentative initial schedule for pilot study and statewide survey

	Months	FY89	FY90	FY91	FY92	FY93
<i>Pilot Study</i>						
Method development	12	X				
Well selection	4	X				
Sample collection	12		X			
Sample analysis	15	X	X			
Training	4			X		
Report	8			X		
<i>Statewide Survey</i>						
Well selection/characterization	12			X		
Sample collection	12				X	
Sample analysis	15				X	
Report	8					X

Therefore, we recommend that the comprehensive long-term groundwater monitoring program mandated in the Illinois Groundwater Protection Act include, as an integral component, an assessment of potential groundwater contamination by agricultural chemicals. A comprehensive monitoring plan should contain the following elements:

- database management to assess trends and evaluate programs.
- continued monitoring of rural private wells by the IDPH and IDOA as warranted by the results of the statewide survey,
- expansion of the current monitoring of public water supply wells by the IEPA,
- research monitoring by the ISGS and ISWS,

**Database management** The Illinois State Surveys should develop and maintain a comprehensive GIS-compatible or transferable database on agricultural chemicals in groundwater in Illinois. The database should include results from routine monitoring by state agencies, special purpose monitoring by state and local agencies, and research by ISGS, ISWS, and university scientists. Information from the database should be used to identify areas for special investigations and to evaluate educational and regulatory programs.

**Monitoring rural private wells** The IDPH and the IDOA should institute a long-term monitoring program for rural private wells. Determination of sampling frequency in various areas of the state should be based on the results of the initial statewide survey and modified as additional data are obtained during the monitoring program. For example, we anticipate that private wells in areas of the state where aquifer materials lie at or near land surface will have a significantly higher occurrence of agricultural chemicals than areas where materials lie at greater depths; those areas with a higher frequency of contamination should be sampled every 2 years. Areas of the state where private wells have not significantly affected by agricultural chemicals might be sampled at 5-year intervals. This long-term monitoring should identify trends in water quality and be useful in assessing the effectiveness of any educational or regulatory programs that might be implemented.

**Monitoring large-diameter dug and bored wells** Because of their design and generally shallow depth, large-diameter dug and bored wells are highly susceptible to contamination from agricultural chemicals. Since inclusion of dug and bored wells might bias the assessment of the validity of using depth to the uppermost aquifer as a measure of contamination potential, these wells are not included in the sample population for the survey proposed in this report.

We recommend that these wells be treated as a special class and that these wells be sampled according to a simple random sampling plan. Dug and bored wells are not distributed uniformly across the state. Therefore, in order to limit the costs of conducting a survey of the occurrence of agricultural chemicals in these wells, we recommend that the study be restricted to areas of Illinois where more than 50 percent of the total number of wells are dug wells. Assuming the same conditions for estimating sample size as in the statewide survey of drilled wells, approximately 380 of these wells would have to be sampled.

**Monitoring private wells in suburban areas** There is growing concern about the potential for groundwater contamination from the use of lawn-care chemicals and household pesticides in urban and suburban areas. Per-acre application rates of lawn-care chemicals have been reported to be much higher than for agricultural uses.

The sample population in this proposed survey does not include urban and suburban areas in which private wells are used. Although many agricultural chemicals are used for nonagricultural purposes, a thorough evaluation of the potential contamination of private wells by nonagricultural uses of pesticides might require additional analyses, and therefore, might substantially increase the costs of the statewide survey.

We recommend that small-scale retrospective studies be conducted in several representative suburban areas of Illinois as an initial step to evaluate this potential problem. These studies should include analyses for the most commonly used lawn-care chemicals.

**Monitoring public water wells** We recommend that the IEPA expand its current monitoring program of public water-supply (PWS) wells by (1) conducting an initial random sampling stratified on the basis of the potential for contamination by agricultural chemicals, and (2) bi-monthly sampling of wells finished at shallow depths in unconfined aquifers. Stratified random sampling of these wells will permit more cost-efficient sampling and aid in identifying those classes of PWS wells most susceptible to contamination. Frequent sampling of wells finished in unconfined aquifers is recommended because unconfined aquifers generally have high recharge rates, and therefore, greater temporal variability in the occurrence of agricultural chemicals would be expected. In addition, the IEPA should expand its list of analytes to include those recommended for the statewide survey of private wells.

**Research monitoring** To increase understanding of the transport and fate of agricultural chemicals in the subsurface, improve our ability to predict contamination potential, and evaluate remediation alternatives, the ISGS and ISWS should develop a coordinated research program to investigate

- temporal variability in the presence of agricultural chemicals in groundwater in various hydrogeologic settings,
- effects of soil and hydrogeologic conditions in Illinois on the persistence and mobility of pesticides,
- potential for adsorption and degradation of pesticides in aquifers.

These objectives can be met by conducting small-scale prospective and retrospective studies in areas of the state with different soil and hydrogeologic conditions. Particular emphasis should be placed on identifying areas for which anomalous results were obtained in the statewide survey. The studies should include detailed characterizations of aquifers and overlying materials by controlled drilling and installation of monitoring wells, frequent sampling of those monitoring wells, and collection of soil cores for pesticide analyses. Soil core studies will be particularly valuable in identifying areas where pesticides have leached below the crop root zone but have not yet reached an aquifer.

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## APPENDIX A. Pesticide Usage and Properties Data

The selection of priority analytes was based on the usage and properties of pesticides as well as the recommendations made by regulatory officials and researchers at the University of Illinois. This appendix presents data summaries for the pesticides listed in tables 5 and 6 in the section, *Selection of Analytes*. Pesticide degradation products (metabolites) are not included.

### Explanation of Data Summaries

Common name	Common name by which the compound active ingredient is known. Common names are approved by the American National Standards Committee.
Trade names	Trademarked names under which the compound is marketed. Parentheses following a specific trade name indicate that that trade name compound is marketed as a mixture of two compounds. The name in parentheses is the common name of the other compound in the mixture.
USEPA priority analyte	Compound that because of its leaching potential was designated as being of particular interest to the U.S. Environmental Protection Agency (USEPA) for the National Pesticide Survey (NPS).
USEPA NPS method no.	Refers to the analytical method developed by the USEPA for the NPS, used for determination of that compound. The method summaries are given in <i>Experimental Design-Analytical Methods</i> .

### Usage

Type	Indicates the primary type of use for the compound: herbicide for weed control, insecticide for insect control, and fungicide for fungus control.
Crop use	Indicates the principal crops in Illinois on which this compound and/or mixtures of this compound are used.
Total acres	Total Illinois acres on which the compound and/or mixture of this compound was reported to be used on the crops listed above (crop use) for the year indicated. The individual compounds may be registered for use on additional crops, but the acreages of use for these crops were not compiled by the sources cited. The following references were used for compilation of this data: <ul style="list-style-type: none"><li>• 1969 - Pesticide use by Illinois farmers 1969, Illinois Department of Agriculture, compiled by the Illinois Cooperative Crop Reporting Service, Springfield, Illinois</li><li>• 1985 - Illinois major crop pesticide use and safety survey report, David R. Pike, State Coordinator, Pesticide Impact Assessment Program, Department of Agronomy, University of Illinois at Urbana-Champaign</li><li>• 1987 - personal communication with Mr. William Curran, Department of Agronomy, University of Illinois at Urbana-Champaign</li></ul>
Typical rates	Range of rates at which the compound is applied to crops in Illinois.
Restricted use	A restricted use pesticide is available for purchase and use only by certified pesticide applicators or persons under their direct supervision and only for those uses covered by the Certified Applicator's certification. These pesticides are not available for use by the general public because of the very high toxicities and/or environmental hazards associated with these materials.

- Chemical Properties** Data for some of the chemical properties can vary depending upon experimental conditions under which they were collected. Thus, where applicable, references are given for the source of the data. The following letters refer to the Reference cited in this section:
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  - N Bostian, Arlin, 1988, personal communication, Rhone Poulenc.
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P Curran, William, 1988, personal communication, Department of Agronomy, University of Illinois at Urbana-Champaign.

Chemical class General chemical classification of the pesticide active ingredient.

Chemical formula Chemical formula for the active ingredient of the compound.

Molecular weight Molecular weight in grams per mole of the compound active ingredient.

Water solubility Solubility of the compound active ingredient in water (the maximum amount that can be dissolved in water). The given number is the highest value reported in the references cited. Solubility varies with temperature, and the specified temperature, if available, is given in degrees Celsius.

Organic carbon partition coefficient ( $K_{oc}$ ) A proportionality constant that represents the normalization of the adsorption coefficient ( $K_d$ ) by the organic carbon content of the soil (adsorbent). When data were not available in the references cited,  $K_{oc}$  was calculated using the following equation:  $\log K_{oc} = 3.95 - 0.62 \log S$ , where S equals the water solubility in mg/L (Hassett et al., 1983).

Adsorption coefficient ( $K_d$ ) A proportionality constant that represents the ratio of the amount of the compound adsorbed by the soil to the equilibrium concentration of the compound in solution. It was calculated using data for the organic carbon partition coefficient ( $K_{oc}$ ) at 1 percent organic carbon content using the following relationship:

$$K_d = \frac{K_{oc} \cdot \% \text{ organic carbon}}{100}$$

Vapor pressure Vapor pressure of the compound at the specified temperature (C = degrees Celsius). At this temperature and pressure the gas and liquid phases can coexist in equilibrium. The lowest vapor pressure found in the references is reported.

Henry's law constant ( $K_H$ ) This is a proportionality term that describes the ratio of the vapor pressure of an ideal gas (P) to its mole fraction (X) in a dilute solution using the relationship:  $K_H = P/X$

It can be estimated by dividing the vapor pressure of the gas or vapor by its solubility in water at the same temperature, where:

$$\begin{aligned} VP &= \text{vapor pressure in atmospheres} \\ S &= \text{water solubility in moles/m}^3 \\ K_H &= VP/S \end{aligned}$$

The Henry's law constant was calculated at the given temperature. If the temperature is not given, the constant was calculated using water solubility and vapor pressure data at different temperatures. In this case, the calculated Henry's law constant may be considered a rough estimate of the true value.

Half-life This is the time in days for one-half of the compound to degrade in the soil by hydrolysis, biodegradation, or photolysis. Values given are the maximum number of days cited if a range of days was given in the references. The half-life values reported represent the degradation of the compound in a soil

environment and may not be representative of purely photochemical, biochemical, or other half-life processes. Half-life data and degradation rates can vary greatly due to experimental conditions, such as soil properties, temperature, and moisture content. Consequently, it is difficult to compare half-life data from different sources.

**Health Risk Information** Health risk information was obtained from USEPA Health Advisories (USEPA, 1987). Health Advisories describe nonregulatory concentrations of drinking water contaminants at which adverse health effects would not be anticipated to occur over specific exposure durations. Health Advisories contain a margin of safety to protect sensitive members of the population. They are not to be construed as legally enforceable Federal standards and are subject to change as new information becomes available.

Health Advisories are developed for One-day, Ten-day, Longer-term, and Lifetime exposures based on data describing noncarcinogenic end points of toxicity. They do not quantitatively incorporate any potential carcinogenic risk from such exposure.

Longer term health advisory Nonregulatory concentration (microgram/liter) of drinking water contaminant at which adverse health effects would not be anticipated to occur over approximately 7 years, or 10 percent of an individual's lifetime.

Lifetime health advisory Nonregulatory concentration (microgram/liter) of drinking water contaminant at which adverse health effects would not be anticipated to occur over an individual's lifetime. It represents that portion of an individual's total exposure that is attributed to drinking water and is considered protective of noncarcinogenic adverse health effects over a lifetime exposure. The Lifetime Health Advisory is derived in a three-step process (USEPA, 1987). For those substances that are known or probable human carcinogens (see Carcinogenicity group), Lifetime Health Advisories are not recommended.

Carcinogenicity group This represents the classification of the compound into a carcinogenicity group (USEPA, 1987) as follows:

- A - known human carcinogen
- B - probable human carcinogen
- C - possible human carcinogen
- D - not classified
- E - evidence of non-carcinogenicity for humans

Maximum allowable concentration (MAC) The maximum concentration (microgram/liter) of the compound allowed in the drinking water supply. The MAC is established by the Illinois Pollution Control Board and is equivalent to Illinois finished drinking water standards. The Safe Drinking Water Act and the Illinois Pollution Control Board Chapter 6 Rules and Regulations require that the owner of a public water supply notify the water consumers when the supply fails to meet an MAC of any parameter (Good and Taylor, 1987).

## Pesticide Data Summaries

<b>Common name</b>	2,4-D
Trade names	2,4-D
USEPA priority analyte	yes
USEPA NPS method no.	3
<b>Usage</b>	
Type	herbicide
Crop use	com, grain
Total acres	1969 - 3,702,000 1985 - 2,153,000 1987
Typical rates	0.25 to 2 lbs active ingredient per acre
Restricted use	no
<b>Chemical Properties</b>	
Chemical class	phenoxyaliphatic acid
Chemical formula	C <sub>8</sub> H <sub>6</sub> Cl <sub>2</sub> O <sub>3</sub>
Molecular weight	221.00
Water solubility	900 mg/L at 25° C (Reference: B,D)
Organic carbon partition coefficient (K <sub>oc</sub> )	20 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.2
Vapor pressure	5.26E-04 atm. at 160° C (Reference: D,E)
Henry's law constant	
Half-life	7.1 days (Reference: I)
<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	70 µg/L
Carcinogenicity group	D
Maximum allowable concentration	100 µg/L

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<b>Common name</b>	<b>2,4-DB</b>
Trade names	Butoxone, Butyrac
USEPA priority analyte	no
USEPA NPS method no.	3
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 - 19,999 1985 - 129,000 1987
Typical rates	0.2 to 2 lbs active ingredient per acre
Restricted use	no
<b>Chemical Properties</b>	
Chemical class	phenoxyaliphatic acid
Chemical formula	C <sub>10</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>3</sub>
Molecular weight	249.10
Water solubility	46 mg/L at 25° C (Reference: E)
Organic carbon partition coefficient (K <sub>oc</sub> )	830 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 8.3
Vapor pressure	
Henry's law constant	
Half-life	
<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

**Common name** acifluorfen  
Trade names Blazer, Tackle  
USEPA priority analyte yes  
USEPA NPS method no. 3

**Usage**  
Type herbicide  
Crop use soybeans  
Total acres 1969  
1985 - 519,000  
1987  
Typical rates 0.125 to 2 lbs active ingredient per acre  
Restricted use no

**Chemical Properties**  
Chemical class phenoxalipahatic acid (biphenyl ether)  
Chemical formula  $C_{14}H_6ClF_3NO_5Na$   
Molecular weight 383.70  
Water solubility 250,000 mg/L at 25° C (Reference: A)  
Organic carbon partition coefficient ( $K_{oc}$ ) 490 (Reference: C)  
Adsorption coefficient ( $K_d$ ) at 1.0% 4.9  
Vapor pressure 3.16E-02 atm. at 25° C (Reference: D)  
Henry's law constant 4.85E-05 atm. m<sup>3</sup>/mole  
Half-life 60 days (Reference: G)

**Health Risk Information**  
Longer term health advisory 437 µ g/L  
Lifetime health advisory 9 µ g/L  
Carcinogenicity group C  
Maximum allowable concentration

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**Common name** alachlor  
Trade names Lasso, Bronco (+glyphosate)  
USEPA priority analyte yes  
USEPA NPS method no. 1

**Usage**  
Type herbicide  
Crop use soybeans, com, grain  
Total acres 1969 - 342,000  
1985 - 4,590,000  
1987-4,441,000  
Typical rates 1.5 to 4 lbs active ingredient per acre  
Restricted use no

**Chemical Properties**  
Chemical class acetanilide  
Chemical formula  $C_{14}H_{20}ClNO_2$   
Molecular weight 269.77  
Water solubility 242 mg/L at 25° C (Reference: B,G)  
Organic carbon partition coefficient ( $K_{oc}$ ) 120 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 1.2  
Vapor pressure 2.89E-08 atm. at 25° C (Reference: D)  
Henry's law constant 3.22E-08 atm. m<sup>3</sup>/mole  
Half-life 18 days (Reference: I)

**Health Risk Information**  
Longer term health advisory  
Lifetime health advisory  
Maximum allowable concentration



**Common name** aldrin  
Trade names Aldrin, Aldrex  
USEPA priority analyte no  
USEPA NPS method no. 2

**Usage**  
Type insecticide  
Crop use com  
Total acres 1969 - 3,512,000  
1985  
1987

Typical rates  
Restricted use registration cancelled

**Chemical Properties**  
Chemical class cyclodiene  
Chemical formula  $C_{12}H_8Cl_6$   
Molecular weight 364.93  
Water solubility 0.013 mg/L (Reference: B)  
Organic carbon partition coefficient ( $K_{oc}$ ) 131,630 (calculated)  
Adsorption coefficient ( $K_d$ ) at 1.0% 1316.3  
Vapor pressure 3.29E-08 atm. at 20° C (Reference: B)  
Henry's law constant 9.24E-04 atm. m<sup>3</sup>/mole  
Half-life 2,190 days (Reference: N)

**Health Risk Information**  
Longer term health advisory  
Lifetime health advisory  
Carcinogenicity group  
Maximum allowable concentration 1 µg/L

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**Common name** atrazine  
Trade names Atrazine, Atrex  
USEPA priority analyte yes  
USEPA NPS method no. 1

**Usage**  
Type herbicide  
Crop use com, grain  
Total acres 1969 - 3,416,000  
1985 - 9,094,000  
1987 - 9,094,000

Typical rates 2 to 4 lbs active ingredient per acre  
Restricted use no

**Chemical Properties**  
Chemical class triazine  
Chemical formula  $C_6H_4ClN_5$   
Molecular weight 215.68  
Water solubility 70 mg/L at 25° C (Reference: A)  
Organic carbon partition coefficient ( $K_{oc}$ ) 160 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 1.6  
Vapor pressure 3.95E-10 atm. at 20° C (Reference: D)  
Henry's law constant 1.22E-09 atm. m<sup>3</sup>/mole  
Half-life 64 days (Reference: I)

**Health Risk Information**  
Longer term health advisory 123 µg/L  
Lifetime health advisory 3 µg/L  
Carcinogenicity group C  
Maximum allowable concentration

<b>Common name</b>	<b>bentazon</b>
Trade names	Basagran
USEPA priority analyte	yes
USEPA NPS method no.	3
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 1985 - 2,324,000 1987 - 3,420,000
Typical rates	0.75 to 2 lbs active ingredient per acre
Restricted use	no
<b>Chemical Properties</b>	
Chemical class	triazole (benzothiadiazole)
Chemical formula	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>
Molecular weight	240.28
Water solubility	500 mg/L at 20° C (Reference: A,D)
Organic carbon partition coefficient (K <sub>oc</sub> )	189 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 1.9
Vapor pressure	1.30E-14 atm. at 20° C (Reference: D,G)
Henry's law constant	6.25E-15 atm. m <sup>3</sup> /mole
Half-life	30 days (Reference: J)
<b>Health Risk Information</b>	
Longer term health advisory	875 µg/L
Lifetime health advisory	17.5 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

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<b>Common name</b>	<b>bromoxynil</b>
Trade names	Buctril, Brominal
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	herbicide
Crop use	corn
Total acres	1969 1985 - 277,000 1987 - 277,000
Typical rates	0.5 to 1 lbs active ingredient per acre
Restricted use	no
<b>Chemical Properties</b>	
Chemical class	nitrite
Chemical formula	C <sub>7</sub> H <sub>3</sub> BR <sub>2</sub> NO
Molecular weight	276.90
Water solubility	130 mg/L at 25° C (Reference: A,D)
Organic carbon partition coefficient (K <sub>oc</sub> )	436 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 4.4
Vapor pressure	6.32E-09 atm. at 25° C (Reference: N)
Henry's law constant	1.36E-08 atm. m <sup>3</sup> /mole
Half-life	14 days (Reference: N)
<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>butylate</b>
Trade names	Genate Plus, Sutan +
USEPA priority analyte	yes
USEPA NPS method no.	1
<b>Usage</b>	
Type	herbicide
Crop use	com
Total acres	1969 - 388,000 1985 - 2,679,000 1987 - 2,679,000
Typical rates	3 to 6 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	thiocarbamate
Chemical formula	C <sub>11</sub> H <sub>23</sub> NOS
Molecular weight	217.37
Water solubility	45 mg/L at 25° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	841 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 8.4
Vapor pressure	1.71E-06 atm. at 25° C (Reference: A,D)
Henry's law constant	8.26E-06 atm. m <sup>3</sup> /mole
Half-life	21 days (Reference: G)

<b>Health Risk Information</b>	
Longer term health advisory	2,400 µg/L
Lifetime health advisory	50 µg/L
Carcinogenicity group	C
Maximum allowable concentration	

<b>Common name</b>	<b>CDAA (allidochlor)</b>
Trade names	CDAA-T, Radox
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	herbicide
Crop use	com, soybeans, vegetables, fruit
Total acres	1969 1985 1987
Typical rates	4 to 5 lbs active ingredient per acre
Restricted use	manufacture discontinued (1984)

<b>Chemical Properties</b>	
Chemical class	amide
Chemical formula	C <sub>8</sub> H <sub>12</sub> ClNO
Molecular weight	173.65
Water solubility	20,000 mg/L at 25° C (Reference: G)
Organic carbon partition coefficient (K <sub>oc</sub> )	19.2 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.2
Vapor pressure	1.24E-05 atm. at 20° C (Reference: G)
Henry's law constant	1.07E-07 atm. m <sup>3</sup> /mole
Half-life	42 days (Reference: G)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

**Common name** carbaryl  
Trade names Sevin, Savit  
USEPA priority analyte yes  
USEPA NPS method no. 5

**Usage**  
Type insecticide  
Crop use com, hay  
Total acres 1969 - 23,000  
1985  
1987  
Typical rates 1 to 4 pints per acre  
Restricted use no

**Chemical Properties**  
Chemical class carbamate  
Chemical formula  $C_{12}H_{11}NO_2$   
Molecular weight 201.22  
Water solubility 120 mg/L at 30° C (Reference: A)  
Organic carbon partition coefficient ( $K_{oc}$ ) 229 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 2.3  
Vapor pressure 5.26E-08 atm. at 25° C (Reference: A)  
Henry's law constant 8.82E-08 atm.  $m^3/mole$   
Half-life 22 days (Reference: I)

**Health Risk Information**  
Longer term health advisory 3,500  $\mu g/L$   
Lifetime health advisory 700  $\mu g/L$   
Carcinogenicity group D  
Maximum allowable concentration

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**Common name** carbofuran  
Trade names Furadan  
USEPA priority analyte yes  
USEPA NPS method no. 5

**Usage**  
Type insecticide  
Crop use com  
Total acres 1969  
1985 - 197,000  
1987 - 197,000  
Typical rates 0.3 to 1.1 lbs active ingredient per acre  
Restricted use yes

**Chemical Properties**  
Chemical class carbamate  
Chemical formula  $C_{12}H_{15}NO_3$   
Molecular weight 221.26  
Water solubility 700 mg/L at 25° C (Reference: A,H)  
Organic carbon partition coefficient ( $K_{oc}$ ) 28 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 0.3  
Vapor pressure 2.63E-08 atm. at 33° C (Reference: H)  
Henry's law constant 8.32E-09 atm.  $m^3/mole$   
Half-life 40 days (Reference: I)

**Health Risk Information**  
Longer term health advisory 180  $\mu g/L$   
Lifetime health advisory 36  $\mu g/L$   
Carcinogenicity group E  
Maximum allowable concentration

<b>Common name</b>	<b>carboxin</b>
Trade names	Vitavax, DCMO
USEPA priority analyte	yes
USEPA NPS method no.	1

<b>Usage</b>	
Type	fungicide
Crop use	com, grains, soybeans
Total acres	1969 1985 1987
Typical rates	
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	oxathiin
Chemical formula	C <sub>12</sub> H <sub>13</sub> O <sub>2</sub> NS
Molecular weight	235.30
Water solubility	170 mg/L at 25° C (Reference: K)
Organic carbon partition coefficient (K <sub>oc</sub> )	369 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 3.7
Vapor pressure	
Henry's law constant	
Half-life	14 days (Reference: O)

<b>Health Risk Information</b>	
Longer term health advisory	3,500 µg/L
Lifetime health advisory	700 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

<b>Common name</b>	<b>chlomozone</b>
Trade names	Command, FMC 57020
USEPA priority analyte	no
USEPA NPS method no	

<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 1985 1987 - 720,000
Typical rates	0.75 to 1.0 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	isoxazolidinone
Chemical formula	
Molecular weight	239.70
Water solubility	1,100 mg/L (Reference: J)
Organic carbon partition coefficient (K <sub>oc</sub> )	116 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 1.2
Vapor pressure	1.90E-07 atm. at 25° C (Reference: H)
Henry's law constant	4.13E-08 atm. m <sup>3</sup> /mole
Half-life	75 days (Reference: J)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>chloramben</b>
Trade names	Amiben
USEPA priority analyte	yes
USEPA NPS method no.	3
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 - 2,586,000 1985 - 447,000 1987 - 360,000
Typical rates	2 to 4 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	arylaliphatic acid or benzoic acid
Chemical formula	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub> NO <sub>2</sub>
Molecular weight	206.02
Water solubility	700 mg/L at 25° C (Reference: A,D)
Organic carbon partition coefficient (K <sub>oc</sub> )	21 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.2
Vapor pressure	9.21E-06 atm. at 100° C (Reference: A,E)
Henry's law constant	
Half-life	42 days (Reference: G)

<b>Health Risk Information</b>	
Longer term health advisory	525 µg/L
Lifetime health advisory	105 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

Common name	chlordane
Trade names	Belt, Chlor Kil
USEPA priority analyte	no
USEPA NPS method no.	2
<b>Usage</b>	
Type	insecticide
Crop use	fruits, vegetables
Total acres	1969 1985 1987
Typical rates	
Restricted use	registration cancelled

<b>Chemical Properties</b>	
Chemical class	
Chemical formula	C <sub>10</sub> H <sub>6</sub> Cl <sub>8</sub>
Molecular weight	409.80
Water solubility	0.056 mg/L (Reference: B)
Organic carbon partition coefficient (K <sub>oc</sub> )	380,000 (Reference I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 3800
Vapor pressure	1.32E-08 atm. at 25° C (Reference: H)
Henry's law constant	9.63E-05 atm. m <sup>3</sup> /mole
Half-life	3,500 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	B2
Maximum allowable concentration	3.0 µg/L

<b>Common name</b>	<b>chlorpropham</b>
Trade names	Furloe
USEPA priority analyte	no
USEPA NPS method no.	1
Usage	
Type	herbicide
Crop use	soybeans
Total acres	1969
	1985 - 15,000
	1987 - 14,400
Typical rates	1 to 3 lbs active ingredient per acre
Restricted use	no

**Chemical Properties**

Chemical class	carbamate
Chemical formula	C <sub>10</sub> H <sub>12</sub> ClNO <sub>2</sub>
Molecular weight	213.68
Water solubility	88 mg/L at 20° C (Reference: D)
Organic carbon partition coefficient (K <sub>oc</sub> )	555 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 5.5
Vapor pressure	1.32E-08 atm. at 25° C (Reference: D)
Henry's law constant	3.20E-08 atm. m <sup>3</sup> /mole
Half-life	65 days (Reference: G)

**Health Risk Information**

Longer term health advisory  
Lifetime health advisory  
Carcinogenicity group  
Maximum allowable concentration

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<b>Common name</b>	<b>chlorpyrifos</b>
Trade names	Lorsban, Dursban
USEPA priority analyte	no
USEPA NPS method no.	
Usage	
Type	insecticide
Crop use	com
Total acres	1969
	1985- 1,642,000
	1987-1,642,000
Typical rates	1.0 to 1.2 lbs active ingredient per acre
Restricted use	no

**Chemical Properties**

Chemical class	heterocyclic organophosphate
Chemical formula	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS
Molecular weight	350.57
Water solubility	2 mg/L at 25° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	6,070 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 60.7
Vapor pressure	2.46E-09 atm. at 25° C (Reference: A)
Henry's law constant	4.31 E-07 atm. m <sup>3</sup> /mole
Half-life	63 days (Reference: I)

**Health Risk Information**

Longer term health advisory  
Lifetime health advisory  
Carcinogenicity group  
Maximum allowable concentration

**Common name** cyanazine  
Trade names Bladex  
USEPA priority analyte yes  
USEPA NPS method no. 4

**Usage**  
Type herbicide  
Crop use com  
Total acres 1969  
1985 - 1,429,000  
1987 - 1,429,000  
Typical rates 1 to 4 lbs active ingredient per acre  
Restricted use yes

**Chemical Properties**  
Chemical class triazine  
Chemical formula  $C_9H_{13}ClN_8$   
Molecular weight 240.68  
Water solubility 171 mg/L at 25° C (Reference: A,D,G)  
Organic carbon partition coefficient ( $K_{oc}$ ) 168 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 1.7  
Vapor pressure 2.11E-12 atm. at 20° C (Reference: A,D)  
Henry's law constant 2.96E-12 atm. m<sup>3</sup>/mole  
Half-life 13.5 days (Reference: I)

**Health Risk Information**  
Longer term health advisory 46 µg/L  
Lifetime health advisory 9 µg/L  
Carcinogenicity group D  
Maximum allowable concentration

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**Common name** DDT  
Trade names Anofex, Arkotine  
USEPA priority analyte no  
USEPA NPS method no. 2

**Usage**  
Type insecticide  
Crop use com, fruits, vegetables  
Total acres 1969  
1985  
1987  
Typical rates  
Restricted use registration cancelled

**Chemical Properties**  
Chemical class  
Chemical formula  $C_{14}H_9Cl_6$   
Molecular weight 354.50  
Water solubility 0.002 mg/L (Reference: B)  
Organic carbon partition coefficient ( $K_{oc}$ ) 240,000 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 2400.0  
Vapor pressure 1.97E-10 atm. at 20° C (Reference: A)  
Henry's law constant 4.12E-05 atm. m<sup>3</sup>/mole  
Half-life 3,837 days (Reference: I)

**Health Risk Information**  
Longer term health advisory  
Lifetime health advisory  
Carcinogenicity group  
Maximum allowable concentration 50.0 µg/L



<b>Common name</b>	<b>diazinon</b>
Trade names	Diazinon, D.z.n.
USEPA priority analyte	yes
USEPA NPS method no.	1
<b>Usage</b>	
Type	insecticide
Crop use	com
Total acres	1969 - 559,000 1985 1987
Typical rates	5.3 to 7.0 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	heterocyclic organophosphate
Chemical formula	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS
Molecular weight	304.36
Water solubility	40 mg/L at 20° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	85 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.9
Vapor pressure	1.84E-07 atm. at 20° C (Reference: A)
Henry's law constant	1.40E-06 atm. m <sup>3</sup> /mole
Half-life	25 days (Reference: M)

<b>Health Risk Information</b>	
Longer term health advisory	17.5 µg/L
Lifetime health advisory	0.63 µg/L
Carcinogenicity group	E
Maximum allowable concentration	

<b>Common name</b>	<b>dicamba</b>
Trade names	Banvel, Marksman (+Atrazine)
USEPA priority analyte	yes
USEPA NPS method no.	3
<b>Usage</b>	
Type	herbicide
Crop use	com
Total acres	1969 - 158,000 1985 - 1,621,000 1987 - 1,621,000
Typical rates	0.06 to 0.5 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	arylaliphatic acid or benzoic acid
Chemical formula	C <sub>8</sub> H <sub>6</sub> Cl <sub>2</sub> O <sub>3</sub>
Molecular weight	221.04
Water solubility	7,900 mg/L at 25° C (Reference: E)
Organic carbon partition coefficient (K <sub>oc</sub> )	2.2 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.02
Vapor pressure	4.49E-08 atm. at 25° C (Reference: D)
Henry's law constant	1.26E-09 atm. m <sup>3</sup> /mole
Half-life	14 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	50 µg/L
Lifetime health advisory	9 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

**Common name** dieldrin  
 Trade names Dieldrin, Dieldrex  
 USEPA priority analyte yes  
 USEPA NPS method no. 2

**Usage**  
 Type insecticide  
 Crop use corn  
 Total acres 1969 - 11,000  
 1985  
 1987  
 Typical rates  
 Restricted use registration cancelled

**Chemical Properties**  
 Chemical class cyclodiene  
 Chemical formula  $C_{12}H_8Cl_6O$   
 Molecular weight 380.93  
 Water solubility 0.022 mg/L (Reference: B)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 12,000 (Reference: I)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 120.0  
 Vapor pressure  $2.34E-10$  atm. at 20° C (Reference: B)  
 Henry's law constant  $4.05E-06$  atm.  $m^3/mole$   
 Half-life 868 days (Reference: I)  
**Health Risk Information**  
 Longer term health advisory 0.5  $\mu g/L$   
 Lifetime health advisory  
 Carcinogenicity group B2  
 Maximum allowable concentration 1.0  $\mu g/L$

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**Common name** dinoseb  
 Trade names Dyanap(+naptalam), Premerge  
 USEPA priority analyte yes  
 USEPA NPS method no. 3

**Usage**  
 Type herbicide  
 Crop use soybeans  
 Total acres 1969  
 1985- 170,000  
 1987 - 170,000  
 Typical rates 3 quarts per acre  
 Restricted use no

**Chemical Properties**  
 Chemical class dinitrophenol (phenol)  
 Chemical formula  $C_{10}H_{12}N_2O_5$   
 Molecular weight 240.20  
 Water solubility 52 mg/L at 25° C (Reference: D)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 124 (Reference: C)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 1.2  
 Vapor pressure  $1.32E-03$  atm. at 151° C (Reference: D,G)  
 Henry's law constant  
 Half-life 32 days (Reference: I)  
**Health Risk Information**  
 Longer term health advisory 35  $\mu g/L$   
 Lifetime health advisory 7  $\mu g/L$   
 Carcinogenicity group D  
 Maximum allowable concentration

**Common name** dlsulfoton  
Trade names Di-Syston  
USEPA priority analyte yes  
USEPA NPS method no. 1

**Usage**  
Type insecticide  
Crop use  
Total acres 1969  
1985  
1987  
Typical rates  
Restricted use yes

**Chemical Properties**  
Chemical class  
Chemical formula  $C_8H_{19}O_2PS_3$   
Molecular weight 274.38  
Water solubility 25 mg/L (Reference: B,H)  
Organic carbon partition coefficient ( $K_{oc}$ ) 1,600 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 16.0  
Vapor pressure  $2.37E-07$  atm. at  $20^\circ C$  (Reference: A)  
Henry's law constant  $3.99E-06$  atm.  $m^3/mole$   
Half-life 5 days (Reference: I)

**Health Risk Information**  
Longer term health advisory  $9 \mu g/L$   
Lifetime health advisory  $3 \mu g/L$   
Carcinogenicity group E  
Maximum allowable concentration

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**Common name** EPTC  
Trade names Genep, Eradicane  
USEPA priority analyte no  
USEPA NPS method no. 1

**Usage**  
Type herbicide  
Crop use com  
Total acres 1969  
1985 - 185,000  
1987 - 185,000  
Typical rates 2 to 6 lbs active ingredient per acre  
Restricted use no

**Chemical Properties**  
Chemical class thiocarbamate  
Chemical formula  $C_9H_{19}NO_5$   
Molecular weight 189.30  
Water solubility 370 mg/L at  $20^\circ C$  (Reference: D)  
Organic carbon partition coefficient ( $K_{oc}$ ) 280 (Reference: I)  
Adsorption coefficient ( $K_d$ ) at 1.0% 2.8  
Vapor pressure  $4.47E-05$  atm. at  $25^\circ C$  (Reference: G)  
Henry's law constant  $2.29E-05$  atm.  $m^3/mole$   
Half-life 30 days (Reference: I)

**Health Risk Information**  
Longer term health advisory  
Lifetime health advisory  
Carcinogenicity group  
Maximum allowable concentration

**Common name** endrin  
 Trade names  
 USEPA priority analyte yes  
 USEPA NPS method no. 2

**Usage**  
 Type insecticide  
 Crop use com, grains, vegetables  
 Total acres 1969  
 1985  
 1987  
 Typical rates  
 Restricted use most uses cancelled

**Chemical Properties**  
 Chemical class cyclodiene  
 Chemical formula  $C_{12}H_8Cl_6O$   
 Molecular weight 380.93  
 Water solubility 0.024 mg/L (Reference: B)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 90,005 (calculated)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 900.1  
 Vapor pressure 2.63E-10 atm. at 25° C (Reference: A,E)  
 Henry's law constant 4.18E-06 atm. m<sup>3</sup>/mole  
 Half-life 5,840 days (Reference: M)

**Health Risk Information**  
 Longer term health advisory 16 µ g/L  
 Lifetime health advisory 0.2 µ g/L  
 Carcinogenicity group E  
 Maximum allowable concentration 0.2 µ g/L

**Common name** ethalfluralin  
 Trade names Sonalan  
 USEPA priority analyte no  
 USEPA NPS method no.

**Usage**  
 Type herbicide  
 Crop use soybeans  
 Total acres 1969  
 1985 - 1,010,000  
 1987 - 900,000  
 Typical rates 0.5 to 2.25 lbs active ingredient per acre  
 Restricted use no

**Chemical Properties**  
 Chemical class aniline  
 Chemical formula  $C_{13}H_{14}F_3N_3O_4$   
 Molecular weight 333.30  
 Water solubility 0.300 mg/L at 25° C (Reference: G)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 18,801 (calculated)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 188.0  
 Vapor pressure 1.08E-07 atm. at 25° C (Reference: D,H)  
 Henry's law constant 1.20E-04 atm. m<sup>3</sup>/mole  
 Half-life 180 days (Reference: J)

**Health Risk Information**  
 Longer term health advisory  
 Lifetime health advisory  
 Carcinogenicity group  
 Maximum allowable concentration

<b>Common name</b>	<b>ethoprop</b>
Trade names	Mocap
USEPA priority analyte	no
USEPA NPS method no.	1
<b>Usage</b>	
Type	insecticide
Crop use	com
Total acres	1969
	1985-45,000
	1987 - 45,000
Typical rates	1.0 lbs active ingredient per acre
Restricted use	yes

<b>Chemical Properties</b>	
Chemical class	phosphorodithioate
Chemical formula	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>2</sub>
Molecular weight	242.32
Water solubility	750 mg/L at 25° C (Reference: A,H)
Organic carbon partition coefficient (K <sub>oc</sub> )	120 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 1.2
Vapor pressure	4.61 E-07 atm. at 26° C (Reference: A)
Henry's law constant	1.49E-07 atm. m <sup>3</sup> /mole
Half-life	35 days (Reference: N)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>fluazifop-butyl</b>
Trade names	Fusilade
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969
	1985 - 150,000
	1987 - 360,000
Typical rates	0.125 to 0.5 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	phenoxy propionate
Chemical formula	C <sub>19</sub> H <sub>20</sub> F <sub>3</sub> NO <sub>4</sub>
Molecular weight	383.38
Water solubility	2 mg/L at 23° C (Reference: G)
Organic carbon partition coefficient (K <sub>oc</sub> )	5,799 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 58.0
Vapor pressure	5.43E-10 atm. at 20° C (Reference: G)
Henry's law constant	1.04E-07 atm. m <sup>3</sup> /mole
Half-life	21 days (Reference: G)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>fonofos</b>
Trade names	Dyfonate
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	insecticide
Crop use	com
Total acres	1969 - 106,000 1985 - 651,000 1987-651,000
Typical rates	1.2 to 1.8 lbs active ingredient per acre
Restricted use	yes

<b>Chemical Properties</b>	
Chemical class	
Chemical formula	C <sub>10</sub> H <sub>15</sub> OPS <sub>2</sub>
Molecular weight	246.32
Water solubility	15.700 mg/L at 20° C (Reference: F)
Organic carbon partition coefficient (K <sub>oc</sub> )	68 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.7
Vapor pressure	2.76E-07 atm. at 25° (Reference: K)
Henry's law constant	4.33E-06 atm. m <sup>3</sup> /mole
Half-life	60 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	70 µ g/L
Lifetime health advisory	14 µ g/L
Carcinogenicity group	D
Maximum allowable concentration	

<b>Common name</b>	<b>glyphosate</b>
Trade names	Roundup
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	herbicide
Crop use	soybeans, com
Total acres	1969 1985 - 361,000 1987-361,000
Typical rates	0.3 to 4 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	substituted amino acid
Chemical formula	C <sub>3</sub> H <sub>8</sub> NO <sub>5</sub> P
Molecular weight	169.07
Water solubility	12,000 mg/L at 25° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	26.40 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.3
Vapor pressure	
Henry's law constant	
Half-life	60 days (Reference: G)

<b>Health Risk Information</b>	
Longer term health advisory	3,500 µ g/L
Lifetime health advisory	700 µ g/L
Carcinogenicity group	D
Maximum allowable concentration	

**Common name** heptachlor  
 Trade names  
 USEPA priority analyte yes  
 USEPA NPS method no. 2

**Usage**  
 Type insecticide  
 Crop use corn  
 Total acres 1969-1,131,000  
 1985  
 1987

Typical rates  
 Restricted use registration cancelled

**Chemical Properties**  
 Chemical class cyclodiene  
 Chemical formula  $C_{10}H_5Cl_7$   
 Molecular weight 373.35  
 Water solubility 0.030 mg/L (Reference: B)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 24,000 (Reference: I)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 240  
 Vapor pressure  $3.95E-07$  atm. at 25° C (Reference: A,H)  
 Henry's law constant  $4.91E-03$  atm.  $m^3/mole$   
 Half-life 2,000 days (Reference: I)

**Health Risk Information**  
 Longer term health advisory  
 Lifetime health advisory  
 Carcinogenicity group B  
 Maximum allowable concentration 0.1  $\mu g/L$

**Common name** imazaquin  
 Trade names Scepter, AC 252,214  
 USEPA priority analyte no  
 USEPA NPS method no.

**Usage**  
 Type herbicide  
 Crop use soybeans  
 Total acres 1969  
 1985  
 1987 - 1,800,000

Typical rates 0.125 lbs active ingredient per acre  
 Restricted use no

**Chemical Properties**  
 Chemical class imidazolinone  
 Chemical formula  
 Molecular weight 311.34  
 Water solubility 60 mg/L at 25° C (Reference: H)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 704 (calculated)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 7.0  
 Vapor pressure  $2.63E-11$  atm. at 45° C (Reference: P)  
 Henry's law constant  
 Half-life 60 days (Reference: P)

**Health Risk Information**  
 Longer term health advisory  
 Lifetime health advisory  
 Carcinogenicity group  
 Maximum allowable concentration

**Common name** linuron  
 Trade names Linex, Lorox  
 USEPA priority analyte no  
 USEPA NPS method no. 4

**Usage**  
 Type herbicide  
 Crop use soybeans  
 Total acres 1969 - 208,000  
 1985 - 496,000  
 1987 - 630,000  
 Typical rates 0.5 to 3 lbs active ingredient per acre  
 Restricted use no

**Chemical Properties**  
 Chemical class substituted urea  
 Chemical formula  $C_9H_{10}Cl_2N_2O_2$   
 Molecular weight 249.10  
 Water solubility 81 mg/L at 25° C (Reference: H)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 863 (Reference: I)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 8.6  
 Vapor pressure 1.97E-08 atm. at 24° C (Reference: A,E)  
 Henry's law constant 6.07E-08 atm. m<sup>3</sup>/mole  
 Half-life 75 days (Reference: I)

**Health Risk Information**  
 Longer term health advisory  
 Lifetime health advisory  
 Carcinogenicity group  
 Maximum allowable concentration

**Common name** metalaxyl  
 Trade names Apron, Ridomil  
 USEPA priority analyte no  
 USEPA NPS method no.

**Usage**  
 Type fungicide  
 Crop use soybeans, vegetables  
 Total acres 1969  
 1985  
 1987  
 Typical rates  
 Restricted use no

**Chemical Properties**  
 Chemical class  
 Chemical formula  
 Molecular weight 279.35  
 Water solubility 7,100 mg/L at 20° C (Reference: A,H)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 36.50 (calculated)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 0.4  
 Vapor pressure 2.89E-09 atm. at 20° C (Reference: A)  
 Henry's law constant 1.14E-10 atm. m<sup>3</sup>/mole  
 Half-life

**Health Risk Information**  
 Longer term health advisory  
 Lifetime health advisory  
 Carcinogenicity group  
 Maximum allowable concentration



**Common name** metolachlor  
 Trade names Dual, Turbo (+Metribuzin)  
 USEPA priority analyte yes  
 USEPA NPS method no. 1

**Usage**  
 Type herbicide  
 Crop use com, soybeans  
 Total acres 1969  
 1985 - 3,984,000  
 1987 - 3,629,000  
 Typical rates 1 0.25 to 3 lbs active ingredient per acre  
 Restricted use no

**Chemical Properties**  
 Chemical class acetanilide or cloroacetamide  
 Chemical formula  $C_{15}H_{22}ClNO_2$   
 Molecular weight 283.81  
 Water solubility 530 mg/L at 20° C (Reference: A,D,H)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 181 (Reference: I)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 1.8  
 Vapor pressure 1.71E-08 atm. at 20° C (Reference: A,D)  
 Henry's law constant 9.16E-09 atm. m<sup>3</sup>/mole  
 Half-life 42 days (Reference: I)

**Health Risk Information**  
 Longer term health advisory 1,050 µg/L  
 Lifetime health advisory 10 µg/L  
 Carcinogenicity group C  
 Maximum allowable concentration

**Common name** methyl parathion  
 Trade names Methyl Parathion  
 USEPA priority analyte no  
 USEPA NPS method no.

**Usage**  
 Type insecticide  
 Crop use fruits, vegetables  
 Total acres 1969  
 1985  
 1987  
 Typical rates  
 Restricted use yes

**Chemical Properties**  
 Chemical class  
 Chemical formula  $C_8H_{10}NO_5PS$   
 Molecular weight 263.23  
 Water solubility 60 mg/L (Reference: H)  
 Organic carbon partition coefficient ( $K_{oc}$ ) 5,100 (Reference: I)  
 Adsorption coefficient ( $K_d$ ) at 1.0% 51.0  
 Vapor pressure 1.28E-08 atm. at 20° C (Reference: K)  
 Henry's law constant 5.62E-08 atm. m<sup>3</sup>/mole  
 Half-life 15 days (Reference: I)

**Health Risk Information**  
 Longer term health advisory 100 µg/L  
 Lifetime health advisory 2 µg/L  
 Carcinogenicity group D  
 Maximum allowable concentration

<b>Common name</b>	<b>metribuzin</b>
Trade names	Lexone, Sencor
USEPA priority analyte	yes
USEPA NPS method no.	1
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 1985 - 4,122,000 1987 - 2,070,000
Typical rates	0.25 to 1 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	triazine
Chemical formula	C <sub>8</sub> H <sub>14</sub> N <sub>4</sub> OS
Molecular weight	214.28
Water solubility	1,220 mg/L at 20° C (Reference: B,D)
Organic carbon partition coefficient (K <sub>oc</sub> )	24 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.2
Vapor pressure	1.32E-08 atm. at 20° C (Reference: D)
Henry's law constant	2.31E-09 atm. m <sup>3</sup> /moie
Half-life	37 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	875 µg/L
Lifetime health advisory	175 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

<b>Common name</b>	<b>pendimethalin</b>
Trade names	Prowl, Stomp
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	herbicide
Crop use	soybeans, corn
Total acres	1969 1985 - 670,000 1987 - 936,000
Typical rates	0.5 to 2 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	dinitroaliline
Chemical formula	C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub>
Molecular weight	281.31
Water solubility	0.500 mg/L at 25° C (Reference: D)
Organic carbon partition coefficient (K <sub>oc</sub> )	13,697 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 137.0
Vapor pressure	3.95E-08 atm. at 25° C (Reference: A,D)
Henry's law constant	2.22E-05 atm. m <sup>3</sup> /mole
Half-life	

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>phorate</b>
Trade names	Thimet
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	insecticide
Crop use	com
Total acres	1969 - 424,000 1985 - 272,000 1987 - 272,000
Typical rates	1.0 to 1.3 lbs active ingredient per acre
Restricted use	yes

<b>Chemical Properties</b>	
Chemical class	phosphorodithioate
Chemical formula	C <sub>7</sub> H <sub>17</sub> O <sub>2</sub> PS <sub>3</sub>
Molecular weight	260.40
Water solubility	50 mg/L at 25° C (Reference: A,B)
Organic carbon partition coefficient (K <sub>oc</sub> )	660 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 6.6
Vapor pressure	1.11E-06 atm. at 20° C (Reference: A)
Henry's law constant	5.76E-06 atm. m <sup>3</sup> /mole
Half-life	82 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>picloram</b>
Trade names	Tordon, Grazon
USEPA priority analyte	yes
USEPA NPS method no.	3
<b>Usage</b>	
Type	herbicide, brush control
Crop use	pasture, grain
Total acres	1969 1985 1987
Typical rates	1 lb per 1000 square feet
Restricted use	yes

<b>Chemical Properties</b>	
Chemical class	
Chemical formula	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>2</sub>
Molecular weight	241.48
Water solubility	430 mg/L at 25° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	48 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 0.5
Vapor pressure	8.11E-10 atm. at 35° C (Reference: A)
Henry's law constant	4.55E-10 atm. m <sup>3</sup> /mole
Half-life	100 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	2450 µg/L
Lifetime health advisory	490 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

<b>Common name</b>	<b>propachlor</b>
Trade names	Ramrod, Bexton
USEPA priority analyte	yes
USEPA NPS method no.	2
<b>Usage</b>	
Type	herbicide
Crop use	corn
Total acres	1969 - 2,452,000 1985 - 57,000 1987 - 57,000
Typical rates	3 to 6 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	substituted amide (acetanilide)
Chemical formula	C <sub>11</sub> H <sub>17</sub> ClNO
Molecular weight	211.70
Water solubility	700 mg/L at 20° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	420 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 4.2
Vapor pressure	3.03E-07 atm. at 25° C (Reference: D)
Henry's law constant	9.15E-09 atm. m <sup>3</sup> /mole
Half-life	7 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	460 µg/L
Lifetime health advisory	92 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

<b>Common name</b>	<b>sethoxydim</b>
Trade names	Poast
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 1985 - 246,000 1987 - 540,000
Typical rates	0.1 to 1 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	2-popp acid (misc.)
Chemical formula	C <sub>17</sub> H <sub>25</sub> NO <sub>3</sub> S
Molecular weight	327.86
Water solubility	48 mg/L at 25° C (Reference: G)
Organic carbon partition coefficient (K <sub>oc</sub> )	808 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 8.1
Vapor pressure	2.11E- atm. at 25° C (Reference: G)
Henry's law constant	1.44E-09 atm. m <sup>3</sup> /mole
Half-life	11 days (Reference: G)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>simazine</b>
Trade names	Princep, Simazine
USEPA priority analyte	yes
USEPA NPS method no.	1

**Usage**

Type	herbicide
Crop use	corn
Total acres	1969
	1985- 117,000
	1987- 117,000
Typical rates	2 to 4 lbs active ingredient per acre
Restricted use	yes

**Chemical Properties**

Chemical class	nitroaniline (triazine)
Chemical formula	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>
Molecular weight	201.67
Water solubility	4.980 mg/L at 20° C (Reference: G)
Organic carbon partition coefficient (K <sub>oc</sub> )	140 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 1.4
Vapor pressure	8.03E-12 atm. at 20° C (Reference: D,E)
Henry's law constant	3.25E- atm. m <sup>3</sup> /mole
Half-life	75 days (Reference: I)

**Health Risk Information**

Longer term health advisory	175 µg/L
Lifetime health advisory	35 µg/L
Carcinogenicity group	D
Maximum allowable concentration	

<b>Common name</b>	<b>terbufos</b>
Trade names	Counter
USEPA priority analyte	yes
USEPA NPS method no.	1

**Usage**

Type	insecticide
Crop use	com
Total acres	1969
	1985- 1,906,000
	1987 - 1,906,000
Typical rates	1.1 to 1.3 lbs active ingredient per acre
Restricted use	yes

**Chemical Properties**

Chemical class	
Chemical formula	C <sub>9</sub> H <sub>21</sub> O <sub>2</sub> PS <sub>3</sub>
Molecular weight	288.40
Water solubility	15 mg/L at 25° C (Reference: A,H)
Organic carbon partition coefficient (K <sub>oc</sub> )	1,663 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 16.6
Vapor pressure	3.14E-07 atm. at 25° C (Reference: K)
Henry's law constant	6.04E-06 atm. m <sup>3</sup> /mole
Half-life	

**Health Risk Information**

Longer term health advisory	0.88 µg/L
Lifetime health advisory	0.18 µg/L
Carcinogenicity group	E
Maximum allowable concentration	

<b>Common name</b>	<b>trifluralin</b>
Trade names	Treflan
USEPA priority analyte	yes
USEPA NPS method no.	2
<b>Usage</b>	
Type	herbicide
Crop use	soybeans
Total acres	1969 - 946,000 1985 - 4,326,000 1987 - 3,780,000
Typical rates	0.5 to 1 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	nitoraliline (dinitroaniline)
Chemical formula	C <sub>13</sub> H <sub>16</sub> F <sub>3</sub> N <sub>3</sub> O <sub>4</sub>
Molecular weight	335.29
Water solubility	24 mg/L (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	7,300 (Reference: I)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 73.0
Vapor pressure	1.45E-07 atm. at 25° C (Reference: G)
Henry's law constant	2.02E-06 atm. m <sup>3</sup> /mole
Half-life	132 days (Reference: I)

<b>Health Risk Information</b>	
Longer term health advisory	25 µg/L
Lifetime health advisory	2 µg/L
Carcinogenicity group	C
Maximum allowable concentration	

<b>Common name</b>	<b>trimethacarb</b>
Trade names	Broot, UC 27867
USEPA priority analyte	no
USEPA NPS method no.	
<b>Usage</b>	
Type	insecticide
Crop use	corn
Total acres	1969 1985 - 104,000 1987 - 104,000
Typical rates	1.2 lbs active ingredient per acre
Restricted use	no

<b>Chemical Properties</b>	
Chemical class	
Chemical formula	
Molecular weight	193.25
Water solubility	58 mg/L at 23° C (Reference: H)
Organic carbon partition coefficient (K <sub>oc</sub> )	719 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 7.2
Vapor pressure	6.58E-08 atm. at 23° C (Reference: H)
Henry's law constant	2.19E-07 atm. m <sup>3</sup> /mole
Half-life	56 days (Reference: N)

<b>Health Risk Information</b>	
Longer term health advisory	
Lifetime health advisory	
Carcinogenicity group	
Maximum allowable concentration	

<b>Common name</b>	<b>vernolate</b>
Trade names	Reward, Vemam Vernam
USEPA priority analyte	no
USEPA NPS method no.	1

**Usage**

Type	herbicide
Crop use	soybeans
Total acres	1969 - 300,000 1985 - 99,000 1987
Typical rates	2 to 4 lbs active ingredient per acre
Restricted use	no

**Chemical Properties**

Chemical class	thiocarbamate
Chemical formula	C <sub>10</sub> H <sub>21</sub> NOS
Molecular weight	203.40
Water solubility	7 mg/L at 25° C (Reference: A)
Organic carbon partition coefficient (K <sub>oc</sub> )	492 (calculated)
Adsorption coefficient (K <sub>d</sub> )	at 1.0% 4.9
Vapor pressure	1.37E-05 atm. at 25° C (Reference: A,D)
Henry's law constant	2.60E-05 atm. m <sup>3</sup> /mole
Half-life	10 days (Reference: G)

**Health Risk Information**

Longer term health advisory
Lifetime health advisory
Carcinogenicity group
Maximum allowable concentration

## APPENDIX B. Selection of Stratification Variables and Mapping Conventions

by Donald A. Keefer

The geologic information used to map the potential for contamination of shallow aquifers by agricultural chemicals was compiled from the *Stack-Unit Map of Illinois* (Berg and Kempton, 1988). This map depicts the distribution of geologic deposits vertically from the surface to a depth of 50 feet as well as horizontally over a specified area. The minimum thickness of continuous mapped units is 5 feet, except where a unit less than 5 feet was mapped over at least 0.4 square miles (Berg and Kempton, 1988). Where a mapped unit is laterally discontinuous within the specified area, the unit is frequently less than 5 feet thick.

Berg, Kempton, and Cartwright (1984) mapped 18 generalized sequences of geologic materials to a depth of 50 feet throughout Illinois. These 18 sequences were rated in terms of the potential for contamination of shallow aquifers from surface and near-surface waste disposal activities. Ratings were made by comparing capacities of geologic materials to accept, transmit, restrict, or remove contaminants. Highly permeable materials (sands, gravels, fractured carbonate rocks, and sandstones) tend to allow rapid migration of contaminants; whereas materials of low permeability (loess, glacial diamicton, shales, cemented sandstone, and unfractured carbonate rocks) tend to restrict contaminant migration (table B-1).

To limit the number of strata for sampling of rural private wells, Berg, Kempton and Cartwright's 18 sequences were combined into four groups based on relative potential for contamination of shallow aquifers from agricultural chemicals. These four groups were differentiated by the distance from the land surface to the top of the first deposit of aquifer materials:

- 1) within 5 feet of land surface;
- 2) between 5 and 20 feet of land surface;
- 3) between 20 and 50 feet of land surface; and
- 4) greater than 50 feet from land surface.

For this study, the distinction between aquifer materials and aquifers is that aquifer materials have the hydrogeologic characteristics to be classified as aquifers, but the materials may not be saturated. Aquifers, by definition, are saturated. In Illinois, the water table generally occurs 5 to 15 feet below ground surface. Below this depth, aquifer materials are generally saturated and capable of yielding water to a well. In areas mapped as having aquifer materials within 5 feet of the surface, these materials may not be saturated. (These areas occupy 17.2 percent of the land area in rural Illinois.) Since these highly permeable materials would not significantly restrict movement of agricultural chemicals, these areas were interpreted to have a potential for contamination equivalent to areas having aquifers within 5 feet of land surface.

Table B-1 Estimated hydraulic conductivity of typical geologic materials in Illinois  
(source: Berg, Kempton, and Cartwright, 1984)

<i>Geologic material</i>	<i>cm/sec</i>
Clean sand and gravel	$1 \times 10^{-3}$
Fine sand and silty sand	$1 \times 10^{-5}$ to $1 \times 10^{-3}$
Silt (loess, colluvium)	$1 \times 10^{-6}$ to $1 \times 10^{-4}$
Gravelly till, less than 10% clay	$1 \times 10^{-7}$ to $1 \times 10^{-5}$
Till, less than 25% clay	$1 \times 10^{-8}$ to $1 \times 10^{-5}$
Clayey tills, greater than 25% clay	$1 \times 10^{-9}$ to $1 \times 10^{-7}$
Sandstone	$>1 \times 10^{-4}$
Cemented fine sandstone	$1 \times 10^{-7}$ to $1 \times 10^{-4}$
Fractured rock	$>1 \times 10^{-4}$
Shale	$1 \times 10^{-11}$ to $1 \times 10^{-7}$
Dense limestone/dolomite (unfractured)	$1 \times 10^{-11}$ to $1 \times 10^{-8}$

Sand and gravel greater than 5 feet thick, sandstone greater than 10 feet thick, and fractured



carbonates greater than 20 feet thick are considered aquifer materials. Loess, glacial diamicton, shale, and nonfractured carbonate rocks generally will not provide a sufficient volume of water to a drilled well and are not considered aquifer materials for this study.

Where deposits of aquifer materials lie at depth from the surface, they generally are overlain by deposits of fine-grained materials that are low in permeability. The thickness of these fine-grained materials controls the susceptibility of the underlying aquifers to contamination. As the thickness of these fine-grained materials increases, the potential for contamination of an underlying aquifer decreases (fig. B-1).

The highest potential for contamination of shallow aquifers from agricultural chemicals was assigned to areas where the top of the aquifer materials lies within 5 feet of land surface. These areas typically consist of thin loess or bedrock residuum over jointed limestone or dolomite, or porous sandstone; or less than 5 feet of loess or silty lacustrine materials over thick deposits of sand and gravel. Principal areas are north-central, northwestern, and extreme southern Illinois and adjacent to the Mississippi River.

The next highest potential for contamination of shallow aquifers was assigned to areas where the top of the aquifer materials lies between 5 and 20 feet from land surface. These areas have a continuous deposit(s) of relatively fine-grained materials (loess, diamicton, or lacustrine deposits) overlying highly permeable aquifer materials. Principal areas are northern, southern, and extreme western Illinois.

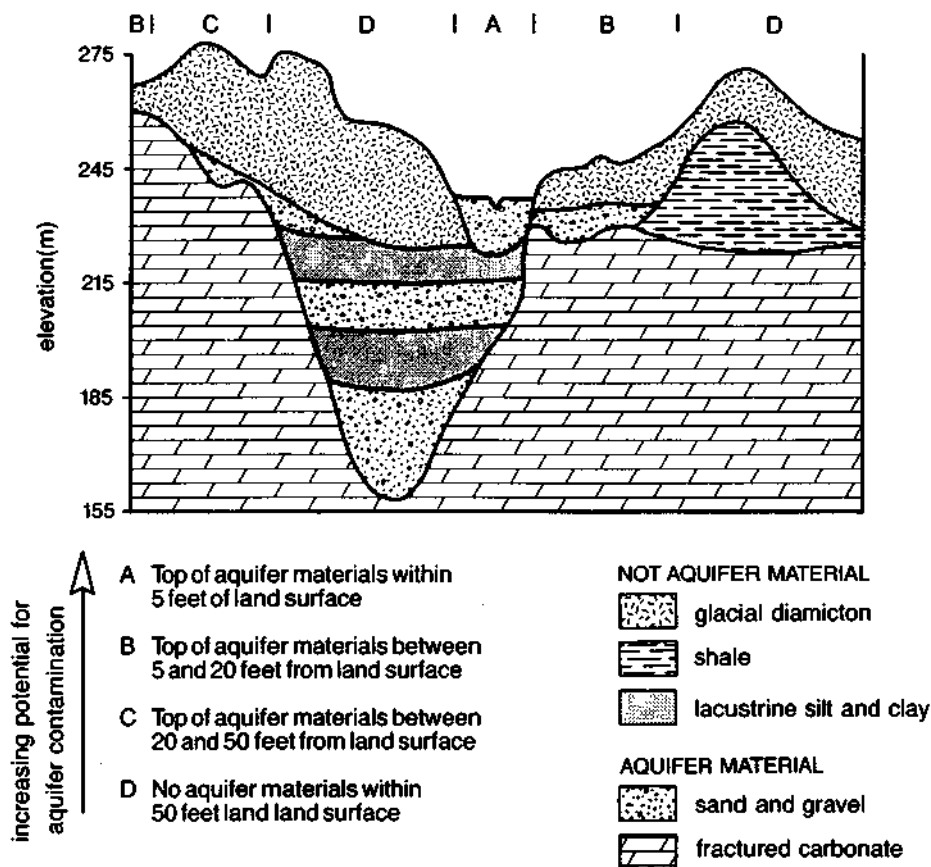


Figure B-1 Example of geologic sequences with ratings for potential for contamination from agricultural chemicals.

The third level of contamination potential was assigned to areas where continuous aquifer materials lie between 20 and 50 feet from land surface. These areas have at least 20 feet of fine-grained material overlying highly permeable deposits. Although these sequences occur throughout Illinois, they are concentrated mainly in the western, south-central, and southern parts of the state.

Areas mapped as having the lowest potential for contamination of shallow aquifers have no continuous aquifers within 50 feet of land surface. These areas are underlain by at least 50 feet of fine-grained glacial deposits or low permeability bedrock. Every county in Illinois contains geologic sequences like these, but the greatest areal coverage occurs in northeastern and central Illinois.

### **Mapping Conventions**

Discontinuous sand and gravel deposits were not mapped as aquifers. As identified in the stack-unit map, these units are frequently less than 5 feet thick and always laterally discontinuous within the mapped area. Continuous, surficial sand and gravel deposits less than 20 feet thick are also not considered to be aquifers.

Another modification to the interpretations by Berg, Kempton, and Cartwright (1984) involved alluvial deposits. Analysis of stack-unit map data indicates that 11.8 percent of Illinois' land surface is covered by alluvial deposits. Alluvium is found in the floodplains and channels of streams and rivers. In Illinois, alluvium generally consists of fine-grained materials eroded from the loess- and diamicton-covered uplands. Where upland deposits are coarse, however, floodplain deposits also tend to be coarse. In most stream and river valleys in Illinois, alluvial deposits are laterally continuous but usually are less than 20 feet thick. In major river valleys, deposits may exceed 50 feet in thickness (Willman and Frye, 1970). Berg, Kempton, and Cartwright (1984) mapped alluvium in a separate potential for contamination group because prediction of the often abrupt lithologic changes was impossible.

For this study, alluvium was considered to be the same general lithology as the first continuous deposit below it. For example, an area with less than 20 feet of alluvium overlying thick glacial diamicton or shale bedrock was mapped as an area of continuous fine-grained deposits (no aquifer materials within 50 feet). An area with continuous alluvium overlying a thick deposit of sand and gravel would be treated as an area of continuous sand and gravel at land surface. Digital land use and land cover information was obtained from the USGS (1984) and used to identify forested areas greater than 1 square mile and urban areas (fig. 2, section *Agricultural Chemical Usage in Illinois*). (The U.S. Census Bureau defines urban areas as municipalities with more than 2500 people.) These urban/forest areas were excluded in mapping the potential for contamination of shallow aquifers.

### **Estimation of Wells per Strata**

Information regarding the number of water wells throughout Illinois was obtained from a computer database compiled by the National Water Well Association (NWWA, 1986). The NWWA utilized U.S. Census Bureau data regarding private water wells for each zip code in the country. The information in the NWWA database for each zip code includes the total number of private water wells; the number of private, drilled water wells; and the number of private, large-diameter, dug or bored wells. This computerized database information was added to a computerized zip code map of Illinois (Board of Trustees, University of Illinois).

The number of private, drilled water wells per square mile per zip code in rural parts of the state was calculated by dividing the total number of wells listed for each zip code by the total area of that zip code. The distribution of wells throughout the zip code areas was assumed constant. The number of rural, private, drilled water wells in each potential for contamination group throughout the state was calculated by combining the well/zip code map with the potential for contamination map. The area of each polygon for each contamination-potential strata was

calculated and multiplied by the average number of rural, private, drilled water wells per square mile for the zip code within that polygon. The estimated total number of drilled wells for each of the four levels of contamination potential are given in table 12 in the section, *Selection of Sample Size*.

To validate the estimates of the number of wells in each of the various potential for contamination strata, a field team would check the average number of wells per square mile. Field checking involves counting the number of rural, private wells within a specified area surrounding each well to be sampled. This could be accomplished most efficiently by reviewing USDA Agricultural Stabilization and Conservation Service aerial photographs.

## APPENDIX C. Statistical Equations

The following formulas are used to compute the stratum mean, stratum variance, population mean, and population variance (Gilbert, 1987). NOTE: definitions of all variables are listed at the end of this appendix.

$$\text{stratum mean, } \bar{x}_h = \frac{1}{n_h} \sum_{i=1}^{n_h} x_{hi}$$

$$\text{population mean, } \bar{x}_{st} = \sum_{h=1}^L w_h \bar{x}_h = \sum_{h=1}^L \left[ \frac{N_h}{N} \right] \bar{x}_h$$

$$\text{stratum variance, } S_h^2 = \frac{1}{n_h - 1} \sum_{i=1}^{n_h} (x_{hi} - \bar{x}_h)^2$$

$$\text{population variance, } S_h^2(\bar{x}_{st}) = \frac{1}{N^2} \sum_{h=1}^L N_h^2 \left[ 1 - \frac{n_h}{N} \right] \frac{S_h^2}{n_h}$$

The formulas to compute stratum and population proportions and the variances are listed below (Cochran, 1963).

$$\text{stratum proportion, } p_h = \frac{a_h}{n_h}$$

$$\text{estimate of proportion in the whole population, } p_{st} = \sum_{h=1}^n \left[ \frac{N_h p_h}{N} \right]$$

$$\text{variance of stratum proportion, } \text{var}(p_h) = \left[ \frac{N_h - n_h}{(n_h - 1)N_h} \right] (p_h q_h)$$

$$\text{variance of population proportion, } \text{var}(p_{st}) = \frac{1}{N^2} \sum_{h=1}^n \left[ \frac{N_h^2 (N_h - n_h)}{N_h - 1} \right] \left[ \frac{p_h q_h}{n_h - 1} \right]$$

The confidence interval for any proportion may be computed with the following formula (Hogg and Tanis, 1983).

approximate  $100(1 - \alpha)\%$   
confidence interval for  $p$ :

$$\frac{a}{n} \pm Z_{\alpha/2} \sqrt{\frac{\left[\frac{a}{n}\right] \left[1 - \frac{a}{n}\right]}{n}}$$

The test statistic for comparison of two proportions is (Hogg and Tanis, 1983).

null hypothesis,  $H_0 : \hat{p}_1 = \hat{p}_2$

alternate hypothesis,  $H_1 : \hat{p}_1 \neq \hat{p}_2$

H rejected if  $|\hat{p}_1 - \hat{p}_2| > Z_{\alpha/2} \sqrt{\frac{\hat{p}_1 \hat{q}_1}{n_1} + \frac{\hat{p}_2 \hat{q}_2}{n_2}}$

#### Definitions of Variables

- $a$  = numbers of samples having a certain attribute
- $a_h$  = number of samples in  $h^{\text{th}}$  stratum having a certain attribute
- $L$  = number of strata
- $n$  = number of samples
- $n_h$  = number of samples in  $h^{\text{th}}$  stratum
- $N_h$  = total number of units in the  $h^{\text{th}}$  stratum
- $N$  = total number of units in all strata
- $q_h$  =  $1 - p_h$
- $Z_{\alpha/2}$  = value from the normal distribution table for  $\alpha/2$ .  
 $1 - \alpha$  defines the probability that the null hypothesis is not rejected.

## APPENDIX D. Recommendations for Quality Assurance/Quality Control Plan

In this appendix, we recommend QA/QC procedures to be used in the analytical laboratories. A formal QA/QC plan would also include sample collection procedures, analytical methods, sample tracking--as presented in the preceding sections, *Sample Custody, Tracking, Laboratory Coordination; Field Procedures; and Analytical Methods*.

### Quality Assurance Objectives

The objective of a QA plan is to ensure that the data obtained are of known, high quality and meet specific accuracy and precision requirements. The plan should document and verify the procedures under which the data are obtained, formalize QA functions, assign responsibilities, and provide information to project managers.

Three major types of activities (prevention, assessment, and evaluation) should be incorporated into a QA plan. Preventative measures, designed to prevent acquisition of incorrect data, include instrument maintenance and calibration, replicate analyses, and standard sampling procedures. Data handling errors can be minimized through the use of a laboratory information management system, which streamlines organization, sample tracking, chain of custody, data management, and statistical analysis. Assessment activities include performance and system audits, documentation review, and performance monitoring. Corrective activities are performed if assessment activities indicate that the validity of experimental procedures and data are questionable.

### Analytical Quality Control Measures

Recommendations for the acceptance criteria for sample analysis and analytical quality-control measures are based on guidelines in the USEPA NPS methods (Mason et al., 1987).

**Acceptance criteria** for sample analysis include measures of precision, bias, representativeness, completeness, and comparability.

*Precision*, used to define the reproducibility of results, is best described in terms of total variance and standard deviation. Precision should be expressed as percentage of relative standard deviation (RSD), where:

$$\text{and } \text{RSD} = \frac{\text{SD}}{\bar{X}} \times 100\%$$

$$\text{SD (standard deviation)} = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}$$

where n = number of measurements for each analyte.

Precision should be assessed for each analyte in the samples and the quality-control standards. Acceptable data should fall within three standard deviations as follows:

$$\text{RSD} \pm 3 \text{ SD}$$

*Bias* (accuracy) is the degree of agreement of a measurement to its accepted or true value. Bias should be expressed as a percentage of the true value using average percent recovery (R), where:

for standards

$$R_i \text{ (individual percent recovery)} = \frac{\text{measured value}}{\text{true value}} \times 100\%$$

or for recovery of spikes

$$R_i \text{ (individual percent recovery)} = \frac{\text{measured value} - \text{background value}}{\text{spike value}} \times 100\%$$

and,

$$R \text{ (average percent recovery)} = \frac{\sum_{i=1}^n R_i}{n}$$

$$SD_R \text{ (standard deviation of the average percent recovery)} = \sqrt{\frac{1}{n-1} \left[ \left( \sum_{i=1}^n R_i^2 \right) - \frac{\left( \sum_{i=1}^n R_i \right)^2}{n} \right]}$$

where n = number of measurements for each analyte.

Acceptable data for percent recovery (bias) should fall within three standard deviations as follows:

$$RSD \pm 3 SD_R$$

*Representativeness* of a sample is obtained by random sampling of the target population. Experimental and sampling design and sample collection procedures should be developed to assure collection of representative samples. The design and procedures, which have been discussed in the preceding report, should be included in a formal QA/QC plan.

*Completeness* is a measure of the amount of valid data obtained compared to the amount that was expected to be obtained. Data losses are most likely to occur because of (1) inaccessible sample sites at the time of sample collection (nonresponse); (2) breakage or loss of samples during handling, shipping, or analysis; and (3) excessive sample storage times before extraction or analysis.

Losses due to inaccessible sample sites or breakage/spillage of samples should be treated as a nonresponse. Samples for which recommended holding times have been exceeded should be evaluated according to results of time-storage studies for each analyte. If the data are considered unacceptable, the sample should be treated as a nonresponse.

*Comparability* data should be reported in SI units accompanied with appropriate quality assurance data, which will assure relative comparability of the data. It is recommended that USEPA standard methods be used for analysis. Where modifications are used, they should be fully documented. Recommended sample collection, storage, and analytical procedures are presented in the preceding report and should be documented in a formal QA/QC plan.

**Quality assurance procedures for organic analyses:** *Initial demonstration of capability* Each laboratory must demonstrate the ability to generate acceptable accuracy (percent bias) and precision for a given analysis through the use of spiked samples and USEPA standards. Demonstration of capability with each method should be accomplished before the analysis of collected field samples.

Initial average percent bias and precision criteria should be established for each of the analytes in each method. Estimated detection limits (EDL) for each analyte should also be documented. The EDL should be calculated by (1) multiplying the standard deviation of replicate measurements by the Student's t value appropriate for a 99-percent confidence level and n-1 degrees of freedom, or (2) calculating the concentration of the compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5. The EDL should be set at the higher value. Quality-control charts for accuracy and precision should be established to ensure the validity of the reported data. Time-storage studies for each analyte should be completed before the analysis of field collected samples, if maximum permissible storage times are unknown for any analyte. Working calibration curves that demonstrate the linearity of response with concentration should also be established. When a new batch of reagents is used, a new standard curve should be prepared, using at least five concentration levels.

*Instrument calibration* should be performed, at least daily, using standards to verify the working calibration curve. The percent recovery of each analyte should be compared with established QC criteria based on laboratory control charts. If the percent recovery of any analyte falls outside the designated range, the instrument should be recalibrated and the laboratory standard rerun. This process should be repeated until the percent recovery of each analyte is within the established range.

*Laboratory contamination* To demonstrate that glassware and reagent interferences are under control, one method blank should be analyzed with each set of samples and at any time a change of reagents occurs. If the method blank exhibits a peak within the retention time window of any analyte greater than or equal to one-half of the EDL for that analyte, the source of contamination and interference problem must be determined and eliminated. If the problem is determined to be due to a systematic contamination of glassware or reagents, the measured peak area or height within the retention time window of interest should be subtracted from the peak area or height obtained for the samples.

*Surrogate standard recovery* Before extraction, all samples and blanks should be fortified with a surrogate spiking compound as a check of the extraction procedure. The percent recovery of the surrogate standard should be compared to the established QC criteria as set forth in the laboratory control charts.

If the percent recovery of the surrogate standard is outside the accepted range, corrective actions should be taken. These should include a check of calculations, degradation or contamination of the internal and surrogate spiking solutions, and instrument performance. If the percent recovery is still unacceptable after corrective actions have been taken, the data should be reported as suspect.

*Internal standard assessment* Each sample extract should be spiked with an internal standard as a check of analyte quantification. Measured peak area or height of the internal standard should be compared using laboratory-control charts with established QC criteria.

If the internal peak area or height for any sample is outside the accepted range, corrective measures should be taken. For a single occurrence, the sample should be reinjected. If the internal standard peak area or height is within the accepted range, the results should be quantified and reported. If it is outside the accepted range but other samples give peak areas or heights within the accepted range, an error was probably made during the addition of the internal standard to that sample. The analysis of that sample should then be repeated and reported.

If peak areas or heights of successive samples are outside the accepted range, the instrument should be checked for proper performance and the calibration curve checked with a calibration standard. If the calibration curve is still applicable and the internal standard is within the accepted



range, the suspect samples should be reanalyzed. If the internal standard peak area or height of the samples now falls within the accepted range, the results should be reported.

If the calibration curve is not applicable, a new calibration curve should be generated and the samples reanalyzed. The results should be reported if the internal standard peak area or height falls within the accepted range.

*Laboratory performance* should be evaluated through the use of three types of quality control standards: laboratory control, QC-check, and performance evaluation. At least one laboratory-control standard should be analyzed per set of samples extracted within a 24-hour period. The stock laboratory-control standard solutions either should be prepared by the individual laboratories by dissolving known amounts of pure analytes in a known amount of reagent water or purchased from an external source. The laboratory control standard should be prepared by diluting known amounts of the stock solutions to known volumes: it should contain analyte concentrations of 15 times the EDL. The laboratory-control charts should be used to compare the percent recovery of each analyte to established QC criteria.

QC-check standards obtained from an outside source should be analyzed on a weekly basis or more frequently if necessary. QC check standards are water-soluble solutions that contain known concentrations of analytes prepared by an outside laboratory. These standards are used to demonstrate that the performing laboratory can obtain acceptable identifications and measurements with a particular method. Corrective measures should be taken if the QC criteria provided with the standards are not met.

The quality assurance (QA) officer or other designated staff member should introduce performance evaluation standards into the analysis process on a quarterly basis. Performance evaluation standards, obtained from the USEPA, should be used to document comparability of data. Corrective measures should be taken if the QC criteria are not met.

*Analyte recovery* At least 10 percent of the analyzed samples should be spiked with each of the target analytes. The spiking concentration should be one to five times the background concentration or 15 times the EDL, if the background concentration is less than the detection limit. The percent recovery for each analyte should be compared with QC criteria established with the analysis of laboratory-control standards. If the QC criteria are not met, corrective actions should be taken.

*Analyte confirmation* Samples for gas chromatography might be analyzed using a sample splitter, after careful consideration of the concentration levels to be expected in the analyses, so that all samples are simultaneously run through the regular and confirmation columns. It is recommended that 10 percent of the positive identifications within quantification limits be confirmed by mass spectroscopy.

Samples for high-performance liquid chromatography analysis should be analyzed with both the regular column and the confirmation column, and 10 percent of the positive identifications should be confirmed by mass spectroscopy.

**Quality assurance procedures for nitrate-nitrogen analyses:** *Initial demonstration of capability* to achieve acceptable accuracy (percent bias) and precision should be accomplished before the analysis of collected field samples. A working calibration curve to demonstrate the linearity of response with concentration should be established. A new standard curve should be prepared, using at least five concentration levels, when each new batch of reagents is used. The EDL should also be determined (See *Quality Assurance Procedures for Organic Analyses*).

*Instrument calibration* The instrument should be calibrated daily with standards to verify the working calibration curve. Accuracy and precision of the calibration standards should be compared with established QC criteria before the analysis of samples.

*Laboratory contamination* Demonstration that glassware and reagent interferences are under control requires that one method blank be analyzed with each set of samples and with every change in reagents. If a response greater than or equal to one-half the EDL is exhibited by the method blank, the source of contamination and interference problem must be determined and eliminated. The response (absorbance) should be subtracted from the samples, if the problem is determined to be due to systematic contamination of glassware or reagents.

*Laboratory performance* should be evaluated by the use of laboratory-control standards, QC-check standards, and performance-evaluation standards. Detailed descriptions are given in *Quality Assurance Procedures for Organic Analyses*.

At least one laboratory-control standard prepared by the laboratory should be analyzed per set of samples. The standard should contain a nitrate-nitrogen concentration of 15 times the EDL.

QC-check standards obtained from an outside source should be analyzed on a weekly basis, or more often if necessary. If the QC criteria provided with the standards are not met, corrective measures should be taken.

The QA officer or a designated staff member should introduce performance-evaluation standards into the analysis process on a quarterly basis. Corrective measures should be taken if results are not within acceptable limits.

*Analyte recovery* Ten percent of the analyzed samples should be spiked with nitrate-nitrogen. The spiking concentration should be one to five times the background concentration or 15 times the EDL if the background concentration is less than the detection limit. The absorbance should be compared with QC criteria established with the analysis of laboratory control standards. If the QC criteria are not met, corrective actions should be taken.

**Laboratory guidelines** Type I water, as described in USEPA guidelines (1979) should be used for the organic analyses. A minimum of type IV water should be used for the nitrate-nitrogen analysis (USEPA, 1979).

A minimum of analytical reagent-grade chemicals and solvents should be used in the preparation of standards. Where applicable, pesticide-quality reagents and solvents should be used.

A minimum of ultrapure certified-grade gases should be used where necessary for chromatography. If necessary, a scrubber or trap should be attached to the chromatograph to provide the required purity of gas.

Standard stock solutions to be used as QC-check standards should be purchased from commercial sources or obtained from the USEPA. Performance-evaluation standards should be obtained from the USEPA.

Glassware and sample bottles for organic analyses should be cleaned according to procedures developed by the USEPA for the National Pesticide Survey (table D-1). Glassware and sample bottles for nitrate-nitrogen analysis should be cleaned in a detergent wash, rinsed three times with tap water, rinsed three times with deionized water, and allowed to drain (Mason et al, 1987). The entire procedure should be performed in an area well away from samples, solvent storage, extraction, or analyses.

**Table D-1** Cleaning procedure for glassware and sample bottles used for organic analyses (Mason et al., 1987)

- 
- 1) Soak and wash with a hot, strong detergent solution (Chem-solv).
  - 2) Immediately rinse the glassware with tap water.
  - 3) Rinse three times with distilled water or deionized water.
  - 4) Bake in an oven for a minimum of 4 hours at 425° C.
  - 5) Remove from oven and allow to cool.
  - 6) Wash Teflon septa and bottle caps with detergent, then rinse them three times with tap and deionized water and air-dry overnight.
  - 7) Rinse Teflon-lined lids with hexane, and allow lids to air-dry in a pesticide-free area.
  - 8) Place hexane-rinsed, Teflon-lined lids on the bottles.
  - 9) Sample bottles are now ready for packaging or storage.
- 

### **Sample Custody and Management**

Laboratory data management, sample tracking, and statistical analysis require the development of a computerized information system. Identical systems should be implemented by each laboratory for ease of data transfer and communication.

Strict chain-of-custody procedures involving locked storage should not be necessary for this program, but limited procedures should be incorporated into the laboratory information management system. On the sample tracking form (described in the section, *Experimental Design --Sample Tracking Scheme*), researchers would record any abnormality or peculiarity encountered during sample collection or analysis. After completing specific tasks for each sample, the sample handler would sign and date the form. Limited chain-of-custody and sample tracking should be documented in this way throughout the monitoring program. This information should be transferred to computer storage during data entry.

A spreadsheet/graphics/statistical program should also be incorporated into the laboratory information management system to aid data manipulation and analysis. Analytical data for samples and quality-control standards should be compiled and analyzed using this feature. The laboratory information management system should also have label-making capabilities for the sample containers. Labels should be coded with information, such as sample identification number, analytical method, laboratory, date and time of collection, and name of collector. Erroneous identification and loss of samples should be minimized using this procedure.

### **Data Reduction and Validation**

**Reduction** Raw data will be in two forms: peak area or height from the pesticide analyses, and absorbance units from the nitrate analyses. A calibration curve for each analyte/analytical method should be constructed by fitting a linear regression equation to the results of the analyses of calibration-standard solutions containing the analyte at five different concentration levels. The raw data should be converted to the concentration of analyte in the sample by the analyst or laboratory manager.

**Data validation:** *Quality-control charts* for precision and bias should be used in each laboratory for evaluating analytical performance. Control charts should be maintained for each analyte and spike compound in each method. Quality-control charts consist of an expected value (mean, percent recovery) and an acceptable range of occurrence (the region between the upper and lower control limits) as shown in figure D-1. The upper control limit (UCL) should be defined as the mean value of the statistic plus three standard deviations, and the lower control limit (LCL) as the mean value of the statistic minus three standard deviations. Quality-control charts for samples, calibration standards, and quality-control standards should be evaluated separately and compared.

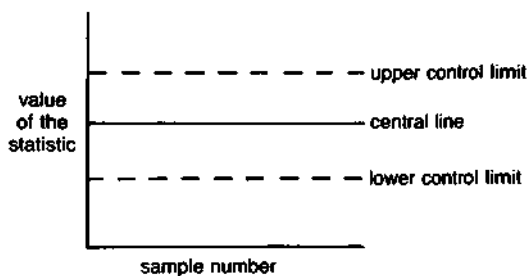


Figure D-1 Sample quality control chart.

Conditions that indicate an out-of-control situation include any point beyond the control limits or seven successive points on the same side of the central line. If an out-of-control situation occurs, analyses must be stopped until the problem has been identified and resolved. The QA officer or designated staff member should verify that quality-control charts are being maintained and that data are of acceptable quality.

*Data reporting* Each laboratory manager should verify that raw data are stored weekly as hard copy and on computer disks. At least 5 percent of the raw data should be examined weekly to verify adequate documentation, peak shape and resolution, and correct calculations. All original output (e.g., chromatograms) should contain information on the date of analysis, analyst, sample identification number, instrument and detector (if necessary), analytical conditions, and sample volume (if necessary). All original output should be permanently stored. All raw data, notebooks, and calculations should also be kept for future reference. All associated blank, standard, and QC data should be reported along with the results for analyses of each batch of samples.

### System and Performance Audits

Prior to the collection of field samples, a system audit of the complete chain of interrelated operations for the implemented program should be completed. This audit should include information on site location protocols, completion of site survey information forms, kit preparation, collection, handling, and transportation of samples, analytical methods, and the sample tracking and laboratory information management system. Any problems encountered in this phase should be resolved before onset of the monitoring program.

During the course of the program, the QA officer or designated staff member should check on all operations. Personnel involved in the program should notify the QA officer or project manager of any problems. QA performance audits or reviews of all project operations by the administering agency may be performed if requested.

### Preventative Maintenance

The minimum schedules for maintenance of major equipment are listed below. In the event that an instrument requires maintenance during actual analyses, the analyst should determine whether that maintenance altered the operating conditions of the instrument (such as standardization, retention times). If so, the analyst should perform the required calibration or corrective action.

#### Gas Chromatograph

<i>Operation</i>	<i>Frequency</i>
Replace carrier gas O <sub>2</sub> scrubber	every 6 months
Recharge carrier gas H <sub>2</sub> O scrubber	every 2 months
Clean chassis air filter	every 6 months
Clean detectors	when poor response is obtained
Replace injector septum	every 80 to 100 runs or as required
Replace column	when poor resolution is obtained

## High Performance Liquid Chromatograph

<i>Operation</i>	<i>Frequency</i>
Check flow rates	weekly
Check connections for leaks	daily
Lubricate pump	monthly
Clean or change eluent tubing	yearly
Replace column	when poor resolution is obtained

## Spectrophotometer

<i>Operation</i>	<i>Frequency</i>
Clean cell	Monthly
Oil and lubricate pump	As needed
Change column	When poor response is obtained
Replace pump tubing	As needed

Adequate supplies of spare parts, including analytical columns, septa, syringes, electrodes, should be maintained by each laboratory so they are available as needed. Field sampling vehicles should be stocked with spare equipment, such as electrodes, Teflon tubing, sample bottles, preservatives, and buffer solutions. Various-sized fittings required to attach the Teflon tubing to various types of water taps should also be kept in the sampling vehicle. Electrical conductivity and pH meters should be checked in the laboratory before each sampling event.

Each sampling team should carry a supply box that contains the following items: sampling instruction sheet, extra questionnaires, tracking forms, and labels, indelible ink pens, strapping tape, scissors, thermometer, extra sample bottles, extra bottle caps, ballpoint pens, and marker pens. Additional materials should be added to the supply box as needed.

## Corrective Action

Laboratory and field managers should have the prime responsibility for recognizing the need for corrective action. The QA officer or other designated staff member should also be responsible for monitoring quality control data and sampling protocol, and determining if corrective measures are necessary. If major problems do occur, the QA officer should consult with the laboratory or field managers, project manager, and other involved personnel to determine the appropriate corrective action.

For each analytical method, precision and bias (accuracy) for each analyte should be regularly calculated and tracked using quality-control charts. Percent recovery and standard deviation for surrogate spikes and analyte spikes should also be calculated. When precision or bias is outside the accepted range ( $\pm 3$  standard deviations), corrective measures should be taken. If problems are encountered during performance or system audits or during implementation of the program, corrective action should be initiated immediately.

Corrective action may include, but not be limited to recalibration of instruments using freshly prepared calibration standards, replacement of solvents or reagents that give unacceptable blank values, additional training of laboratory or field sampling personnel, and reassignment of personnel.

**APPENDIX E. Well-Site Observation Record**

**Rural Private Water Well Survey  
for Agricultural Chemicals**

**Well-Site Observation**

WELL IDENTIFICATION NUMBER \_\_\_\_\_  
(Base number for sample)

Staff member \_\_\_\_\_ Date of survey \_\_\_\_\_

Owner name \_\_\_\_\_ Phone number \_\_\_\_\_

Location of well \_\_\_\_\_

Legal description of well: Twp \_\_\_\_\_ Rng \_\_\_\_\_ Sec \_\_\_\_\_

Ten-acre plot \_\_\_\_\_ and/or

Quarter-quarter-quarter section \_\_\_\_\_

Type of well:

Drilled \_\_\_\_\_ Dug/bored \_\_\_\_\_ Sandpoint \_\_\_\_\_

Well depth: \_\_\_\_\_ Year drilled/dug \_\_\_\_\_

**N O T E      A N Y      L I M I T A T I O N S      O N      A C C E S S**

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**Please answer the following questions as carefully as possible.**

1. What is this well used for?

Private water supply \_\_\_\_\_  
Animal water supply \_\_\_\_\_  
Irrigation \_\_\_\_\_  
Other (specify) \_\_\_\_\_

Is the well used for more than one purpose? Please list them: \_\_\_\_\_

\_\_\_\_\_

**IF THE WELL IS NOT USED FOR PRIVATE WATER SUPPLY OR IF IT IS A LARGE-DIAMETER DUG OR BORED WELL, DISCONTINUE THE INTERVIEW. THANK THE WELL USER FOR HIS COOPERATION AND REPORT THIS INFORMATION TO THE PROJECT MANAGER SO THAT AN ADDITIONAL WELL CAN BE SELECTED.**

2. Can the well be sampled?

No \_\_\_\_\_  
Yes \_\_\_\_\_  
Unknown \_\_\_\_\_

3. If the well can be sampled, can the sample be collected before the treatment point?

No \_\_\_\_\_  
Yes \_\_\_\_\_  
Unknown \_\_\_\_\_

4. Can the sample be collected before the holding tank? (if applicable)

No \_\_\_\_\_  
Yes \_\_\_\_\_  
Unknown \_\_\_\_\_

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

Hilltop \_\_\_\_\_  
Hill slope \_\_\_\_\_  
Terrace \_\_\_\_\_  
Depression \_\_\_\_\_  
Floodplain \_\_\_\_\_  
Other (specify) \_\_\_\_\_  
Unknown \_\_\_\_\_

6. Is the well open or closed at the surface?

Open \_\_\_\_\_  
Closed \_\_\_\_\_  
Unknown \_\_\_\_\_

7. Is the well protected at the surface?

No \_\_\_\_\_  
Yes \_\_\_\_\_  
Unknown \_\_\_\_\_

If yes, how?

Well house or shed \_\_\_\_\_  
Concrete pad \_\_\_\_\_  
Sanitary or grouted seal \_\_\_\_\_  
Covered pit \_\_\_\_\_  
Other (specify) \_\_\_\_\_

8. Is this protection adequate to prevent seepage into the well?

Yes \_\_\_\_\_  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

9. Are there any of the following within 500 feet of the well?

Body of water (pond, stream, river, other?) \_\_\_\_\_  
Drainage ditch \_\_\_\_\_  
Septic tank \_\_\_\_\_  
Septic field \_\_\_\_\_  
Cesspool \_\_\_\_\_  
Animal grazing area \_\_\_\_\_  
Animal housing facility \_\_\_\_\_  
Pesticide mixing point \_\_\_\_\_  
Pesticide storage \_\_\_\_\_  
Crop storage \_\_\_\_\_  
Irrigation well \_\_\_\_\_  
Cropland \_\_\_\_\_  
What crops in 1989? \_\_\_\_\_  
1988? \_\_\_\_\_  
1987? \_\_\_\_\_  
1986? \_\_\_\_\_  
1985? \_\_\_\_\_

10. If the soil within 500 feet of the well is not exposed, how is it covered?

Roofed or covered \_\_\_\_\_  
Paved \_\_\_\_\_  
Graveled \_\_\_\_\_  
Rock \_\_\_\_\_  
Grass/vegetation \_\_\_\_\_  
Other cover (specify) \_\_\_\_\_  
Unknown \_\_\_\_\_

11. Is the well water treated? \_\_\_\_\_ No \_\_\_\_\_ Yes

Mechanically \_\_\_\_\_  
Chemically \_\_\_\_\_

How? (describe the treatment) \_\_\_\_\_  
\_\_\_\_\_

12. Describe and sketch (below) the location of the sampling point.



**APPENDIX F. Well-User Interview Report**

**Rural Private Water Well Survey  
for Agricultural Chemicals**

Well-User Interview

WELL IDENTIFICATION NUMBER \_\_\_\_\_  
(base number for sample)

The state of Illinois is conducting an assessment of the potential impact of agricultural chemicals on rural private wells. This survey is one part of that assessment program. The purpose of this survey is to determine the uses and history of each domestic well.

**Fill out at the time of the site survey, while on site.** Show the user a diagram of a well to aid in the discussion of construction details.

Staff member \_\_\_\_\_

Date of survey \_\_\_\_\_

User name \_\_\_\_\_

User address \_\_\_\_\_  
\_\_\_\_\_

User phone number \_\_\_\_\_

Well user other than owner \_\_\_\_\_

Reason why user is other than owner \_\_\_\_\_  
\_\_\_\_\_

Location of well \_\_\_\_\_

Legal description of well site: Twp \_\_\_\_\_ Rng \_\_\_\_\_ Sec \_\_\_\_\_  
10-acre plot \_\_\_\_\_ or Quarter-quarter-quarter \_\_\_\_\_

Type of well:

Drilled \_\_\_\_\_ or dug/bored \_\_\_\_\_ (diameter) \_\_\_\_\_

Sandpoint \_\_\_\_\_



8. What is the diameter of the hole M O R

• drilled for the well outside the casing? \_\_\_\_\_ (inches)  
unknown \_\_\_\_\_

• of the inside of the well? \_\_\_\_\_ (inches) M O R  
unknown \_\_\_\_\_

9. In what type of material is the well finished? M O R

Limestone/dolomite \_\_\_\_\_  
Sandstone \_\_\_\_\_  
Sand & gravel \_\_\_\_\_  
Other unconsolidated material (describe) \_\_\_\_\_  
Unknown \_\_\_\_\_

10. Does this well have a casing (i.e. a protective covering used to line the well hole)?

Yes \_\_\_\_\_ M O R  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

11. What material was used to case the well?

Plastic pipe (PVC) \_\_\_\_\_ M O R  
Concrete or cement \_\_\_\_\_  
Metal \_\_\_\_\_  
Tile, brick, or stone \_\_\_\_\_  
Other (specify) \_\_\_\_\_  
Unknown \_\_\_\_\_

12. Is the well cased to its total depth?

Yes \_\_\_\_\_ M O R  
No \_\_\_\_\_  
Near surface only: \_\_\_\_\_  
Depth below surface \_\_\_\_\_ (feet)  
Unknown \_\_\_\_\_

13. Does the well have a screen? M O R

Yes \_\_\_\_\_  
Describe (material, slot size) \_\_\_\_\_  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

14. If the well is screened, is there more than one screen? M O R

Yes (how many?) \_\_\_\_\_  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

15. What is the depth to the top of the highest screen?

Unknown \_\_\_\_\_ (feet) M O R  
\_\_\_\_\_

16. What is the depth to the bottom of the lowest screen?

Unknown \_\_\_\_\_ (feet) M O R  
\_\_\_\_\_

17. Is the well grouted?

Yes (with what?) \_\_\_\_\_ M O R  
How deep? \_\_\_\_\_ (feet)  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

18. Has the well been plugged back to its present depth?

Yes \_\_\_\_\_ M O R  
Previous depth? \_\_\_\_\_ (feet)  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

19. Is the well capped or plugged at the ground surface?

Yes \_\_\_\_\_ M O R  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

20. What material was used to cap or plug the well?

Cement \_\_\_\_\_ M O R  
Plastic \_\_\_\_\_  
Other (specify) \_\_\_\_\_

21. What is the depth to water in the well? M O R

Unknown \_\_\_\_\_ (feet)  
\_\_\_\_\_

22. What is the depth to the pump setting? M O R

Unknown \_\_\_\_\_ (feet)  
\_\_\_\_\_

23. Is this well used continuously or seasonally?

Continuously \_\_\_\_\_ M O R  
Seasonally \_\_\_\_\_

If not continuously,

how often is it used? \_\_\_\_\_  
When it is used? \_\_\_\_\_  
How long? \_\_\_\_\_  
Unknown \_\_\_\_\_

24. What is the capacity of the pump? (How many gallons per minute *can* it pump?)

Gallons per minute \_\_\_\_\_ M O R  
Unknown \_\_\_\_\_

25. How many gallons a minute is the average pumping rate during normal usage? (How many gallons per minute *does it usually* pump?)

Gallons per minute \_\_\_\_\_ M O R  
Unknown \_\_\_\_\_

26. Does this well ever run dry? M O R

Yes \_\_\_\_\_  
Seasonally \_\_\_\_\_  
In drought \_\_\_\_\_  
Other (specify) \_\_\_\_\_  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

27. Is the well water being treated currently?

Yes \_\_\_\_\_ M O R  
No \_\_\_\_\_  
Unknown \_\_\_\_\_

28. If treated, how?

Water softener	_____	M O R
Is the water hard?	_____	
Filter:	_____	
on the well	_____	
for the house	_____	
on the tap	_____	
Fluoride	_____	
Chlorination	_____	
Activated carbon/charcoal	_____	
Other (specify)	_____	

29. Has the well been disinfected recently?

M O R

Yes (when?)	_____
No	_____
Unknown	_____

30. Are there any operating wells within 500 feet of this well?

Yes	_____	No	_____	Unknown	_____
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31. Indicate the type of wells within 500 feet of the well and the number of each type.

	Type	Number	M O R
Private drinking water supply	_____	_____	
Community drinking water supply	_____	_____	
Irrigation	_____	_____	
Animal water supply	_____	_____	
Other (specify)	_____	_____	

32. Are there any abandoned (A) or non-operating (N) wells within 500 feet of the well? What type? How many?

	A/N	Number	M O R
Private drinking water supply	_____	_____	
Community drinking water supply	_____	_____	
Irrigation	_____	_____	
Animal water supply	_____	_____	
Other (specify)	_____	_____	

33. Have you had the water from this well tested?

M O R

Yes (when?)	_____
By whom?	_____
Purpose?	_____
Results	_____
No	_____
Unknown	_____

34. Has this well ever been contaminated?

M O R

Yes	_____
By what?	_____
No	_____
Unknown	_____

## Pesticide Usage

This part of the survey is concerned with the usage of pesticides near this well. Pesticides include all insecticides, herbicides, fungicides, nematocides, rodenticides, and other chemical agents except fertilizers.

35. In the past year has any pesticide been used, mixed, stored, or loaded within 500 feet of the well?

Used	_____	Mixed	_____	M O R
Stored	_____	Disposed	_____	

How was it stored? M O R

In the open	_____	In an enclosure	_____
On bare ground	_____	On concrete pad	_____
Unknown	_____		

36. In the past 2 years has any pesticide been used, mixed, stored, or loaded within 500 feet of the well?

Used	_____	Mixed	_____	M O R
Stored	_____	Disposed	_____	

How was it stored? M O R

In the open	_____	In an enclosure	_____
On bare ground	_____	On concrete pad	_____
Unknown	_____		

37. In the past 5 years has any pesticide been used, mixed, stored, or loaded within 500 feet of the well?

Used	_____	Mixed	_____	M O R
Stored	_____	Disposed	_____	

How was it stored? M O R

In the open	_____	In an enclosure	_____
On bare ground	_____	On concrete pad	_____
Unknown	_____		

38. Is water from the well used to mix pesticides for spraying? M O R

Yes \_\_\_\_\_ No \_\_\_\_\_ Unknown \_\_\_\_\_

Is water taken directly from the well to the sprayer tank? M O R

Yes \_\_\_\_\_ No \_\_\_\_\_ Unknown \_\_\_\_\_

Has the sprayer tank ever overflowed? M O R

Yes (when?) \_\_\_\_\_  
 No \_\_\_\_\_ Unknown \_\_\_\_\_

Has the tank ever back-siphoned? M O R

Yes (when?) \_\_\_\_\_  
 No \_\_\_\_\_ Unknown \_\_\_\_\_

39. Starting with this year, back through 1986, which pesticides have been used within 500 feet of the well? (Give either the brand name or the active ingredient.)

1988 \_\_\_\_\_ M O R

Unknown \_\_\_\_\_  
 How close to the well? \_\_\_\_\_ (feet)  
 Unknown \_\_\_\_\_

1987 \_\_\_\_\_ M O R

Unknown \_\_\_\_\_  
 How close to the well? \_\_\_\_\_ (feet)  
 Unknown \_\_\_\_\_

1986 \_\_\_\_\_ M O R

Unknown \_\_\_\_\_  
 How close to the well? \_\_\_\_\_ (feet)  
 Unknown \_\_\_\_\_

40. Starting with this year, back through 1986, what pesticides have been stored within 500 feet of the well? (Give either the brand name or the active ingredient.)

1988 \_\_\_\_\_ M O R

How was it stored? M O R  
 In the open \_\_\_\_\_ In an enclosure \_\_\_\_\_  
 On bare ground \_\_\_\_\_ On concrete pad \_\_\_\_\_  
 Unknown \_\_\_\_\_  
 How close to the well? \_\_\_\_\_ (feet)  
 Unknown \_\_\_\_\_

1987 \_\_\_\_\_ M O R

How was it stored? M O R  
 In the open \_\_\_\_\_ In an enclosure \_\_\_\_\_  
 On bare ground \_\_\_\_\_ On concrete pad \_\_\_\_\_  
 Unknown \_\_\_\_\_  
 How close to the well? \_\_\_\_\_ (feet)  
 Unknown \_\_\_\_\_

1986 \_\_\_\_\_ M O R

How was it stored? M O R  
 In the open \_\_\_\_\_ In an enclosure \_\_\_\_\_  
 On bare ground \_\_\_\_\_ On concrete pad \_\_\_\_\_  
 Unknown \_\_\_\_\_  
 How close to the well? \_\_\_\_\_ (feet)  
 Unknown \_\_\_\_\_



41. Starting with this year, back through 1986, what pesticides containers have been disposed of within 500 feet of the well? (Give either the brand name or the active ingredient.)

1988 \_\_\_\_\_ M O R

How was it disposed of? \_\_\_\_\_

Unknown \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

Are containers triple rinsed near the well? \_\_\_\_\_

Is the well used to rinse containers or tanks? \_\_\_\_\_

1987 \_\_\_\_\_ M O R

How was it disposed of? \_\_\_\_\_

Unknown \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

Are containers triple rinsed near the well? \_\_\_\_\_

Is the well used to rinse containers or tanks? \_\_\_\_\_

1986 \_\_\_\_\_ M O R

How was it disposed of? \_\_\_\_\_

Unknown \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

Are containers triple rinsed near the well? \_\_\_\_\_

Is the well used to rinse containers or tanks? \_\_\_\_\_

42. Starting with this year, back through 1986, what pesticides have been accidentally spilled down or within 500 feet of the well? (Give either the brand name or the active ingredient.)

1988 \_\_\_\_\_ M O R

Unknown \_\_\_\_\_

What volume? \_\_\_\_\_

Mixed or from original container? \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

1987 \_\_\_\_\_ M O R

Unknown \_\_\_\_\_

What volume? \_\_\_\_\_

Mixed or from original container? \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

1986 \_\_\_\_\_

M O R

Unknown \_\_\_\_\_

What volume? \_\_\_\_\_

Mixed or from original container? \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

43. Starting with this year, back through 1986, what pesticides have been accidentally backsiphoned into the well? (Give either the brand name or the active ingredient.)

1988 \_\_\_\_\_

M O R

Unknown \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

1987 \_\_\_\_\_

M O R

Unknown \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

1986 \_\_\_\_\_

M O R

Unknown \_\_\_\_\_

How close to the well? \_\_\_\_\_ (feet)

Unknown \_\_\_\_\_

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