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Hydrogeologic Framework and Sampling Design for an Assessment of Agricultural Pesticides in Ground Water in Pennsylvania

by Bruce D. Lindsey and Tammy M. Bickford

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Area	
square mile (mi^2)	2.590	square kilometer

Other abbreviations used in report:

- m, meter
- µg/L, micrograms per liter
- mL/g, milliliters per gram

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ABSTRACT

State agencies responsible for regulating pesticides are required by the U.S. Environmental Protection Agency to develop state management plans for specific pesticides. A key part of these management plans includes assessing the potential for contamination of ground water by pesticides throughout the state. As an example of how a statewide assessment could be implemented, a plan is presented for the Commonwealth of Pennsylvania to illustrate how a hydrogeologic framework can be used as a basis for sampling areas within a state with the highest likelihood of having elevated pesticide concentrations in ground water. The framework was created by subdividing the state into 20 areas on the basis of physiography and aquifer type. Each of these 20 hydrogeologic settings is relatively homogeneous with respect to aquifer susceptibility and pesticide use—factors that would be likely to affect pesticide concentrations in ground water. Existing data on atrazine occurrence in ground water was analyzed to determine (1) which areas of the state already have sufficient samples collected to make statistical comparisons among hydrogeologic settings, and (2) the effect of factors such as land use and aquifer characteristics on pesticide occurrence. The theoretical vulnerability and the results of the data analysis were used to rank each of the 20 hydrogeologic settings on the basis of vulnerability of ground water to contamination by pesticides. Example sampling plans are presented for nine of the hydrogeologic settings that lack sufficient data to assess vulnerability to contamination. Of the highest priority areas of the state, two out of four have been adequately sampled, one of the three areas of moderate to high priority has been adequately sampled, four of the nine areas of moderate to low priority have been adequately sampled, and none of the three low priority areas have been sampled.

Sampling to date has shown that, even in the most vulnerable hydrogeologic settings, pesticide concentrations in ground water rarely exceed U.S. Environmental Protection Agency Drinking Water Standards or Health Advisory Levels. Analyses of samples from 1,159 private water supplies reveal only 3 sites for which samples with concentrations of pesticides exceeded drinking-water standards. In most cases, samples with elevated concentrations could be traced to point sources at pesticide loading or mixing areas. These analyses included data from some of the most vulnerable areas of the state, indicating that it is highly unlikely that pesticide concentrations in water from wells in other areas of the state would exceed the drinking-water standards unless a point source of contamination were present. Analysis of existing data showed that water from wells in areas of the state underlain by carbonate (limestone and dolomite) bedrock, which commonly have a high percentage of corn production, was much more likely to have pesticides detected. Application of pesticides to the land surface generally has not caused concentrations of the five state priority pesticides in ground water to exceed health standards; however, this study has not evaluated the potential human health effects of mixtures of pesticides or pesticide degradation products in drinking water. This study also has not determined whether concentrations in ground water are stable, increasing, or decreasing.

INTRODUCTION

The U.S. Environmental Protection Agency (USEPA) requires that state agencies responsible for regulating pesticides develop management plans for specific pesticides. In Pennsylvania, the Pennsylvania Department of Agriculture (PDA) is the agency that has regulatory authority for registration and use of pesticides. In 1996, the USEPA proposed restricting the legal sale and use of the five pesticides—alachlor, atrazine, cyanazine, metolachlor, and simazine—that had been identified as either probable or possible human carcinogens (U.S. Environmental Protection Agency, 1996b). Because of their potential to contaminate ground water, the USEPA determined these pesticides may cause unreasonable adverse effects on the environment in absence of effective management measures provided by the states. The PDA has developed a draft Pesticides and Ground Water Strategy that outlines a reasonable approach for managing pesticides and preserving ground-water quality. This strategy for managing pesticides will serve as a framework for the PDA to manage specific pesticides as required by the USEPA. The goal of this strategy is to protect all sources of drinking water from degradation. An important part of the Pesticides and Ground Water Strategy is an assessment of the entire state to determine (1) the vulnerability of various areas of the state to pesticide contamination, (2) the amount of data available to characterize the occurrence of pesticides in ground water, and (3) an approach to characterizing the occurrence of pesticides in ground water throughout the state. As used in this report, the term susceptibility implies that an aquifer has characteristics that would allow movement of contaminants through the aquifer materials (without consideration of whether or not those contaminants are present); the term vulnerability implies both susceptibility of an aquifer and availability of a contaminant. The U.S. Geological Survey (USGS), in cooperation with the PDA, completed the study described herein to ensure that pesticide data-collection efforts by both agencies would be more consistent, and therefore, more useful to any agency using the data to manage pesticide use or water resources.

Purpose and Scope

This report illustrates how a hydrogeologic framework can be used as a basis for sampling a state (in this case, Pennsylvania) for occurrence of pesticides in ground water. The term hydrogeologic framework, as used in this report, refers to using physiography and aquifer type (surficial aquifer or bedrock type) to subdivide the state for pesticide sampling and management. This report also presents a prioritized plan for sampling ground water in areas of the state that have not been adequately characterized for the occurrence of pesticides. Pesticide analyses for 1,159 wells were available for use in the initial prioritization. Datasets of land cover, physiography, geology, and pesticide vulnerability were used to develop the plan. The five pesticides designated in the state management plan—atrazine, simazine, cyanazine, alachlor, and metolachlor—were the focus of this study. Although these pesticides are primarily associated with corn production in agricultural areas, all areas in the state were evaluated with respect to potential uses of these pesticides, as well as the potential for these pesticides to leach into ground water.

Approach

The study consisted of subdividing the state into homogeneous areas for sampling and management, compiling existing data, ranking the vulnerability of all of the areas in the state, and prioritizing those areas needing additional ground-water sampling. The process began by subdividing the state on the basis of the physiography and aquifer type into hydrogeologic settings that were relatively homogeneous with respect to potential for pesticide contamination in ground water. The purpose of this was to allow characterization of large areas of the state with the minimum sampling cost. Following the subdivision of the state, the availability of water-quality data, potential for pesticide use, and the potential for leaching of pesticides was determined in each hydrogeologic setting. The ranking of vulnerability of hydrogeologic settings to leaching of pesticides was initially assigned on the basis of information from previous studies of aquifer susceptibility and pesticide use. Data from previous studies with documentation of analytical methods and quality assurance, were used to (1) determine which areas have adequate sampling for initial characterization of the occurrence of pesticides and (2) conduct statistical tests to assess which areas were most likely to have pesticides detected. The results of the statistical tests were used to adjust the initial rankings. For those areas in which sufficient samples were not available to characterize the occurrence of pesticides, sampling plans were created and presented in the order based on the vulnerability rank of the area.

Acknowledgments

The authors would like to thank David Bingaman and John Pari of the PDA who provided a great deal of assistance in developing the project and providing input to USGS personnel as the project was being implemented. The authors would also like to acknowledge the assistance of a report team that included Kevin Beer, Patricia Lietman, and Dennis Risser of the USGS; John Diehl

and Stuart Reese of the Pennsylvania Department of Environmental Protection (PaDEP), and John Pari of the PDA.

Previous Investigations

Regional assessments of occurrence of contaminants in ground water have been conducted using various approaches. Several of these studies are evaluated to assist in developing the approach for the Pennsylvania Pesticides in Ground Water Strategy. Data from previous investigations within Pennsylvania can be used to assist in developing the Pesticides in Ground Water Strategy, and each of these studies are evaluated herein.

Approaches Used in Similar Investigations

The USGS National Water-Quality Assessment (NAWQA) Program is conducting a nationwide study that includes assessments of pesticides in ground water. The approach of the NAWQA studies is to subdivide large study areas into smaller areas with common natural and human-related factors, such as physiography, geology, and land use, so comparisons of water quality among different types of systems can be made (Gilliom and others, 1995). Samples are collected in each area in a similar manner so statistical comparisons can be made among the different systems or hydrogeologic settings. This approach has been successful in helping to determine which areas have a higher occurrence of certain contaminants and will be useful in the assessments the PDA will be conducting. Several of these studies include part of Pennsylvania.

The Pennsylvania State University conducted a study on the occurrence of atrazine in ground water in Pennsylvania in cooperation with Ciba-Giegy corporation (Harrison and others, 1995; Balu and Holden, 1996). In this study, physiography, corn production, and soil type were used as a way to subdivide the state into vulnerable and nonvulnerable aquifers. Sampling targeted agricultural areas. Physiographic provinces were found to be too large to explain the extent of pesticide contamination because they encompassed a broad range of vulnerabilities within the provinces, as well as a broad range of agricultural practices. The Penn State study was not designed to collect sufficient samples in each hydrogeologic setting to allow statistical comparisons among the different hydrogeologic settings.

The Pennsylvania State University Environmental Resources Research Institute developed a model to represent the potential vulnerability of public water supplies in Pennsylvania to pesticide pollution from agricultural activities (Petersen and others, 1996). This vulnerability assessment used a predictive model called DRASTIC (Depth to ground water, Recharge, Aquifer media, Soil permeability, Topography, Impact of the vadose zone, and hydraulic Conductivity), originally developed by Aller and others (1987). The model was altered by Petersen and others (1996) and used to assign a pesticide susceptibility score to each 100×100 m cell within a grid designed to cover the state of Pennsylvania. The crop usage and probable pesticide usage were incorporated into the DRASTIC score, providing the basis for the PaDEP to grant waivers to public water suppliers from monitoring requirements for pesticides. Because the model is based on a small-scale grid, it does not provide a framework for planning or conducting sampling efforts or managing pesticide use after sampling. It is, however, helpful for determining the variation in ground-water susceptibility throughout the state.

In New Jersey, a study was conducted to evaluate the vulnerability of public supply wells to contamination by pesticides (Vowinkel and others, 1993). The approach of this study was similar to the study conducted by Penn State in that an empirical model was used to predict the vulnerability of each well to pesticide contamination. The variables related to aquifer vulnerability were distance from the aquifer outcrop area, organic-matter content of the soil at the well, depth to the top of the open interval of the well, surrounding land use, distance from the nearest parcel of agricultural land, and distance from the nearest golf course. This study also focused on predicting presence or absence of pesticides at a sampling point or well, and although the study provides insight into the variables that would affect pesticide concentrations, the approach used in the New Jersey study would not provide a method to assess an area or to manage pesticides in an area.

Investigations Used as Sources of Data

Previous studies that analyzed for the state priority pesticides (alachlor, atrazine, cyanazine, metolachlor, and simazine) in ground water have been conducted in Pennsylvania (table 1). These studies have been done at statewide, regional, basin-wide, and local scales from 1991 to 1998. The paragraphs that follow give a brief synopsis of each study. These data were compiled and evaluated to determine sample-collection methodology, analytical methodology, and quality assurance of the data collected. This information was used in determining whether or not to include the existing dataset in statistical analysis. The total number of wells available with pesticide analyses was 4,388; however, only 1,159 of these samples were considered to be accurate enough to use to determine whether or not health standards were exceeded. A subset of 582 samples had quality-assurance programs that indicated an acceptable degree of confidence in the reported concentration to be used in the statistical analysis. In general, samples analyzed at a lab by gas chromatography / mass spectrometry (GCMS) in a study that included a quality-assurance program were used for the statistical analysis. Samples from studies without quality-assurance programs were included in the determination of whether or not health standards were exceeded if resampling was used to verify high-level concentrations.

USGS Studies

The USGS has conducted 11 regional studies as part of the NAWQA programs in the Lower Susquehanna, the Potomac, and the Allegheny and Monongahela River Basins that included analyses of pesticides in ground water. These regional studies started in 1991 and included large parts of the state of Pennsylvania. Five of the regional studies were aquifer studies based on large hydrogeologic settings without regard to land use. The other six regional studies were based on hydrogeologic setting and a targeted land use. These six studies were called “land-use studies” by the NAWQA Program. Five of the six land-use studies were in agricultural areas underlain by carbonate bedrock, and the other was in an urban area underlain by carbonate bedrock. All samples collected for the USGS regional studies were analyzed by the USGS National Water-Quality Laboratory (NWQL) using the same analytical methodology. Wells for each regional study were selected using a stratified random-selection process. This involved using a computerized program (Scott, 1990) to select sampling locations from an area that was defined on the basis of aquifer characteristics, and in the case of land-use studies, the targeted land use. The random-selection program ensured spatial distribution and allowed for wells in specific types of aquifers to be selected in an unbiased manner.

Sub-county level studies of pesticides in ground water also have been conducted by the USGS. These studies were focused on more localized areas and had various methods of site selection and sample analysis. The USGS study of ground water in the Red Clay Creek Basin in Chester County was conducted in 1993 at 82 wells (Senior, 1996). State priority pesticides were included in these analyses, as well as many other potential contaminants. Quality-assurance samples were collected. A USGS study of pesticides and nutrients in ground water in Lancaster and Chester Counties was conducted in the Pequea Creek and Mill Creek Basins (Durlin and Schaffstall, 1992, p. 279-337). This study also included the state priority pesticides. All wells were sampled at least once (total of 377 well samples) and 20 quality-assurance samples were collected (approximately 10 percent of all sites analyzed). Initial triazine screenings were performed by enzyme-linked immunosorbent assay (ELISA) analysis in the Pennsylvania District Laboratory to determine presence or absence of herbicides. Herbicides were analyzed by the USGS NWQL by gas chromatography / mass spectrometry (GCMS) analysis for both studies mentioned above.

Water samples were collected for analysis of pesticides as part of a cooperative program between the USGS and the PDA during the summer of 1998 to provide a screening tool in areas where no acceptable data were available. Samples were collected at 30 wells—at 5 wells in each of 6 hydrogeologic settings. The most vulnerable areas for which no data were available were chosen for this sampling. The protocols of the USGS Lower Susquehanna River Basin NAWQA, summarized in Siwiec and others (1997), were followed for well selection and sampling. Samples were analyzed at the PaDEP Laboratory in Harrisburg, Pa. Quality-assurance samples were submitted to the PaDEP laboratory and the USGS NWQL in Arvada, Colo. The quality-assurance program followed the guidelines established for a USGS / PDA cooperative study on quality assurance (Kevin Breen, U.S. Geological Survey, written commun., 1999). The results of the quality-assurance program indicated

Table 1. *Studies of pesticides in ground water in Pennsylvania*

[NAWQA, National Water-Quality Assessment Program; USGS, U.S. Geological Survey; GCMS, gas chromatography/mass spectrometry; NWQL, National Water-Quality Laboratory; PDA, Pennsylvania Department of Agriculture; PaDEP, Pennsylvania Department of Environmental Protection]

Study name	Agency conducting study	Years study conducted	Type of pesticide sampling	Number of sites sampled in Pennsylvania	Quality assured? (yes or no)	Data included in statistical analysis? (yes or no)	Data included in qualitative analysis? (yes or no)
Lower Susquehanna NAWQA	USGS	1993-95	GCMS analyses, USGS NWQL	163	Yes	Yes	Yes
Potomac NAWQA	USGS	1993-95	GCMS analysis, USGS NWQL	13	Yes	Yes	Yes
Allegheny-Monongahela NAWQA	USGS	1996-97	GCMS analysis, USGS NWQL	40	Yes	Yes	Yes
USGS / PDA Cooperative Sampling Program	USGS	1998	GCMS analysis, USGS NWQL	10	Yes	Yes	Yes
			PaDEP lab	20	Yes	Yes	Yes
Penn State / Ciba-Geigy	Penn State / Ciba-Geigy	1993	GCMS or HPLC analyses, Penn State's Pesticide Research Lab	187	Yes	Yes	Yes
Chester County, Red Clay Creek Study	USGS	1993	GCMS analysis, USGS NWQL	82	Yes	Yes	Yes
Chester County Water-Quality Monitoring Program	USGS	1993	GCMS analysis, USGS NWQL	21	Yes	Yes	Yes
Clearfield, Jefferson, and Indiana County, Ground Water Quality in Mahoning Creek Basin	USGS	1995	Triazine Scan, Pennsylvania District Laboratory	46	Yes	No	Yes
Cumberland County, Hydrogeology of Ground Water and Springs	USGS	1990-91	Triazine Scan, Pennsylvania District Laboratory GCMS analysis, USGS NWQL	50	Yes	No	Yes
Lancaster County, Pequea and Mill Creek	USGS	1992	Triazine Scan, Pennsylvania District Laboratory (all samples)	251	Yes	No	Yes
			GCMS analysis, USGS NWQL (select subset of samples)	35		Yes	Yes
Lancaster County, Pequea and Mill Creek	PDA	1995	Immunoassay triazine scan GCMS analysis, PaDEP lab	136	No	No	Yes
Morrison Cove, Bedford and Blair Counties	PDA	1996	PDA contract lab	189	No	No	Yes
Delaware River Basin, Great Valley	PDA	1997	GCMS analysis, PaDEP lab (all samples) /	76	Yes	No	Yes
			GCMS analysis, USGS NWQL (subset of samples)	11	Yes	Yes	Yes
Pennsylvania public water supply database	PaDEP	1993-98	Unknown	3,240	No	No	No

no evidence of sample contamination. The analysis of samples spiked with known concentrations of analytes showed acceptable recovery levels.

Pennsylvania Department of Agriculture Studies

Sub-county level studies also were conducted by the PDA. One such study was conducted in 1995 in the Pequea Creek and Mill Creek Basins in Lancaster County where ground water from 68 wells and springs was sampled for pesticides (John Pari, Pennsylvania Department of Agriculture, written commun., 1998). Another study by the PDA was conducted in 1996 in the Morrison Cove area of Bedford and Blair Counties (John Pari, Pennsylvania Department of Agriculture, written commun., 1998). Ground-water samples were collected from 189 wells and springs and were analyzed by a contract laboratory. In 1997, the PDA conducted a study of the Great Valley Physiographic Section in the Delaware River Basin in an area underlain by carbonate bedrock (John Pari, Pennsylvania Department of Agriculture, written commun., 1998). The analyses were done at the PaDEP Laboratory in Harrisburg, Pa. A total of 88 ground-water samples were collected.This hydrogeologic setting was sampled using a representative sampling plan similar to the plans presented in this report.

The PDA studies in the Morrison Cove and Pequea / Mill Creek Basins cover a small area with a large sampling density. Data from many different types of wells were collected in these studies. The diversity of well depths and ages and nonrandom site locations of these studies make the data difficult to analyze and interpret for resource assessments. In addition, the Morrison Cove and Pequea / Mill Creek studies were completed without submission of any samples of known concentration (spikes), and the lab that analyzed these samples did not meet the quality-assurance standards set in their contract with the PDA. For those reasons, these samples were not included in the statistical analyses; however, because the PDA verifies high-level detections with additional sampling, this data was used when calculating the number of samples exceeding the drinking-water standards.

During the study of the carbonate area of the Great Valley Physiographic Province in the Delaware River Basin, a quality-assurance program was implemented in conjunction with the USGS. The plan included submitting samples fortified with known quantities of pesticides (spikes) and also splitting replicate samples between the PaDEP Laboratory and the USGS NWQL in Arvada, Colo. The results of the quality-assurance plan showed that the PDA could be confident that sample-collection procedures and field and laboratory sample-processing activities in 1997-98 did not introduce trace levels of the eight priority pesticides as contaminants to environmental samples. False positive results were insignificant. The PDA could also be confident that a pesticide was detected in water when the pesticide was present at concentrations above 0.13 µg / L. False negative results were not a problem, and detections were reproducible. Results from both replicate and spike samples supported this conclusion (Kevin Breen, U.S. Geological Survey, written commun., 1999).

Pennsylvania State University Pesticide Study

The only study to date that analyzed pesticides in ground water in the entire state of Pennsylvania was conducted by the Pennsylvania State University in conjunction with the Ciba-Giegy Corporation (Harrison and others, 1995; Balu and Holden, 1996). The Penn State study was conducted simultaneously with the Ciba-Giegy study using the same set of wells and data-collection protocols; however, samples were analyzed by Ciba-Giegy and Penn State independently. Ciba-Giegy's objective was to study atrazine and its chloro- and hydroxy- degradates in ground-water samples collected from vulnerable hydrogeologic settings in Pennsylvania in areas of high corn production, as part of the requirements to reregister atrazine with the USEPA. The main objective of the Penn State study was to identify areas of the state that were most vulnerable to ground-water contamination to aid the PDA in developing a state management plan for pesticide use. The Penn State study included all of the state priority pesticides. Farm and nonfarm wells were sampled in pairs to determine if site-specific conditions contribute to pesticide detection in ground water. The Ciba-Giegy laboratory analysis had a quality-assurance component, including adherence to the USEPA Good Laboratory Practices standards, and submission of samples spiked with a known quantity of pesticides. The results of the Ciba-Giegy quality-assurance plan indicate acceptable laboratory and field procedures. The Penn State laboratory analysis did not have a quality-assurance component (Harrison and others, 1995).

The design of the Penn State / Ciba-Giegy study was targeted toward sampling wells in corn-producing areas. A predetermined number of wells was selected in each physiographic province of the state with a ratio of approximately 60 percent of the wells in areas with low vulnerability and 40 percent of the wells in areas with high vulnerability. The basic subdivisions of the state for this study were based on the seven major physiographic provinces, with wells selected to represent high and low vulnerability areas. The data collected for the Penn State / Ciba-Giegy study were not quantitatively sufficient to be statistically analyzed by physiographic sections, bedrock type, or soil type; however; the information was useful in helping to design the hydrogeologic framework for the Pennsylvania Pesticides in Ground Water Strategy described in this report. The Penn State / Ciba-Giegy study represented the only data available in many areas of the state for initial determinations of vulnerability.

Pennsylvania Public Water-Supply Database

Another source of data available for analysis of the occurrence of pesticides in Pennsylvania was the PaDEP’s public water-supply database. The database was created to store the results of samples collected by public water suppliers as part of their regulatory sampling requirements. The database consists of samples collected at 3,240 sites from 1,340 water suppliers in Pennsylvania and analyzed at commercial, certified drinking-water laboratories. These laboratories sent the results of their analyses to the PaDEP for inclusion in the public-water-supply database. The data supplied to the PaDEP by the laboratories prior to 1998, however, were not verified or checked, and the PaDEP’s database commonly was not updated if erroneous data were found. The quality of the database is questionable because of the number of samples where data are erroneous. Several analyses in the database were found to have reporting errors. Some reporting labs were contacted directly to verify specific analyses, and these checks confirmed data entry errors had occurred. In some cases, the samples in this database were collected from the distribution system and represented treated ground water. Because of the known errors in the database and lack of a quality-assurance plan, this database was not used for statistical data analysis.

HYDROGEOLOGIC FRAMEWORK FOR PESTICIDE ANALYSIS

The approach to characterizing the occurrence of pesticides in an area as large and diverse as the state of Pennsylvania was to subdivide the state into areas that were relatively homogeneous with respect to potential for pesticide occurrence in ground water. The intent of this approach was to allow characterization of large areas of the state with a minimum number of samples and, therefore, a minimum cost for analysis. This process began with subdividing the state on the basis of physiography. In cases where the ground-water vulnerability within a physiographic section varied greatly, the section was further subdivided on the basis of aquifer type.

Description of the Study Area

The state of Pennsylvania covers 44,820 mi^2 and is composed of seven physiographic provinces: Atlantic Coastal Plain, Piedmont, New England, Blue Ridge, Ridge and Valley, Appalachian Plateaus, and Central Lowlands. These physiographic provinces are further subdivided into 18 physiographic sections (Sevon, 1995) (fig. 1). Major bedrock aquifers (Berg and others, 1980) in Pennsylvania include: limestone and dolomite (carbonate aquifers); sandstone, siltstone, conglomerate, and shale (siliciclastic aquifers); and igneous and metamorphic rocks (crystalline aquifers) (fig. 2). Additionally, bedrock aquifers in some areas of the state are overlain by unconsolidated material (Soller and Packard, 1998), such as sand and gravel, of sufficient depth to serve as an aquifer such as glacial outwash, alluvium, and beach deposits (surficial aquifers) (fig. 2). Areas of the state where surficial materials consist of coarse-grained sediments were designated as surficial aquifers for this report.

Soils in Pennsylvania are classified on the basis of the parent bedrock material from which they formed (U.S. Department of Agriculture, 1972). Most soils are derived from carbonate bedrock, crystalline bedrock, or siliciclastic bedrock, and their locations can be deduced from the locations of the bedrock types. The infiltration capacity of the soils is based on the parent material, slope, soil thickness, land use, and land cover (Susquehanna River Basin Study Coordinating Committee, 1970) and is an important factor in determining if pesticides are likely to leach into the aquifer. Infiltration capacity classifications for soils are excel-

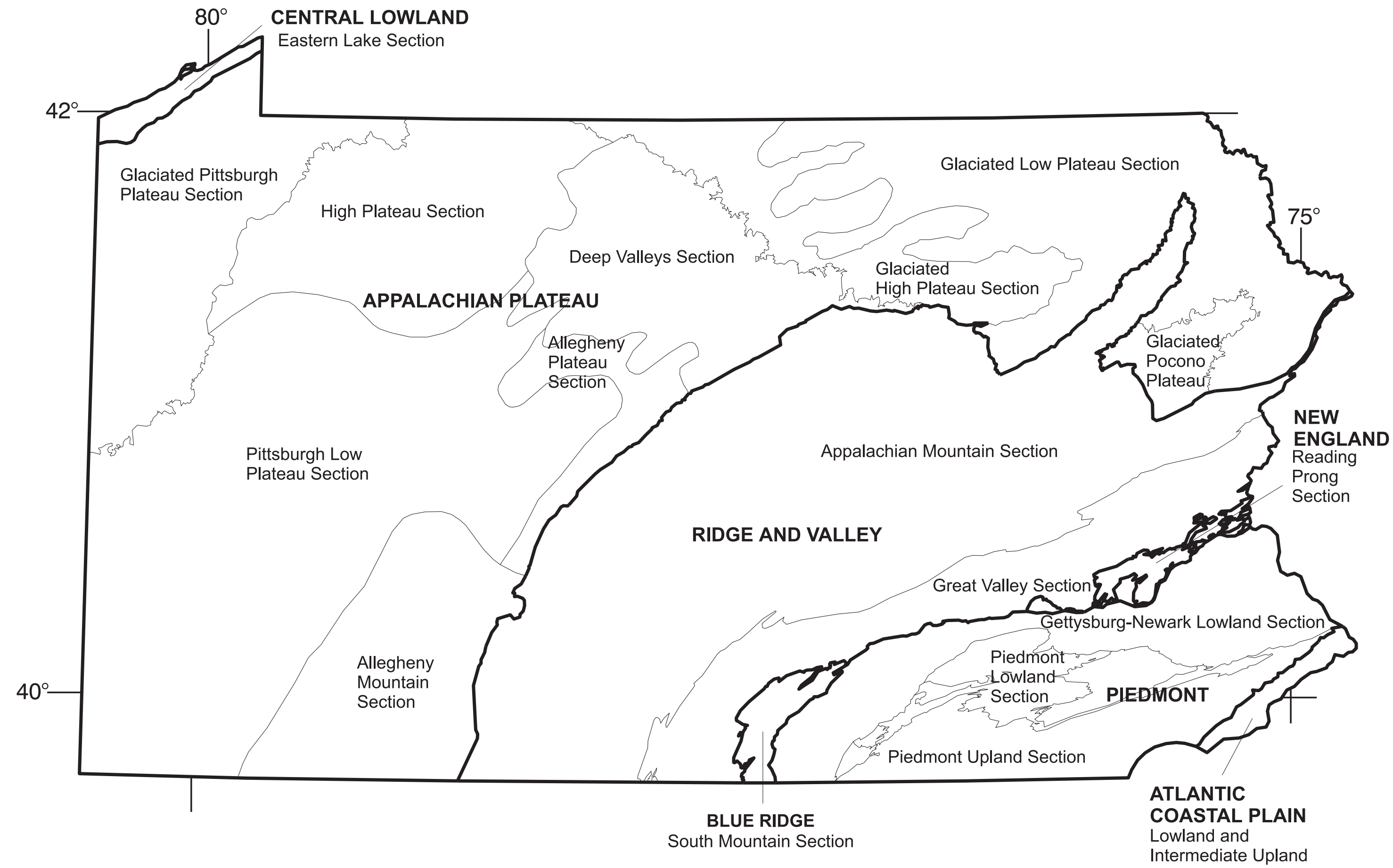


Figure 1. Physiographic provinces and sections of Pennsylvania (Sevon, 1995).

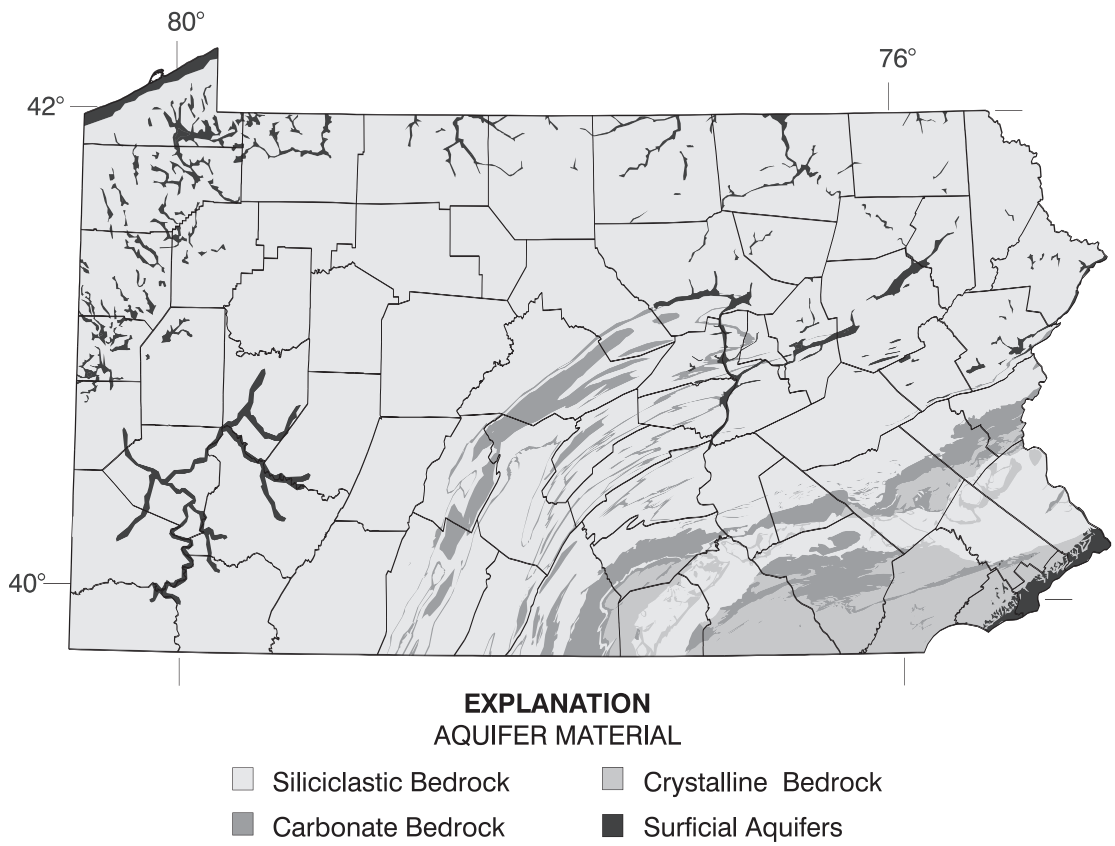


Figure 2. Major aquifer types of Pennsylvania (Berg and others, 1980; Soller and Packard, 1998).

lent (soils derived from carbonate bedrock), good (soils derived from crystalline bedrock and sandstone), and poor (soils derived from shale). The infiltration capacity of soils in unconsolidated stream terrace deposits is classified as very poor, and the infiltration capacity of soils in unconsolidated sand and gravel deposits is classified as good.

Land use in the state is diverse and important in determining the potential for pesticide use. Land-cover data from the early 1990's (Vogelmann and others, 1998a; Vogelmann and others, 1998b) shows that forests—predominantly deciduous forests—cover 65 percent of the land area (fig. 3). Agricultural land covers about 28 percent of the state; 18 percent of the area is in row crops, and 10 percent is in hay or pasture. Urban land covers about 4 percent of the land area including low intensity developed areas, high-intensity commercial areas, and high-intensity residential areas. The remaining 3 percent is covered by quarries and mines, wetlands, lawns, parks, golf courses, and barren land. The distribution of these land-cover types varies across the state as topography, physiography, and agricultural practices vary. In some areas, a single land cover is dominant; however, many areas contain a mixture of agricultural, forested, and other land covers. The distribution of the agricultural land in particular is important in determining priorities for pesticide sampling.

Ground water is an important resource for drinking-water supply for the residents of Pennsylvania. In a population of nearly 12 million people, approximately 3 million rely on private wells for domestic supply (U.S. Bureau of the Census, 1992), and an additional 2 million are served by public water suppliers that use ground water as a source of supply (Russell Ludlow, U.S. Geological Survey, written commun., 1998). Many of the 3 million residents who use private wells live in rural areas of the state in proximity to agricultural land. These private water supplies are not subject to the testing and treatment regulations that govern public water supplies. This is one reason why the Pesticides and Ground Water Strategy has a goal of protecting aquifers from contamination by pesticides.

Hydrogeologic Settings

Physiographic provinces (Sevon, 1995) were used as the basic unit for subdividing the state into relatively homogeneous hydrogeologic settings. Other studies, however, have demonstrated that the amount of variation in aquifer vulnerability and agricultural practices within the major physiographic provinces is too great for the provincial subdivisions to be useful (Harrison and others, 1995). Therefore, physiographic sections within the provinces were used as a basis for subdividing the state. This creates areas large enough to cover the state but small enough to conduct sampling or implement management plans. In some physiographic sections, there were no major differences in aquifer susceptibility, so the section was not further subdivided. The general approach was to delineate a framework that would provide relatively homogeneous settings with respect to potential for pesticide contamination *within* hydrogeologic settings and with most of the variation in potential for pesticide contamination being *among* hydrogeologic settings. Therefore, if large differences in aquifer characteristics and susceptibility existed within a physiographic section, the section was further subdivided on the basis of aquifer type.

Physiographic sections were adequate units for providing homogeneous subdivisions of the state with a few exceptions. The Great Valley Physiographic Section was subdivided into areas underlain by carbonate and siliciclastic bedrock. The Appalachian Mountain Physiographic Section was subdivided into three areas: one area underlain by carbonate bedrock of Ordovician Age, one area underlain by carbonate bedrock of Devonian and Silurian Age, and one area underlain by siliciclastic bedrock. The Ordovician and Devonian-Silurian age carbonate-bedrock aquifers were considered as separate settings because of differences in aquifer characteristics. The Devonian-Silurian carbonate aquifers consist of narrow bands of limestone mixed with shale and siltstone in steep, narrow valleys. The Ordovician carbonate aquifers consist of wider bands of pure limestone and dolomite formations in wide, flat valleys. A small area in the Piedmont Lowlands Physiographic Section underlain by siliciclastic bedrock was included in the Triassic Lowlands setting because that setting also had siliciclastic bedrock. Surficial aquifers over bedrock aquifers also were considered separately. The Eastern Lake Physiographic Section and the Atlantic Coastal Plain Lowland and Intermediate Upland Physiographic Sections are predominantly comprised of unconsolidated surficial aquifers so no further subdivisions were made in these sections. The glacial

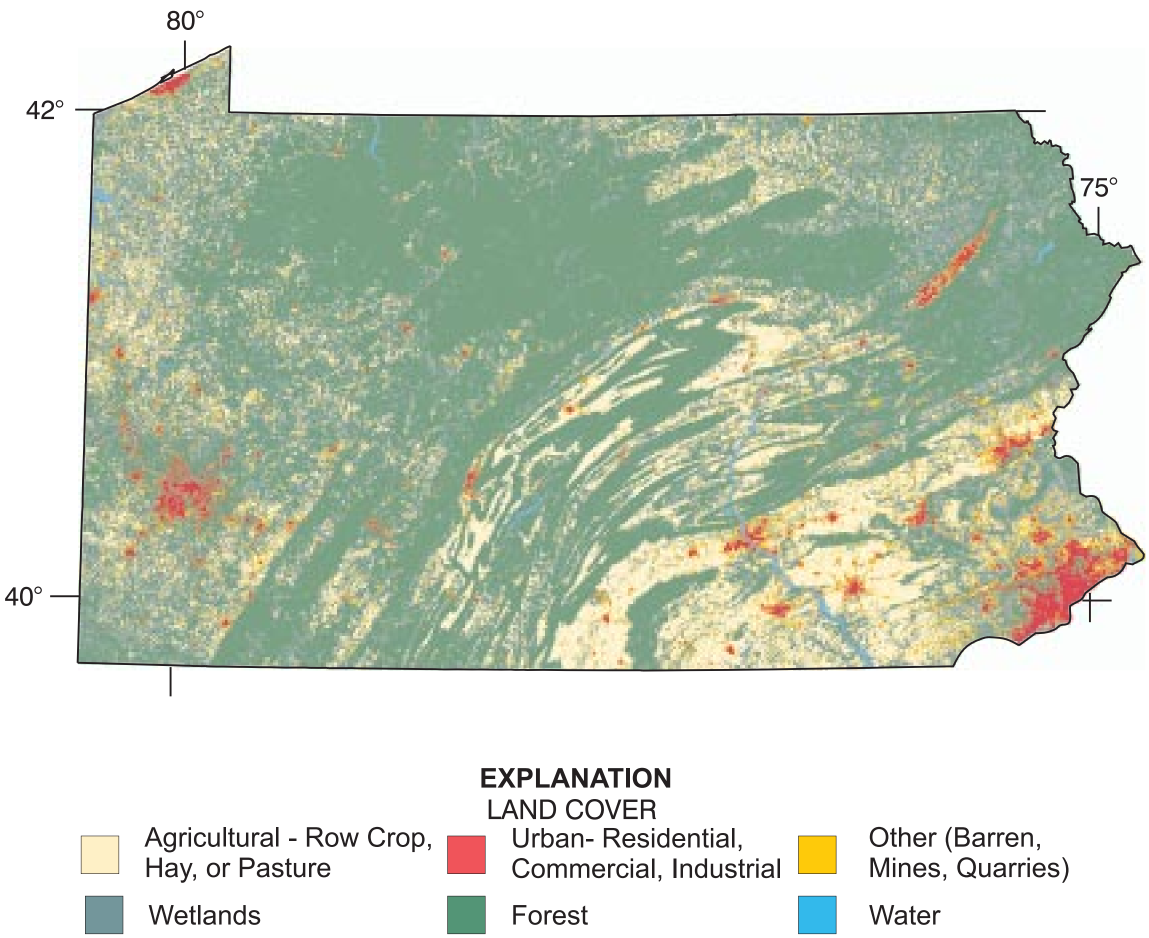


Figure 3. Land covers of Pennsylvania (Vogelmann and others, 1998a; Vogelmann and others, 1998b).

deposits with coarse-grained sediments in the northern part of the state were divided into a northeastern and a northwestern hydrogeologic setting because of apparent variation in the agricultural practices in these two areas of the state. These two glaciated settings were considered as three-dimensional settings with depths that extended to the top of the bedrock. The glaciated settings also spanned several physiographic provinces and sections. Additionally, river terrace deposits in the Allegheny-Monongahela River comprise an important aquifer and were considered as a separate setting. Land-use analysis indicated some subdivisions had a very high percentage of forested land and similar bedrock type. In this case, the five physiographic sections were grouped together and considered as a single hydrogeologic setting. The result of this process was the creation of 20 hydrogeologic settings to be used as a basis for assessing the occurrence of pesticides in Pennsylvania (table 2, fig. 4).

Factors Affecting Occurrence of Pesticides in Ground Water

The general vulnerability of ground water to pesticide contamination is based on two factors: (1) aquifer susceptibility—the ease with which the pesticide can reach the aquifer—determined by natural factors, and (2) contaminant availability—the sources of pesticides at the land surface—determined by human actions on the land surface (Erwin and Tesoriero, 1997). The leachability, or ability of the pesticide to travel with the ground water and not stay attached to particles of soil, is also a factor that determines whether or not pesticide contamination is likely. The leachability is based on the properties unique to each pesticide, such as solubility (the likelihood of the pesticide to stay dissolved in the water), adsorption potential (the likelihood of the pesticide to adhere to the soil) and half-life (the likelihood of the pesticide to degrade significantly before reaching the water table). Within each of the 20 hydrogeologic settings, the aquifer types and agricultural practices are relatively homogeneous. For each setting, the susceptibility of the aquifers to contamination was evaluated, and the use of pesticides was determined. Each pesticide was evaluated with respect to leaching potential.

Aquifer Susceptibility

The major aquifer types in Pennsylvania differ with respect to their inherent properties that may allow contaminants to enter the ground water, which is why aquifer types were used to create the subdivisions. Results of one previous study will be used to illustrate the differences in susceptibility among aquifer types. A regional assessment of pesticides and nitrate in ground water was conducted by Ator and Ferrari (1997). This study assessed the occurrence of pesticides in the four major aquifer types that are present in Pennsylvania but included data from aquifers in Pennsylvania, Maryland, Virginia, West Virginia, North Carolina, New York, and New Jersey. Using more than 500 samples, Ator and Ferrari ranked the aquifers on the basis of the percentage of pesticide detections. The ranking, determined by this study from the highest numbers of detections to the lowest number of detections, was carbonate, crystalline, unconsolidated, and siliciclastic. This ranking was consistent for atrazine, metolachlor, and simazine. The ranking of these four aquifers for nitrate concentrations, commonly used as an indicator of ground-water susceptibility, was in the same order as the ranking for pesticides. Most samples analyzed in this study were collected in agricultural settings, so differences among aquifers were more likely to be related to aquifer susceptibility than land use. The general order of susceptibility of aquifers was used when considering the rankings of vulnerability of aquifers in Pennsylvania.

Four of the hydrogeologic settings are underlain by carbonate bedrock. Areas underlain by carbonate bedrock are highly susceptible to pesticide contamination because of the rapid movement of water from the surface to the ground-water system. Limestone and dolomite bedrock commonly have large fractures caused by weathering, and in many areas of the state, karst features such as sinkholes and caverns have a significant effect on ground-water flow. The infiltration capacity of soils overlying the carbonate bedrock is excellent, and the topography is commonly flat. In carbonate areas, much of the precipitation infiltrates through the soil into large fractures or sinkholes in the bedrock instead of running off into streams. This process commonly carries contaminants directly into the ground water. Studies have shown that water from wells in areas underlain by carbonate bedrock is more likely to contain pesticides (Fishel and Lietman, 1986; Hippe and others,

Table 2. *Physiographic provinces, physiographic sections, bedrock type, and dominant land covers for hydrogeologic settings in Pennsylvania*

Name of hydrogeologic setting	Physiographic province[1]	Physiographic section[1]	Aquifer type[2]	Dominant land covers (percent)[3]		Average DRASTIC score in setting[4]
Eastern Lake Section	Central Lowland	Eastern Lake	Unconsolidated aquifers, inter-bedded sands and clays, siliciclastic bedrock	Forest Row crop Urban Hay / past.	38.8 17.2 17.0 14.9	157
Glaciated Pittsburgh Plateau	Appalachian Plateaus	Glaciated Pittsburgh Plateau	Siliciclastic	forest Hay / past. Row crop	51.1 22.7 18.4	147
Northwestern Glaciated Surficial Aquifers	Appalachian Plateaus	Glaciated Pittsburgh Plateau High Plateau	Coarse grained sediment	Forest Hay / past. Row crop Urban	52.2 19.6 17.1 4.8	150
Pittsburgh Low Plateau	Appalachian Plateaus	Pittsburgh Low Plateau	Siliciclastic	Forest Row crop Hay / past.	65.3 17.1 9.3	153
Allegheny-Monongahela Terrace	Appalachian Plateaus	Pittsburgh Low Plateau	Coarse grained sediment	Forest Urban Row crop Hay / past.	55.1 20.4 10.5 5.4	
Appalachian Plateaus Forested	Appalachian Plateaus	Glaciated Pocono Plateau	Siliciclastic	Forest Woody wetlands	83.6 7.9	153
	Appalachian Plateaus	Glaciated High Plateau	Siliciclastic	Forest Row crop	88.0 7.4	
	Appalachian Plateaus	Deep Valleys	Siliciclastic	Forest	93.5	
	Appalachian Plateaus	Allegheny Plateau	Siliciclastic	Forest	93.5	
	Appalachian Plateaus	High Plateau	Siliciclastic	Forest	91.1	
Allegheny Mountain	Appalachian Plateaus	Allegheny Mountain	Siliciclastic	Forest Row crop	77.9 14.8	162
Appalachian Mountain Siliciclastic	Ridge and Valley	Appalachian Mountain	Siliciclastic	Forest Row crop Hay / past.	70.1 17.2 6.9	156
Devonian-Silurian Carbonate	Ridge and Valley	Appalachian Mountain	Devonian-Silurian Age Carbonate	Forest Row crop Hay / past.	43.9 34.0 15.3	158
Appalachian Mountain Carbonate	Ridge and Valley	Appalachian Mountain	Cambrian-Ordovician Age Carbonate	Row crops Forest	45.8 33.3	186
Glaciated Low Plateau	Appalachian Plateaus	Glaciated Low Plateau	Siliciclastic	Forest Row crop Hay / past.	68.2 19.6 6.9	131
Northeastern Glaciated Surficial Aquifers	Appalachian Plateaus Ridge and Valley	Glaciated Low Plateau Glaciated High Plateau Appalachian Mountain	Coarse grained sediment	Forest Row crop Urban Hay / past.	33.9 28.3 15.3 19.6	147
Great Valley Siliciclastic	Ridge and Valley	Great Valley	Siliciclastic	Row crop Forest Hay / past. Urban	39.2 31.1 22.2 4.7	165
Great Valley Carbonate	Ridge and Valley	Great Valley	Carbonate	Row crop Hay / past. Urban Forest	45.8 22.2 14.7 14.3	185

Table 2. *Physiographic provinces, physiographic sections, bedrock type, and dominant land covers for hydrogeologic settings in Pennsylvania—Continued*

Name of hydrogeologic setting	Physiographic province[1]	Physiographic section[1]	Aquifer type[2]	Dominant land covers (percent)[3]		Average DRASTIC score in setting[4]
Blue Ridge	Blue Ridge	South Mountain	Crystalline	Forest	85.3	148
				Row crop	7.4	
				Hay / past.	4.9	
Triassic Lowlands[5]	Piedmont	Gettysburg-Newark Lowland	Siliciclastic	Forest	41.9	159
				Row crop	30.7	
				Hay / past.	15.7	
				Low int. dev	6.3	
Reading Prong	New England	Reading Prong	Crystalline	Forest	73.3	142
				Hay / past.	8.7	
Piedmont Carbonate	Piedmont	Piedmont Lowland	Carbonate	Row crop	44.7	172
				Hay / past.	25.7	
				Forest	11.3	
				Low int. dev.	9.3	
Piedmont Crystalline	Piedmont	Piedmont Upland	Crystalline	Forest	37.3	150
				Row crop	29.8	
				Hay / past.	19.1	
				Low int. dev.	7.8	
Coastal Plain	Atlantic Coastal Plain	Lowland and Intermediate Upland	Unconsolidated deposits of sand, gravel, silt, and clay, and crystalline bedrock	Urban	64.7	184
				Forest	8.3	

[1] Physiographic provinces and sections from Sevon (1995).
[2] Aquifer types from Berg and others (1980) and Soller and Packard (1998).
[3] Land covers from Vogelmann and others (1998a) and Vogelmann and others (1998b). Land covers comprising greater than 5 percent of the subdivision are shown.
[4] Average vulnerability score within setting from DRASTIC model by Petersen and others (1996). Score based on Depth to ground water, Recharge, Aquifer media, Soil permeability, Topography, Impact of the vadose zone, and hydraulic Conductivity. Higher scores indicate greater vulnerability.
[5] The Gettysburg-Newark Lowlands Physiographic Section is commonly called the Triassic Lowlands based on the age of the rocks and is referred to by that name in this report.

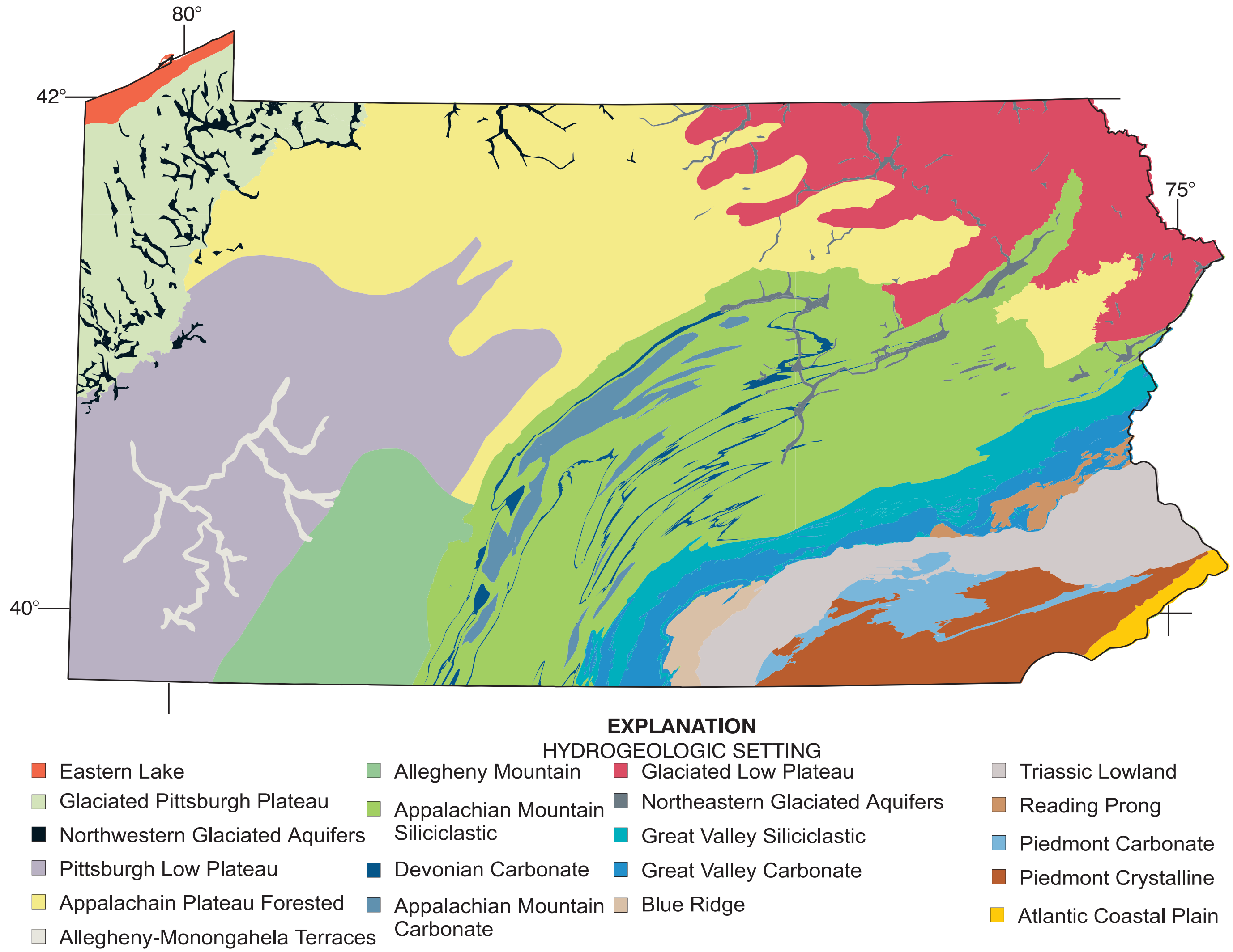


Figure 4. Hydrogeologic settings of Pennsylvania.

1994) and is more likely to contain other contaminants such as nitrate (Lindsey and others, 1997) than water from wells in other bedrock types. Because areas underlain by carbonate bedrock usually have intense agricultural activity, it is difficult to distinguish whether the contaminants detected in these areas are from the susceptibility of the carbonate aquifers or the intensity of agricultural activity. Most likely, it is a combination of both factors.

Three of the hydrogeologic settings are underlain by crystalline bedrock, which in some cases is as susceptible to contamination as areas underlain by carbonate bedrock. Crystalline rock includes igneous and metamorphic rocks such as schist, gneiss, gabbro, phyllite, metavolcanic rocks, and quartzite. Flow through the consolidated bedrock is primarily in small fractures. Ground water in areas underlain by crystalline bedrock exists primarily in the bedrock fractures and pores in the saturated part of the regolith above the crystalline bedrock. The infiltration capacity of the soil overlying crystalline bedrock is classified as good. Previous studies have shown ground-water contamination by pesticides (Harrison and others, 1995) and other contaminants (Lindsey and others, 1997) in areas underlain by crystalline bedrock.

Five of the hydrogeologic settings have surficial aquifers that consist of unconsolidated materials. The susceptibility of unconsolidated deposits that form a mantle over the bedrock throughout the state is not well understood. In some areas, these unconsolidated deposits are thick enough and produce enough water that they become important aquifers. These areas are referred to as surficial aquifers because it is the surface material storing and producing the water, and not the bedrock below. Important surficial aquifers are present in the Atlantic Coastal Plain Province, the Eastern Lake Province, in river terrace deposits near the Allegheny-Monongahela River, and in glaciated areas of the northern part of the state (fig. 2). Surficial aquifers consisting of coarse-grained sediments, such as sand or gravel, are generally productive aquifers. In the northern glaciated valleys, glacial deposits, such as stratified drift or outwash consisting of sand and gravel, were considered as a separate aquifer from the bedrock aquifer below. In the glaciated areas where the glacial deposits include till, a material with a high clay content, the till was not considered as a separate aquifer. Aquifers with coarse-grained materials, such as sand and gravel, theoretically would be vulnerable to the leaching of pesticides; however, Buckwalter and others (1996) found very few pesticide detections in the Eastern Lake Province. Harrison and others (1995) had designated areas with glacial outwash as being highly vulnerable to pesticide leaching prior to their sampling; however, that study found no pesticide detections in water from wells in agricultural areas in glacial outwash in any of the physiographic provinces.

Eight of the hydrogeologic settings are underlain by siliciclastic aquifers, which generally have less potential for leaching of contaminants into ground water than aquifers underlain by the other bedrock types in Pennsylvania (Lindsey and others, 1997). Soils weathered from sandstone generally have good infiltration capacity, whereas soils weathered from shale have poor infiltration capacity. Because of the topography in the siliciclastic valleys, the ground-water recharge areas commonly include forested and agricultural land, even if the well is located in an agricultural setting. The siliciclastic aquifers in Pennsylvania commonly have smaller fractures and more tortuous flow paths than other bedrock aquifers.

Other factors besides aquifer type affect the susceptibility of the aquifer to pesticide contamination. A model that accounts for many of these factors is called DRASTIC. In this model, each factor is assigned weight and rating to calculate a score for each area. The Pennsylvania State University has created a DRASTIC model for Pennsylvania for predicting potential for pesticide contamination (Petersen and others, 1996). The results of this modeling show susceptibility varies in a pattern that generally follows the areas delineated as hydrogeologic settings (fig. 5). Areas underlain by carbonate bedrock are generally shown to be more susceptible, as are areas underlain by unconsolidated aquifers; however, the DRASTIC model does not account for all of the potential effects of karst features such as sinkholes on susceptibility. Areas underlain by siliciclastic bedrock and crystalline bedrock are shown to have lower susceptibility by this model. Some variability of DRASTIC scores within each of the selected hydrogeologic settings is evident (fig. 5). In some cases, this is because of the topography factor, where flat valleys are rated more vulnerable than the ridges. Other variation is evident in stream terraces and glaciated areas, where variation in soil type affects the predicted susceptibility of ground water.

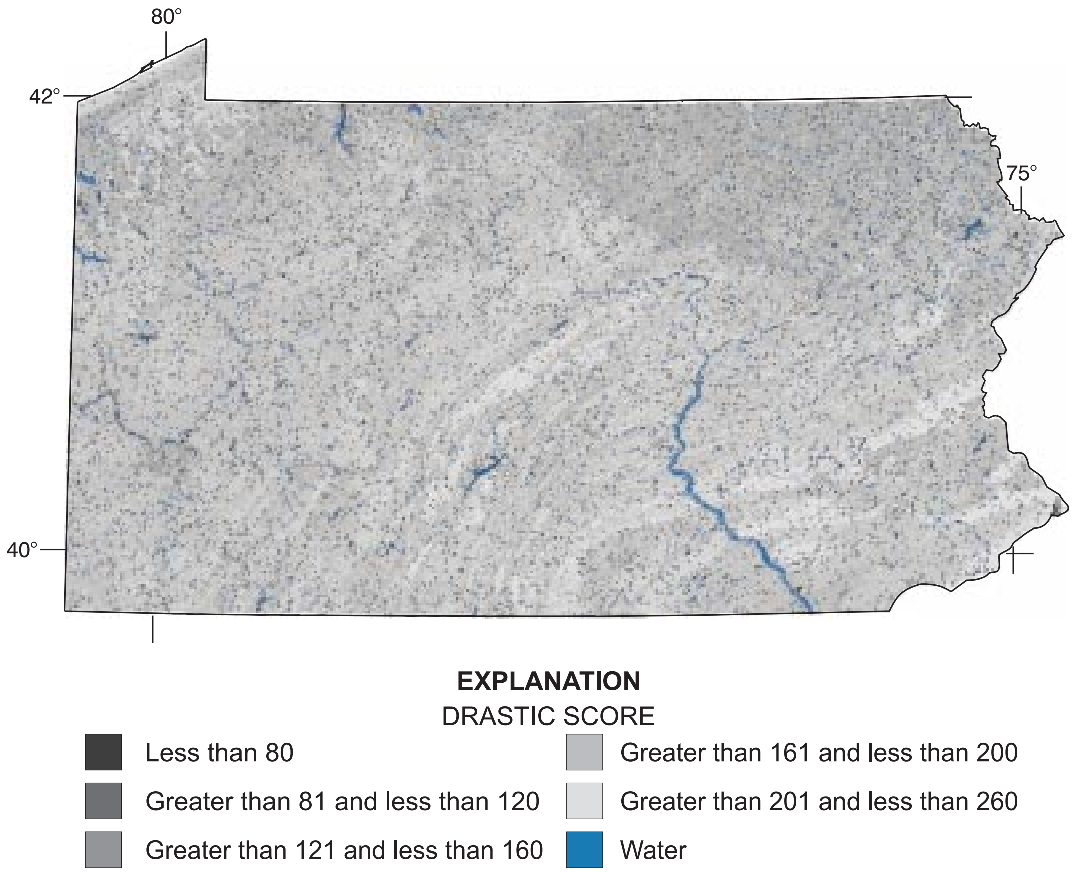


Figure 5. Generalized pesticide DRASTIC scores for the state of Pennsylvania (Petersen and others, 1996). Higher scores indicate more vulnerable areas and are shown in lighter colors.

Contaminant Availability

The availability of contaminants is another important factor in determining aquifer vulnerability. The best way to quantify the availability of pesticides is to know the actual amount of each pesticide applied on a small scale; however, this information is not available. Several approaches have been used successfully to approximate pesticide usage. These approaches use cropland, corn production, or pesticide sales data as surrogates for pesticide application rates.

County-level estimates of pesticide use were derived for compound and crop combinations found within the conterminous United States (Andersen and Gianessi, 1995) (fig. 6). These estimates were based on (1) state-level pesticide-use data collected by Federal agencies from 1990 to 1993 and 1995, (2) pesticide application coefficients of application rates for specific crops, and (3) crop acreage from the 1992 Census of Agriculture. Because these data represent the average application and treatment rates by state, they do not yield precise estimates of use at the county level. The state-use coefficients represent an average for the entire state and, consequently, do not reflect the local variability of cropping and management practices found within many states and counties. In addition, the county-level acreage data used to calculate county use are based on the 1992 Census of Agriculture and may not represent all crop acreage because of Census nondisclosure rules. Despite these limitations, however, these estimates are useful for discerning the overall use patterns and probable distribution of pesticide usage throughout the state.

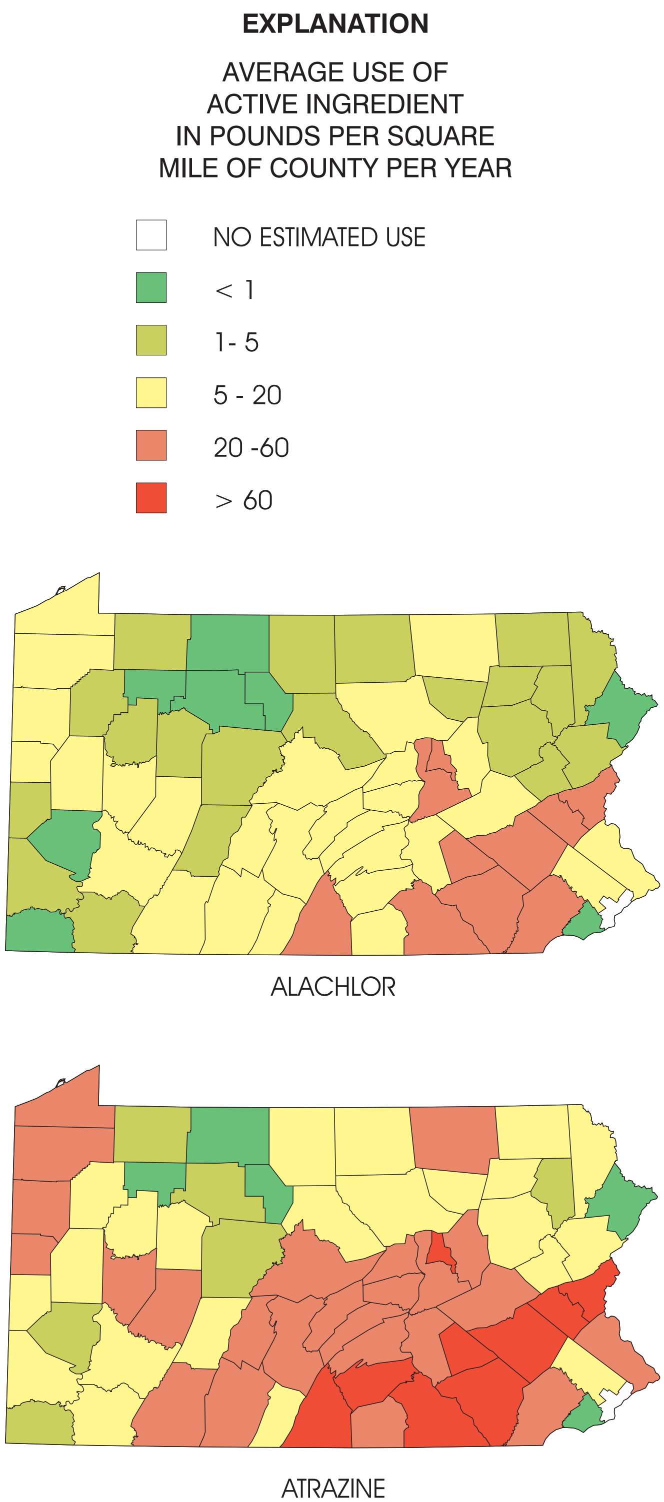


Figure 6. Pesticide-use estimates by county for the state of Pennsylvania from 1990-93 and 1995. (Andersen and Gianessi, 1995).

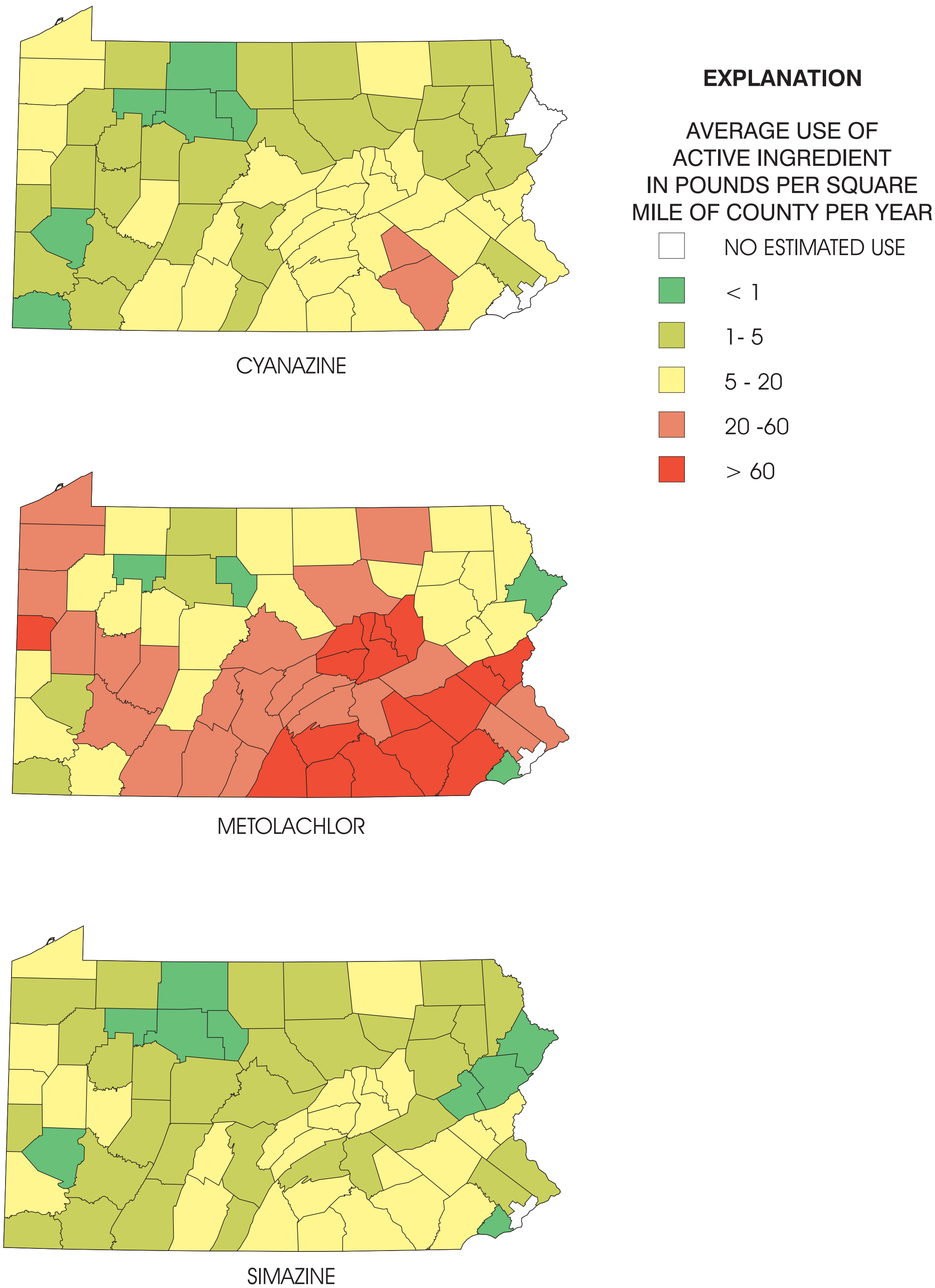


Figure 6. Pesticide-use estimates by county for the state of Pennsylvania from 1990-93 and 1995 —Continued.

The most widely used pesticides in the state of Pennsylvania (among the five priority pesticides), on the basis of pounds of active ingredient, are metolachlor and atrazine (table 3). On the basis of pesticide-use surveys conducted by the PDA, chlorpyrifos, pendimethalin, chlorothalonil, metribuzin, and hexchlorocyclopentadiene are widely used and are included as analytes with all samples submitted for analysis for the Pesticides and Ground Water Strategy (John Pari, Pennsylvania Department of Agriculture, written commun., 1998). The five priority pesticides, with the exception of simazine, also are predominantly applied to corn. This information is useful because it shows that determining areas with higher percentages of corn production would be a viable method for determining areas with higher pesticide application amounts for four of the five pesticides. Small-scale data on corn production are not available; however, a comparison between the percentage of harvested cropland in each county and the use of pesticides in each county shows use of the five priority pesticides is strongly correlated to the percentage of harvested cropland (table 3). This strong positive correlation establishes that contaminant availability, or pesticide use, can be approximated by assessing the amount of cropland in a given area. Spatial data on amounts of cropland are available at a fine scale (about 30 m^2) from interpreted satellite photography for the entire state of Pennsylvania (Vogelmann and others, 1998a; Vogelmann and others, 1998b). Therefore, the percentage of an area in row crops will be used as an indicator of contaminant availability.

The studies conducted by PDA include a pesticide-use survey, which provides detailed information on actual pesticide use (Bingaman and others, 1994). These surveys are not estimates and provide much more accuracy than the estimates based on statewide data; however, these data are only available for those areas where PDA studies have been conducted and are not available for the entire state. The data from the Pequea-Mill Creek survey (table 4) show that the ranking of pesticide use and the patterns of pesticide use for corn production are similar to the estimates based on statewide data.

Table 3. *Pesticide usage and the relation of pesticide use to cropland in Pennsylvania (Andersen and Gianessi, 1995)*

[lb, pounds]

Active ingredient	Use for corn (lb active ingredient)	Use for other crops (lb active ingredient)	Total pesticide use (lb active ingredient)	Percentage used on corn	Correlation between percentage of harvested cropland by county and total pesticide use by county (Spearman's coefficient/ p value)
Alachlor	310,000	72,000	382,000	81	0.947 / 0.0001
Atrazine	1,171,000	18,000	1,189,000	99	.907 / .0001
Cyanazine	279,000	0	279,000	100	.951 / .0001
Metolachlor	1,446,000	279,000	1,725,000	84	.463 / .0001
Simazine	70,000	141,000	211,000	33	.880 / .0001

Table 4. *Pesticide usage in the Pequea-Mill Creek Basin (Bingaman and others, 1994)*

[lb, pounds]

Active ingredient	Use for corn (lb active ingredient)	Use for other crops (lb active ingredient)	Total pesticide use (lb active ingredient)	Percentage used on corn
Alachlor	2,094	0	2,094	100
Atrazine	9,326	10	9,336	99
Cyanazine	2,171	0	2,171	100
Metolachlor	10,394	1,046	11,440	91
Simazine	0	452	452	0

Pesticide Leaching Potential

Pesticide leachability can be evaluated by assessing the mobility of the pesticide through soil and the persistence of the pesticide. A model developed by Gustafson (1989) can be used to rate the leaching potential of specific pesticides. The model uses the half-life of the pesticide in soil ($t_{1/2}$) and the linear adsorption coefficient for organic carbon (K_{oc}) to assign a value, referred to as the Gustafson Ubiquity Score, for each pesticide. These scores provide an index to allow comparisons of the leaching potential of pesticides. Pesticides with a score of less than 1.8 have a low leaching potential; those scoring between 1.8 and 2.8 have a medium leaching potential; and those with a score above 2.8 have a high leaching potential. This model was used to evaluate the five state priority pesticides. The results show that atrazine, metolachlor, and simazine have a high leaching potential, whereas alachlor and cyanazine have a medium leaching potential (table 5).

Table 5. *Leaching potential of the state priority pesticides (Gustafson, 1989)*

[K_{oc}, linear adsorption coefficient for organic carbon; mL/g, milliliters per gram]

Active ingredient	Soil half-life (days)	Soil sorption index (K_{oc}, mL/g)	Gustafson Ubiquity Score	Leaching potential
Alachlor	15	170	2.08	Medium
Atrazine	60	100	3.56	High
Cyanazine	20	168	2.31	Medium
Metolachlor	90	200	3.32	High
Simazine	60	130	3.35	High

PRIORITIZATION OF AREAS FOR SAMPLING

The data on aquifer susceptibility, contaminant availability, and leaching potential can be combined to determine overall vulnerability of ground water to contamination. Because the relative importance of aquifer susceptibility, contaminant availability, and leaching potential is not well known, the initial rankings of vulnerability were based on a combination of the known factors, and this initial ranking was adjusted by use of available water-quality data. Prioritization of areas for sampling was accomplished in a series of steps. The first step was to assign an initial ranking of vulnerability to each hydrogeologic setting on the basis of aquifer susceptibility and pesticide use. For example, areas underlain by carbonate bedrock, with a high percentage of cropland (implying a high application rate of pesticides), would be likely to have numerous detections of atrazine (the second most widely used pesticide with a high leaching potential). The initial ranking consisted of grouping the hydrogeologic settings into groups with high, moderate, and low percentages of pesticide use on the basis of percentage of row crop in the hydrogeologic setting. Within those groupings, hydrogeologic settings underlain by carbonate bedrock were given a high priority on the basis of the susceptibility of those aquifers. If more than one carbonate hydrogeologic setting existed in a pesticide-use group, the average DRASTIC score of the setting was used to rank those settings. The other hydrogeologic settings within each pesticide-use group were ranked on the basis of the DRASTIC score, and in cases where the DRASTIC scores were equal, the percentage of row crop land cover in the hydrogeologic setting was used to determine the initial ranking. The initial rankings of vulnerability on the basis of the stated criteria are listed in table 6.

The next step was to compile existing data on pesticide concentrations in ground water to determine which areas had adequate sampling for initial characterization of the occurrence of pesticides. Supplemental data were collected in some areas that had insufficient data. Then, supplemental data and data from each of the previous studies was statistically analyzed to determine if the data confirmed initial rankings. Finally, the results of the statistical tests were used to adjust vulnerability rankings. Sampling priority for continued studies will be given to areas that have the highest vulnerability rankings and that lack sufficient data.

Table 6. *Initial prioritization of hydrogeologic settings of Pennsylvania*
[>, greater than]

Hydrogeologic setting	Aquifer type	DRASTIC scores[1]	Land cover[2] and percentage of area		Pesticide use group	Initial vulnerability ranking
Appalachian Mountain Carbonate	Carbonate	196	Row crop	45.8	High	1
Great Valley Carbonate	Carbonate	193	Row crop	45.8	High	2
Piedmont Carbonate	Carbonate	182	Row crop	44.7	High	3
Devonian-Silurian Carbonate	Carbonate	166	Row crop	34.0	High	4
Great Valley Siliciclastic	Siliciclastic	172	Row crop	39.2	High	5
Triassic Lowlands	Siliciclastic	168	Row crop	30.7	High	6
Piedmont Crystalline	Crystalline	157	Row crop	29.8	High	7
Northeastern Glaciated Surficial Aquifers	Unconsolidated	170	Row crop	28.3	Moderate	8
Appalachian Mountain Siliciclastic	Siliciclastic	165	Row crop	17.2	Moderate	9
Eastern Lake Section	Unconsolidated	162	Row crop	17.2	Moderate	10
Northwestern Glaciated Surficial Aquifers	Unconsolidated	164	Row crop	17.1	Moderate	11
Allegheny Mountain	Siliciclastic	162	Row crop	14.8	Moderate	12
Glaciated Pittsburgh Plateau	Siliciclastic	156	Row crop	18.4	Moderate	13
Pittsburgh Low Plateau	Siliciclastic	159	Row crop	17.1	Moderate	14
Glaciated Low Plateau	Siliciclastic	138	Row crop	19.6	Moderate	15
Allegheny-Monongahela Terraces	Unconsolidated	153	Row crop	10.5	Moderate	16
Coastal Plain	Unconsolidated	209	Urban	64.7	Low	17
Blue Ridge	Crystalline	152	Row crop	7.4	Low	18
			Forest	85.3		
Reading Prong	Crystalline	142	Forest	73.3	Low	19
Appalachian Plateaus Forested	Siliciclastic	153	Forest	>90	Low	20

[1] From Petersen and others (1996).
[2] Row crop percentages are shown for comparison purposes only unless the percentage of row crops comprise less than 5 percent of the hydrogeologic setting, in which case the dominant land covers are shown.

Relations Between Pesticides in Ground Water and Hydrogeologic Setting

For this study, atrazine was chosen as an indicator of overall pesticide vulnerability because it has a high leaching potential and is used extensively on corn in Pennsylvania. Additionally, more data were available for atrazine than for the other pesticides, and atrazine was detected most frequently in previous studies in Pennsylvania. For these reasons, atrazine was used for the statistical analysis of pesticides in water from wells.

Statistical tests were selected to determine relations between atrazine and categorical variables such as subunit (hydrogeologic setting or a combination of hydrogeologic setting and land use) and bedrock type. Other tests were selected to determine the relations between atrazine and continuous variables such as the percentage of agricultural land surrounding a well and DRASTIC scores. All statistical analyses discussed in this section are based on data from the studies that were determined to have consistent methodology and quality assurance as listed in table 1. These studies provided 582 atrazine samples to conduct statistical analyses. Because of different method reporting limits among laboratories, pesticide data for analysis of the entire pesticide dataset was censored to the highest reporting limit of 0.1 µg/L before statistical tests were conducted. The resulting dataset contained a large amount of censored data or nondetects. The atrazine data also were not normally distributed (skewed toward left). According to Helsel and Hirsch (1992, p. 367), if greater than 50 percent of the data are censored, nonparametric tests based on ranks have less power to detect differences in central values than nonparametric tests based on a categorical variable of detections and nondetections. For this reason, atrazine concentration was represented as either “detect” or “nondetect” instead of the actual concentration or rank for categorical tests. Conversion of the atrazine data from a concentration to a detect/nondetect category was performed after the data were censored to the common reporting limit. For some hydrogeologic settings, much information was lost by censoring the data to the higher detection limit because for many of the samples, reported concentrations were between 0.001 µg/L and 0.1 µg/L. Therefore, some statistical tests were conducted on a subset of the data that were analyzed at the lower reporting limit to determine whether the results differed. Correlations between atrazine and other continuous variables used the rank of atrazine (after censoring to 0.01 µg/L).

Statistical tests were conducted to identify any relations between the presence or absence of atrazine and hydrogeologic settings or bedrock types. The Kruskal-Wallis test was used to make this comparison. When the Kruskal-Wallis test is used on categorical variables, the test is a measure of whether or not differences in the distribution of the number of detections among the categories exist (Helsel and Hirsch, 1992, p. 382). As a follow-up to this test, a multiple comparison test is used to determine how the categories vary. This was accomplished by use of the multiple-stage Kruskal-Wallis (MSKW) test using an overall alpha value of 0.05. Categories that did not have significant differences in the distribution of detections of atrazine were assigned the same letter. Groups could be assigned more than one letter.

Detections of atrazine were analyzed by aquifer type. Detections of atrazine were most prevalent in hydrogeologic settings underlain by carbonate bedrock types (fig. 7). The results of the output from the MSKW test analyzing the presence or absence of atrazine among hydrogeologic settings in which at least 20 samples had been collected are shown on figure 8. The difference between detections of atrazine in areas underlain by carbonate bedrock and areas underlain by the other types of bedrock is statistically significant. The Great Valley carbonate, Appalachian Mountain carbonate, and Piedmont carbonate hydrogeologic settings had the highest percentages of detections of atrazine in Pennsylvania (figs. 8 and 9).

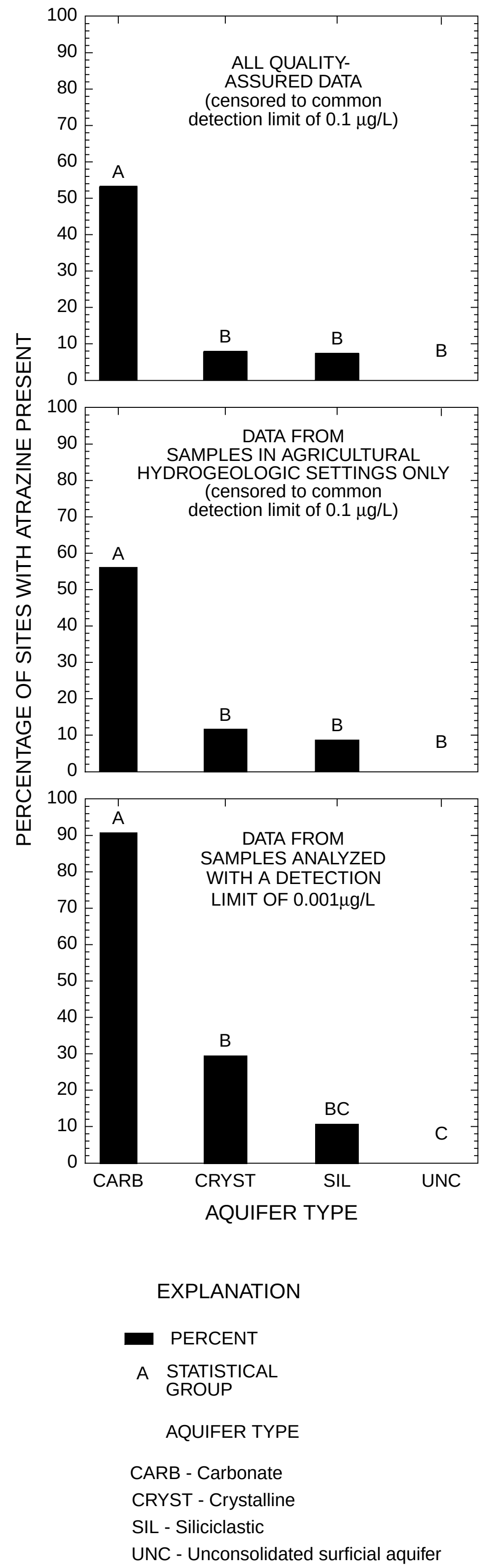


Figure 7. Percentage of detections of atrazine by bedrock type.

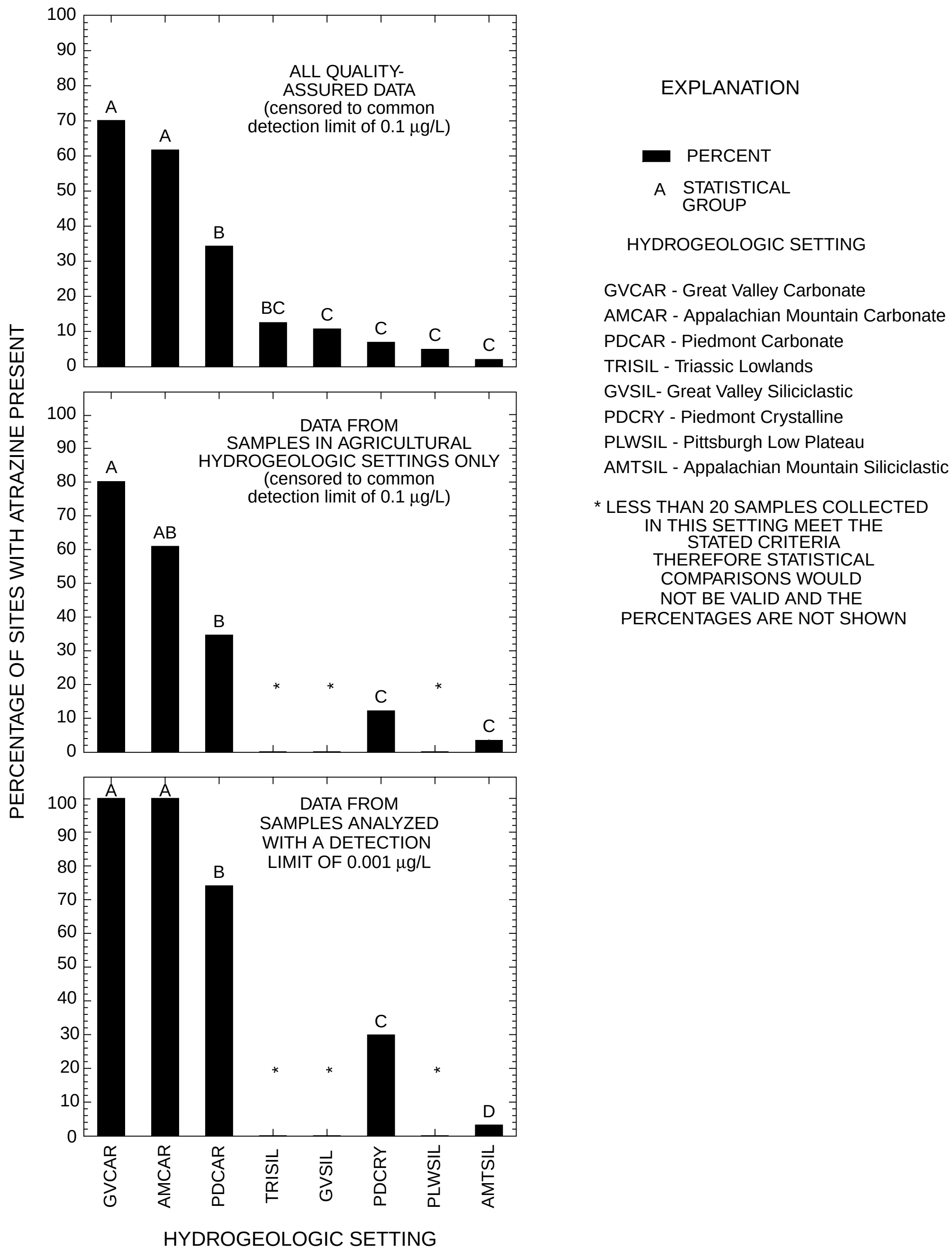
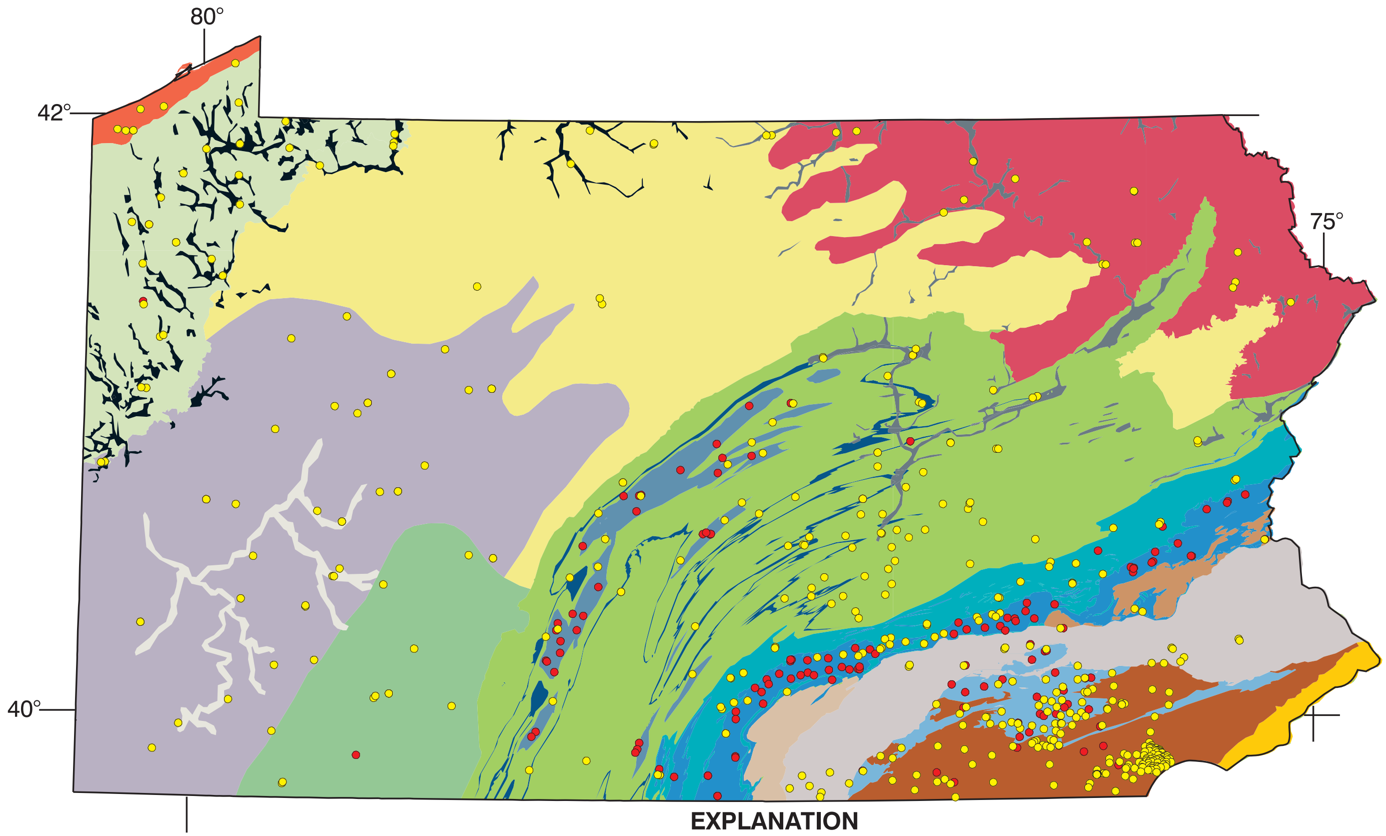


Figure 8. Percentage of detections of atrazine by hydrogeologic setting.



EXPLANATION

HYDROGEOLOGIC SETTING

- Eastern Lake
- Glaciated Pittsburgh Plateau
- Northwestern Glaciated Aquifers
- Pittsburgh Low Plateau
- Appalachian Plateau Forested
- Allegheny-Monongahela Terraces
- Allegheny Mountain
- Appalachian Mountain Siliciclastic
- Devonian Carbonate
- Appalachian Mountain Carbonate
- Glaciated Low Plateau
- Northeastern Glaciated Aquifers
- Great Valley Siliciclastic
- Great Valley Carbonate
- Blue Ridge
- Triassic Lowland
- Reading Prong
- Piedmont Carbonate
- Piedmont Crystalline
- Atlantic Coastal Plain

- ATRAZINE CONCENTRATION GREATER THAN OR EQUAL TO 0.1 MICROGRAMS PER LITER
- ATRAZINE CONCENTRATION LESS THAN 0.1 MICROGRAMS PER LITER

Figure 9. Atrazine detections by hydrogeologic settings.

Lack of data and lack of consistency in detection limits make it difficult to assess the relations among the hydrogeologic settings. The detection rate of atrazine is dependent on whether or not low-level detections are included. For example, the detection rate for the Piedmont Crystalline hydrogeologic setting goes from 30 percent to 7 percent if the detections below 0.1 µg/L are not included, but in the Glaciated Pittsburgh Plateau hydrogeologic setting, the detection rate remains at 9 percent. This means there are a small number of detections with higher concentrations in the Glaciated Pittsburgh Plateau hydrogeologic setting and a large number of detections with low-level concentrations in the Piedmont Crystalline hydrogeologic setting. Also, when analyzing all data censored at a common reporting limit of 0.1 µg/L, the Triassic Lowlands is ranked as having a higher rate of detection of atrazine than the Piedmont Crystalline hydrogeologic setting. When the lower detection limit of 0.001 µg/L is used to analyze the data, the Piedmont Crystalline area has a much higher rate of detection. However, the Triassic Lowlands does not have sufficient samples analyzed at that low reporting limit to make such a comparison.

The effect of land use surrounding the well on atrazine detections in the various hydrogeologic settings and bedrock types also was evaluated. A 300-m radius around each well was assessed, and wells with at least 25 percent of row crop land within that radius or at least 50 percent agricultural (row crop, hay, or pasture) land within that radius were classified as 'agricultural.' The intent of this method was to conduct statistical analyses on only the subset of wells that had a good possibility of having pesticides applied near the well. The results of the categorical comparisons (detections against nondetections) previously described did not change when only those data from wells in agricultural areas were analyzed. The areas underlain by carbonate bedrock still had a significantly higher rate of atrazine detection, and the detection rates among hydrogeologic settings were ranked in the same order as previously described.

Other statistical tests were conducted to determine the relations between atrazine concentrations and continuous variables, such as the percentage of row crops around the well or the average DRASTIC score in areas surrounding the well. The Spearman's rank correlation procedure tests whether a monotonic relation exists between two continuous variables. The monotonic relation may be nonlinear but shows an association between the two variables. An alpha value of 0.05 was used to indicate that the relation between the two variables was statistically significant, and the value of Spearman's rho was used to indicate the strength of the relation (higher values of Spearman's rho indicate stronger relations). Atrazine was ranked for the Spearman's test but was not transformed into detects and nondetects.

The results of the Spearman's correlation test showed that the percentage of row crops and average DRASTIC score in a 300-m radius around the well were positively correlated to the atrazine rank (table 7). The percentage of forested land was negatively correlated to the atrazine rank. As with the categorical statistical analyses, tests also were conducted on subsets of the data that had lower reporting limits and subsets of the data collected in agricultural hydrogeologic settings. Similar to the categorical comparisons, only small changes in statistics were observed when analyzing subsets with lower detection limits or subsets with data collected in agricultural areas. The correlation between atrazine and the average DRASTIC score

Table 7. *Summary of statistical correlations between ranks of atrazine concentrations (after censoring to 0.1 micrograms per liter) and selected characteristics of area surrounding wells*

	Spearman's correlation coefficient	Probability	Number of samples
Percentage of row crop within 300 meter radius around well	0.31	0.0001	432
Percentage of forested land within 300 meter radius around well	-.34	.0001	579
Average DRASTIC[1] score within 300 meter radius around well	.36	.0001	460
Score based on bedrock type[2]	.52	.0001	582

[1] From Petersen and others (1996).

[2] Samples from carbonate aquifers were assigned a score of 3, crystalline and siliciclastic aquifers were assigned a score of 2, and unconsolidated aquifers were assigned a score of 1.

was expected to be improved when only wells surrounded by agricultural land use were considered. The lack of improvement in this correlation is probably because the variables in the DRASTIC score already account for land use. For example, slope, soil-infiltration capacity, and bedrock type are included in the DRASTIC score. As these variables increase, the DRASTIC score (low percentage of slope, high infiltration capacity, and carbonate bedrock) increases, as does the likelihood of that parcel of land being used for row crops and having pesticides applied.

Because categorical analysis showed significant differences between aquifer categories, a correlation was tested by assigning a score to each sample in the database on the basis of aquifer type. Samples from carbonate aquifers were assigned a score of 3, crystalline and siliciclastic aquifers were assigned a score of 2, and unconsolidated aquifers were assigned a score of 1. These scores were based on the order of pesticide detections from the categorical analysis of aquifers. Interestingly, this simple model of assigning a score on the basis of the aquifer type showed a stronger correlation coefficient to the rank of atrazine score than the more complex DRASTIC model. The implication is that aquifer type encompasses many variables that influence both susceptibility and potential for pesticide application. This may not be a universally applicable model; however, it does show hydrogeologic settings based on aquifer type provide a good basis for predicting pesticide occurrence.

Other observations also were made from the analysis of the existing data on pesticides in ground water. The number of samples exceeding the USEPA's Maximum Contaminant Levels (MCL's) (U.S. Environmental Protection Agency, 1996a) or health advisories was very small. Only 3 wells of the 1,029 private wells sampled had concentrations that exceeded a MCL or Heath Advisory Level, and in each of these cases, the contamination was determined to be from a point source. One case was from a known spill of a pesticide. In the other two cases, the wells were located in close proximity to a pesticide loading or mixing area. These three wells also were located in the areas underlain by carbonate bedrock, which have been shown to be the most vulnerable to contamination. The pesticide detections seem to have both a geologic and geographic distribution across the state. The majority of all detections were in areas underlain by carbonate bedrock, and the pesticide detections were most likely to be in the southeastern part of the state. Of the 135 samples where atrazine exceeded 0.1 µg/L, 112 (83 percent) were in areas underlain by carbonate bedrock, and only 6 of the 135 were collected from wells in noncarbonate bedrock north and west of the Great Valley Physiographic Province. The possible explanation for the geographic distribution of the pesticide detections is that the most intense agricultural activity is in the southeastern part of the state, which would indicate higher pesticide-use rates in this area (fig. 6).

Vulnerability Rankings of Hydrogeologic Settings

The final vulnerability rankings of the hydrogeologic settings were determined by adjusting the initial rankings on the basis of existing data. If sufficient atrazine data existed, and those data indicated a reason to adjust the rankings (such as statistically significant differences in the percentage of detections), changes were made to the prioritization table (table 8). Vulnerability rankings were adjusted to reflect the order of percentage of detections even when differences among the hydrogeologic settings were not statistically significant. Because adjustments to the rankings were only made when sufficient data existed, the rankings of the areas that need additional sampling generally remain the same. The decision on whether or not sampling was adequate is based on the number of samples collected and how those samples were collected. Generally, if 20 to 30 samples were collected in a hydrogeologic setting by one agency in a coordinated effort, the sampling was considered adequate. If 20 to 30 samples were collected by several agencies as parts of different projects, with no single agency collecting the majority of samples, the adequacy of sampling was determined on a case by case basis. If fewer than 20 samples had been collected, the sampling was generally considered inadequate.

Prioritization of Areas Needing Further Study

The preliminary analysis of existing pesticide data showed the combination of carbonate bedrock type accompanied by agricultural land use accounted for most of the pesticide detections in ground water. Carbonate areas have a high percentage of land planted in corn (table 2). Additionally, the carbonate bedrock is overlain by soils with high infiltration capacity, and the bedrock is highly weathered, which allows pesticides to rapidly infil-

Table 8. *Final vulnerability (to pesticides contamination) rankings of hydrogeologic settings in Pennsylvania*

Hydrogeologic setting	Initial ranking	Number of samples	Statistical ranking (censored)[1]	Rate of detection (percent exceeding 0.1 μg/L)	Sufficient data to characterize hydrogeologic setting[2]	Relative vulnerability[3]	Final ranking
Great Valley Carbonate	2	83	1	71	Yes	High	1
Appalachian Mountain Carbonate	1	47	2	31	Yes	High	2
Piedmont Carbonate	3	67	3	34	Yes	High	3
Devonian-Silurian Carbonate	4	11		9	No	High	4
Triassic Lowlands	6	24	4	13	No	Moderate / high	5
Great Valley Siliciclastic	5	28	5	11	No	Moderate / high	6
Piedmont Crystalline	7	145	6	7	Yes	Moderate / high	7
Northeastern Glaciated Surficial Aquifers	8	15	--	0	No	Moderate / low	8
Appalachian Mountain Siliciclastic	9	50	8	2	Yes	Moderate / low	9
Eastern Lake Section	10	7	--	0	No	Moderate / low	10
Northwestern Glaciated Surficial Aquifers	11	10	--	0	Yes	Moderate / low	11
Allegheny Mountain	12	11	--	9	No	Moderate / low	12
Glaciated Pittsburgh Plateau	13	25		8	Yes	Moderate / low	13
Pittsburgh Low Plateau	14	41	7	5	Yes	Moderate / low	14
Glaciated Low Plateau	15	10	--	0	No	Moderate / low	15
Blue Ridge	18	0	--	No samples	No	Moderate / low	16
Allegheny-Monongahela Terraces	16	0	--	No samples	No	Moderate / low	17
Coastal Plain	17	0	--	No samples	No	Low	18
Reading Prong	19	2	--	50	No	Low	19
Appalachian Plateaus Forested	20	6	--	0	No	Low	20

[1] Censored data refers to the data analysis performed on all available data censored to a common detection limit of 0.1 microgram per liter. This allows the data analysis to be performed on the largest amount of samples possible, but some low-level detections are counted as nondetections to allow accurate comparisons to data that were analyzed with a higher detection limit.

[2] Approximately 20 samples collected by a single agency generally needed for a hydrogeologic setting to have sufficient data.

[3] This would be the recommended order of sampling if no areas had been assessed, this order is the overall rank and could be used for other purposes, such as deciding which area was a high priority for resampling.

trate into the aquifer. Overall, 83 percent (112 of 135) of the pesticide detections were in areas underlain by carbonate bedrock. In southeastern Pennsylvania, pesticide detections were common in all bedrock types north and west of the Great Valley Physiographic Section; however, only 6 of the 135 pesticide detections were in noncarbonate areas. Because of the association between carbonate bedrock and pesticides in ground water, areas of the state underlain by carbonate bedrock that do not have adequate sampling were given high priority for characterization studies (table 9). One of the areas for which no data were available was the Appalachian Mountain Carbonate hydrogeologic setting within the West Branch Susquehanna River Basin. These carbonate valleys were studied by the Lower Susquehanna NAWQA project, but the parts of the valleys that extended out of the Lower Susquehanna River Basin were not sampled as part of the NAWQA project. Another area without adequate sampling was the Devonian-Silurian hydrogeologic setting. The NAWQA study had focused on the larger Cambrian and Ordovician Valleys; however, only a few samples from other studies had been collected in the Devonian-Silurian hydrogeologic setting.

Although areas underlain by siliciclastic bedrock generally had fewer pesticide detections than areas underlain by carbonate bedrock, a small number of samples collected in the siliciclastic areas of the southeastern part of the state had a higher rate of pesticide detections than other areas underlain by siliciclastic bedrock. These areas included the Great Valley and the Triassic Lowlands. These areas have some differences in topography and land use from other siliciclastic areas of the state. Most significantly, the percentage of row crops in this area is higher. For this reason, these two siliciclastic areas were given high priority for characterization studies (table 9).

Table 9. *Prioritization of hydrogeologic settings in Pennsylvania needing additional sampling*
[Shaded areas indicate very low priority for sampling based on low pesticide usage and aquifer susceptibility]

Hydrogeologic setting	Final ranking (from table 7)	Priority for additional sampling
Appalachian Mountain Carbonate (unsampled area)	2	1
Devonian-Silurian Carbonate	4	2
Triassic Lowlands	5	3
Great Valley Siliciclastic	6	4
Northeastern Glaciated Surficial Aquifers	8	5
Eastern Lake	10	6
Allegheny Mountain	12	7
Glaciated Low Plateau	15	8
Blue Ridge	16	9
Allegheny-Monongahela Terraces	17	10
Reading Prong	18	11
Coastal Plain	19	12
Appalachian Plateaus Forested	20	13

Areas underlain by unconsolidated coarse-grained sediments have a high potential for pesticide detections, but existing sampling data do not show a high level of detections in these areas. Two areas underlain by unconsolidated sediment with a high percentage of row crops, the Eastern Lake and the Northeastern Glaciated Surficial Aquifers hydrogeologic settings, were selected for further study. Few samples have been collected in the Eastern Lake setting (fig. 1), an area that has different agricultural practices than most of the state. A study in the Eastern Lake hydrogeologic setting in Erie County, however, showed triazine herbicides were present in tile drains draining agricultural fields, indicating the potential for pesticides to be detected in wells in this area (Buckwalter and others, 1996). A study conducted in the Northwestern Glaciated Surficial Aquifers hydrogeologic setting by the Allegheny-Monongahela NAWQA study found no pesticide detections in these aquifers in Pennsylvania. Few samples had been collected in the Northeastern Glaciated Surficial Aquifers hydrogeologic setting; however, this area has a higher percentage of cropland than the Northwestern Glaciated Surficial Aquifers hydrogeologic setting (table 2). The unconsolidated sediments in the Coastal Plain in Pennsylvania have essentially no agricultural cropland; therefore, state priority pesticides are not likely to be applied in this hydrogeologic setting.

The Glaciated Low Plateau and Allegheny Mountain hydrogeologic settings (fig. 4) have a significant amount of agricultural activity, although less than the areas underlain by siliciclastic bedrock in the Great Valley or Triassic Lowlands. Application of state priority pesticides is likely in these areas. These areas are given a lower priority for additional sampling because of the combination of moderate agricultural land use and low aquifer susceptibility. Although the Blue Ridge hydrogeologic setting is dominated by forested land cover, a small agricultural area of the Blue Ridge hydrogeologic setting is dominated by orchards. This area would not be likely to have high usage of most state priority pesticides; however, simazine is registered for usage on orchards. Because this is a small area with unique herbicide-use patterns, this is a low priority area for sampling; however, plans for sampling in this hydrogeologic setting will be included.

The lowest priority areas include the Appalachian Plateau Forested, the Reading Prong, and the Coastal Plain hydrogeologic settings. Most agricultural land within the Appalachian Plateau Forested hydrogeologic setting is included in the studies of glaciated surficial aquifers; the remaining area in this hydrogeologic setting is almost entirely forested and has a very low pesticide-application rate. The Reading Prong hydrogeologic setting also has an extremely small amount of agricultural land. The Coastal Plain Physiographic Province was considered a low priority for agricultural pesticides on the basis of the high percentage of urban land; however, other studies have shown that nonagricultural pesticides may be an issue of concern in urban hydrogeologic settings. On the basis of the low pesticide-use rates in these areas, these hydrogeologic settings are considered a very low priority for sampling, and sampling plans for these areas will not be presented.

SAMPLING PLAN

An overall strategy that follows scientifically accepted practices is essential in conducting a statewide pesticide assessment that may be used to manage pesticide usage. Plans for sampling in each of the areas that are not adequately characterized for pesticide occurrence are presented for completing a statewide assessment. The hydrogeologic framework presented also may have other uses for the Pesticides and Ground Water Strategy.

Statistical Sampling Design Considerations

The Pesticides and Ground Water Strategy includes components to determine the spatial distribution of pesticides in ground water as well as temporal variation of pesticides in ground water. The spatial distribution of pesticides in ground water has several components: (1) an assessment of the vulnerability of and occurrence of pesticides in ground water throughout the state, (2) an assessment of the occurrence of pesticides in aquifers used for public supply, and (3) an assessment of local areas with high levels of contamination, or hot spots. The temporal variation of pesticides in ground water is a follow-up task to determine if the pesticide concentrations in aquifers, public-supply wells, or hot-spot wells are increasing, decreasing, or remaining the same.

One of the initial goals of the Pesticides and Ground Water Strategy is to identify areas of special protection that are vulnerable to pesticide contamination. A vulnerability assessment supplemented by sampling data can be used as an initial characterization or a resource assessment to identify these areas of special protection. A carefully designed sampling plan will allow statistical comparisons among various areas of the state that have been sampled. These comparisons can be used for determining future monitoring needs and priorities. Other goals of the Pesticides and Ground Water Strategy include detecting local areas of contamination or hot spots and assessing the effects of pesticides on public-supply wells. The random-selection plan described herein will serve as an overall resource assessment of the occurrence of pesticides in ground water. Plans to identify local areas of contamination or hot spots and sampling of public-supply wells are addressed separately.

To make statistical comparisons among the selected hydrogeologic settings in the state, the target populations of sampling points for various areas of the state must be similarly defined. For example, if samples in one area of the state were collected from wells on farms and samples in another area were collected from rural nonfarm wells, comparisons of those two areas may not be valid. The on-farm wells would have potential for point-source contamination from pesticide mixing areas, whereas the rural nonfarm wells would be more likely to reflect the occurrence of pesticides in the aquifer from nonpoint pesticide sources. Additionally, a set of shallow drilled wells would not represent the same population as a set of dug wells or deeper drilled wells. Therefore, it is important to use similarly defined populations of wells when comparing pesticide occurrence. Another important design issue is to ensure wells *within* each given area have similar potential for pesticide occurrence, as determined by aquifer susceptibility and contaminant availability.

Another consideration in designing a sampling plan is determining the number of samples needed to characterize an area with respect to pesticide occurrence. If the target population is well defined, the precision of the estimation of statistics such as the mean is determined by the number of samples collected rather than the density of sampling (Alley, 1993). This allows for a large population to be characterized by sampling only a small percentage of the population. A sample size of about 30 is considered large enough to approximate the summary statistics (Alley, 1993).

All sampling designs have inherent bias. The wells selected may or may not accurately represent the conditions in the aquifer. Use of data from previously sampled wells can be biased if prior sampling was done because of a suspected water-quality problem. The wells available for sampling may not cover the targeted area in an evenly distributed manner. A random-selection process can minimize the potential biases of sampling wells, and it is a prerequisite for valid statistical comparisons of sampling results. All of these issues make well selection an important issue in being able to draw accurate conclusions from the data collected.

The well-selection method used for the sampling plans included herein is described in Scott (1990). This method uses a computerized process to subdivide an area into cells, each of which has a similar amount of the targeted land use. The program then randomly selects a point in each of the cells, and this location is used to begin the search for a well that meets the designated criteria. This method has been accepted as a way to ensure random location of sites and adequate spatial coverage of the sampling areas. The potential sampling points are selected in agricultural areas, particularly corn-production areas, because the focus of this continuing study is herbicides used on corn. Wells will be selected in areas where corn production is evident, in wells that are of recent construction, and relatively shallow wells. These criteria create a set of wells that is biased in that it does not represent the general water-quality conditions throughout the state; using these wells as the target population, however, makes the data representative of aquifers in agricultural areas.

Example Sampling Plans

Sampling plans were developed for areas of the state classified as not having sufficient samples available to assess pesticide occurrence. Sampling plans are presented in the order of their suggested prioritization for additional sampling (table 9). Sampling in some hydrogeologic settings ranked as very low priority may not be necessary. The PDA may determine that sampling these extremely low-priority areas is not as important as returning to some more vulnerable areas to conduct resampling or determining the trends in pesticide concentrations. If some quality-assured data already existed within the selected sampling area, the sampling plan was still created with a specific number of cells to adequately cover the area, usually 30 samples. The existing data could be used to characterize cells where samples have previously been collected.

The PDA sampling policy includes plans to assess the geographic extent of contamination if detections of pesticides exceed two thirds of the USEPA MCL. This entails collecting additional samples from wells near any well that has elevated pesticide concentrations, as well as resampling the original well to determine the seasonal fluctuations in pesticide concentrations.

Some hydrogeologic settings do not meet the criteria for being adequately characterized with respect to pesticide occurrence, but the PDA may want to consider these areas adequately characterized for other reasons. The Northwestern Glaciated Surficial hydrogeologic setting does not have adequate characterization as previously defined. Although only 19 samples have been collected in this hydrogeologic setting in Pennsylvania, the USGS NAWQA project in the Allegheny-Monongahela River Basin specifically studied this hydrogeologic setting. The area studied by the NAWQA project collected 30 samples in this hydrogeologic setting; however, the basin extends into New York State, so the number of samples in Pennsylvania does not meet the criteria for characterization. The PDA may want to consider the sampling in the Northwestern Glaciated Surficial Aquifers hydrogeologic setting as adequately characterized.

Appalachian Mountain Carbonate

The area of the Appalachian Mountain Carbonate hydrogeologic setting that does not fall in the Lower Susquehanna or Potomac River Basins is the highest priority area that has not been sampled. The sampling plan presented herein includes only that part of the hydrogeologic setting not previously sampled, and the sampling density to complete this remaining area was chosen to be similar to the sampling density of the previous sampling in the Appalachian Mountain Carbonate hydrogeologic setting. For this reason, only 15 samples will be needed to adequately characterize this area (fig. 10). The supplemental sampling conducted in 1998 by the USGS included five samples from this hydrogeologic setting: cells 3, 6, 9, 12, and 15. When the remaining samples are collected in this hydrogeologic setting, the entire set of 15 should be considered as a part of the overall assessment of the Appalachian Mountain Carbonate hydrogeologic setting, including the samples previously collected.

Devonian-Silurian Carbonate

The areas of carbonate bedrock of Devonian-Silurian Age will need 30 samples to be adequately characterized (fig. 11). The supplemental sampling conducted in 1998 by the USGS included five samples from this hydrogeologic setting: cells 5, 10, 15, 20, and 25. The geographic distribution of the Devonian-Silurian Age carbonate bedrock is banded throughout central Pennsylvania, so to accurately characterize this area, the wells need to be positively identified with respect to their location. The horizontal extent of outcrops of carbonate bedrock are as thin as 100 m in some areas, so driller's logs with lithologic descriptions showing limestone also would be necessary to ensure the wells were completed in the correct aquifer.

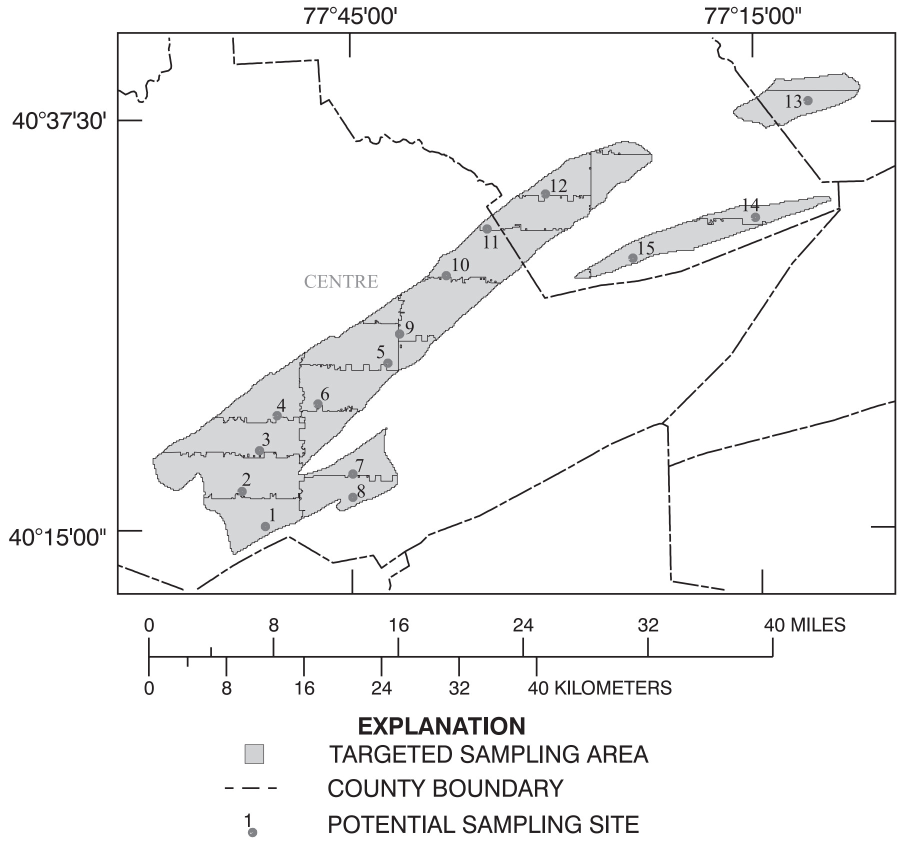


Figure 10. Sampling cells and locations in the unsampled area of the Appalachian Mountain Carbonate hydrogeologic setting.

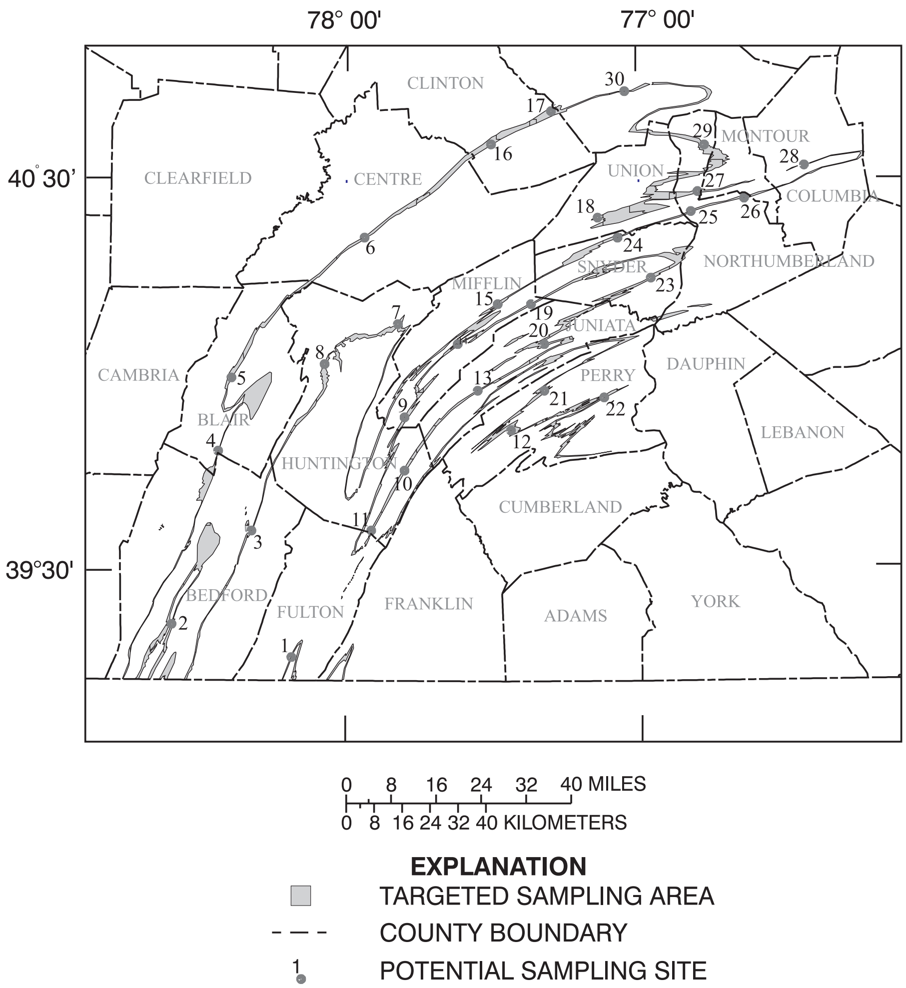


Figure 11. Sampling cells and locations in the Devonian-Silurian Carbonate hydrogeologic setting.

Triassic Lowlands

The area aquifers of the Triassic Lowland Siliciclastic hydrogeologic setting will need 30 samples to be adequately characterized (fig. 12). The PDA began sampling this area in the fall of 1998, and, to date, 44 samples have been collected in this hydrogeologic setting. This hydrogeologic setting was the second area sampled using the plans presented in this report.

Great Valley Siliciclastic

The area aquifers of the Great Valley Siliciclastic hydrogeologic setting will need 30 samples to be adequately characterized (fig. 13). The supplemental sampling conducted in 1998 by the USGS included five samples from this hydrogeologic setting: cells 5, 9, 15, 20, and 25. The Great Valley Siliciclastic hydrogeologic setting is a high priority study area for the ground-water sampling for the Delaware River NAWQA project. The results of any NAWQA studies may help to characterize this hydrogeologic setting.

Northeastern Glaciated Surficial Aquifers

The unconsolidated aquifers of the Northeastern Glaciated Surficial Aquifer hydrogeologic setting will need 30 samples to be adequately characterized (fig. 14). The supplemental sampling conducted in 1998 by the USGS included five samples from this hydrogeologic setting: cells 5, 9, 15, 20, and 25. Sampling in this area should be conducted shortly after the pesticide application period (generally late April to late June) because the contaminants in these aquifers may travel through the

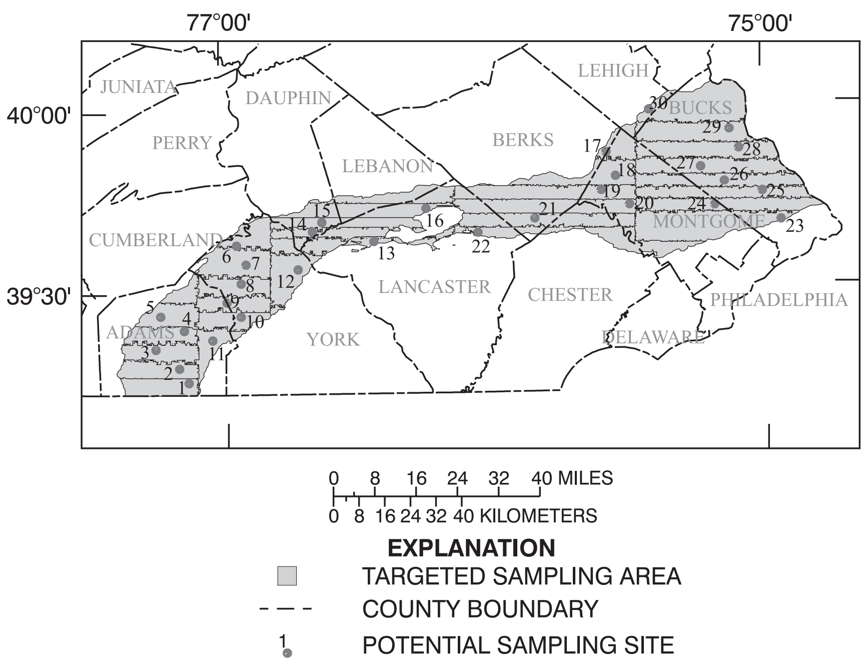


Figure 12. Sampling cells and locations in the Triassic Lowlands hydrogeologic setting.

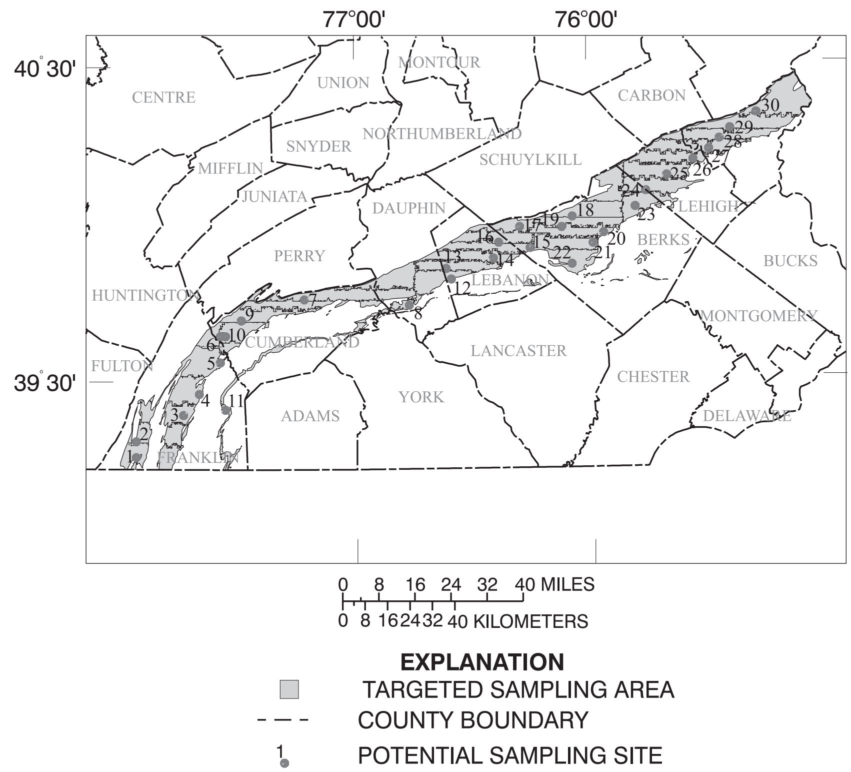


Figure 13. Sampling cells and locations in the Great Valley Siliciclastic hydrogeologic setting.

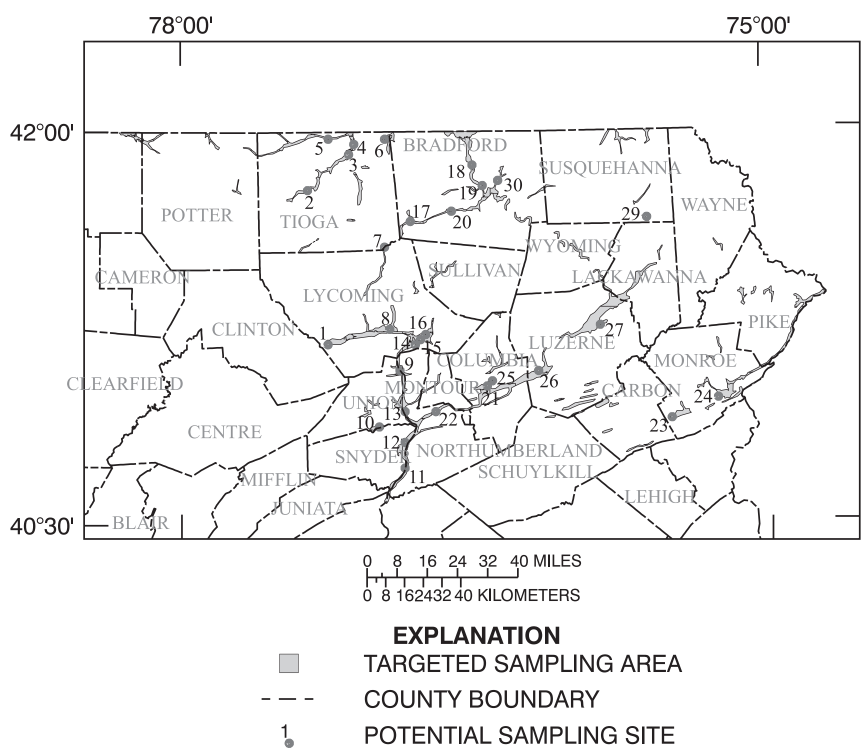


Figure 14. Sampling cells and locations in the Northeastern Glaciated Surficial Aquifer hydrogeologic setting.

shallow ground water rapidly. The movement of contaminants in this hydrogeologic setting may be closely related to the type of unconsolidated materials where the well is located. Wells completed in stream terraces consisting of fine-grained sediments deposited on floodplains may be less vulnerable to pesticide contamination than wells completed in glacial deposits with coarse grained sand and gravel. Wells in this aquifer are commonly shallow, and in a given location, a well could be drilled through the unconsolidated aquifer and completed in the bedrock below. When selecting wells in this area, it is very important to determine the depth and well-construction characteristics to ensure the sample is drawn from the surficial aquifer and not the underlying bedrock aquifer.

Eastern Lake

The unconsolidated aquifers of the Eastern Lake Physiographic Section will need 30 samples to be adequately characterized (fig. 15). The supplemental sampling conducted in 1998 by the USGS included five samples from this hydrogeologic setting: cells 5, 10, 15, 20, and 25. Sampling in this area should follow the pesticide application period because the contaminants in these aquifers may travel rapidly through the shallow ground water. In this area, it is important to note the well construction because the targeted aquifer is the unconsolidated deposits. Wells in this aquifer are commonly 20 to 60 ft deep, with an open-ended casing or slotted screen. Agricultural land use in the northeastern part of this setting differs from much of the rest of the state. Vineyards are the dominant agricultural crop in this area. The pesticides used for vineyards are different than the corn herbicides that are the focus of the rest of these studies, and therefore, additional pesticides should be analyzed when sampling this area.

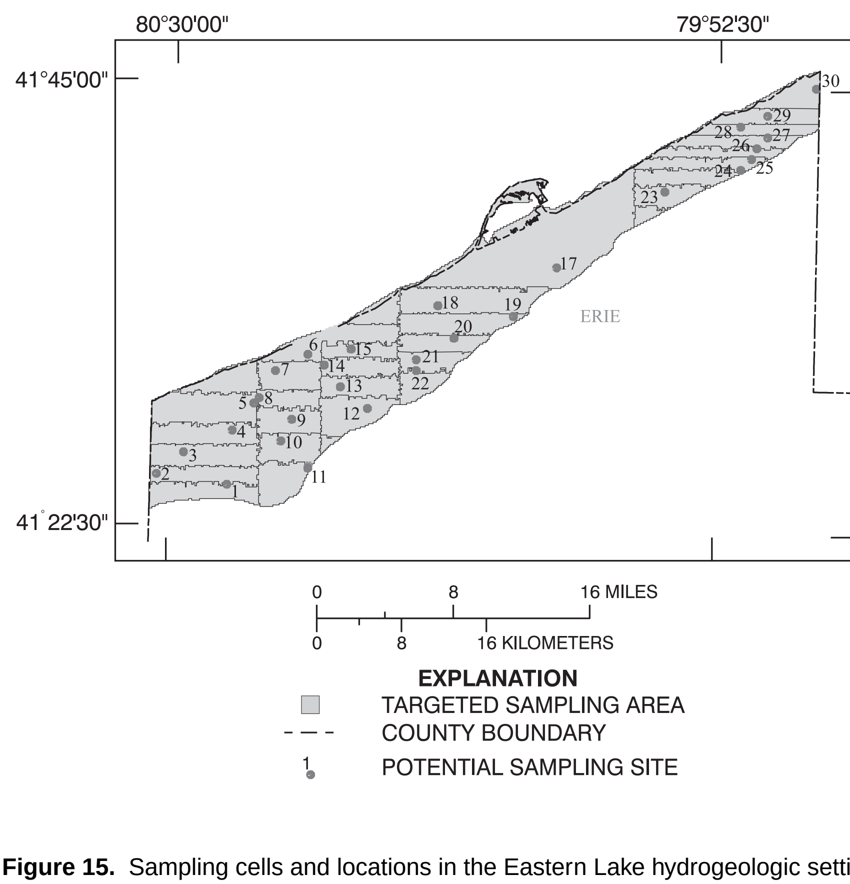


Figure 15. Sampling cells and locations in the Eastern Lake hydrogeologic setting.

Allegheny Mountain

The Allegheny Mountain hydrogeologic setting will need 30 samples to be adequately characterized (fig. 16). No supplemental sampling was conducted in 1998 by the USGS; however, several samples were collected in this hydrogeologic setting by the Allegheny-Monongahela NAWQA study. The coverage of this area was considered to be near to completion because of the NAWQA study; however, the NAWQA study sampled a broader area that extended beyond the state boundaries.

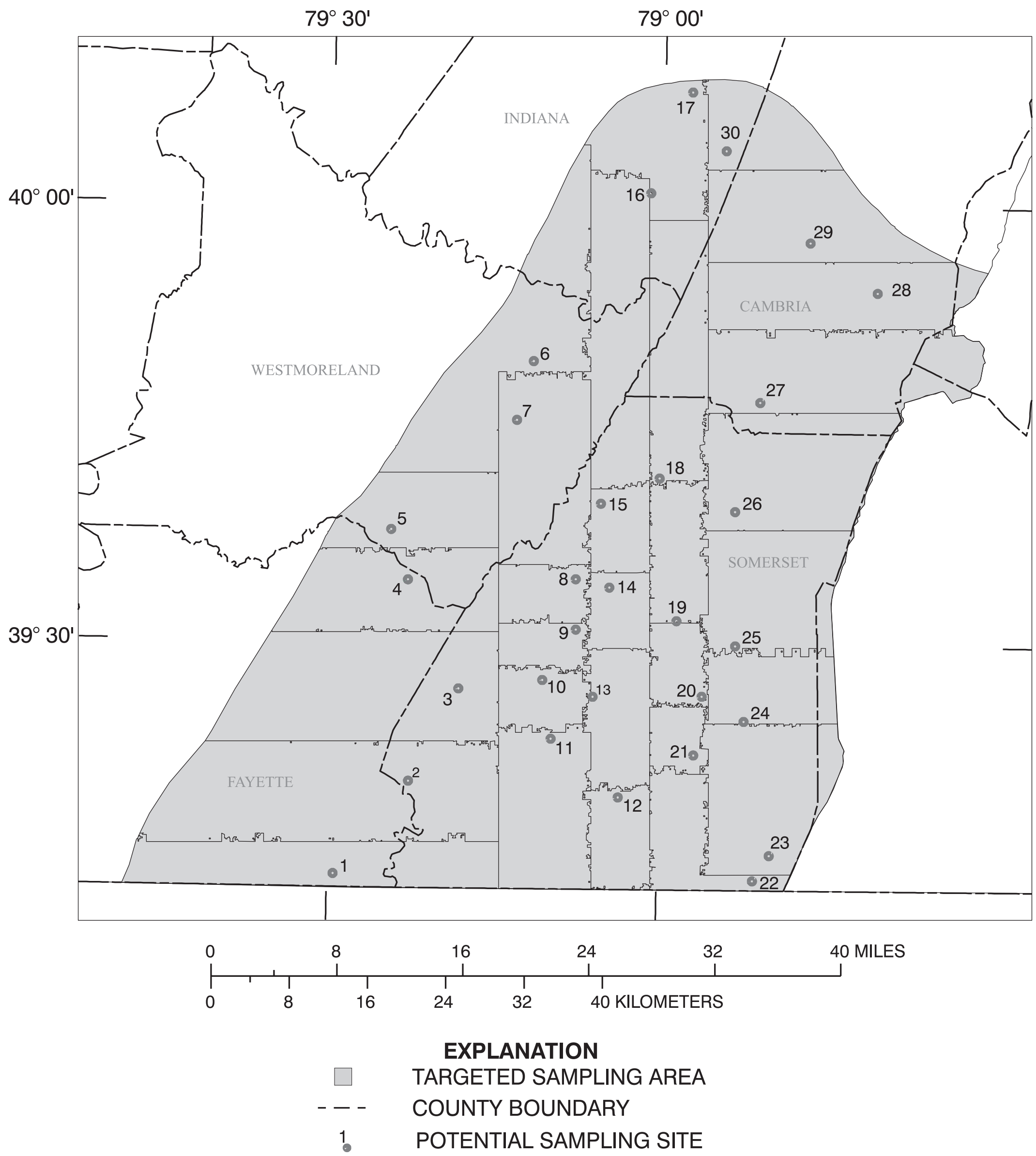


Figure 16. Sampling cells and locations in the Allegheny Mountain hydrogeologic setting.

Glaciated Low Plateau

The Glaciated Low Plateau hydrogeologic setting will need 30 samples to be adequately characterized (fig. 17). The supplemental sampling conducted in 1998 by the USGS included five samples from this hydrogeologic setting: cells 5, 10, 15, 20, and 25. During the collection of supplemental samples, it was noticed that the amount of agricultural cropland is much lower in this area than in other parts of the state. It was more difficult in this area to locate wells that were downgradient from agricultural activities; however, an attempt was made to locate wells that were potentially affected by pesticides (contaminant availability at the land surface).

Blue Ridge

The Blue Ridge hydrogeologic setting will need 30 samples to be adequately characterized (fig. 18). No supplemental sampling was conducted in 1998 by the USGS in this hydrogeologic setting. Generally, land use in the Blue Ridge hydrogeologic setting indicates a small amount of agricultural activity and low pesticide usage. However, this area is characterized by the largest concentration of orchards in the state. The orchard area straddles the Blue Ridge setting and the western boundary of the Triassic setting. The geology in this area includes the igneous and metamorphic bedrock of the Blue Ridge and the siliciclastic bedrock of the Triassic setting. A sampling plan that focuses on this area is included for consideration by the PDA. The state priority pesticides are primarily used for corn; however, simazine is also registered for use on orchards. Sampling in this area is considered a low priority because it comprises a very small area of the state, is not considered to have a high potential for leaching of pesticides, and is a unique area with respect to pesticide application. Pesticide-use surveys in this area could be used as a basis for selecting the pesticides to analyze for when conducting this sampling.

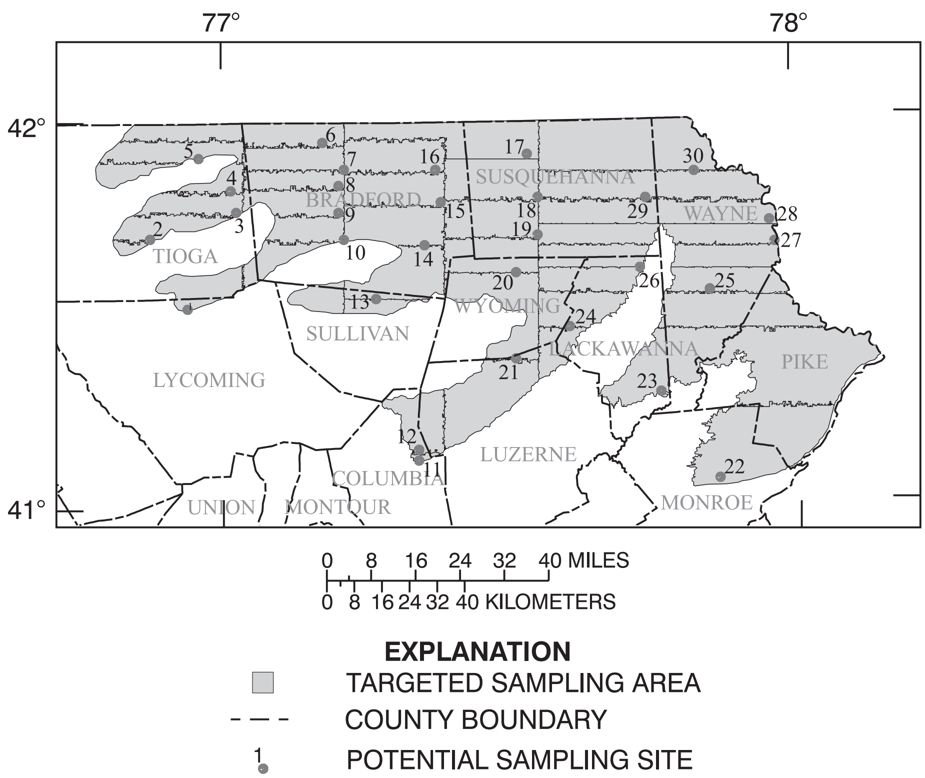


Figure 17. Sampling cells and locations in the Glaciated Low Plateau hydrogeologic setting.

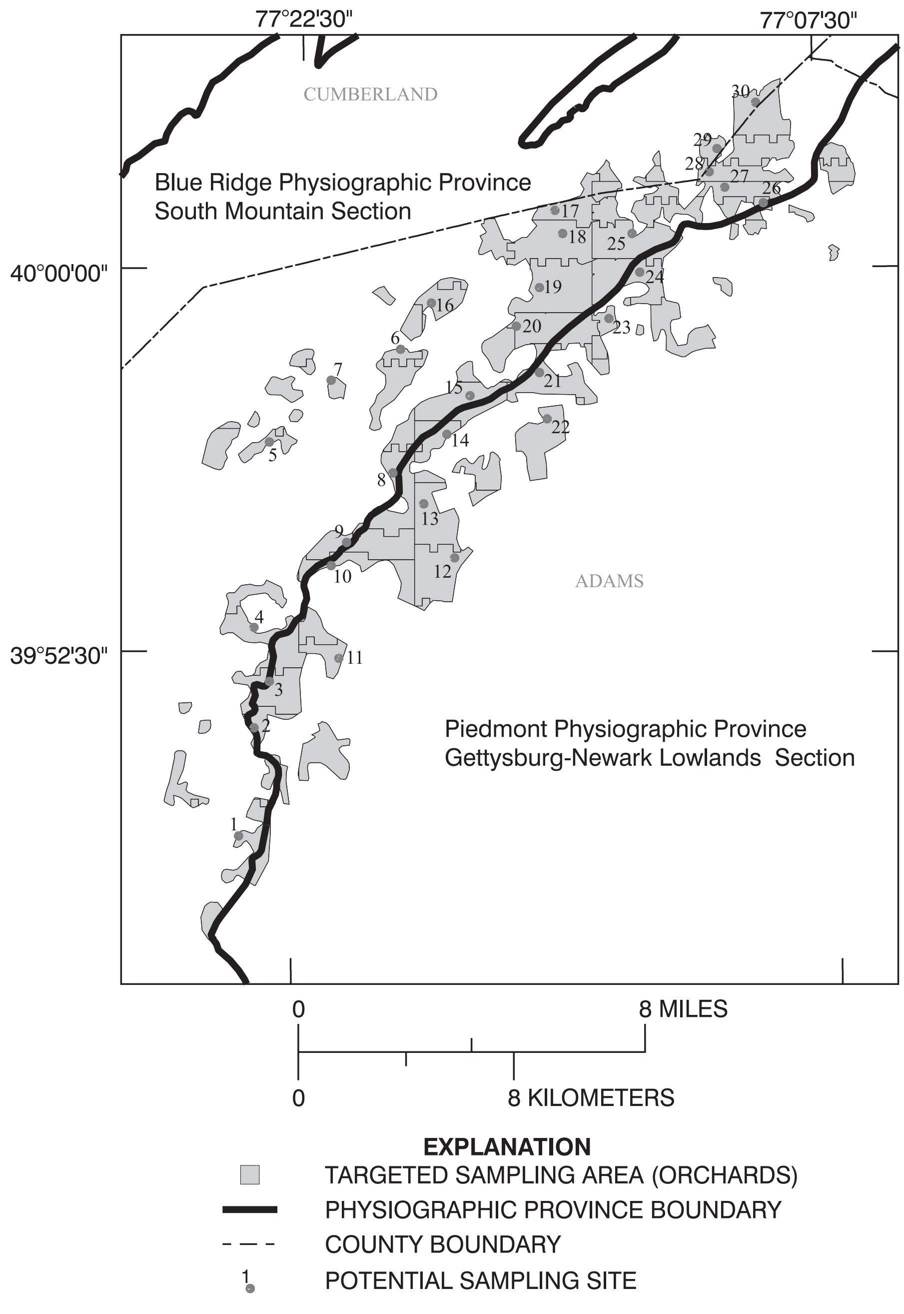


Figure 18. Sampling cells and locations in the Blue Ridge hydrogeologic setting.

Allegheny-Monongahela Terraces

The Allegheny-Monongahela Terraces setting will need 30 samples to be adequately characterized (fig. 19). No supplemental sampling was conducted in 1998 by the USGS in this hydrogeologic setting. Generally, land use in the Allegheny-Monongahela Terraces hydrogeologic setting indicates a small amount of agricultural activity and low pesticide usage. However, this aquifer is widely used for water supply and is therefore a setting to consider for additional sampling. The aquifer in this setting is a shallow unconsolidated aquifer. A sampling plan that focuses on this area is included for consideration by the PDA. Sampling in this area is considered a low priority because it comprises a very small area of the state and is not considered to have a high potential for leaching of pesticides.

Additional Applications of Hydrogeologic Framework

The hydrogeologic framework designed for the assessment of pesticides in ground water could have other uses. Other states required to develop a state management plan for pesticides in ground water could use a similar approach for their plans. This would be particularly useful in states that have diverse geology and aquifer types. Management practices could be implemented on the basis of hydrogeologic settings rather than political boundaries. Also, other types of sampling could be conducted using this framework.

Resampling and Follow-Up Studies

The framework and prioritization can be used as the basis for subsequent rounds of sampling after the initial characterization is completed. To determine whether pesticide concentrations are increasing or decreasing, settings can be resampled using the designs presented herein. The priority for resampling can be based on the ranking shown in this report and augmented by additional sampling data. Future studies also could assess a list of analytes modified to represent changes in pesticide use. The modified list could include pesticides that have been introduced since the original studies were conducted and drop others that are no longer on the priority list. For example, cyanazine is currently a priority pesticide but is likely to be phased out completely in the future. Patterns of herbicide use show increases in use of acetochlor, which was not in use when initial studies were conducted. Because of the changes in pesticide-use patterns, the PDA may determine that resampling some more vulnerable areas would be a higher priority than continuing to sample in less vulnerable areas.

Hot-Spot Surveys

Conducting a grid-based approach for detecting hot spots would require an extremely large number of samples to obtain an acceptable certainty of detecting existing hot spots. An approach to increasing the probability of detecting hot spots would be to define a population of wells that were most likely to be contaminated and then sample a selected subset of those wells. This approach would incorporate the results of existing sampling to select aquifers identified as being vulnerable to contamination, then select a subset of wells from that area that would be most likely to have high pesticides levels. This subset of wells would include wells near pesticide mixing and loading sites. Wells on sites where commercial pesticide mixing and handling takes place would make a good target population for conducting a hot-spot survey. The PDA could identify licensed applicators from their records to define the target population. The hot-spot survey would consist of sampling a selected number of wells from the target population in each hydrogeologic setting. This type of sampling would represent a ‘worst case’ scenario and would not be representative of the entire resource or aquifer sampled.

Public Water Supplies

A large percentage of the state population relies on water from public-supply wells; therefore, assessing the occurrence of pesticides in these wells would be desirable. One way to efficiently assess these wells would be to sample a high proportion of the public-supply wells located in the aquifers that were identified in the resource assessment phase as having a high pesticide occurrence and then to sample a lower proportion of the public-supply wells located in the aquifers that were identified in the resource assessment phase as having a low pesticide occurrence. A coordinated assessment of pesticides in ground water in public water supplies would help clarify the weaknesses in the data currently in the PaDEP public water-supply database.

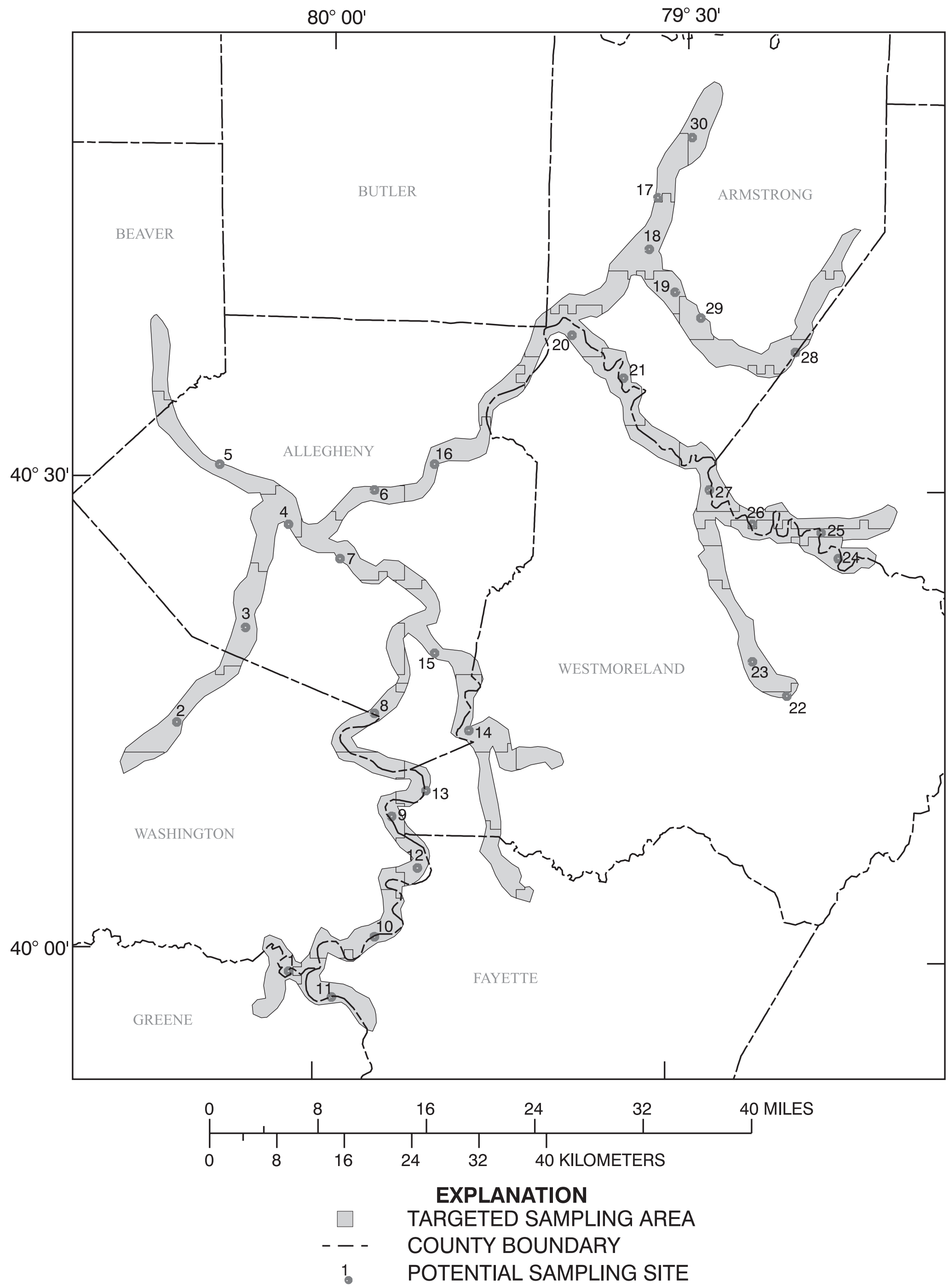


Figure 19. Sampling cells and locations in the Allegheny-Monongahela Terraces hydrogeologic setting.

SUMMARY

The USEPA requires states to have systematic plans to assess the occurrence of pesticides in ground water. A hydrogeologic framework that subdivides the state of Pennsylvania into areas that are relatively homogeneous with respect to aquifer susceptibility and pesticide use has been presented as an example of how these assessments could be conducted. The framework was created by subdividing the state into 20 areas on the basis of physiography, aquifer characteristics, and land use. The existing data on pesticides in ground water have been analyzed to determine (1) the quality of the data, (2) the availability of data within each hydrogeologic setting, (3) the factors that had the most significant effect on pesticide concentrations, and (4) the rank of each of the 20 hydrogeologic settings on the basis of vulnerability of ground water to contamination by pesticides.

Sampling to date has shown that, even in the most vulnerable hydrogeologic settings, pesticide concentrations in ground water rarely exceed USEPA Drinking-Water Standards or Health Advisory Levels. Analyses of samples from 1,159 private wells revealed only 3 wells from which samples contained concentrations of the state priority pesticides—atrazine, simazine, cyanazine, alachlor, and metolachlor—that exceeded drinking-water standards. In each of these three cases, concentrations can be traced to point sources at pesticide loading or mixing areas. These three sites also were in areas underlain by carbonate bedrock. Application of pesticides to the land surface generally has not caused concentrations of the five state priority pesticides in ground water to exceed health standards; however, this study has not evaluated the potential human health effects of mixtures of pesticides in drinking water. This study also has not determined whether concentrations in these areas are stable, increasing, or decreasing.

Sampling plans are presented for each of the 20 areas that lack sufficient data for assessing pesticide occurrence. Of the highest priority areas of the state, the areas underlain by carbonate bedrock, two out of four have been sampled in a manner that offers complete spatial coverage and adequate numbers of samples for statistical comparisons. One of the remaining areas, the Appalachian Mountain Carbonate hydrogeologic setting, is sufficiently characterized; however, the spatial coverage is not complete and will need some additional sampling. The fourth carbonate hydrogeologic setting has neither sufficient numbers of samples nor adequate spatial coverage. Only one of the three areas of moderately high priority has been adequately sampled. The Piedmont Crystalline hydrogeologic setting has adequate numbers of samples and spatial coverage. The Triassic Lowlands and Great Valley Siliciclastic hydrogeologic settings have a large number of samples, but these samples have been collected in different studies. Therefore, both of these areas would be better characterized by a coordinated sampling effort. Almost half of the areas of moderate to low priority (four of nine areas) have been adequately sampled, and none of the three low priority areas have been sampled. A methodical implementation of this plan would result in a scientifically based characterization of the status of pesticides in ground water of all high priority areas within 1 to 2 years, and the entire state probably could be characterized within 3 to 4 years.

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