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Quality-Assurance Design Applied to an Assessment of Agricultural Pesticides in Ground Water from Carbonate Bedrock Aquifers in the Great Valley of Eastern Pennsylvania

by Kevin J. Breen

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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
	Volume	
gallon (gal)	3.785	liter
	Mass	
pound avoirdupois (lb)	0.4536	kilogram

Other Abbreviations

µg/L	micrograms per liter
mg/mL	milligrams per milliliter
L	liter

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

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ABSTRACT

Assessments to determine whether agricultural pesticides are present in ground water are performed by the Commonwealth of Pennsylvania under the aquifer monitoring provisions of the State Pesticides and Ground Water Strategy. Pennsylvania's Department of Agriculture conducts the monitoring and collects samples; the Department of Environmental Protection (PaDEP) Laboratory analyzes the samples to measure pesticide concentration. To evaluate the quality of the measurements of pesticide concentration for a ground-water assessment, a quality-assurance design was developed and applied to a selected assessment area in Pennsylvania. This report describes the quality-assurance design, describes how and where the design was applied, describes procedures used to collect and analyze samples and to evaluate the results, and summarizes the quality-assurance results along with the assessment results.

The design was applied in an agricultural area of the Delaware River Basin in Berks, Lebanon, Lehigh, and Northampton Counties to evaluate the bias and variability in laboratory results for pesticides. The design—with random spatial and temporal components—included four data-quality objectives for bias and variability. The spatial design was primary and represented an area comprising 30 sampling cells. A quality-assurance sampling frequency of 20 percent of cells was selected to ensure a sample number of five or more for analysis. Quality-control samples included blanks, spikes, and replicates of laboratory water and spikes, replicates, and 2-lab splits of ground-water. Two analytical laboratories, the PaDEP Laboratory and a U.S. Geological Survey Laboratory, were part of the design. Bias and variability were evaluated by use of data collected from October 1997 through January 1998 for alachlor, atrazine, cyanazine, metolachlor, simazine, pendimethalin, metribuzin, and chlorpyrifos.

Results of analyses of field blanks indicate that collection, processing, transport, and laboratory-analysis procedures did not contaminate the samples; there were no false-positive results. Pesticides were detected in water when pesticides were spiked into (added to) samples. There were no false negatives for the eight pesticides in all spiked samples. Negative bias was characteristic of analytical results for the eight pesticides, and bias was generally in excess of 10 percent from the 'true' or expected concentration (34 of 39 analyses, or 87 percent of the ground-water results) for pesticide concentrations ranging from 0.31 to 0.51 µg/L (micrograms per liter). The magnitude of the negative bias for the eight pesticides, with the exception of cyanazine, would result in reported concentrations commonly 75-80 percent of the expected concentration in the water sample. The bias for cyanazine was negative and within 10 percent of the expected concentration. A comparison of spiked pesticide-concentration recoveries in laboratory water and ground water indicated no effect of the ground-water matrix, and matrix interference was not a source of the negative bias. Results for the laboratory-water spikes submitted in triplicate showed large variability for recoveries of atrazine, cyanazine, and pendimethalin. The relative standard deviation (RSD) was used as a measure of method variability over the course of the study for laboratory waters at a concentration of 0.4 µg/L. An RSD of about 11 percent (or about ±0.05 µg/L) characterizes the method results for alachlor, chlorpyrifos, metolachlor, metribuzin, and simazine. Atrazine and pendimethalin have RSD values of about 17 and 23 percent, respectively. Cyanazine showed the largest RSD at nearly 51 percent. The pesticides with low variability in laboratory-water spikes also had low variability in ground water.

The assessment results showed that atrazine was the most commonly detected pesticide in ground water in the assessment area. Atrazine was detected in water from 22 of the 28 wells sampled, and recovery results for atrazine were some of the worst (largest negative bias). Concentrations of the eight pesticides in ground water from wells were generally less than 0.3 µg/L. Only six individual measurements of the concentrations in water from six of the wells were at or above 0.3 µg/L, five for atrazine and one for metolachlor. There were eight additional detections of metolachlor and simazine at concentrations less than 0.1 µg/L. No well water contained more than one pesticide at concentrations at or above 0.3 µg/L. Evidence exists, however, for a pattern of co-occurrence of metolachlor and simazine at low concentrations with higher concentrations of atrazine.

Large variability in replicate samples and negative bias for pesticide recovery from spiked samples indicate the need to use data for pesticide recovery in the interpretation of measured pesticide concentrations in ground water. Data from samples spiked with known amounts of pesticides were a critical component of a quality-assurance design for the monitoring component of the Pesticides and Ground Water Strategy.

Trigger concentrations, the concentrations that require action under the Pesticides and Ground Water Strategy, should be considered maximums for action. This consideration is needed because of the magnitude of negative bias.

INTRODUCTION

In areas of Pennsylvania where pesticides are used extensively for agricultural purposes, there is concern about pesticides entering aquifers that supply water to wells and springs. The Pennsylvania Department of Agriculture (PDA) is the agency responsible for regulating pesticide registration and use, including protecting all environmental resources from deleterious effects of pesticides. The U.S. Environmental Protection Agency (USEPA) requires PDA to develop state management plans for five pesticides—alachlor, atrazine, cyanazine, metolachlor, and simazine—identified as either probable or possible human carcinogens with a potential to contaminate ground water. PDA developed a Pesticides and Ground Water Strategy (Pennsylvania Department of Agriculture, 1998) as an approach to managing pesticide use and preserving ground-water quality. The goal of the Strategy is to protect all drinking-water sources from degradation.

Monitoring for pesticides in ground water is an important component of the Strategy and is done statewide. The monitoring to determine the occurrence and distribution of pesticides in ground water of Pennsylvania evolved during 1996-97 to focus on spatial characterization. This focus has roots in the U.S. Geological Survey (USGS) National Water-Quality Assessment Program (Gilliom and others, 1995, p. 26). Areas of the State are prioritized on the basis of geologic setting, hydrogeology, presence of agricultural lands and pesticide use, and on the availability of data from previous studies of pesticides in ground water (Lindsey and Bickford, 1999). In addition to the five pesticides for which state management plans are required, PDA tests water samples for the herbicides pendimethalin and metribuzin and the insecticide chlorpyrifos due to the quantities that are used as determined by PDA pesticide-use surveys. A priority area for sampling is divided into subareas of equal size, and a single sampling location is randomly selected to start to represent each subarea. This is a “stratified random spatial” selection. To supplement the data from a single location in a subarea, PDA collects samples from and monitors additional wells for assurance that each subarea is adequately represented. The subareas were termed sampling cells.

To monitor ground water, the PDA regularly samples wells and submits the water samples to the Pennsylvania Department of Environmental Protection (PaDEP) Laboratory to analyze for the presence of pesticides in ground water at concentrations above the Maximum Contaminant Level (MCL) (Pennsylvania Department of Agriculture, 1998, p. 2). A concentration of one-third of the MCL for any of the five pesticides in ground water triggers action by PDA. The concentrations for five pesticides that trigger action by PDA as part of the Strategy are summarized in table 1. The concentration of 1 µg/L (micrograms per liter) for cyanazine requires that laboratories analyzing ground-water samples for PDA are capable of measuring 0.3 µg/L of cyanazine. The 0.3 µg/L concentration is also the reporting level for the other pesticides.

Quality assurance of the laboratory analytical measurements and aspects of sample collection are also part of the monitoring component because data from PDA assessments are for regulatory pur-

Table 1. *Priority (State Management Plan) pesticides for monitoring as specified by the Pesticides and Ground Water Strategy and concentrations that trigger actions by Pennsylvania Department of Agriculture*

[MCL, U.S. Environmental Protection Agency Maximum Contaminant Level; H indicates an MCL is not developed for the pesticide and the U.S. Environmental Protection Agency Health Advisory Level is used]

Pesticide	Concentration, in micrograms per liter	
	MCL	One-third of MCL
Alachlor	2	0.7
Atrazine	3	1.0
Cyanazine	1 H	.3
Metolachlor	100 H	33
Simazine	4	1.3

poses and data quality must be documented. Because pesticide concentrations in ground water are usually extremely small (usually smaller than one part per billion), quality assurance is a critical part of the monitoring component.

The USGS, in cooperation with PDA, completed the study described herein to demonstrate the application of a quality-assurance design to an assessment of an area prioritized for study by the monitoring component of the Pesticides and Ground Water Strategy. The USGS role was to develop the quality-assurance design, assist PDA in the application of the design to a selected assessment area, evaluate the results, and report the quality-assurance and assessment results.

Purpose and Scope

This report 1) describes a quality-assurance design developed primarily to evaluate the quality of laboratory analytical results for pesticide concentrations in ground water, 2) evaluates the bias and variability of laboratory results, and 3) summarizes quality-assurance data and data for pesticide concentrations in ground-water samples from the assessment area. The data used for the evaluation were collected from October 1997 through January 1998. The pesticides include five herbicides (alachlor, atrazine, cyanazine, metolachlor, and simazine) for which specific state management plans are required, two additional high-use herbicides (pendimethalin and metribuzin), and a high-use insecticide, chlorpyrifos. The ground-water data presented herein are for the 8 pesticides in water samples collected from 28 wells in the Delaware River Basin in eastern Pennsylvania. The wells were drilled into carbonate bedrock aquifers in agricultural areas of the Great Valley Section of the Ridge and Valley Physiographic Province.

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QUALITY-ASSURANCE DESIGN AND APPLICATION

The primary design goals were to (1) establish if there was bias in laboratory analytical measurements of pesticide concentrations, including determining whether results were free from field and laboratory contamination, and (2) define the variability of pesticide-concentration measurements in ground water. The evaluation of the bias and variability for measured concentrations had to be documented so that actions by PDA

as part of the Pesticides and Ground Water Strategy were supported by quality-assurance information.

The design was used 1) to be confident that contamination (false-positive detections or contamination bias) introduced by sample-collection procedures and field and laboratory sample-processing activities was not the source of trace amounts of the eight pesticides in ground-water samples, 2) to be confident that false-negative results would not be a problem and that a pesticide would be detected in ground water when the pesticide was present, 3) to quantify bias in pesticide recoveries, 4) to determine if bias was related to interferences from the ground water itself, and 5) to quantify overall variability in pesticide recovery.

Data-Quality Objectives and the Types of Quality-Control Samples

Four data-quality objectives are presented. The types of quality-control samples used to assess the objective are given in italics.

The first data-quality objective was that bias due to sample contamination from all processing sources (field processing, transport, and lab analysis) would not be found (concentration less than the detection level for the analysis). This objective was evaluated with *field blanks*.

The second data-quality objective was for small numbers (less than 5 percent) of false negatives (negative detection bias). Pesticides deliberately added to the samples of ground water and laboratory water (spikes) were used to evaluate this objective. Reagent-grade water was spiked (*laboratory-water spikes*) to determine detection and recovery in a sample matrix free of environmental interferences. Ground water was spiked (*ground-water spikes)* to determine detection and recovery in a sample matrix that may have properties that interfere with extraction or analysis. Unspiked ground-water splits submitted to two laboratories (*2-lab splits*) were another check on false-negative results.

The third data-quality objective was that the bias in the recovery would be within 10 percent of the 'true' (100-percent recovery) result. The laboratory-water spikes and ground-water spikes used for the second data-quality objective also were used to evaluate this objective. Recoveries and recovery percentages for both types of spikes were used to evaluate overall bias resulting from the sample matrix and other factors.

The fourth data-quality objective was that recovery variability would be low or small. On the basis of data presented by the USEPA (1995, p. 507-27), a small variability would be 10 percent or less. This objective was evaluated with split *replicate samples*—duplicate samples of ground water and triplicate samples of spiked laboratory water. A single volume of water was split for each sample; thus, recoveries and recovery percentages for both types of replicates were used to evaluate overall analytical variability with sampling and sample-processing variability assumed constant within each replicate.

Design Components

The quality-assurance design had spatial and temporal components. The spatial design was primary and represented an area comprising 30 sampling cells assessed as part of the monitoring component for the PDA Pesticides and Ground Water Strategy during the 1997-98 field season. A quality-assurance sampling frequency of 20 percent of cells was selected to ensure a sample number of five or more for analysis. Sampling cells for the blanks, spikes, and replicates collected in the field were chosen by use of a random number table (Taylor, 1987, p. 274-275); thus, the term 'random spatial' design.

The temporal design component was intended to gather quality-assurance information throughout the field season. Because of the complex nature of pesticide analysis methods, results from laboratories can take months to be completed and made available. During a 3- to 4-month field season, it was reasonable to assume that some quality-assurance results might not be returned from the laboratory until after the season had ended. Visiting the selected randomly chosen cells at the beginning of the field season and submitting quality-control samples such as field blanks and selected spikes as early in the season as possible were emphasized. Laboratory-water spikes were to be analyzed at discrete intervals during the study period and were not randomly chosen cells. In this way, results were available across the sampling period.

Quality-Control Samples and the Role of the USGS Laboratories

Two analytical laboratories, the PaDEP Laboratory in Harrisburg, Pa., and the USGS National Water-Quality Laboratory in Arvada, Colo., were part of the design. The quality-assurance design was not developed to compare laboratories but to compare specific types of quality-control samples that were submitted with routine samples of ground water to evaluate the objectives. The purpose of using the USGS Laboratory was to provide (1) an independent check of results from the PaDEP Laboratory for blank samples to evaluate false positives, (2) independent confirmation that preparation of laboratory-water spikes and ground-water spikes by the USGS field personnel was valid and resulted in the concentrations expected based on spike calculations, (3) an independent check of the PaDEP Laboratory results to evaluate false negatives, and (4) an independent set of ground-water-sample results to evaluate whether the sample matrix affected pesticide recovery. In addition, using two laboratories to analyze split samples provided additional documentation of the measured concentrations in ground water.

All quality-control samples were *blind samples*; that is, the laboratories did not know the quality-control samples were any different than routine ground-water samples. Replicate samples were processed and spike samples were prepared in the laboratory at the USGS in Lemoyne, Pa., hereafter termed "Lemoyne laboratory." The reason the samples were prepared and how the laboratories were used are described below.

Field Blanks

Blank samples were used to determine if contamination was occurring in any stage of sample processing in either the field or laboratory that would result in false positives. Blanks were for evaluation of false positives. The random spatial design called for blanks at 20 percent of the sampling cells. Five field blanks were collected during the field season at five field sites for analysis by the PaDEP Laboratory. Four of the five blanks were split at the Lemoyne laboratory and submitted to both the PaDEP Laboratory and the USGS Laboratory for analysis.

Spikes

Spikes were for evaluation of false negatives and bias in pesticide recovery. A spike not detected was a false-negative result. The random spatial design called for ground-water spikes at 20 percent of the sampling cells. Ground water for five spikes were collected at five field sites. All were split at the Lemoyne laboratory and submitted to both the PaDEP Laboratory and the USGS Laboratory for analysis. The temporal design was to check for false negatives at 10 percent of the sampling cells using laboratory waters spiked with pesticides. These waters were submitted to the PaDEP Laboratory with samples from three cells—10, 20, and 30—in an attempt to distribute the information throughout the field season. Two of the three laboratory-water spikes were split at the Lemoyne laboratory and submitted to the PaDEP Laboratory and the USGS Laboratory for analysis. The triplicate samples, prepared for cells 10, 20, and 30, were designated lab spike 10-1, 10-2, 10-3, 20-1, and so forth. A second aspect of the temporal design was to compare spike recovery for samples collected on the same day. This involved analysis of results for two sets of spikes prepared from waters on the same day. This was done twice (on two different days) and involved samples from four sites.

Spike recovery was used to evaluate bias. Concentrations in a 0.3 to 0.5 µg/L range were selected for spikes in order to evaluate bias near the trigger concentration for action by PDA under the Pesticides and Ground Water Strategy. The range also was selected to match measured concentrations in ground water determined by earlier studies. Concentrations from earlier studies were summarized by Lindsey and Bickford (1999). All laboratory-water spikes were prepared at a concentration of 0.4 µg/L.

Recovery results from laboratory-water spikes and ground-water spikes were used for evaluation of bias from ground-water matrix interference. Matrix interference is not expected for laboratory-water spikes. The design compared recoveries of spikes in laboratory water and in ground water. The three laboratory-water spikes and five ground-water spikes were again used for this evaluation.

Replicates

Replicates were used for evaluation of overall variability. The design involved 1) evaluation of the triplicate results from the PaDEP Laboratory

for three laboratory-water spikes and 2) evaluation of duplicate results from the PaDEP Laboratory for seven ground-water samples. The triplicates and duplicates were from the temporal and random spatial components of the design, respectively.

For the three replicates of spiked laboratory waters, four-way splits were prepared at the Lemoyne laboratory for determination of variability. Three triplicates were submitted to the PaDEP Laboratory, and twice, a single sample was submitted to the USGS laboratory as a independent verification check on spike concentration.

Seven replicates of ground waters were prepared at the Lemoyne laboratory, three as two-way splits of samples and four as three-way splits for evaluation of variability. The two-way splits were submitted as duplicate samples only to the PaDEP Laboratory. The three-way splits of the samples were used to prepare a duplicate for the PaDEP Laboratory and a single sample submitted to the USGS laboratory as an independent verification check on concentration. A split submitted to both laboratories is hereafter termed a 2-lab split.

Splits (2-lab)

Four additional samples, not part of other quality-control sample types, were prepared as 2-lab splits and were used to further evaluate false negatives and bias. The interest was in determining how often the PaDEP Laboratory detected the 'true' presence of a pesticide. The USGS Laboratory results were used to help determine the 'true' values. The unspiked ground water analyzed with each of the five spiked ground waters also was categorized as a 2-lab split. In total, 11 samples were prepared as 2-lab splits, including the 5 spike-related ground waters, 2 additional samples prepared as three-way split replicates, and these 4 additional samples.

Assessment Area for Application of the Design

The 30 sampling cells subdividing the assessment area in Lebanon, Berks, Lehigh, and Northampton Counties are shown in figure 1 along with the locations and local well numbers of the 29 wells chosen to represent 28 of the cells. The wells were assigned a local number and another identifier for the USGS and PDA computer systems, respectively. The identification numbers and records of wells sampled for the assessment and for the quality-assurance design are provided in table S-1 (Supplemental Data section). Wells representative of agricultural areas could not be located for sampling in cells 17 and 23. Two wells were sampled in cell 14. The assessment was completed with 28 samples from 27 of the 30 cells. The sample from cell 15 was lost. The cells and local well numbers associated with the types of quality-control samples are provided in table 2.

Field and Lemoyne Laboratory Procedures

Sample collection for the monitoring component of the Pesticides and Ground Water Strategy is not restricted to a specific time of year. In well waters having high concentrations of pesticides, PDA has found that the concentrations show little fluctuation with season (John W. Pari, Pennsylvania Department of Agriculture, oral commun., 1997). The sampling for this assessment started during the harvest season in October 1997 and ended in February 1998, months after the primary pesticide-application period for row crops in the spring and early summer of 1997.

Sampling supplies were prepared at the Lemoyne laboratory each day before field work began. The 3-L Teflon bottles used to collect samples were cleaned with Liquinox detergent and triple rinsed with both tap water and deionized water. The bottles were allowed to dry, and an empty weight was determined.

Samples for analysis were submitted to the laboratories in 1-L amber glass bottles. Bottles from two suppliers were used. I-Chem brand bottles were provided by the PaDEP Laboratory for use by PDA and were certified by the manufacturer to be free of organics. Bottles used for samples submitted to the USGS Laboratory were supplied for field use by the USGS Quality of Water Services Unit in Ocala, Fla.

Water for preparation of blank samples and laboratory-water spikes was obtained through the USGS Laboratory from commercial sources of laboratory supplies. Waters from three lot numbers were used for the study. Each lot was certified as laboratory water for use in blanks; the eight pesticides were not detected by independent analyses of the lots by the USGS Laboratory. For field preparation of blank samples, pesticide-free laboratory waters were transported to the field with the bottles and other supplies. The pesticide-free laboratory water was added to the 3-L Teflon bottles to simulate the procedures used in collection of ground-water samples.

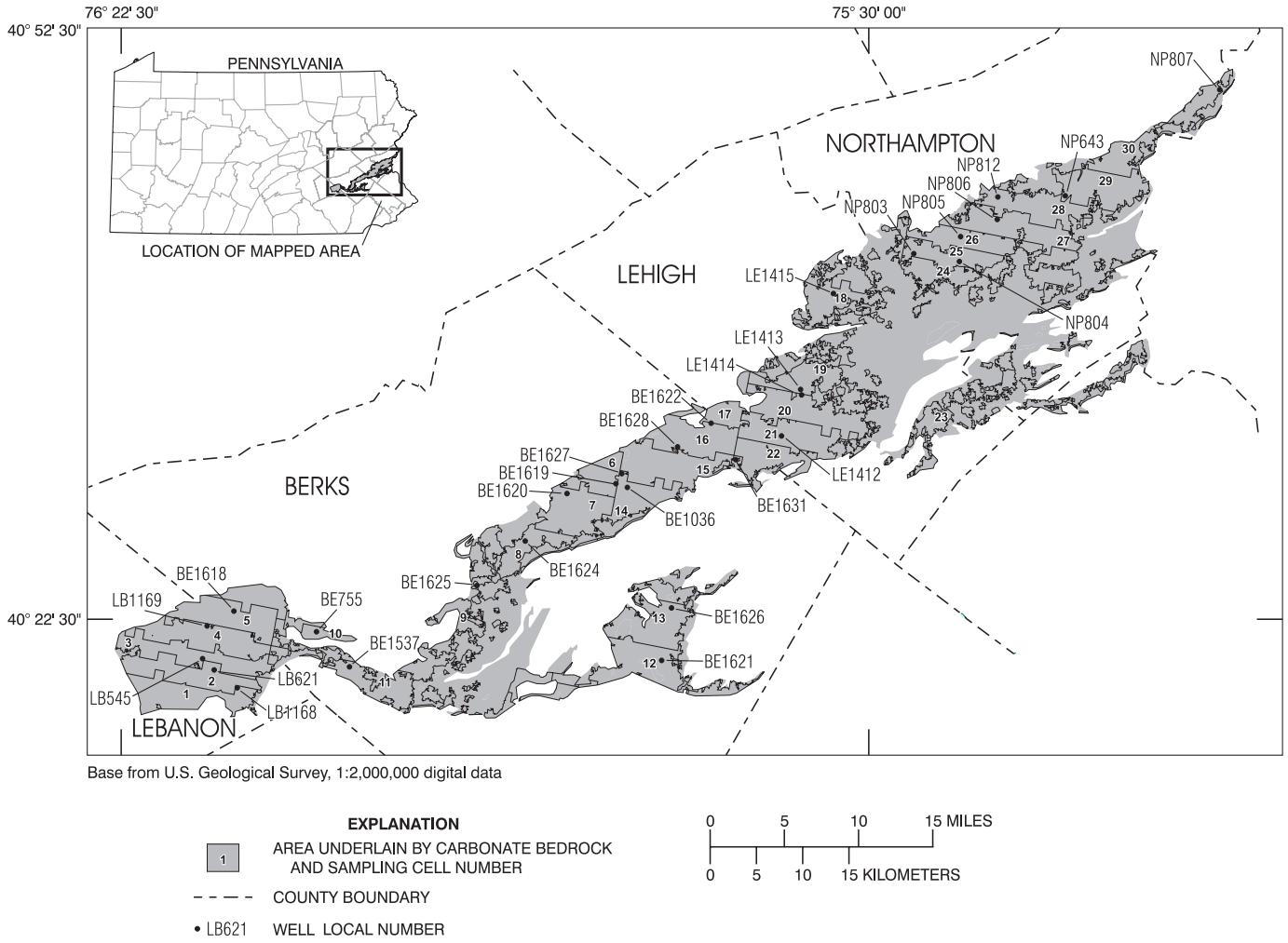

Figure 1. Location of data-collection sites used for the quality-assurance design in the 30 sampling cell areas subdividing the Great Valley agricultural area underlain by carbonate bedrock aquifers in Berks, Lebanon, Lehigh, and Northampton Counties, eastern Pennsylvania.

Table 2. *Quality-control sample types and sampling cell numbers for application of the quality-assurance design in the agricultural areas underlain by carbonate bedrock aquifers in the Great Valley of eastern Pennsylvania*

[PaDEP, Pennsylvania Department of Environmental Protection; USGS, U.S. Geological Survey]

Quality-control sample type	Sampling cell identification number	Local well number where sample collected	Laboratory to analyze sample		Comments
			PaDEP	USGS	
Blank, field	2	LB 621	X	X	Before first sample
Blank, field	4	LB 1169	X	X	--
Blank, field	5	BE 1618	X	--	--
Blank, field	12	BE 1621	X	X	--
Blank, field	27	NP 806	X	X	--
Spike, laboratory water	10	BE 755	X	--	To PaDEP in triplicate
Spike, laboratory water	20	LE 1414	X	X	To PaDEP in triplicate
Spike, laboratory water	30	NP 807	X	X	To PaDEP in triplicate
Spike, ground water	4	LB 1169	X	X	--
Spike, ground water	6	BE 1619	X	X	--
Spike, ground water	14	BE 1036	X	X	--
Spike, ground water	19	LE 1413	X	X	--
Spike, ground water	24	NP 803	X	X	--
Replicate, laboratory water	10	BE 755	X	--	To PaDEP in triplicate
Replicate, laboratory water	20	LE 1414	X	--	To PaDEP in triplicate
Replicate, laboratory water	30	NP 807	X	--	To PaDEP in triplicate
Replicate, ground water--3-way split	4	LB 1169	X	X	To PaDEP in duplicate
Replicate, ground water--2-way split	8	BE 1624	X	--	To PaDEP in duplicate
Replicate, ground water--2-way split	9	BE 1625	X	--	To PaDEP in duplicate
Replicate, ground water--3-way split	16	BE 1622	X	X	To PaDEP in duplicate
Replicate, ground water--3-way split	19	LE 1413	X	X	To PaDEP in duplicate
Replicate, ground water--3-way split	29	NP 643	X	X	To PaDEP in duplicate
Replicate, ground water--2-way split	30	NP 807	X	--	To PaDEP in duplicate
2-lab split, ground water	1	LB 1168	X	X	--
2-lab split, ground water	3	LB 545	X	X	--
2-lab split, ground water	10	BE 755	X	X	--
2-lab split, ground water	12	BE 1621	X	X	--

At the sampling site prior to sample collection, a raw-water faucet was opened to allow the water from the well to flow into a bucket. Temperature and specific conductance of the water were monitored until measurements were stable at 5-minute intervals. Samples from the raw-water faucet were then collected in one or more of the 3-L bottles. If sediment or particulate matter was visible in the samples, the waters were to be filtered through glass-fiber membranes with pore-size openings of 0.7 microns. None of the samples required this filtration step. The waters submitted to the laboratories were free of visible sediment and particulates. No preservatives were added.

Depending on the type of quality-assurance sample being prepared, the water from the 3-L bottles was either transferred directly to the 1-L glass bottles and stored in a cooler on ice or the 3-L bottles were placed in a cooler on ice for processing and shipment to the analytical laboratories. Samples were transported to the Lemoyne laboratory for processing and shipment.

At the Lemoyne laboratory, spiked samples were prepared by adding known herbicide amounts to the samples. The samples in the 3-L Teflon bottles were weighed for volume determination, using unit density to convert mass to volume. Spike mixtures manufactured by Supelco, Inc., and certified by the USGS Laboratory were obtained from the USGS Laboratory. A 100-microliter variable-volume micropipet with replaceable glass bores was used to dispense predetermined aliquots of the spike mixture to the water samples in the 3-L Teflon bottles. Calculations for spike concentrations in the 0.3 to 0.5 µg/L range were made from concentration data (Supelco, Inc.) for pesti-

cide spike mixtures. The two lots of spike mixture used for the study have pesticide concentrations listed in table 3. The overall errors in measuring sample volume and the volume of spike mixture were estimated to be 2 percent of the final spiked concentration. After spiking, the total sample volume from multiple 3-L bottles was thoroughly mixed by shaking and stirring and then split by pouring waters from the 3-L bottles into 1-L glass bottles in equal-volume aliquots. The water samples in glass bottles were kept chilled and delivered to the laboratories for analysis within 24 hours after collection.

Table 3. *Concentrations of selected pesticide compounds in commercial mixtures used for preparation of laboratory-water and ground-water spike samples*

[Data from Supelco, Inc., certificate of composition for pesticide/herbicide spike mix.]

Pesticide	Spike-mixture concentrations, (micrograms per milliliter of solvent)	
	Supelco Lot LA-62435	Supelco Lot LA-66096
Alachlor	1.0	1.0
Atrazine	1.0	1.0
Chlorpyrifos	1.0	1.0
Cyanazine	1.0	.9
Metolachlor	.9	1.0
Metribuzin	1.0	.9
Pendimethalin	1.0	1.0
Simazine	1.0	1.0

A single water sample submitted to the PaDEP Laboratory comprised two 1-L glass bottles of sample. Thus, a duplicate sample to PaDEP (or intra-lab split) comprised four 1-L glass bottles of sample all split from two 3-L bottles of the initial sample. One 1-L glass bottle was submitted to the USGS Laboratory for each sample.

Analytical Laboratory Procedures

The two laboratories used different methods for pesticide extraction from water prior to analysis. Extraction methods used by the PaDEP Laboratory involved a liquid-liquid extraction procedure as described in USEPA Method 507 (U.S. Environmental Protection Agency, 1988). USGS used a solid-phase extraction procedure described by Zaugg and others (1995). USGS methods concentrate the extract to about one-fifth of the volume used in Method 507.

Analytical methods for the eight pesticides differed between laboratories and resulted in different method detection limits (MDL's). The MDL is statistically determined and is defined to be the minimum pesticide concentration that can be identified, measured, and reported with 99-percent confidence that the concentration is greater than zero. The MDL is intended to protect against false-positive results.

The PaDEP Laboratory used a modification of USEPA Method 507; a mass spectrometer detector was substituted for the nitrogen-phosphorus detector specified in Method 507. The PaDEP Laboratory operated the detector in full-scan monitoring mode. The PaDEP set the reporting levels for the pesticides to 0.3 µg/L and set the MDL's at 0.1 µg/L. USGS used a mass spectrometer detector operated in the selected-ion monitoring mode. The concentrations measured by the USGS laboratory were at reporting levels of 0.005 µg/L or less for the eight pesticides. A summary of the reporting levels or quantitation limits for the two laboratories is provided in table 4.

Table 4. *Analytical reporting levels (quantitation limits) for selected pesticides*

[PaDEP, Pennsylvania Department of Environmental Protection Laboratory; USGS, U.S. Geological Survey National Water-Quality Laboratory]

Pesticide	Reporting level, by laboratory, in micrograms per liter	
	PaDEP	USGS
State Management Plan herbicides		
Alachlor	0.3	0.002
Atrazine	.3	.001
Cyanazine	.3	.004
Metolachlor	.3	.002
Simazine	.3	.005
Additional high-use herbicides		
Pendimethalin	.3	.004
Metribuzin	.3	.004
High-use insecticide		
Chlorpyrifos	.3	.004

Data Analysis

The procedures or statistical methods used to analyze the results by sample type are described in this section. The description begins with methods for blanks and then includes methods for analysis of data resulting from spikes, replicates, and splits.

Field Blanks

To determine if there was sample contamination and how that may bias an environmental sample, analyses results of field blanks were tabulated to determine the number of detections (false positives) and obtain summary statistics for the concentrations in blanks. Results from the PaDEP Laboratory and the USGS Laboratory were compiled for splits of the blank samples submitted to both laboratories. This compilation ensured that pesticide concentrations in blanks were described over the range of reporting limits listed in table 4 for the two laboratories.

Spikes

Bias was determined by evaluating how close the measured concentrations are to the 'true' or known sample concentration. The rate of false-negative results was determined for the eight pesticides in laboratory water spikes and in ground-water spikes as a percentage of the total number of each type of spike.

Analysis of the recovery of pesticides spiked into water at concentrations ranging from 0.31 µg/L to 0.51 µg/L was used to assess bias of results. The spike-recovery calculations require the following information for each pesticide:

$C_{mix,}$ Spike mixture concentration of pesticide, in micrograms per milliliter (see table 3);

V_{wat}, Volume of water sample, in milliliters;

V_{mix}, Volume of spike mixture added to water sample, in milliliters;

$C_{spkmeas}$, Concentration, in micrograms per liter, of pesticide measured by laboratory in the spiked water sample; and

$C_{unsmeas}$, Concentration, in micrograms per liter, of pesticide measured by laboratory in the unspiked water sample.

Percent recovery was calculated in three steps:

1. Calculate the spike concentration prepared in the spiked water sample, in micrograms per liter:

$$C_{prp} = V_{mix} \times C_{mix} \times [1/V_{wat}] \times 1{,}000 \quad (1a)$$

2. Calculate the spike concentration measured by the laboratory, in micrograms per liter:

$$C_{difmeas} = C_{spkmeas} - C_{unsmeas} \quad (1b)$$

3. Take the ratio of measured to prepared concentrations to determine recovery, in percent:

$$\text{Recovery Percentage} = [C_{difmeas}/C_{prp}] \times 100 \quad (1c)$$

In the calculations for laboratory-water samples, $C_{unsmeas}$ was set to zero.

Graphical techniques and summary statistics were used to compare recoveries among samples for each pesticide. Recovery results were tabulated, summary statistics were computed, and results were compared to the data-quality objective that recoveries be within plus or minus 10 percent of the 'true' or 100-percent value.

To evaluate the use of internal surrogate recoveries to estimate recoveries of spiked pesticides, internal surrogate recoveries were correlated with pesticide recoveries for the same sample. Recoveries of the internal surrogate 1,3-dimethyl-2-nitrobenzene were reported by the PaDEP Laboratory, and three other internal surrogates—diazinon-d_{10}, terbuthylazine, and lindane (*alpha*-HCH-d_6)—were reported by the USGS Laboratory. The laboratories monitor these recoveries to determine if the analysis is within a control-limit range set for the analytical method. The range for the PaDEP method was 60-120 percent or 70-120 percent depending on the sample. Results that show poor (or out-of-range) surrogate recoveries generally require samples be reanalyzed by the laboratory. In some instances, if the original water sample cannot be re-extracted, water may need to be resampled from the well.

The exact form of the rank-sum test (Helsel and Hirsch, 1992, p. 120) was used to compare the recovery summary statistics for laboratory-water spikes and ground-water spikes to determine if there was a significant bias caused by interference from the ground-water matrix.

Replicates

Variability is a measure of how well detections, concentrations, and recoveries can be reproduced. To evaluate variability of detections, equivocal detection results (a measured detection and nondetection for splits of the same sample) were tabulated for duplicate ground-water samples submitted to the PaDEP Laboratory. The result from the USGS Laboratory for the sample was then used as an independent check in cases of disparate results from the PaDEP Laboratory. The USGS result provided an independent way to determine if the nondetection or the detection was correct. To evaluate concentration variability, replicate samples submitted to the PaDEP Laboratory were analyzed two ways. For determination of differences between duplicate samples where results were greater than the reporting limit, the Relative Percent Difference (RPD) was calculated. The RPD, a statistic that represents the difference between two measurements (X_1, X_2) relative to their average, was calculated as follows:

$$RPD = [(2|X_2 - X_1|)/(X_2 + X_1)] \times 100 \qquad (2)$$

For determination of differences between triplicate samples where results were greater than the reporting limit, the Relative Standard Deviation (RSD) was calculated as follows:

$$RSD = s/C\text{-}bar \qquad (3)$$

where s is the standard deviation of triplicate results, and

C-bar is the mean concentration of the triplicate results.

The RSD is also known as the coefficient of variation.

Splits (2-lab)

Detection summaries were prepared as part of the overall assessment of agricultural pesticides in ground water. The percentages of false negatives combined with graphical techniques were used to evaluate results for the 11 ground-water samples analyzed by both laboratories.

QUALITY-ASSURANCE RESULTS

The results are presented by type of quality-control sample. Discussion of the results focuses on addressing the design goals and whether the results met the data-quality objectives.

Field Blanks

The results of analyses of five field-prepared blank samples of laboratory water showed no evidence of any sample contamination at or above a concentration of 0.3 µg/L. Data for the blank samples are given in tables S-2 and S-3 (Supplemental Data section) for the PaDEP Laboratory and USGS Laboratory, respectively. The data indicate the three lots of pesticide-free laboratory water used for quality assurance had no detectable concentrations of the eight pesticides. The results for five field blanks indicate that collection, processing, transport, and laboratory-analysis procedures did not contaminate the samples. In addition, the last four field blanks were collected following collection of samples in which pesticides were detected, which demonstrates the cleaning procedures were effective in decontaminating the sampling equipment. Therefore, pesticide detections in ground waters were due to the presence of the pesticide in ground water and were not to be attributed to contamination from sample processing in either the field, the Lemoyne laboratory, or the analytical laboratories. The first data-quality objective was met.

Spikes

Results for laboratory water are presented first, then the ground-water results are presented. The results were evaluated to first address the question of false negatives (data-quality objective 2) and then to evaluate bias (data-quality objective 3). Matrix interference from ground water, as a cause of bias, was then addressed.

Evaluation of false negatives began with the results of the analyses by the PaDEP Laboratory of laboratory-water spikes with pesticide concentrations at 0.4 µg/L (table S-4 in Supplemental Data section). The results of analyses of two four-way splits submitted to the USGS Laboratory as independent concentration checks are given in table S-5 (Supplemental Data section) and show the spikes had concentrations close to that expected from the spike-preparation calculations. On the basis of results in table S-4 from 64 analyses for individual pesticides in 3 samples of laboratory water spiked with known amounts of pesticides, all spiked pesticides were detected. For laboratory-water spikes, there were no false-negative results at the 0.4 µg/L concentration.

The evaluation of false negatives in ground water used analyses by the PaDEP Laboratory of spiked samples of ground water at concentrations

ranging from 0.31 µg/L (the reporting level) to 0.51 µg/L. On the basis of results from 40 analyses by the PaDEP Laboratory for individual pesticides in 5 ground-water samples spiked with known pesticide amounts, no analytical measurements failed to detect the presence of a pesticide (table S-6 in Supplemental Data section). The check samples analyzed by the USGS Laboratory showed the pesticides to be present (table S-7 in Supplemental Data section).

In summary, there were no false negatives for the eight pesticides in all spiked samples. The second data-quality objective, for small numbers (less than 5 percent) of false negatives in analyses of ground water, was met.

To evaluate bias (data-quality objective 3), the results in tables S-4, S-5, S-6, and S-7 (Supplemental Data section) were used in equation 1 to calculate pesticide recoveries. On the basis of results from the laboratory blanks, setting $C_{unsmeas}$ to zero in equation 1b for laboratory water was a valid procedure. The results of the calculations of recoveries are given in table S-8 (Supplemental Data section) along with summary statistics for recovery in laboratory water and in ground water. Recovery data for pesticides in addition to the eight evaluated herein are summarized by Durlin and Schaffstall (1999, p. 395-399).

Negative bias is a normal and accepted characteristic of analytical methods for pesticides (U.S. Environmental Protection Agency, 1988, p. 167; Zaugg and others, 1995). Negative bias comes from measured concentrations that are generally lower than expected. In samples with very small concentrations of pesticides, a small (0.1 µg/L) difference in measured concentration can result in a large difference in recovery. In a sample spiked for example at 0.5 µg/L, a result of 0.3 µg/L would yield a recovery of 60 percent; a result of 0.4 µg/L would yield a recovery of 80 percent. Bias results for PaDEP analyses were compared against Method 507 results in U.S. Environmental Protection Agency (1995).

Negative bias was characteristic of results for the eight pesticides. Spike recoveries in laboratory water by the PaDEP Laboratory ranged from medians near 76 percent for alachlor, atrazine, chlorpyrifos, metolachlor, and pendimethalin to 107 percent for cyanazine. The median recovery for pesticide spikes in ground water was as low as 65 percent for atrazine and as high as 97 percent for cyanazine. The results for cyanazine were dissimilar from the other pesticides and were characterized by high positive bias in 7 of the 13 spikes analyzed for cyanazine. The recoveries for cyanazine in Lab-Spike-10 were in excess of 250 percent. The median results for alachlor, atrazine, metolachlor, metribuzin, and simazine in laboratory water and ground water were lower than the results, some by as much as 20 percent, reported in the Method 507 documentation (U.S. Environmental Protection Agency, 1995). The USEPA results were for recovery of concentrations between 0.75 µg/L (simazine) and 7.5 µg/L (metolachlor)—concentrations generally many times higher than the concentrations used in this study—and were not directly comparable to the results presented here. The USEPA results also do not include data for chlorpyrifos, cyanazine, or pendimethalin. Standard deviation of recovery was as low as 7 percent for alachlor and simazine and as high as 17 percent for cyanazine. The standard deviations of the percent recovery in table S-8 were similar to the USEPA results for ground water.

A rank-sum test of the results for laboratory water and ground water showed no significant difference (alpha=0.05) in spike recovery for any of the eight pesticides. Thus, the ground-water matrix did not contribute to matrix interference.

The magnitude of the negative bias for the eight pesticides, with the exception of cyanazine, would result in reported concentrations commonly 75-80 percent of the expected ('true') concentration in the water sample. To relate recovery results to data-quality objective 3, spike recovery for the five state management plan pesticides in ground water and the 20 percentage point range (from 90 to 110 percent) acceptable for objective 3 are illustrated in figure 2. The results (table S-8 and figure 2) show that the bias in the recovery was not within 10 percent of the 'true' (100 percent recovery) result for at least half of the results for each pesticide. The laboratories were unable to consistently provide results to within 10 percent of known concentrations for ground water over the course of the study.

The recovery data for the internal surrogate 1,3-dimethyl-2-nitrobenzene (tables S-4 and S-6 in Supplemental Data section) were checked for correlation with the spike recovery. For the six spikes, three of laboratory water and three of ground water, where surrogate recovery and spike recovery were quantified, correlations were too small for

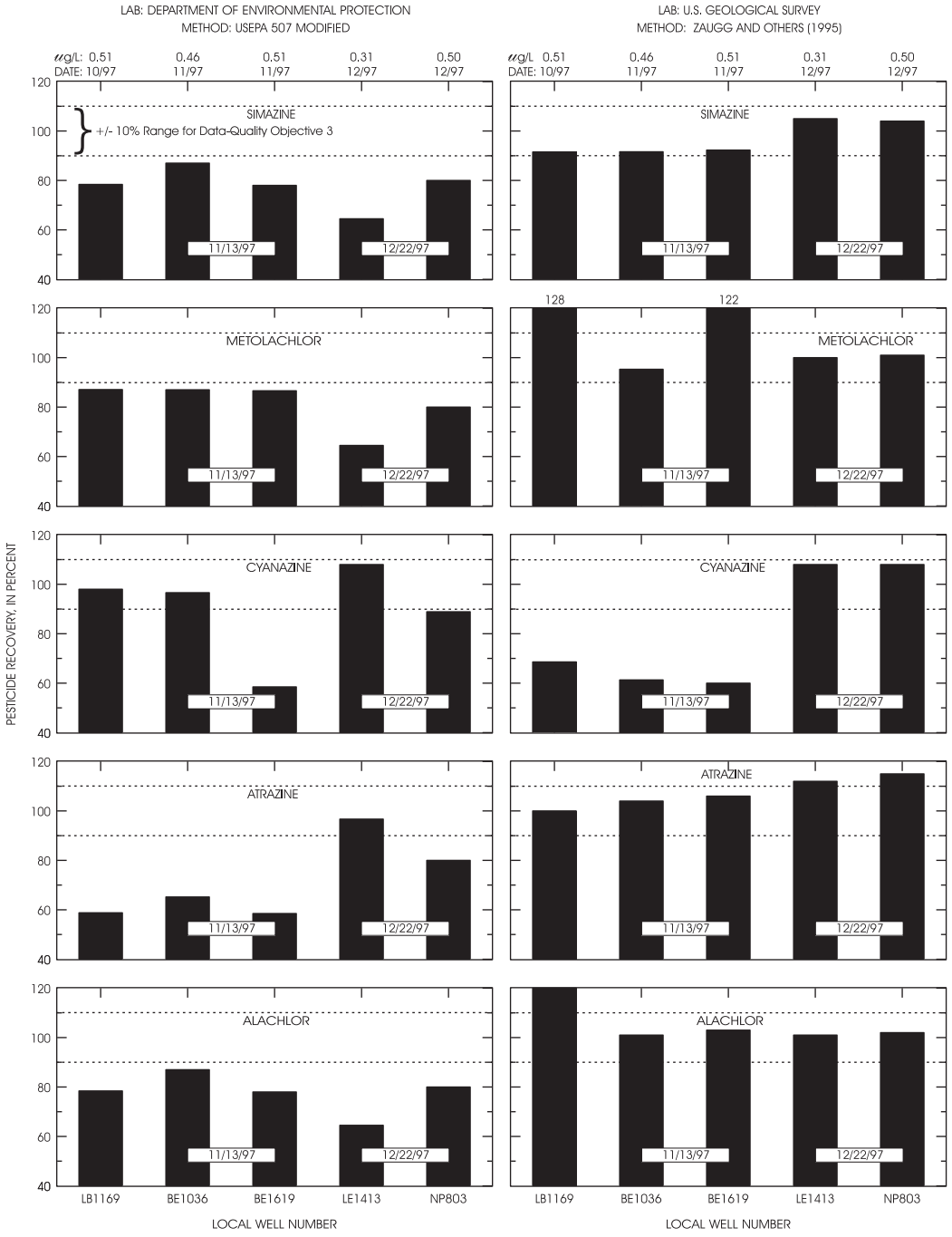

Figure 2. Percentage recovery of alachlor, atrazine, cyanazine, metolachlor, and simazine in spiked ground-water samples analyzed by Pennsylvania Department of Environmental Protection Laboratory and U.S. Geological Survey, National Water-Quality Laboratory.

the relations to be of any practical use. Two other spikes of ground water analyzed by the PaDEP Laboratory had "poor" internal surrogate recoveries. Poor internal surrogate recovery did not correspond to anomalous results for spike recovery. Internal surrogate recoveries for 1,3-dimethyl-2-nitrobenzene could not be used to determine the pesticide recoveries.

Bias from laboratory rounding of measured concentrations to the tenth of a microgram for reporting purposes was an issue not addressed for this study. Rounding, as a source of bias, could contribute about 10 percent to the overall bias if, for example, a 0.44 µg/L concentration in a sample was reported as 0.4 µg/L. This type of bias could be negative, as in the example, or positive. Relating to this issue, for the last samples analyzed by the PaDEP Laboratory for the assessment in April 1998, the results were reported to hundreths of a microgram.

In summary, the majority of results did not meet data-quality objective 3. For analytical results from the PaDEP Laboratory, bias was nearly always negative (38 of 39 analyses or 97 percent of the ground-water results) and generally in excess of 10 percent from the 'true' or expected concentration (34 of 39 analyses or 87 percent of the ground-water results) for pesticides at concentrations ranging from 0.31 to 0.51 µg/L. Cyanazine results were unusual, meeting the data-quality objective in three of the five ground-water spikes yet overall exhibiting the largest (50 point) range in recovery percentage. Results were better for laboratory-water spikes than for ground water; 63 percent of laboratory-spike results were in excess of 10 percent from the 'true' or expected concentration. A rank-sum test of the results for laboratory water and ground water showed no significant difference (alpha=0.05) in spike recovery for any of the eight pesticides. From this test result, the ground-water matrix did not contribute to bias.

To put the negative bias in the context of concentrations that would trigger actions by PDA (0.7 µg/L of alachlor, for example; see table 1), a 75-percent recovery value means an alachlor concentration of 0.53 µg/L measured by the PaDEP Laboratory would be equal to an environmental concentration of 0.7 µg/L. Thus, a laboratory report showing a concentration of 0.53 µg/L alachlor should prompt PDA to trigger action for the Pesticides and Ground Water Strategy.

Replicates

Spiked replicates (laboratory water) were used for evaluating variability in pesticide recovery. Unspiked replicates (ground water) were used for evaluating variability in pesticide concentration. Results for laboratory water are presented first, then the ground-water results are presented. The results were evaluated to determine if variability was small (10 percent or less, data-quality objective 4).

Variability was estimated using the results for the laboratory-water spikes submitted in triplicate to the PaDEP Laboratory (table S-4). The RPD was calculated for lab-spike 10 and the RSD for lab-spikes 20 and 30. The RPD was zero for all pesticides except cyanazine (RPD of 10 percent) in lab-spike 10. In the two triplicates, the RSD was zero for chlorpyrifos, metolachlor, metribuzin, and simazine; the RSD for alachlor, cyanazine, and pendimethalin ranged from zero in lab-spike 30 to as high as 20 percent in lab-spike 20; and the RSD for atrazine in the two triplicates ranged from 13 to 18 percent. The recovery percentages that characterize these samples are shown in table S-8. In both cases, the result for one sample of the three in the triplicate series was different.

No ground-water samples were prepared as replicate spikes for this study. Summary statistics for variability in recovery for laboratory-water spikes, including the RSD, for the eight samples are listed in table S-8. The RSD in table S-8 is a measure of variability of the method over the course of the study for laboratory waters at a concentration of 0.4 µg/L. An RSD of about 11 percent (or about ±0.05 µg/L) characterizes the method results for alachlor, chlorpyrifos, metolachlor, metribuzin, and simazine. Atrazine and pendimethalin have RSD values of about 17 and 23 percent, respectively. Cyanazine showed a large RSD at nearly 51 percent.

The statistics summarizing variability in recovery results for spiked ground-water samples also are listed in table S-8. The pesticides with low variability in laboratory-water spikes also had low variability in ground water. The RSD for PaDEP lab results is about 10 percent for alachlor, chlorpyrifos, metolachlor, metribuzin, and simazine (table S-8). The RSD values for atrazine, pendimethalin, and cyanazine are high relative to the five other pesticides. Ground-water results were consistent with results for laboratory water.

By combining the results for laboratory water and ground water in table S-8, a combined RSD was calculated for the eight pesticides. The combined percent RSD was 11 for alachlor, 19 for atrazine, 12 for chlorpyrifos, 52 for cyanazine, 12 for metolachlor, 13 for metribuzin, 22 for pendimethalin, and 13 for simazine. The combined RSD for alachlor, chlorpyrifos, metolachlor, metribuzin, and simazine is considered low enough to meet the requirement of data-quality objective 4. Results for atrazine, cyanazine, and pendimethalin do not meet data-quality objective 4. The nature and magnitude of RSD values for the different pesticides underscores the importance of using spikes and the results of spike recovery when evaluating pesticide concentrations in ground water.

Concentration variability in unspiked ground water was difficult to determine because of the large proportion of "less than quantitation limit" results (table S-9). For seven ground-water samples submitted to the PaDEP Laboratory in duplicate, only one duplicate analysis had two measured concentrations greater than the reporting level (atrazine in samples from BE 1622). Two other samples had estimated concentrations in duplicate atrazine analyses (samples from LB 1169 and NP 643). Metolachlor also was detected in the duplicate from NP 643. In an attempt to quantify the differences, the RPD was calculated for these samples. The RPD was zero for atrazine and 40 percent for metolachlor. Two samples in seven had an inconsistency in results between duplicate analyses—an estimated detection of 0.2 µg/L and a "less than reporting level" result for atrazine in samples from well BE 1624 and well BE 1625. The samples from wells BE 1624 and BE 1625 were not among the 3-way split samples analyzed by the USGS Laboratory and the disparate results could not be further qualified. For two of the seven duplicate samples or about 25 percent, the presence of atrazine remained in question. Again, these results for atrazine do not meet data-quality objective 4.

The evaluation of variability from the perspective of the temporal design was accomplished primarily with the triplicate samples of laboratory-water spikes. In addition, the variability of recovery results among ground-water samples collected on the same day is shown in figure 2 and provides additional insight on use of a temporal design. The five samples included in figure 2 were collected on 3 days; bars showing recovery for samples collected on the same day are labeled with the date of collection. Although the spike concentrations were different for each sample on the 2 days, the within-day variability is apparent. The magnitude of variability for samples on a single day contributes to and appears to be described well by the overall variability summarized above.

The description of variability reinforces the point that the only way to assure the quality of the concentration data is to regularly submit spike samples to evaluate recovery in ground water. Both random spatial and temporal designs could be used to guide submission of these samples.

Splits (2-lab)

The results for the 11 samples are listed in table S-10 (Supplemental Data section). In the split samples, there were eight detections of atrazine, one detection of metolachlor, and no detections of alachlor, chlorpyrifos, cyanazine, metribuzin, pendimethalin, or simazine by the PaDEP Laboratory. The results from the USGS Laboratory supported the PaDEP results and showed no detections for the 11 splits at concentrations greater than 0.05 µg/L for alachlor, chlorpyrifos, cyanazine, metribuzin, pendimethalin, or simazine. For metolachlor, the results from the USGS Laboratory supported the PaDEP results in the one sample where metolachlor was detected by the PaDEP Laboratory. The eight other metolachlor detections by USGS were at concentrations too small (less than 0.06 µg/L) to be reported even as estimated concentrations in the PaDEP Laboratory results. Atrazine concentrations less than 0.13 µg/L reported by the USGS Laboratory were not detected or reported as estimated concentrations by the PaDEP Laboratory (fig. 3). Atrazine concentrations greater than 0.13 µg/L reported by the USGS Laboratory also were reported as detections by the PaDEP Laboratory. These results, no false-negative results for atrazine and metolachlor, support the earlier findings for data-quality objective 2.

ASSESSMENT RESULTS FOR PESTICIDE CONCENTRATIONS IN GROUND WATER

Results showed measured concentrations of the eight pesticides in ground water from wells in carbonate bedrock aquifers in the assessment area were generally less than 0.3 µg/L. In water samples from 28 wells, only 6 individual measurements of the concentrations in water from 6 of the wells were at or above 0.3 µg/L, 5 for atrazine and

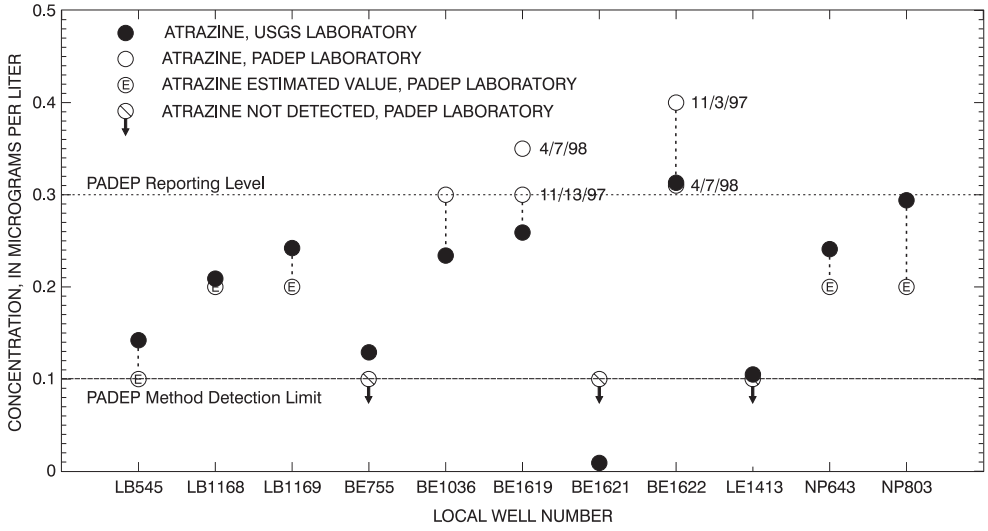

Figure 3. Concentration of atrazine in splits of ground-water samples analyzed using two different methods by Pennsylvania Department of Environmental Protection (PADEP) Laboratory and U.S. Geological Survey (USGS), National Water-Quality Laboratory.

1 for metolachlor. No well water had more than one pesticide at concentrations at or above 0.3 µg/L. In addition, the assessment results showed:

• No chlorpyrifos, cyanazine, metribuzin, or pendimethalin was detected in ground water.

• Atrazine was detected in water from 22 of the 28 wells sampled. Two of the 22 detections were in question on the basis of results of duplicate analyses.

• The atrazine concentration of 0.5 µg/L in water from well NP 805 was the largest atrazine concentration measured. The atrazine concentration that triggers action by PDA under the Pesticides and Ground Water Strategy would be a measured concentration of approximately 0.75 µg/L if the spike-recovery data from this study hold true at concentrations greater than 0.5 µg/L.

• At four wells, resampling in April 1998 confirmed atrazine detections from November 1997 and indicated atrazine concentrations were the same or differed less than 0.1 µg/L in ground-water samples collected 5 months apart.

• Metolachlor was reported at a concentration of 0.3 µg/L in water from well NP 643. The 0.3 µg/L metolachlor concentration is well below the 33 µg/L trigger concentration for metolachlor. Eight additional detections of metolachlor were at concentrations below 0.06 µg/L in other well waters. All eight were in waters where atrazine was detected.

• Simazine was detected in water from eight wells at concentrations of 0.04 µg/L or less. Seven of the eight detections were in water where metolachlor also was detected. All eight waters where simazine was detected contained atrazine.

• Evidence exists for a pattern of co-occurrence of metolachlor and simazine at low concentrations with higher atrazine concentrations.

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey (USGS) in cooperation with Pennsylvania Department of Agriculture (PDA) completed a study to demonstrate the application of a quality-assurance design to the monitoring component of the Pesticides and Ground Water Strategy. The design was to evaluate the bias and variability of laboratory measurements of pesticide concentration. The USGS role was to develop the quality-assurance design, assist PDA in the application of the design to a selected assessment area, evaluate the results, and report the quality-assurance and assessment results. This report describes the quality-assurance design, describes how the design was applied to a selected assessment area in eastern Pennsylvania, describes procedures used to collect and analyze samples

and to evaluate the results, and summarizes the quality-assurance results along with the assessment results.

The design had random spatial and temporal components. Four types of quality-control samples were used to evaluate data-quality objectives: 1) field blanks were used to test for false-positive results, 2) spikes of laboratory water and ground water were used to test for false-negative results and determine bias, 3) replicates of laboratory water and ground water were used to determine variability, and 4) 2-lab splits were used as an additional check for bias. The design included use of two laboratories. The Department of Environmental Protection (PaDEP) Laboratory analyzes the samples collected by PDA for the monitoring component of the Pesticides and Ground Water Strategy to determine pesticide concentration. The second laboratory, a USGS Laboratory, was used to provide supporting information and an independent check on results for the four types of quality-control samples.

The design was applied to an assessment area that included agricultural areas of the Great Valley Section of the Ridge and Valley Physiographic Province in Berks, Lebanon, Lehigh, and Northampton Counties. Wells drilled into carbonate bedrock aquifers were sampled. Bias and variability were evaluated using data collected from October 1997 through January 1998 for five herbicides (alachlor, atrazine, cyanazine, metolachlor, and simazine) for which specific state management plans were required, two additional high-use herbicides (pendimethalin and metribuzin) and a high-use insecticide chlorpyrifos.

Results of the evaluation of bias showed:

• False positives (analyses reporting pesticides to be present when there actually were none present) were not a problem. Results for five field blanks indicate collection, processing, transport, and laboratory-analysis procedures did not contaminate the samples. The last four field blanks were collected following collection of samples in which pesticides were detected. These results demonstrate the cleaning procedures were effective in decontaminating the sampling equipment. The first data-quality objective was met; there were no false-positive results.

• Pesticides were detected in water when pesticides were spiked into (added to) samples. There were no false negatives for the eight pesticides in all spiked samples. The second data-quality objective, for small numbers (less than 5 percent) of false negatives in analyses of ground water, was met.

• Negative bias is a normal and accepted characteristic of analytical methods for pesticides. Negative bias comes from measured concentrations that are generally lower than expected. Negative bias was characteristic of results for the eight pesticides. The magnitude of the bias was large enough that the third data-quality objective—for pesticide recovery to be within 10 percent of the 'true' (100 percent recovery) result—was not met. For analytical results from the PaDEP Laboratory, bias was nearly always negative (38 of 39 analyses or 97 percent of the ground-water results) and generally in excess of 10 percent from the 'true' or expected concentration (34 of 39 analyses or 87 percent of the ground-water results) for pesticides at concentrations ranging from 0.31 to 0.51 µg/L (micrograms per liter). The results for cyanazine were unusual, meeting the data-quality objective in three of the five ground-water spikes yet overall exhibiting the largest (50 point) range in recovery percentage. The magnitude of the negative bias for the eight pesticides, with the exception of cyanazine, would result in reported concentrations commonly 75-80 percent of the expected ('true') concentration in the water sample. Therefore, data from calculations of spike recovery need to be used when interpreting measured pesticide concentrations in ground water.

• Neither the pesticide analysis method used by the PaDEP Laboratory nor the method used by the USGS Laboratory could always provide unbiased results to within 10 percent of known concentrations for ground water over the course of the study. Expecting concentrations to be within 10 percent of a true value is unrealistic at the extremely small concentrations at which pesticides commonly are present in ground water. Determining the magnitude of the bias is more important than setting a numerical data-quality objective.

• Even though the third data-quality objective may have been too stringent a requirement, the magnitude of the negative bias, especially for atrazine, was important to document. Atrazine was the pesticide most commonly detected, and recovery results for atrazine were some of the

worst (largest negative bias). Atrazine had recoveries in ground water ranging from 58 to 97 percent and a median recovery of 65 percent.

• The magnitude of negative bias indicates the importance of incorporating a quality-assurance design that periodically and routinely includes samples spiked at concentrations expected in ground water as part of the monitoring component of the PDA Pesticides and Ground Water Strategy. Random spatial and temporal designs that provide at least five recovery results to evaluate bias are desirable. The recovery results need to be evaluated before making conclusions about the atrazine concentrations (and other pesticides) in ground water.

• Trigger concentrations, the concentrations that require action under the Pesticides and Ground Water Strategy, should be considered maximums for action. This consideration is needed because of the negative bias in concentration results. Concentrations of alachlor, atrazine, chlorpyrifos, metolachlor, pendimethalin, and simazine measured by the PaDEP laboratory were commonly 20 to 25 percent less than expected in the 0.31 to 0.51 µg/L range.

• Interference in laboratory analyses caused by the composition of the ground-water matrix was not a source of bias for this assessment. Results for spiked laboratory water (no matrix interference) and ground water were compared. A rank-sum test of the results for laboratory water and ground water showed no significant difference (alpha=0.05) in spike recovery for any of the eight pesticides. Thus, the ground-water matrix did not contribute to matrix interference.

Results of the evaluation of variability showed:

• Large variability for recoveries of atrazine, cyanazine, and pendimethalin. Data for the laboratory-water spikes submitted in triplicate to the PaDEP Laboratory were evaluated to determine if variability was small (10 percent or less, data-quality objective 4). The relative standard deviation (RSD) was used as a measure of variability of the method over the course of the study for laboratory waters at a concentration of 0.4 µg/L. An RSD of about 11 percent (or about 0.05 µg/L) characterizes the method results for alachlor, chlorpyrifos, metolachlor, metribuzin, and simazine. Atrazine and pendimethalin have RSD values of about 17 and 23 percent, respectively. Cyanazine showed the largest RSD at nearly 51 percent. The pesticides with low variability in laboratory-water spikes also had low variability in ground water. The RSD's for alachlor, chlorpyrifos, metolachlor, metribuzin, and simazine are considered low enough to meet the requirement of data-quality objective 4. Results for atrazine, cyanazine, and pendimethalin do not meet data-quality objective 4.

• Large variations in pesticide recovery from spiked samples further indicate the need to use data for pesticide recovery in the interpretation of measured pesticide concentrations in ground water. Data from replicate samples spiked with known pesticide amounts are a critical component of a quality-assurance design for the monitoring component of the Pesticides and Ground Water Strategy.

• Variability of concentrations in unspiked ground water was difficult to determine because of the large proportion of samples with pesticide concentrations too small to be detected by the PaDEP Laboratory. In addition to the types of quality-control samples used for this study, replicate samples of spiked ground water would add quality-assurance information. These samples can provide important data on bias and variability. Although no matrix interference from ground water was significant for this assessment area, the quality assurance is especially important as the monitoring is done in the varied geologic settings where variations in the chemistry of the ground-water matrix would be expected.

The use of two laboratories in the quality-assurance design was useful for:

• Certification that spike mixtures obtained from a commercial supplier were manufactured according to the concentration specifications.

• Certification that laboratory water obtained from commercial suppliers for preparing field blanks and laboratory-water spikes did not contain pesticides at concentrations greater than the method detection limit.

• Verification that spikes were prepared correctly by field personnel and had concentrations that were expected on the basis of spike-concentration calculations.

• Verification of pesticide detections. The atrazine results showed that concentrations greater than 0.13 µg/L measured by the USGS Laboratory were detected by the PaDEP Laboratory.

REFERENCES CITED

Durlin, R.R., and Schaffstall, W.P., 1999, Water resources data, Pennsylvania, water year 1998, v. 1, Delaware River Basin: U.S. Geological Survey Water-Data Report PA-98-1, 405 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishing Company, Inc., 522 p.

Lindsey, B.D., and Bickford, T.M., 1999, Hydrogeologic framework and sampling design for an assessment of agricultural pesticides in ground water in Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 99-4076, 44 p.

Pennsylvania Department of Agriculture, 1998, Pesticides and ground water strategy, January 2, 1998: Harrisburg, Pa., 36 p.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Boca Raton, Fla., CRC Press, Inc. (Lewis Publishers, Inc.), 328 p.

U.S. Environmental Protection Agency, 1988, Methods for the determination of organic compounds in drinking water: EPA-600/4-88/039, 382 p.

_____1995, Methods for the determination of organic compounds in drinking water, Supplement III: EPA-600/R-95/131, 552 p.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.

SUPPLEMENTAL DATA TABLES

A listing, by topic, of the tables of data that appear in this section is as follows:

Topic	Laboratory	
	PaDEP	USGS
Well records		
Table S-1		
Field Blanks		
Pesticide concentration and surrogate recovery, laboratory water	Table S-2	Table S-3
Spikes		
Pesticide concentration and surrogate recovery, laboratory water	Table S-4	Table S-5
Pesticide concentration and surrogate recovery, ground water	Table S-6	Table S-7
Spike recovery percentages and summary statistics, laboratory water and ground water	Table S-8	
Replicates		
Pesticide concentration and surrogate recovery, laboratory-water spikes (triplicates)	Table S-4	--
Pesticide concentration and surrogate recovery, ground water (duplicates)	Table S-9	
2-lab splits and routine samples		
Ground water	Table S-10	

Table S-1. *Records of selected wells in Berks, Lebanon, Lehigh, and Northampton Counties sampled for the Quality-Assurance Project for the Pennsylvania Department of Agriculture Pesticides and Ground Water Strategy, 1997-98*

Local well number - Well number shown on index map and county prefix (BE, Berks; LB, Lebanon; LE, Lehigh; NP, Northampton).

PDA sample identifier - Sample-identification number assigned by Pennsylvania Department of Agriculture (PDA).

Cell number - Sampling-cell number in study area.

Latitude and longitude - Location, to the nearest second, of well as determined by USGS personnel from topographic maps and confirmed by Global Positioning System.

Aquifer code - Abbreviation of carbonate rock geologic unit where well is completed.
Middle Ordovician:
364BKMN, Beekmantown Group; 364HRSY, Hershey Formation; 364JKBG, Jacksonburg Formation;
364MRSN, Myerstown Formation; 364ONLN, Ontelaunee Formation.
Lower Ordovician:
367EPLR, Epler Formation; 367RCKB, Rickenbach Formation; 367SNNG, Stonehenge Formation.
Upper Cambrian:
371ALNN, Allentown Formation; 371MDCK, Maiden Creek Member of Allentown Formation; 371RCLD, Richland Formation; 371SZCK, Snitz Creek Formation;
371TCKR, Tuckertown Member of Allentown Formation.

Depth to top - Depth, in feet, to bedrock as reported on driller's log.

Use of water - The primary way water from the well is used: C, commercial; H, rural domestic; P, public supply; S, livestock; T, institutional

Depth of well - Depth of drilled well, in feet, as reported on driller's log.

Casing length - Feet of casing used to complete well, as reported on driller's log.

Casing material - S, steel; P, PVC plastic.

Date well constructed - Date of well construction as reported on driller's log, in mm-yy or mm-dd-yy format.

Elevation of land surface - Land surface at well site, in feet above sea level (National Geodetic Vertical Datum of 1929).

Water-level date - Date of water-level measurement, in mm-dd-yy format.

Water level - Depth of water, in feet below land surface, as measured by USGS personnel.

All columns - A double dash indicates no information was obtained.

Table S-1. *Records of selected wells in Berks, Lebanon, Lehigh, and Northampton Counties sampled for the Quality Assurance Project for the Pennsylvania Department of Agriculture Pesticides and Ground Water Strategy, 1997-98—Continued*

Local well number	PDA sample identifier	Cell number	Latitude	Longitude	Aquifer code	Depth to top (feet)	Use of water	Depth of well (feet)	Casing length (feet)	Casing material	Date well constructed	Elevation of land surface (feet)	Water-level date	Water level (feet)
BE 755	06002	10	40°22'20"	76°08'58"	367EPLR	--	H, S	128	--	--	01-65	410	--	--
BE 1036	06016	14	40°29'23"	75°47'29"	371MDCK	--	S	192	58	--	01-63	400	--	--
BE 1537	06003	11	40°20'30"	76°06'46"	364MRSN	--	P	90	--	--	--	390	--	--
BE 1618	06001	5	40°23'27"	76°14'36"	364HRSY	--	S	220	60	P	11-01-95	475	10-21-97	8.1
BE 1619	06015	6	40°29'34"	75°48'18"	371MDCK	25	H	150	120	S	06-26-89	400	11-13-97	37.7
BE 1620	06030	7	40°29'07"	75°51'39"	367RCKB	3	H	225	41	S	05-10-85	424	12-04-97	83.7
BE 1621	06028	12	40°20'32"	75°45'24"	371RCLD	52	H	238	60	S	05-01-88	310	12-04-97	10.7
BE 1622	06005	16	40°32'32"	75°41'39"	367RCKB	53	H	180	100	S	10-07-96	480	11-03-97	80.6
BE 1624	06010	8	40°26'45"	75°54'35"	367SNNG	40	H	200	92	S	08-03-89	320	11-04-97	42.9
BE 1625	06008	9	40°24'32"	75°57'57"	367EPLR	41	H	436	63.5	S	03-01-90	270	11-04-97	46.1
BE 1626	06029	13	40°23'11"	75°44'40"	371ALNN	18	H	95	39	S	09-29-92	320	12-04-97	19.3
BE 1627	06017	14	40°30'05"	75°47'52"	364ONLN	53	C	180	80	S	06-11-88	430	11-13-97	56.8
BE 1628	06007	15	40°31'22"	75°44'00"	367EPLR	12	H	172	45.5	S	12-01-89	440	--	--
BE 1631	06035	22	40°30'40"	75°40'02"	371TCKR	70	H	100	100	S	04-05-95	430	--	--
LB 545	38012	3	40°21'03"	76°16'47"	367EPLR	--	H	200	--	S	--	480	10-21-97	69.0
LB 621	38007	2	40°20'28"	76°15'59"	367RCKB	--	H	300	--	--	--	510	--	--
LB 1168	38011	1	40°19'33"	76°14'28"	371SZCK	25	H	70	34	S	02-01-88	520	10-21-97	27.3
LB 1169	38008	4	40°22'43"	76°16'25"	364MRSN	--	H	137	106	S	07-21-77	470	10-16-97	59.7
LE 1412	39001	21	40°31'48"	75°36'52"	371ALNN	100	H	150	120	S	04-17-97	395	12-09-97	14.5
LE 1413	39004	19	40°34'09"	75°35'29"	364BKMN	33	H	125	100	S	03-17-95	438	--	--
LE 1414	39003	20	40°33'52"	75°35'25"	364BKMN	39	T	105	100	S	04-26-94	428	12-17-97	39.8
LE 1415	39002	18	40°39'00"	75°33'05"	364BKMN	87	H	165	100	S	12-27-93	430	12-17-97	117.0
NP 643	48003	29	40°43'40"	75°17'00"	367EPLR	--	H	200	95	S	10-04-80	380	--	--
NP 803	48001	24	40°40'54"	75°27'30"	367EPLR	--	H	200	60	S	03-13-97	360	--	--
NP 804	48007	25	40°40'28"	75°24'22"	367EPLR	--	H	120	--	S	01-72	400	01-14-98	100.8
NP 805	48006	26	40°41'44"	75°24'15"	367EPLR	115	H	140	114	S	05-01-95	400	01-14-98	78.5
NP 806	48002	27	40°42'33"	75°21'42"	367EPLR	--	H	125	103	S	07-01-89	370	12-29-97	34.5
NP 807	48008	30	40°48'52"	75°06'10"	364JKBG	--	H	--	--	--	01-72	370	01-27-98	136.1
NP 812	48005	28	40°43'29"	75°21'43"	367EPLR	28	C	300	60	S	03-01-84	405	--	--

Table S-2. *Analytical results for pesticide concentration and surrogate compound recovery determined by Pennsylvania Department of Environmental Protection Laboratory for field blanks of pesticide-free laboratory water*

[<, indicates compound was analyzed for but not detected and the quantitation limit is reported]

Lot number of pesticide-free laboratory water	Local well number where blank prepared	Date (yyyymmdd)	Time (hhmm)	Blank concentration, in micrograms per liter								Surrogate recovery, in percent
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine	1,3-dimethyl-2-nitrobenzene
Lot L01251	BE 1618	19971021	1536	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	83.88
Lot G51317	BE 1621	19971204	1206	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	88.12
Lot 37149	LB 621	19971016	0946	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	107.61
Lot 37149	LE 1412	19971209	1413	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	90.91
Lot 37149	NP 806	19971229	1040	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	68.18

Table S-3. *Analytical results for pesticide concentration and surrogate compound recovery determined by U.S. Geological Survey, National Water-Quality Laboratory, for field blanks of pesticide-free laboratory water*

[<, indicates compound was analyzed for but not detected and the quantitation limit is reported]

Lot number of pesticide-free laboratory water	Local well number where blank prepared	Date (yyyymmdd)	Time (hhmm)	Blank concentration, in micrograms per liter								Surrogate recovery, in percent		
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine	Diazinon-d_{10}	Terbuthylazine	*alpha*-HCH-d_6
Lot L01251	BE 1618	19971021	1535	<0.002	<0.004	<0.004	<0.004	<0.002	<0.004	<0.004	<0.005	104	132	104
Lot G51317	BE 1621	19971204	1205	<.002	<.001	<.004	<.004	<.002	<.004	<.004	<.005	98.1	105	92.4
Lot 37149	LB 621	19971016	0945	<.002	<.001	<.004	<.004	<.002	<.004	<.004	<.005	89.8	114	94.1
Lot 37149	LE 1412	19971209	1425	<.002	<.001	<.004	<.004	<.002	<.004	<.004	<.005	107	112	89.5

Table S-4. *Analytical results for pesticide concentration and surrogate compound recovery determined by Pennsylvania Department of Environmental Protection Laboratory for spiked pesticide-free laboratory-water samples submitted as triplicate-blind samples for assessment of laboratory bias and variability*

[E, indicates an estimated value below the quantitation limit but above the method detection limit. --, No data received. For a 1-liter sample, the spike volume is equivalent to the prepared spike concentration, C_{prp}, in micrograms per liter (see equation 1a).]

Sample identifier	Local well number of sample preceding preparation of spiked blank	Date (yyyymmdd)	Time (hhmm)	Analyzed concentration of spiked blank, in micrograms per liter								Spike volume, in milliliters per liter of sample	Surrogate recovery, in percent	Lot number of Supelco Brand pesticide spike mix
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine		1,3-dimethyl-2-nitrobenzene	
Lab Spike 10-1	BE 755	19971023	1101	0.3	0.3	0.3	1	0.3	0.3	0.3	0.4	0.40 ± .01	112.14	LA-66096
Lab Spike 10-2	BE 755	19971023	1102	.3	.3	.3	.9	.3	.3	.3	.4	.40 ± .01	108.85	LA-66096
Lab Spike 10-3	BE 755	19971023	1103	--	--	--	--	--	--	--	--	.40 ± .01	--	LA-66096
Lab Spike 20-1	LE 1414	19971217	1622	.3	.2E	.3	.4	.3	.3	.2E	.3	.39 ±. 01	115.74	LA-66096
Lab Spike 20-2	LE 1414	19971217	1623	.3	.3	.3	.3	.3	.3	.3	.3	.39 ± .01	97.72	LA-66096
Lab Spike 20-3	LE 1414	19971217	1624	.3	.3	.3	.3	.3	.3	.2E	.3	.39 ± .01	93.62	LA-66096
Lab Spike 30-2	NP 807	19980127	1333	.4	.3	.4	.4	.4	.4	.4	.4	.42 ± .01	83.64	LA-66096
Lab Spike 30-3	NP 807	19980127	1334	.4	.4	.4	.4	.4	.4	.4	.4	.42 ± .01	75.89	LA-66096
Lab Spike 30-4	NP 807	19980127	1335	.3	.4	.4	.4	.4	.4	.4	.4	.42 ± .01	82.73	LA-66096

Table S-5. *Analytical results for pesticide concentration and surrogate compound recovery determined by U.S. Geological Survey, National Water-Quality Laboratory for spiked pesticide-free laboratory-water samples*

[For a 1-liter sample, the spike volume is equivalent to the prepared spike concentration, C_{prp} , in micrograms per liter (see equation 1a).]

Sample identifier	Date (yyyymmdd)	Time (hhmm)	Analyzed concentration of spiked blank, in micrograms per liter								Spike volume, in milliliters per liter of sample	Surrogate recovery, in percent		
			Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine		Diazinon-d_{10}	Terbuthylazine	*alpha*-HCH-d_6
Lab Spike 20-4	19971217	1625	0.409	0.442	0.398	0.442	0.405	0.404	0.343	0.432	0.39 ± .01	110	126	116
Lab Spike 30-1	19980127	1332	.487	.454	.470	.467	.464	.384	.288	.444	.42 ± .01	108	119	99.1

Table S-6. *Analytical results for pesticide concentration and surrogate-compound recovery determined by Pennsylvania Department of Environmental Protection Laboratory for spiked ground-water samples and unspiked ground-water samples and concentration differences calculated from the analytical results for pesticide concentration*

[Shaded rows are recovery values for concentration (by difference); E, indicates an estimated value below the quantitation limit but above the method detection limit; <, indicates compound was analyzed for but not detected, the quantitation limit is reported, and zero was used for difference calculations. Surrogate recoveries reported as "poor" were quantified as less than 60 percent by the PaDEP Laboratory. For a 1-liter sample, the spike volume is equivalent to the prepared spike concentration, C_{prp} , in micrograms per liter (see equation 1a).]

Local well number and lot number of Supelco Brand pesticide spike mix	Sample type	Date (yyyymmdd)	Time (hhmm)	Concentration, in micrograms per liter								Spike volume, in milliliters per liter of sample	Surrogate recovery, in percent
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine		1,3-dimethyl-2-nitrobenzene
BE 1036 LA-66096	Spiked ground water	19971113	1233	0.4	0.6	0.4	0.4	0.4	0.4	0.4	0.4	0.46±.01	Poor
	Ground water	19971113	1239	<.3	.3	<.3	<.3	<.3	<.3	<.3	<.3	--	Poor
	Difference	--	--	.4	.3	.4	.4	.4	.4	.4	.4	--	--
BE 1619 LA-62435	Spiked ground water	19971113	1112	.4	.6	.4	.3	.4	.4	.3	.4	.51±.01	Poor
	Ground water	19971113	1109	<.3	.3	<.3	<.3	<.3	<.3	<.3	<.3	--	Poor
	Difference	--	--	.4	.3	.4	.3	.4	.4	.3	.4	--	--
LB 1169 LA-62435	Spiked ground water	19971016	1233	.4	.5	.4	.5	.4	.4	.3	.4	.51±.01	98.47
	Ground water	19971016	1239	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	--	96.78
	Difference	--	--	.4	.3	.4	.5	.4	.4	.3	.4	--	--
LE 1413 LA-66096	Spiked ground water	19971222	1303	.2E	.3	.2E	.3	.2E	.2E	.2E	.2E	.31±.01	74.36
	Ground water	19971222	1309	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	--	72.26
	Difference	--	--	.2	.3	.2	.3	.2	.2	.2	.2	--	--
NP 803 LA-66096	Spiked ground water	19971222	1133	.4	.6	.4	.4	.4	.4	.4	.4	.50±.01	67.46
	Ground water	19971222	1139	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	--	69.58
	Difference	--	--	.4	.4	.4	.4	.4	.4	.4	.4	--	--

Table S-7. *Analytical results for pesticide concentration and surrogate-compound recovery determined by U.S. Geological Survey, National Water-Quality Laboratory for spiked ground-water samples, unspiked ground-water samples, and concentration differences calculated from the analytical results for pesticide concentration*

[Shaded rows are recovery values for concentration (by difference); E, indicates an estimated value below the quantitation limit but above the method detection limit; <, indicates compound was analyzed for but not detected, the quantitation limit is reported, and zero was used for difference calculations. For a 1-liter sample, the spike volume is equivalent to the prepared spike concentration, C_{prp} , in micrograms per liter (see equation 1a).]

Local well number and lot number of Supelco Brand pesticide spike mix	Sample type	Date (yyyymmdd)	Time (hhmm)	Concentration, in micrograms per liter								Spike volume, in milliliters per liter of sample	Surrogate recovery, in percent		
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine		Diazinon-d_{10}	Terbuthylazine	*alpha*-HCH-d_6
BE 1036 LA-66096	Spiked ground water	19971113	1232	0.463	0.713	0.390	0.254	0.443	0.309	0.235	0.433	0.46 ± .01	99.1	107	86.5
	Ground water	19971113	1230	<.002	.234	<.004	<.004	.004	<.004	<.004	.011	--	97.2	101	80.9
	Difference	--	--	.463	.479	.390	.254	.439	.309	.235	.422	--			
BE 1619 LA-62435	Spiked ground water	19971113	1102	.527	.802	.454	.308	.569	.341	.288	.485	.51 ± .01	106	99.1	82.3
	Ground water	19971113	1100	<.002	.259	<.004	<.004	.007	<.004	<.004	.011	--	104	98.1	82.3
	Difference	--	--	.527	.543	.454	.308	.562	.341	.288	.474	--			
LB 1169 LA-62435	Spiked ground water	19971016	1232	.612	.753	.478	.350	.617	.319	.292	.475	.51 ± .01	142	129	105
	Ground water	19971016	1230	<.002	.242	<.004	<.004	.029	<.004	<.004	.008	--	92.3	120	92.4
	Difference	--	--	.612	.511	.478	.350	.588	.319	.292	.467	--			
LE 1413 LA-66096	Spiked ground water	19971222	1302	.314	.453	.239	.303	.322	.234	.195	.332	.31 ± .01	87.1	121	101
	Ground water	19971222	1300	<.002	.105	<.004	<.004	.010	<.004	<.004	.006	--	71.7	113	94.3
	Difference	--	--	.314	.348	.239	.303	.312	.234	.195	.326	--			
NP 803 LA-66096	Spiked ground water	19971222	1132	.514	.871	.298	.487	.540	.384	.309	.525	.50 ± .01	87.5	121	99.1
	Ground water	19971222	1130	.005	.294	<.004	<.004	.034	<.004	<.004	.003E	--	68.6	114	102
	Difference	--	--	.509	.577	.298	.487	.506	.384	.309	.522	--			

Table S-8. *Spike recovery data and summary statistics for analyses of pesticides in spiked laboratory-water and ground-water samples by Pennsylvania Department of Environmental Protection Laboratory and U.S. Geological Survey, National Water-Quality Laboratory*

[PaDEP, Pennsylvania Department of Environmental Protection Laboratory; USGS, U.S. Geological Survey, National Water-Quality Laboratory; --, sample not analyzed or statistic not calculated; cnbd, could not be determined; SD, Standard Deviation; RSD, Relative Standard Deviation]

Sample identifier	Lot number of Supelco Brand pesticide spike mix	Spike recovery, in percent															
		Alachlor		Atrazine		Chlorpyrifos		Cyanazine		Metolachlor		Metribuzin		Pendimethalin		Simazine	
		PaDEP	USGS	PaDEP	USGS	PaDEP	USGS	PaDEP	USGS	PaDEP	USGS	PaDEP	USGS	PaDEP	USGS	PaDEP	USGS
Laboratory Water																	
Lab Spike 10-1	LA-66096	75.2	--	75.2	--	75.2	--	278	--	75.2	--	83.5	--	75.2	--	100	--
Lab Spike 10-2	LA-66096	75.2	--	75.2	--	75.2	--	251	--	75.2	--	83.5	--	75.2	--	100	--
Lab Spike 10-3	LA-66096	cnbd	--	cnbd	--	cnbd	--	cnbd	--	cnbd	--	cnbd	--	cnbd	--	cnbd	--
Lab Spike 20-1	LA-66096	76.3	--	50.9	--	76.3	--	113	--	76.3	--	84.8	--	50.9	--	76.3	--
Lab Spike 20-2	LA-66096	76.3	--	76.3	--	76.3	--	84.8	--	76.3	--	84.8	--	76.3	--	76.3	--
Lab Spike 20-3, 4	LA-66096	76.3	104	76.3	112	76.3	101	84.8	125	76.3	103	84.8	114	50.9	87.2	76.3	110
Lab Spike 30-2	LA-66096	96.2	--	72.1	--	96.2	--	107	--	96.2	--	107	--	96.2	--	96.2	--
Lab Spike 30-3	LA-66096	96.2	--	96.2	--	96.2	--	107	--	96.2	--	107	--	96.2	--	96.2	--
Lab Spike 30-4,1	LA-66096	72.1	117	96.2	109	96.2	113	107	125	96.2	112	107	103	96.2	69.3	96.2	107
Median		76.3	--	75.8	--	76.3	--	107	--	76.3	--	84.8	--	75.8	--	96.2	--
Mean		80.5	--	77.3	--	83.5	--	142	--	83.5	--	92.8	--	77.1	--	89.7	--
SD		9.2	--	13.5	--	9.9	--	72	--	9.9	--	11.0	--	17.6	--	10.5	--
RSD, percent		11.4	--	17.4	--	11.8	--	50.8	--	11.8	--	11.9	--	22.8	--	11.7	--
Ground Water																	
BE 1036	LA-66096	87.0	101	65.2	104	87.0	84.7	96.6	61.3	87.0	95.4	96.6	74.6	87.0	51.0	87.0	91.7
BE 1619	LA-62435	78.0	103	58.5	106	78.0	88.4	58.5	60.0	86.6	122	78.0	66.4	58.8	56.1	78.0	92.3
LB 1169	LA-62435	78.4	120	58.8	100	78.4	93.6	98.0	68.6	87.1	128	78.4	62.5	58.8	57.2	78.4	91.5
LE 1413	LA-66096	64.5	101	96.7	112	64.5	77.0	108	108	64.5	100	71.7	83.7	64.5	62.8	64.5	105
NP 803	LA-66096	80.0	102	80.0	115	80.0	59.6	88.9	108	80.0	101	88.9	85.3	80.0	61.8	80.0	104
Median		78.4	102	65.2	106	78.4	84.7	96.6	68.6	86.6	101	78.4	74.6	64.5	57.2	78.4	92.3
Mean		77.6	105	71.8	107	77.6	80.7	90.0	81.2	81.0	109	82.7	74.5	69.8	57.8	77.6	96.9
SD		7.3	7.3	14.7	5.4	7.3	11.8	16.9	22.1	8.7	13.1	8.9	9.1	11.6	4.3	7.3	6.2
RSD, percent		9.4	7.0	20.4	5.1	9.4	14.7	18.8	27.2	10.7	12.0	10.7	12.2	16.6	7.4	9.4	6.4

Table S-9. *Analytical results for pesticide concentration and surrogate-compound recovery determined by Pennsylvania Department of Environmental Protection Laboratory and U.S. Geological Survey, National Water-Quality Laboratory for replicate samples of ground water*

[E, indicates an estimated value below the quantitation limit but above the method detection limit; <, indicates compound was analyzed for but not detected and the quantitation limit is reported. Surrogate for PaDEP Laboratory: Surrogate 1, 1,3-dimethyl-2-nitrobenzene. Surrogate recoveries reported as "poor" were quantified as less than 60 percent by the PaDEP Laboratory. Surrogates for USGS Laboratory: Surrogate 1, diazinon-d_{10}; Surrogate 2, terbuthylazine; Surrogate 3,*alpha*-HCH-d_6]

Local well number	Analyzing laboratory	Date (yyyymmdd)	Time (hhmm)	Ground-water concentration, in micrograms per liter								Surrogate recovery, in percent		
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine	Surrogate 1	Surrogate 2	*Surrogate 3*
BE 1622	PaDEP	19971103	1249	<0.3	0.4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	Poor	--	--
	PaDEP	19971103	1247	<.3	.4	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
	USGS	19971103	1240	<.002	.313	<.004	<.004	.057	<.004	<.004	.041	98.1	110	92.1
BE 1624	PaDEP	19971104	1530	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
	PaDEP	19971104	1532	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1625	PaDEP	19971104	1230	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
	PaDEP	19971104	1232	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
LB 1169	PaDEP	19971016	1239	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	96.78	--	--
	PaDEP	19971016	1231	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	98.95	--	--
	USGS	19971016	1230	<.002	.242	<.004	<.004	.029	<.004	<.004	.008	92.3	120	92.4
LE 1413	PaDEP	19971222	1309	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	72.26	--	--
	PaDEP	19971222	1301	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	69.57	--	--
LE 1413	USGS	19971222	1300	<.002	.105	<.004	<.004	.010	<.004	<.004	.006	71.7	113	94.3
NP 643	PaDEP	19971229	1439	<.3	.2E	<.3	<.3	.3	<.3	<.3	<.3	69.50	--	--
	PaDEP	19971229	1437	<.3	.2E	<.3	<.3	.2E	<.3	<.3	<.3	69.91	--	--
	USGS	19971229	1430	<.002	.241	<.004	<.004	.288	<.004	<.004	.021	94.4	108	112
NP 807	PaDEP	19980127	1100	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	83.31	--	--
	PaDEP	19980127	1102	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	80.02	--	--

Table S-10. *Analytical results for pesticide concentration and surrogate-compound recovery determined by Pennsylvania Department of Environmental Protection Laboratory and U.S. Geological Survey, National Water-Quality Laboratory for routine ground-water samples and for 2-lab splits of ground-water samples*

[R, in date column indicates resample; E, indicates an estimated value below the quantitation limit but above the method detection limit;
<, indicates compound was analyzed for but not detected and the quantitation limit is reported. Surrogate for PaDEP Laboratory:
Surrogate 1, 1,3-dimethyl-2-nitrobenzene. Surrogate recoveries reported as “poor” were quantified as less than 60 percent by the PaDEP Laboratory.
Surrogates for USGS Laboratory: Surrogate 1, diazinon-d_{10}; Surrogate 2, terbuthylazine; Surrogate 3,*alpha*-HCH-d_6]

Local well number	Analyzing laboratory	Date (yyyymmdd)	Time (hhmm)	Ground-water concentration, in micrograms per liter								Surrogate recovery, in percent		
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine	Surrogate 1	Surrogate 2	Surrogate 3
BE 755	PaDEP	19971023	1109	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	101.54	--	--
BE 755	USGS	19971023	1100	<.002	.129	<.004	<.004	<.002	<.004	<.004	.004E	109	136	108
BE 1036	PaDEP	19971113	1239	<.3	.3	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1036	USGS	19971113	1230	<.002	.234	<.004	<.004	.004	<.004	<.004	.011	97.2	101	80.9
BE 1036	PaDEP	19980407 R	1140	<.3	.3	<.3	<.3	<.3	<.3	<.3	<.3	69.62	--	--
BE 1537	PaDEP	19971023	1445	<.3	.09E	<.3	<.3	<.3	<.3	<.3	<.3	111.77	--	--
BE 1618	PaDEP	19971021	1539	<.3	.1E	<.3	<.3	<.3	<.3	<.3	<.3	No data	--	--
BE 1619	PaDEP	19971113	1109	<.3	.3	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1619	USGS	19971113	1100	<.002	.259	<.004	<.004	.007	<.004	<.004	.011	104	98.1	82.3
BE 1619	PaDEP	19980407 R	1045	<.3	.35	<.3	<.3	<.3	<.3	<.3	<.3	91.37	--	--
BE 1620	PaDEP	19971204	1550	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	87.74	--	--
BE 1621	PaDEP	19971204	1239	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	97.35	--	--
BE 1621	USGS	19971204	1230	<.002	.009	<.004	<.004	.003E	<.004	<.004	.002E	109	113	93.1
BE 1622	PaDEP	19971103	1249	<.3	.4	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1622	USGS	19971103	1240	<.002	.313	<.004	<.004	.057	<.004	<.004	.041	98.1	110	92.1
BE 1622	PaDEP	19980407 R	1355	<.3	.31	<.3	<.3	<.3	<.3	<.3	<.3	77.01	--	--
BE 1624	PaDEP	19971104	1530	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1625	PaDEP	19971104	1230	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1626	PaDEP	19971204	1440	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	98.65	--	--
BE 1627	PaDEP	19971113	1305	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	Poor	--	--
BE 1627	PaDEP	19980407 R	1115	<.3	.24E	<.3	<.3	<.3	<.3	<.3	<.3	90.80	--	--
BE 1628	PaDEP	19971103	1500			no	data	received				--	--	--

Table S-10. *Analytical results for pesticide concentration and surrogate-compound recovery determined by Pennsylvania Department of Environmental Protection Laboratory and U.S. Geological Survey, National Water-Quality Laboratory for routine ground-water samples and for 2-lab splits of ground-water samples—Continued*

[R, in date column indicates resample; E, indicates an estimated value below the quantitation limit but above the method detection limit; <, indicates compound was analyzed for but not detected and the quantitation limit is reported. Surrogate for PaDEP Laboratory: Surrogate 1, 1,3-dimethyl-2-nitrobenzene. Surrogate recoveries reported as "poor" were quantified as less than 60 percent by the PaDEP Laboratory. Surrogates for USGS Laboratory: Surrogate 1, diazinon-d_{10}; Surrogate 2, terbuthylazine; Surrogate 3,*alpha*-HCH-d_6]

Local well number	Analyzing laboratory	Date (yyyymmdd)	Time (hhmm)	Ground-water concentration, in micrograms per liter								Surrogate recovery, in percent		
				Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Metribuzin	Pendimethalin	Simazine	Surrogate 1	Surrogate 2	Surrogate 3
BE 1631	PaDEP	19971209	1140	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	94.52	--	--
LB 545	PaDEP	19971021	1409	<.3	.1E	<.3	<.3	<.3	<.3	<.3	<.3	87.08	--	--
LB 545	USGS	19971021	1400	<.002	.142	<.004	<.004	.015	<.004	<.004	<.005	99.1	130	98.1
LB 621	PaDEP	19971016	0949	<.3	.3	<.3	<.3	<.3	<.3	<.3	<.3	99.02	--	--
LB 1168	PaDEP	19971021	1129	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	100.48	--	--
LB 1168	USGS	19971021	1120	<.002	.209	<.004	<.004	<.002	<.004	<.004	<.005	107	135	103
LB 1169	PaDEP	19971016	1239	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	96.78	--	--
LB 1169	USGS	19971016	1230	<.002	.242	<.004	<.004	.029	<.004	<.004	.008	92.3	120	92.4
LE 1412	PaDEP	19971209	1420	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	96.54	--	--
LE 1413	PaDEP	19971222	1309	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	72.26	--	--
LE 1413	USGS	19971222	1300	<.002	.105	<.004	<.004	.010	<.004	<.004	.006	71.7	113	94.3
LE 1414	PaDEP	19971217	1545	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	104.84	--	--
LE 1415	PaDEP	19971217	1250	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	92.58	--	--
NP 643	PaDEP	19971229	1439	<.3	.2E	<.3	<.3	.3	<.3	<.3	<.3	69.50	--	--
NP 643	USGS	19971229	1430	<.002	.241	<.004	<.004	.288	<.004	<.004	.021	94.4	108	112
NP 803	PaDEP	19971222	1139	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	69.58	--	--
NP 803	USGS	19971222	1130	.005	.294	<.004	<.004	.034	<.004	<.004	.003E	68.6	114	102
NP 804	PaDEP	19980114	1220	<.3	.1E	<.3	<.3	<.3	<.3	<.3	<.3	87.91	--	--
NP 805	PaDEP	19980114	1025	<.3	.5	<.3	<.3	<.3	<.3	<.3	<.3	94.28	--	--
NP 806	PaDEP	19971229	1050	<.3	.2E	<.3	<.3	<.3	<.3	<.3	<.3	73.40	--	--
NP 807	PaDEP	19980127	1100	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	83.31	--	--
NP 812	PaDEP	19971229	1525	<.3	<.3	<.3	<.3	<.3	<.3	<.3	<.3	84.02	--	--