In cooperation with the Pennsylvania Department of Agriculture

Pesticides in Ground Water in Selected Agricultural Land-Use Areas and Hydrogeologic Settings in Pennsylvania, 2003–07

Scientific Investigations Report 2009-5139

U.S. Department of the Interior
U.S. Geological Survey

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Cover:

1. Application of pesticides in a fruit orchard by use of an air-blast sprayer, May 2008. Photograph taken by Joanne Irvin, U.S. Geological Survey.
2. Application of pesticides to a field near a home with a domestic well by use of a tractor with a spray tank and boom-type applicator, April 2008. Photograph taken by Connie Loper, U.S. Geological Survey.
3. Application of pesticides on corn by use of helicopter with boom-type applicator, July 2007.
   Photograph taken by John Clune, U.S. Geological Survey.
4. Pesticide application to row crops by use of a commercial or custom boom-type applicator, May 2007.
   Photograph by Connie Loper, U.S. Geological Survey.

Pesticides in Ground Water in Selected Agricultural Land-Use Areas and Hydrogeologic Settings in Pennsylvania, 2003–07

By Connie A. Loper, Kevin J. Breen, Tammy M. Zimmerman, and John W. Clune

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U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

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Conversion Factors

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
gallon (gal)	3.785	cubic decimeter (dm^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per second per square mile [(ft^3/s)/mi^2]	0.01093	cubic meter per second per square kilometer [(m^3/s)/km^2]
cubic foot per day (ft^3/d)	0.02832	cubic meter per day (m^3/d)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
	Application rate	
pounds per acre per year [(lb/acre)/yr]	1.121	kilograms per hectare per year [(kg/ha)/yr]
pounds per year (lb/yr)	0.4536	kilograms per year (kg/yr)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

CAAT	2-chloro-4-isopropylamino-6-amino-s-triazine, deethyldeisopropylatrazine
CEAT	2-chloro-6-ethylamino-4-amino-s-traizine, deisopropylatrazine
CIAT	2-chloro-4-isopropylamino-6-amino-s-triazine, deethylatrazine
DCPA	dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid, dacthal
DMFM	demethylfluometuron
EPTC	s-ethyl dipropylthiocarbamate
ESA	ethane sulfonic acid
ESA SA	ethane sulfonic acid second amide
FSRW	field-spiked reagent water
GC	gas chromatography
GCMS	gas chromatography/mass spectrometry
GIS	Geographic Information System
GWSI	Ground-Water Site Inventory
HCH	hexachlorocyclohexane
HPLC	high-performance liquid chromatography
HPLCMS	high-performance liquid chromatography/mass spectrometry
LHA	lifetime health advisory
LRS	lab reagent spike
MCPA	2-methyl-4-chlorophenoxyacetic acid
MCPB	4-(2-methyl-4-chlorophenoxy) butyric acid
MDL	method detection limit
MRL	minimum reporting level
N	nitrogen
NTU	nephelometric turbidity unit
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OEAT	deisopropylhydroxyatrazine
OGRL	Organic Geochemistry Research Laboratory
OIAT	deethylhydroxyatrazine
OIET	hydroxyatrazine
OWML	Ohio Water Microbiology Laboratory
OXA	oxanilic acid
p,p’-DDE	p,p’-dichlorodiphenyldichloroethylene
PADEPL	Pennsylvania Department of Environmental Protection Laboratory

PATGS	Pennsylvania Topographic and Geologic Survey
PA WSC	Pennsylvania Water Science Center
PDA	Pennsylvania Department of Agriculture
PPGWS	Pennsylvania Pesticides and Ground Water Strategy
QA	quality assurance
QC	quality control
QAPP	quality assurance project plan
RSD	relative standard deviation
RPA	Rhone Poulenc Agro (Kim Morris, Bayer Crop Science, oral commun., Dec. 2008)
SAA	sulfynil acetic acid
SD	standard deviation
SRWS	standard reference water sample (prepared by Branch of Quality Systems, USGS)
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Pesticides in Ground Water in Selected Agricultural Land-Use Areas and Hydrogeologic Settings in Pennsylvania, 2003–07

By Connie A. Loper, Kevin J. Breen, Tammy M. Zimmerman, and John W. Clune

Abstract

This report was prepared by the U.S. Geological Survey (USGS) in cooperation with the Pennsylvania Department of Agriculture (PDA) as part of the Pennsylvania Pesticides and Ground Water Strategy (PPGWS). Monitoring data and extensive quality-assurance data on the occurrence of pesticides in ground water during 2003–07 are presented and evaluated; decreases in the land area used for agriculture and corresponding changes in the use of pesticides also are documented. In the Pennsylvania ground waters assessed since 2003, concentrations of pesticides did not exceed any maximum contaminant or health advisory levels established by the U.S. Environmental Protection Agency; PPGWS actions are invoked by the PDA at fractions of these levels and were needed only in areas designated by the PDA for special ground-water protection.

Previous investigations through 1998 of pesticides in Pennsylvania ground water identified land use, as a surrogate for pesticide use, and rock type of the aquifer combined with physiography as key hydrogeologic setting variables for understanding aquifer vulnerability to contamination and the common occurrence of atrazine and metolachlor in ground water. Of 20 major hydrogeologic settings in a framework established in 1999 for pesticide monitoring in Pennsylvania, 9 were identified as priorities for data collection in order to change the monitoring status from “inadequate” to “adequate” for the PPGWS.

Agricultural and forested land-use areas are decreasing because of urban and suburban growth. In the nine hydrogeologic settings evaluated using 1992 and 2001 data, decreases of up to 12 percent for agricultural land and 10 percent for forested land corresponded to increases of up to 11 percent for urban land. Changes in agricultural pesticide use were computed from crop data. For example, from 1996 to 2004–05, atrazine use declined by about 15 percent to 1,314,000 lb/yr (pounds per year) and metolachlor use increased by about 20 percent to 895,000 lb/yr; these compounds are the two most-used agricultural pesticides statewide.

In 2003–07, a baseline assessment of pesticides was conducted in five of nine hydrogeologic settings with inadequate monitoring data—the Blue Ridge crystalline and Triassic Lowland siliciclastic, Eastern Lake surficial, Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial settings. Between 20 and 30 wells in each setting were monitored. Of the 126 wells sampled, 96 well-water samples were analyzed for at least 52 pesticide compounds at the USGS National Water Quality Laboratory (NWQL) using a method with a minimum reporting level (MRL) at or above 0.002 µg/L (micrograms per liter). Of the 96 well waters analyzed by NWQL, 43 had measureable concentrations of one or more pesticides. Atrazine and (or) deethylatrazine (CIAT), a degradation product of atrazine, were reported at or above the MRL in 39 of the 43 well waters. Neither atrazine nor CIAT were reported at concentrations exceeding 0.10 µg/L; all measured concentrations in these five settings were below PPGWS action levels. Metolachlor was present in 7 of the 43 well waters with measureable concentrations of 1 or more pesticides; however, concentrations were below the MRL. The other 30 samples (10 of 20 wells in the Blue Ridge crystalline and Triassic Lowland siliciclastic setting and all 20 wells in the Eastern Lake surficial setting) were analyzed for at least 19 pesticide compounds at the Pennsylvania Department of Environmental Protection Laboratory (PADEPL); the PADEPL reported no concentrations of pesticides at or above an MRL of 0.10 µg/L.

Statistical tests using the NWQL analytical results showed correlations between pesticide occurrence and two indicators of water-quality degradation—the occurrence of total coliform bacteria and nitrate concentration. A 2 × 2 contingency-table test indicated a relation between presence or absence of atrazine or metolachlor and presence or absence of bacteria only for the 10 wells representing the Blue Ridge crystalline and Triassic Lowland siliciclastic setting. Results of Spearman’s rank test showed strong positive correlations in the Devonian-Silurian carbonate setting between 1) the number of pesticides above the MRLs and nitrate concentration, and 2) concentrations of atrazine and nitrate. Atrazine concentration and nitrate concentration also showed a statistically significant positive correlation in the Great Valley siliciclastic setting.

An additional component of baseline monitoring was to evaluate changes in pesticide concentration in water from wells representing hydrogeologic settings most vulnerable to contamination from pesticides. In 2003, 16 wells originally sampled in the 1990s were resampled—4 each in the Appalachian Mountain carbonate, Triassic Lowland siliciclastic, Great Valley carbonate, and Piedmont carbonate settings. Nine of these wells, where pesticide concentrations from 1993 and 2003 were analyzed at the NWQL, were chosen for a paired-sample analysis using concentrations of atrazine and metolachlor. A statistically significant decrease in atrazine concentration was identified using the Wilcoxon signed-rank test ($p = 0.004$); significant temporal changes in metolachlor concentrations were not observed ($p = 0.625$).

Monitoring in three areas of special ground-water protection, where selected pesticide concentrations in well water were at or above the PPGWS action levels, was done at wells BE 1370 (Berks County, Oley Township), BA 437 (Blair County, North Woodbury Township), and LN 1842 (Lancaster County, Earl Township). Co-occurrence of pesticide-degradation products with parent compounds was documented for the first time in ground-water samples collected from these three wells. Degradation products of atrazine, cyanazine, acetochlor, alachlor, and metolachlor were commonly at larger concentrations than the parent compound in the same water sample. Pesticide occurrence in water from wells neighboring the hot-spot wells was highly variable; however, the same sets of pesticide compounds that were present in wells BA 437, BE 1370, and LN 1842 were present to some degree in water from neighboring wells. To evaluate temporal changes in concentration, nonparametric statistical tests were used to determine overall and seasonal monotonic trends. Concentrations of alachlor, atrazine, metolachlor, and nitrate were examined using the 5-year (2003–07) and the long-term data from wells BA 437 and LN 1842 (1996–2007 and 1995–2007, respectively), and the long-term data for well BE 1370 (1998–2007); results showed either downward trends or no trends. Trends in acetochlor concentrations were tested only at well LN 1842 using the 5-year data; no trends were observed. Homogeneity of trend tests indicated statistically significant downward concentration trends in the long-term data were due to seasonal trends as follows: BA 437—alachlor and atrazine (summer); BE 1370—atrazine and metolachlor (winter) and alachlor (winter and spring); LN 1842—alachlor (summer and fall) and atrazine (spring and fall).

Introduction

Pesticides are used to improve yields of agricultural crops throughout Pennsylvania. Use of pesticides also is common in urban and suburban areas statewide. The Pennsylvania Department of Agriculture (PDA) has regulatory authority for registration and use of all pesticide products. The PDA is also responsible for ensuring the application of pesticides does not contaminate Pennsylvania's ground-water resources. A draft Pennsylvania Pesticides and Ground Water Strategy (PPGWS) developed by the Pennsylvania Department of Agriculture (1998) outlines an approach for managing pesticides and preserving ground-water quality. The goal of this strategy is to protect all sources of drinking water from degradation. This strategy serves as a framework for the PDA to manage specific pesticides, as required by the U.S. Environmental Protection Agency (USEPA). The PPGWS specifies requirements for assessment of aquifer vulnerability and monitoring of pesticides in ground water.

As a result of detailed studies linking rock type and land use to pesticides in ground water (Lietman, 1997; Lindsey and others, 1998), monitoring for pesticides in Pennsylvania's ground water is structured with land use as a surrogate for pesticide use and rock type of the aquifer combined with physiography to establish "hydrogeologic setting" as a key design variable to represent vulnerability to pesticide contamination. Consistent with this structure, Lindsey and Bickford (1999) established a framework for characterizing the occurrence of pesticides in ground water throughout the state. Hydrogeologic settings previously assessed to a limited extent or not assessed at all and that were predominated by agricultural land use were given high priority for characterization studies. Agricultural row-crop areas were the focus of the statewide sampling design because the agricultural use of pesticides was substantial and was better defined than other uses. Hence, the focus of ground-water monitoring has been in rural areas where 1) pesticide applications are predominantly related to agriculture, and 2) rural residents obtain water supplies primarily from private household water wells.

PDA's responsibilities under the PPGWS are to establish pesticide-occurrence monitoring and assess for trends in pesticide concentrations for 1) areas of selected hydrogeologic settings vulnerable to pesticide contamination where baseline assessments of pesticide concentrations are needed (hereafter termed baseline-assessment areas) and 2) areas of special ground-water protection, defined as areas where concentrations of pesticides in ground water are at or above action levels specified in the PPGWS (wells in these areas are referred to as hot-spot wells). An investigation to address both monitoring responsibilities began in 2003 by the U.S. Geological Survey (USGS), in cooperation with the PDA.

Purpose and Scope

This report summarizes an investigation of pesticides in Pennsylvania ground water by presenting:

- Estimates of statewide and county pesticide use on agricultural crops for the mid-1990s and the study period 2003–07, and land-use estimates for 1992 and 2001 in nine hydrogeologic settings;
- A summary of previous investigations with an emphasis on 1997–2002;

- Results of 126 analyses during 2003–07 to assess occurrence of pesticides in water from aquifers in baseline-assessment areas representing five selected hydrogeologic settings vulnerable to pesticide contamination and that were previously assessed to a limited extent or not assessed at all (the focus of the current study was on settings with row-crop agriculture; urban or suburban settings with non-agricultural use of pesticides, including transportation and power-line rights-of-way, were excluded);
- An evaluation of long-term changes in pesticide concentration for waters from nine wells in baseline-assessment areas in each of four hydrogeologic settings vulnerable to pesticide contamination where concentrations of selected pesticides were compared to concentrations in water from the same wells measured approximately 10 years earlier;
- An evaluation of long-term changes in pesticide concentration for waters from wells in areas of special ground-water protection; these detailed investigations of pesticide occurrence, seasonal concentration change related to changing water levels, and persistence in areas of special ground-water protection in Berks, Blair, and Lancaster Counties involved three “hot-spot” well locations (a well from each of the areas of special ground-water protection where selected pesticide concentrations in well water were at or above the PPGWS action levels) sampled in winter, spring, summer, and fall 2003–07.
- An examination of concentrations of 15 pesticides, 39 pesticide degradation products, and other indicators of water-quality degradation in water from wells neighboring the hot-spot wells in the three areas of special ground-water protection listed above. A total of 16 sites (15 wells and 1 spring) were sampled one time.
- An examination of concentrations of nitrate nitrogen, nitrite nitrogen, (henceforth referred to as nitrate and nitrite, respectively), and most probable numbers of total coliform and *Escherichia coli (E. coli)* bacteria as indicators of water-quality degradation and their correlation with pesticide results in baseline-assessment areas representing four selected hydrogeologic settings.

Because of the regulatory authority of the PDA related to pesticide use, quality control was extensive. Approximately 46 percent of all samples collected were for quality-control testing. An evaluation of bias and variability is presented on the basis of 191 quality-control (QC) samples (42 blanks, 58 replicates, 73 field-spiked reagent water [FSRW] samples, 6 standard reference water samples [SRWS], and 12 two-lab splits). The intent of the QC split samples analyzed at two laboratories (2-lab splits) was to verify the concentrations received from the primary laboratory used. Results from laboratory reagent spikes analyzed by both the PADEPL and the NWQL were also used as measures of QC.

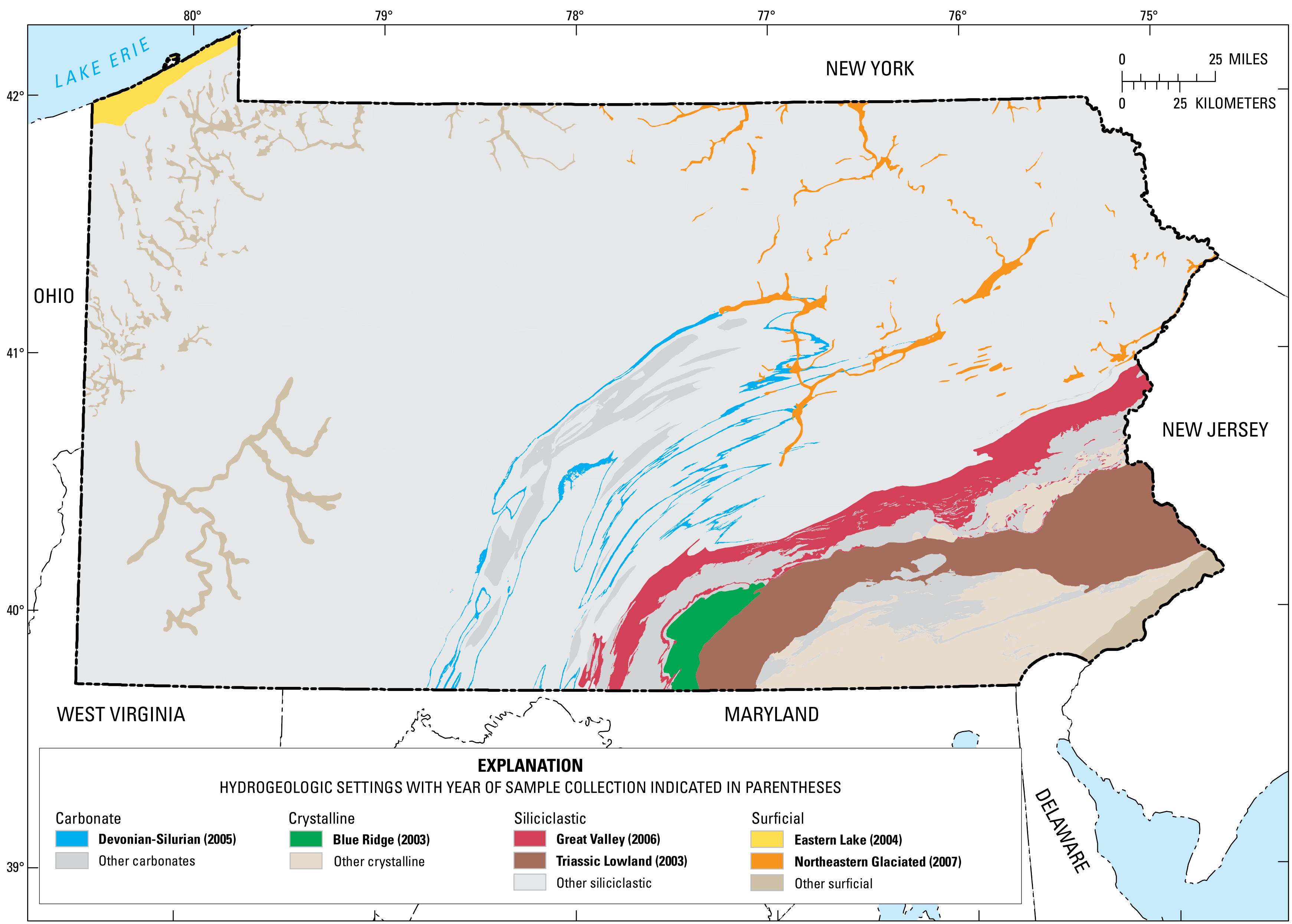
Hydrogeologic Settings

The 20 hydrogeologic settings for assessment of pesticide occurrence in Pennsylvania ground water were defined and prioritized by Lindsey and Bickford (1999). Pesticide occurrence was assessed to a limited extent or not previously assessed at all in five hydrogeologic settings, which were selected for sampling in 2003–07. The five settings (fig. 1) included 1) an area straddling the boundary between the Blue Ridge crystalline and Triassic Lowland siliciclastic (assessed as one setting for this report), 2) Eastern Lake surficial, 3) Devonian-Silurian carbonate, 4) Great Valley siliciclastic, and 5) Northeastern Glaciated surficial. The Blue Ridge crystalline and the Triassic Lowland siliciclastic settings were considered one setting because of land use—an area straddling the two settings is characterized by the largest concentration of orchards in the state. Areas of row-crop agriculture (primarily corn and soybeans) were targeted for assessment except in settings 1 and 2, where orchards and vineyards, respectively, were major components of the agricultural activity.

Patterns of Pesticide Use

Statewide pesticide-use data were available for 2003–06. The major crop commodities that require substantial pesticide use are shown in figure 2 in order by the acres harvested. Corn was dominant in areal terms with an average of 1,375,000 acres harvested over the 4 years. Annually, acres harvested did not vary substantially for any commodity shown in figure 2.

Annual pesticide use for agricultural purposes in Pennsylvania was estimated to 1) ensure the pesticides selected for ground-water sampling were in widespread use, and 2) determine if there were major changes in usage patterns from the mid-1990s to the period of this study (2003–07). The methods for estimating pesticide use for this report are presented in appendix 1. At the time data were compiled, no data was available for 2007; hence, data from 2003–06 were used to represent the period of this study. There were 134 pesticides used on Pennsylvania crops from 2003 to 2006 (U.S. Department of Agriculture National Agricultural Statistics Service, 2004, 2005a, 2006a, 2006b, 2007a, 2007b). Pesticide use amounted to greater than 14,000 lb/yr for each of 21 pesticides (fig. 3). Amounts of S-metolachlor and metolachlor were combined on figure 3 because of similar chemical structure and use. In a similar manner, glyphosate and the “iso-salt” of glyphosate also were combined on figure 3. Atrazine, metolachlor, and acetochlor were selected as representative triazine and acetamide compounds for focus in this study on the basis of heavy use and properties that can lead to contamination of water resources. Atrazine and metolachlor, 1,314,000 and 895,000 lb/yr, respectively, were the most-used pesticides (primarily on field corn [grain and silage] and sweet corn, fig. 3). Acetochlor was introduced in 1994 as a possible replacement for alachlor (Kolpin and others, 2004) and atrazine. Current



Hydrogeologic settings digital data from the U.S. Geological Survey, 2007

Base from U.S. Census Bureau digital data, 1990
1:100,000 Albers Equal-Area Conic projection: standard parallels 40° N and 42° N,
Central meridian -78° W, latitude of origin 39°

Figure 1. Hydrogeologic settings of Pennsylvania used for assessments of pesticides in ground water. For detailed maps of the areas sampled each year of this study, see figure 8 (2003), figure 9 (2004), figure 10 (2005), figure 11 (2006), and figure 12 (2007).

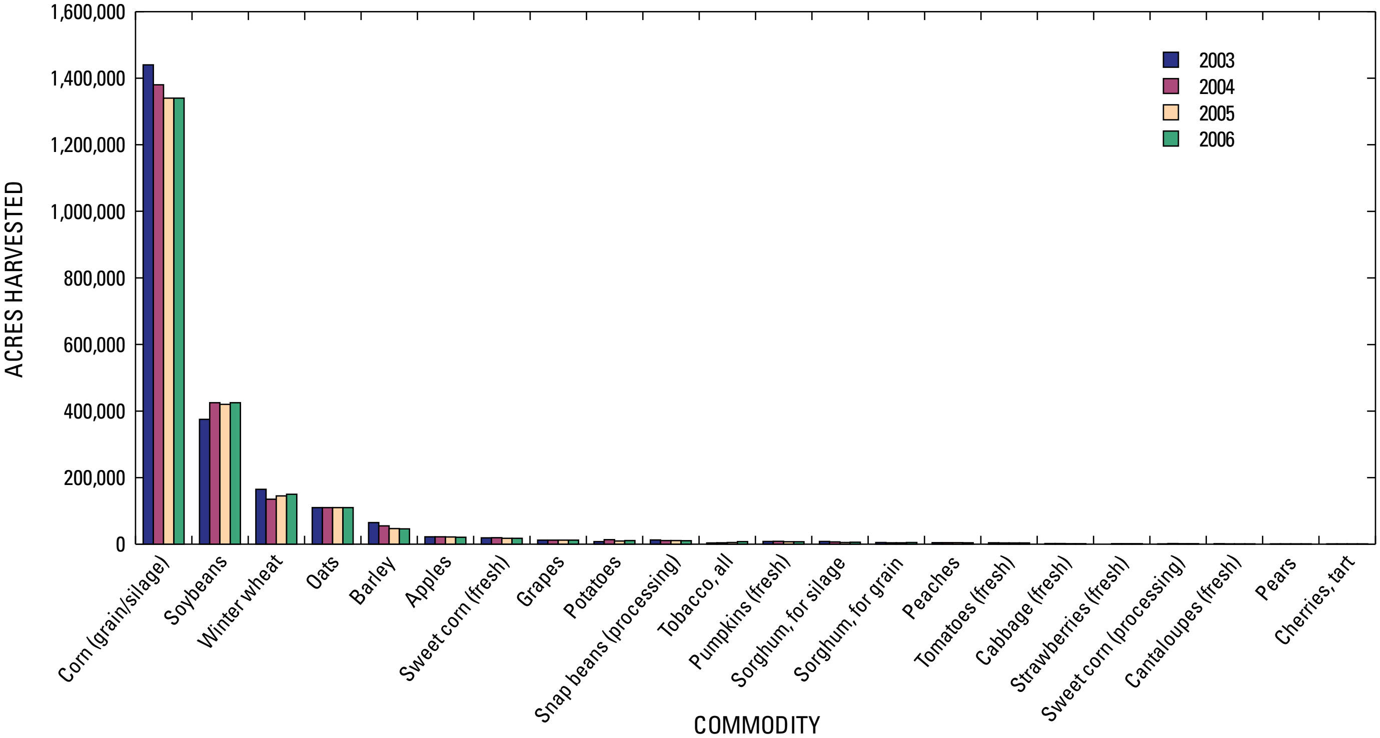


Figure 2. Acres harvested statewide in 2003–06 for Pennsylvania crop commodities likely produced with use of pesticides. Data obtained from the Pennsylvania Agricultural Statistics Bulletin for 2003–06 (Pennsylvania Department of Agriculture, 2004, 2005, 2006, 2007).

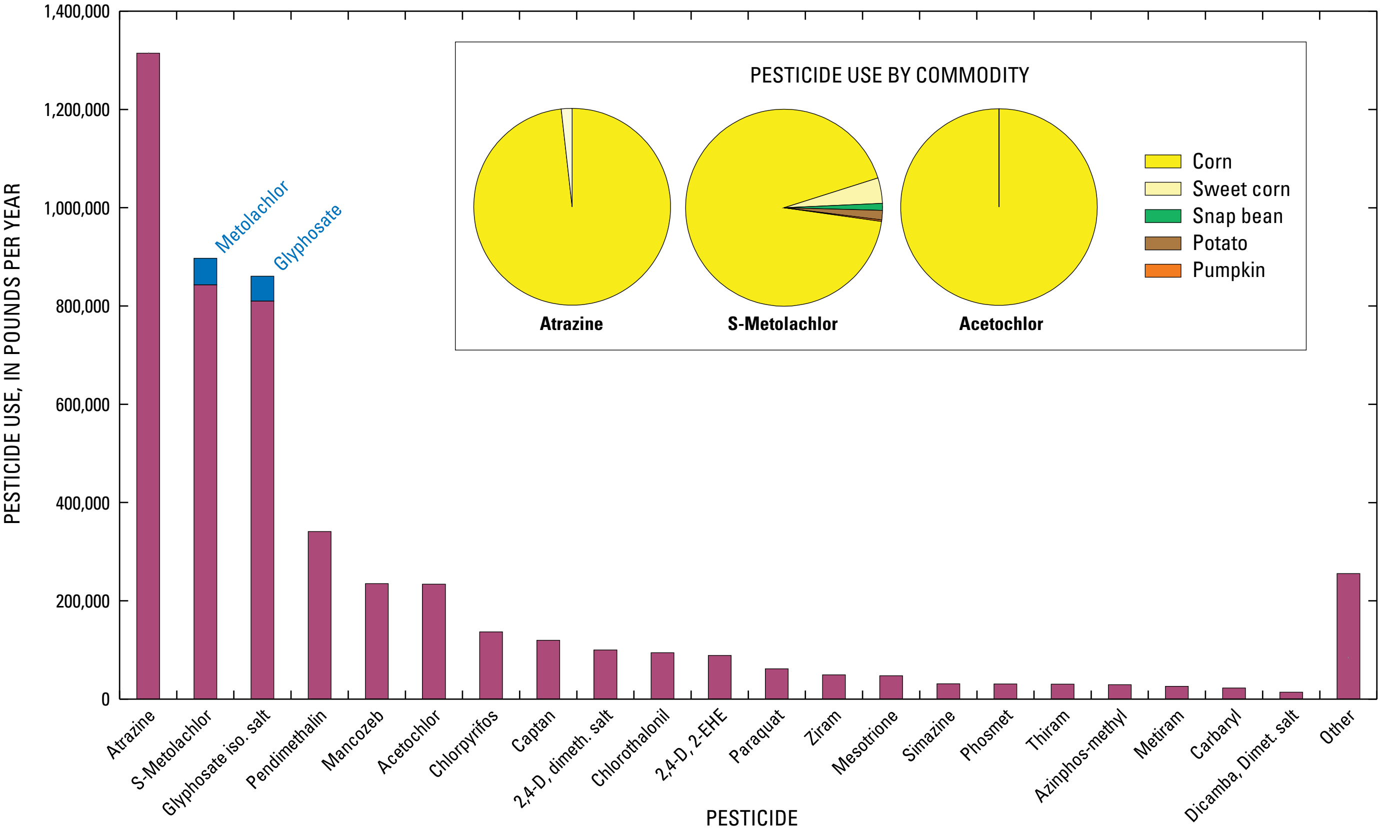


Figure 3. Annual use of pesticides in Pennsylvania, 2003–06, and a breakdown of use by crop commodity for atrazine, metolachlor, and acetochlor. [Based on acres of crop commodity planted for Pennsylvania (U.S. Department of Agriculture National Agricultural Statistics Service, 2004, 2005a, 2006a, 2006b, 2007a, 2007b) and not acres harvested.]

(2006) acetochlor use is about 234,000 lb/yr statewide; acetochlor is used solely on corn (fig. 3). Compounds whose use in Pennsylvania has been terminated are not shown on figure 3 (for example, any existing stock of cyanazine was to be used by December 31, 2002; U.S. Environmental Protection Agency, 2000b).

Statewide use of atrazine, metolachlor, and acetochlor on corn crops in 1996 (field corn and sweet corn data were combined) and in 2004–05 (2004 data were for field corn and 2005 data were for sweet corn) is shown in figure 4. Pesticide use for selected pesticides on crops besides corn such as snap beans, potatoes, or pumpkins represents less than 3 percent of the crops to which atrazine, metolachlor, and acetochlor were applied. Atrazine use on corn decreased from 1,506,000 lb/yr in 1996 to 1,298,000 lb/yr in 2004–05, a decrease of about 13 percent. Metolachlor use increased from 725,000 to 852,000 lb/yr, an increase of about 16 percent; S-metolachlor usage has largely replaced metolachlor over the past decade. Acetochlor use decreased from 507,000 lb/yr in 1996 to 237,000 lb/yr in 2004–05, in part because of lower application rates, less area on which the pesticide is applied, and decreased acreage of harvested corn (table 1-1 in appendix 1)

Atrazine-use estimates are illustrated in figure 5A by county for corn in 1996 (field corn and sweet corn data were combined) and in 2004–05 (2004 data were for field corn and 2005 data were for sweet corn); 2004–05 patterns in atrazine use by county in Pennsylvania are shown in figure 5B. Atrazine use decreased from 1996 to 2004 for 50 of 66 counties. Lancaster County accounted for 12.9 percent of all atrazine use (2004–05) in Pennsylvania. Lancaster County combined with eight other southeast counties (York, Franklin, Berks, Chester, Lebanon, Dauphin, Cumberland, and Adams) accounted for 40.7 percent of the atrazine use (2004–05) in Pennsylvania; those nine counties comprise 13.9 percent of the land area in Pennsylvania.

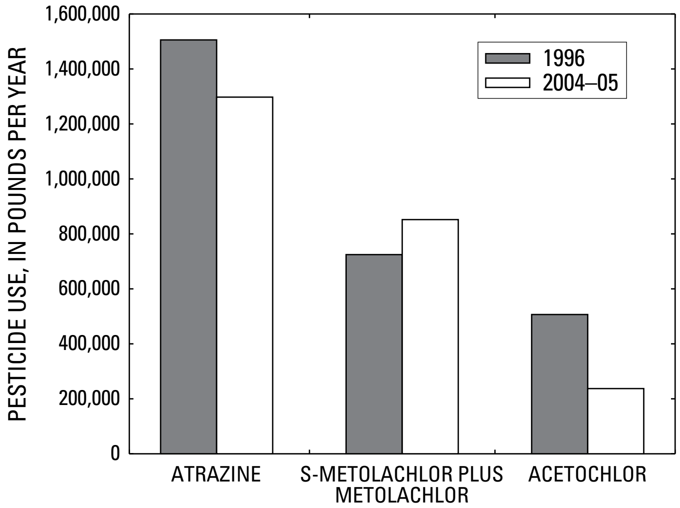


Figure 4. Statewide use of selected pesticides on corn in 1996 (field corn and sweet corn) and in 2004–05 (field corn data from 2004 plus sweet corn data from 2005). Use estimates are calculated on the basis of area of crop commodity harvested for Pennsylvania counties, in acres (Pennsylvania Department of Agriculture, 1997; U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, 1997b, 2005a, 2005b, 2006a, 2006c). Methodology is presented in appendix 1.

Acetochlor and metolachlor are not used as heavily as atrazine; however, acetochlor and metolachlor show similar patterns of use by county. Acetochlor use decreased from 1996 to 2004–05 for 65 of 66 counties (fig. 6A), and metolachlor use on corn increased from 1996 to 2004–05 in 43 of 66 counties (fig. 6B).

Changing Patterns of Land Use

The National Land Cover Database 2001 (Multi-Resolution Land Characteristics, 2001) was compared to the National Land Cover Database 1992 (Multi-Resolution Land Characteristics, 1992) to quantify and relate changing patterns in three major land-cover categories (agriculture, forest, and urban) for nine hydrogeologic settings where agricultural land use was important historically (table 1). From 1992 to 2001 in the nine settings, agricultural land generally decreased up to 12 percent (median decrease 7.2 percent), forested land decreased up to 10 percent (median decrease 4.5 percent), and urban land increased up to 11 percent (median increase 2 percent).

Previous Investigations with Emphasis on the Period 1997–2002

Numerous investigations have contributed to the current knowledge of pesticide occurrence in Pennsylvania ground water. A compilation of investigations that analyzed for alachlor, atrazine, cyanazine, metolachlor, and simazine in ground water through 1998 was presented by Lindsey and Bickford (1999, p. 5). Investigations subsequent to the Lindsey and Bickford compilation and selected references to source data through 2002 are presented in table 2. Most are regional investigations by the USGS in the Delaware River Basin (see table 2 entries for USGS Delaware NAWQA [National Water-Quality Assessment] and USGS/PDA Delaware River Basin Quality Assurance Design). In addition to the data-source references provided in table 2, data were available in a compilation by Low and others (2008).

Primary findings of the previous investigations were 1) atrazine, metolachlor, and simazine are the three pesticide parent compounds reported most often in analyses of ground-water samples (concentrations are low with none exceeding USEPA drinking-water standards); 2) two or more compounds typically occur together and the health effects of co-occurring compounds are unknown; and 3) degradation products of the parent compounds typically have reported concentrations at or above the parent compounds; however, degradation products are not routinely measured in studies of ground-water quality, and applicable drinking-water standards are not established.

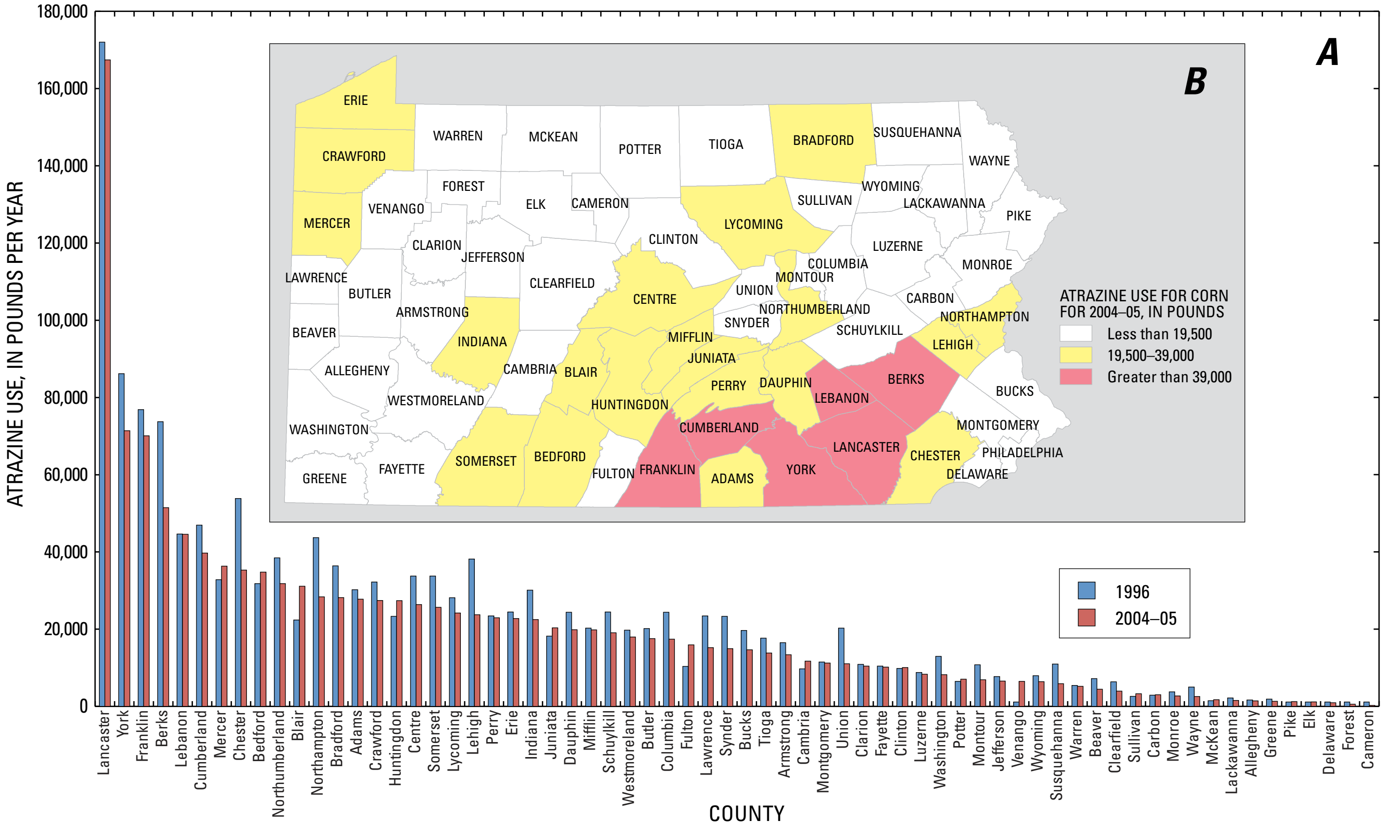


Figure 5. Atrazine use on corn crops for 66 Pennsylvania counties (no data for Philadelphia County) as *A*) chart comparing 1996 data (field corn and sweet corn) and 2004–05 data (field corn data from 2004 plus sweet corn data from 2005), and *B*) map for 2004–05 data for three use-per-year categories. Use estimates are calculated on the basis of area of crop commodity harvested for Pennsylvania counties, in acres (Pennsylvania Department of Agriculture, 1997; U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, 1997b, 2005a, 2005b, 2006a, 2006c).

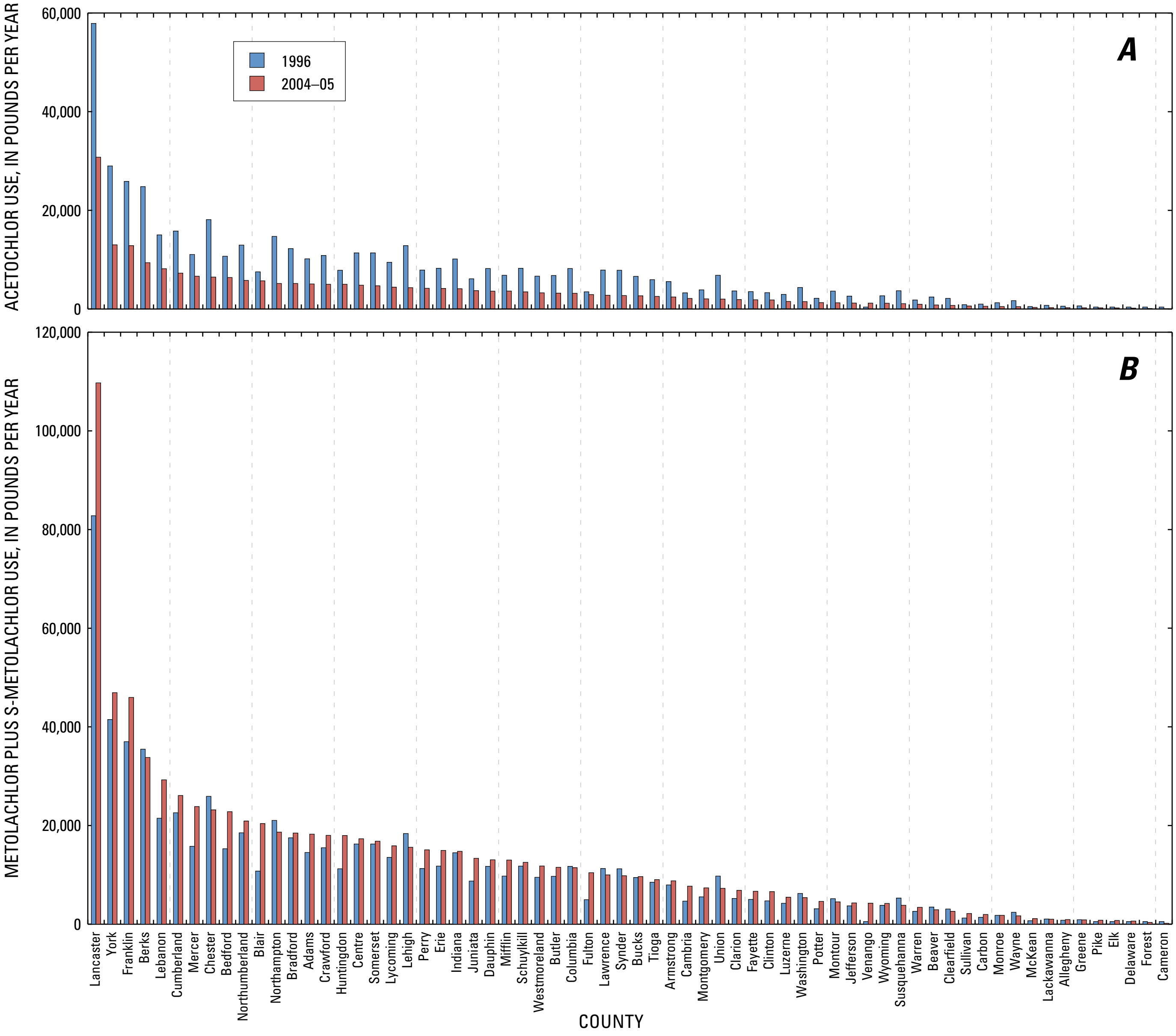


Figure 6. Pesticide use on corn crops for 66 Pennsylvania counties (Philadelphia County not shown) in 1996 (field corn and sweet corn) and in 2004–05 (field corn data from 2004 plus sweet corn from 2005) for *A*) acetochlor, and *B*) metolachlor plus S-metolachlor. Use estimates are calculated on the basis of area of crop commodity harvested for Pennsylvania counties, in acres (Pennsylvania Department of Agriculture, 1997; U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, 1997b, 2005a, 2005b, 2006a, 2006c).

Table 1. Physiographic provinces, physiographic sections, and change in dominant land covers for selected hydrogeologic settings in Pennsylvania using 1992 and 2001 National Land Cover Databases.

[NLCD, National Land Cover Database]

Hydrogeologic setting	Physiographic province[1]	Physiographic section[1]	Dominant land covers[2]	NLCD 1992 (percent)[3]	NLCD 2001 (percent)[4]
Eastern Lake surficial	Central Lowland	Eastern Lake	Forest	39.4	29.8
			Agriculture	31.9	28.9
			Urban	18.0	29.1
Devonian-Silurian carbonate	Ridge and Valley	Appalachian Mountain	Forest	43.0	43.2
			Agriculture	49.6	41.2
			Urban	5.0	6.2
Appalachian Mountain carbonate	Ridge and Valley	Appalachian Mountain	Forest	27.4	30.4
			Agriculture	66.0	54.0
			Urban	2.3	4.3
Northeastern Glaciated surficial	Appalachian Plateaus	Glaciated Low Plateau	Forest	33.9	27.9
		Glaciated High Plateau	Agriculture	36.9	30.8
	Ridge and Valley	Appalachian Mountain	Urban	16.9	16.3
Great Valley siliciclastic	Ridge and Valley	Great Valley	Forest	31.4	28.3
			Agriculture	61.0	52.9
			Urban	4.8	7.7
Great Valley carbonate	Ridge and Valley	Great Valley	Forest	14.1	9.6
			Agriculture	67.8	57.8
			Urban	14.9	20.0
Blue Ridge crystalline	Blue Ridge	South Mountain	Forest	85.6	82.9
			Agriculture	12.1	10.1
			Urban	.5	1.1
Triassic Lowland siliciclastic	Piedmont	Gettysburg-Newark Lowland	Forest	41.7	31.6
			Agriculture	46.1	46.6
			Urban	8.6	9.8
Piedmont carbonate	Piedmont	Piedmont Lowland	Forest	11.2	5.3
			Agriculture	70.1	62.9
			Urban	14.9	17.1

[1] Physiographic province and physiographic section from Lindsey and Bickford, (1999).

[2] Forest dominant land cover is the combination of deciduous, evergreen, and mixed forest. Agriculture dominant land cover is the combination of row crop and hay/pasture land covers. Urban dominant land cover is the combination of low-intensity residential, high-intensity residential, and commercial/industrial/transportation in the 1992 NLCD and low-intensity developed, medium-intensity developed, and high-intensity developed in the 2001 NLCD.

[3] Multi-Resolution Land Characteristics (1992).

[4] Multi-Resolution Land Characteristics (2001).

Table 2. Six U.S. Geological Survey investigations of major-use pesticides in ground water of Pennsylvania, 1997–2002, where data quality assurance could be documented.

[Investigations of major-use pesticides in ground water of Pennsylvania conducted 1990-98 are summarized in Lindsey and Bickford (1999); NAWQA, National Water-Quality Assessment; USGS, U.S. Geological Survey; NWQL, USGS National Water Quality Laboratory; PADEPL, Pennsylvania Department of Environmental Protection Laboratory; PDA, Pennsylvania Department of Agriculture; OGRL, USGS Organic Geochemistry Research Laboratory; GCMS, gas chromatography/mass spectrometry; HPLCMS, High Performance Liquid Chromatography/Mass Spectrometry]

Investigation name	Years investigation conducted	Settings sampled	Number of sites sampled in Pennsylvania	Number of pesticides, analysis source, and method	Data-source reference
Carroll Valley Ground Water, Adams County	2002	Blue Ridge crystalline	6	11, NWQL GCMS	Low and Conger (2002, p. 75-76)
Martinsburg Ground Water, Blair County	2002	Appalachian Mountain carbonate	10	11, NWQL GCMS	Durlin and Schaffstall (2003, p. 460-469) Lindsey and Koch (2004, p. 23-26)
Chester County Water-Quality Monitoring Project	2001	Piedmont crystalline	10	47, NWQL GCMS	Durlin and Schaffstall (2002, p. 390-400)
Delaware NAWQA	2001	Northeastern Glaciated surficial	6	47, NWQL GCMS 65, NWQL HPLCMS 10, OGRL HPLCMS	Durlin and Schaffstall (2002, p. 423, 426-427, 505-521)
	2000	Appalachian Mountain siliciclastic	13	[1]47, NWQL GCMS	Durlin and Schaffstall (2001, p. 463, 624-646)
	2000	Great Valley siliciclastic	11	[1]47, NWQL GCMS	Durlin and Schaffstall (2001, p. 463, 624-646)
	1999	Triassic Lowland siliciclastic	23	[1]47, NWQL GCMS	Durlin and Schaffstall (2001, p. 463, 599-622)
USGS/PDA Design Framework	1998	Eastern Lake surficial	1	47, NWQL GCMS	Coll and Siwicki (1999, p. 346-349)
	1998	Eastern Lake surficial	5	9, PADEPL GCMS	Coll and Siwicki (1999, p. 346-349)
	1998	Great Valley siliciclastic	5	9, PADEPL GCMS	Durlin and Schaffstall (1999a, p. 392-393; 1999b, p. 444-452)
	1998	Northeastern Glaciated surficial	3	47, NWQL GCMS	Durlin and Schaffstall (1999a, p. 392-393; 1999b, p. 444-452)
	1998	Northeastern Glaciated surficial	4	9, PADEPL GCMS	Durlin and Schaffstall (1999a, p. 392-393; 1999b, p. 444-452)
	1998	Appalachian Mountain carbonate	5	47, NWQL GCMS	Durlin and Schaffstall (1999b, p. 444-452)
	1998	Appalachian Mountain carbonate	5	9, PADEPL GCMS	Durlin and Schaffstall (1999b, p. 444-452)
	1998	Devonian-Silurian carbonate	3	47, NWQL GCMS	Durlin and Schaffstall (1999b, p. 444-452)
	1998	Devonian-Silurian carbonate	5	9, PADEPL GCMS	Durlin and Schaffstall (1999b, p. 444-452)
	1998	Glaciated Low Plateau siliciclastic	4	9, PADEPL GCMS	Durlin and Schaffstall (1999b, p. 444-452)
	1998	Glaciated Low Plateau siliciclastic	1	1, PADEPL GCMS	Durlin and Schaffstall (1999b, p. 444-452)
USGS/PDA Delaware River Basin Quality Assurance Design	1997	Great Valley carbonate	11	47, NWQL GCMS	Breen (2000)
	1997	Great Valley carbonate	29	8, PADEPL GCMS	Breen (2000)

[1] Data for 65 additional pesticides are available in the USGS National Water Information System for these wells.

Methods

Ground-water studies were conducted in baseline-assessment areas, for trends assessment or occurrence monitoring, and in areas of special ground-water protection. A description of methods for these studies follows.

Baseline-Assessment Areas

To understand trends in concentrations of pesticides, wells in vulnerable settings that were part of assessments of pesticide occurrence from 1993 to 2001 and had waters with one or more pesticides were resampled in 2003 and 2004. Previous PDA and USGS pesticide data were reviewed to evaluate candidates for repeat sampling. Site reconnaissance was conducted to confirm site status and obtain written permission from the landowner to sample. The frequency of sampling was set at one time per year. Water samples were collected from 4 wells in each of the Great Valley carbonate, Appalachian Mountain carbonate, Piedmont carbonate, and Triassic Lowland siliciclastic settings in 2003, and 14 of those 16 wells were resampled in 2004 (2 new wells had to be located for the 2004 sample collection). Pesticide samples collected in April 2003 for trends assessments were analyzed at the USGS NWQL, and those collected in March-April 2004 were analyzed at the PADEPL.

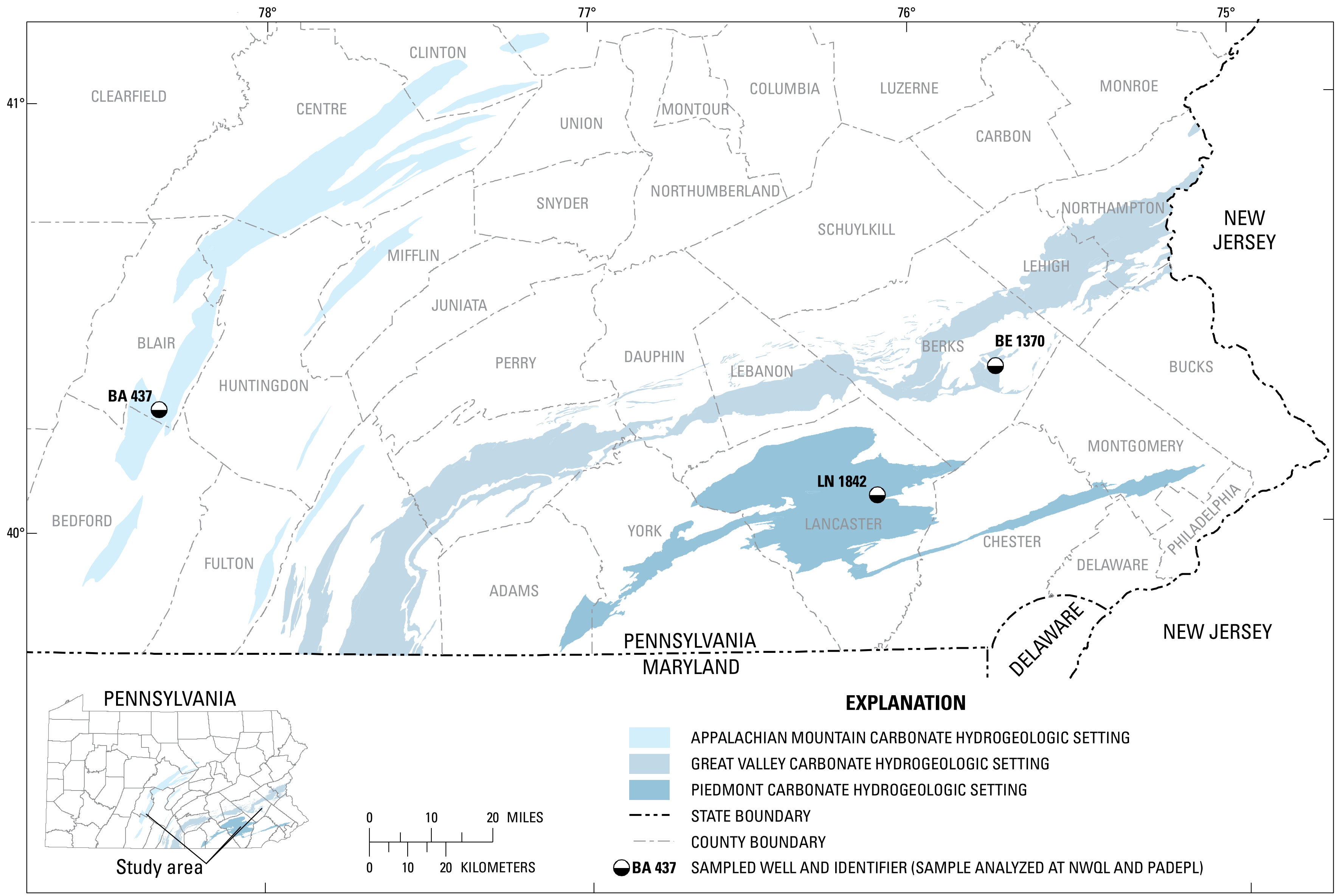
For the baseline-assessment component, a 5-year plan for monitoring was developed to obtain data for settings with little or no data using documented vulnerability rankings for hydrogeologic settings found in Lindsey and Bickford (1999) and the most recent data from well-water sampling completed by PDA and other agencies (table 2). The plan called for sampling one setting per year. The Blue Ridge crystalline and Triassic Lowland siliciclastic setting was sampled in 2003, the Eastern Lake surficial setting was sampled in 2004, the Devonian-Silurian carbonate setting was sampled in 2005, the Great Valley siliciclastic setting was sampled in 2006, and the Northeastern Glaciated surficial setting was sampled in 2007. Each setting was subdivided using a 20- or 30-cell equal area grid of the assessment area, and a random point was assigned for starting the process of well selection in each grid cell (Scott, 1990). For the Blue Ridge crystalline and Triassic Lowland siliciclastic setting, a 20-cell grid was based on a land-use coverage subset for orchards. In the Eastern Lake surficial setting, a 20-cell grid was based on agricultural land use (vineyards primarily); the large urban area occupied by the city of Erie was excluded. For the Great Valley siliciclastic and Devonian-Silurian carbonate settings, a 30-cell grid was based on agricultural land use comprised of hay/pasture and row crops classifications. For the Northeastern Glaciated surficial setting, the boundary of the setting from Lindsey and Bickford (1999) was expanded to include additional glacial deposits shown in Williams and others (1998); a 30-well grid was based on hay/pasture and row crops agricultural land use. The five baseline-assessment areas and year of sample collection are noted on figure 1. More detailed discussions of the study areas sampled are found in the “Pesticides in Ground Water for the Baseline Assessment of Hydrogeologic Settings, 2003–07” section of this report.

Pennsylvania Topographic and Geologic Survey (PATGS) online well-record data, scanned well records available from PATGS on compact disc (CD), and well records from drilling companies were used to verify well depth and lithology. Site reconnaissance established that wells were generally within 75 ft of targeted land use. After permission to sample the well was obtained from the homeowner, plumbing was inspected to establish a raw-water sampling point. A Global Positioning System (GPS) unit was used to establish a latitude and longitude for the well, and well-construction data were entered into the USGS Ground-Water Site Inventory (GWSI) database. The records of wells sampled are given in table 3 (back of report).

Sampling of wells for occurrence monitoring was planned for May through August to reflect conditions when the majority of pesticides were applied. Wells were sampled once. In most settings, the number of wells sampled equaled the number of grid cells; in the Devonian-Silurian carbonate and Northeastern Glaciated surficial settings, only 28 wells were sampled because of difficulties in finding wells meeting the well-selection criteria (discussed in Quality Assurance section). Pesticides samples were analyzed predominantly at the USGS NWQL. The PADEPL analyzed water from 10 wells sampled in the Blue Ridge crystalline and Triassic Lowland siliciclastic setting in August 2003 and from 20 wells sampled in the Eastern Lake surficial setting May-August 2004. Minimum reporting levels (MRLs) for pesticides analyzed at the PADEPL were greater than those reported at the USGS NWQL, and fewer pesticides per sample were analyzed by the PADEPL.

Areas of Special Ground-Water Protection

Areas of special ground-water protection are designated by the PDA where concentrations of pesticides in ground water are at or above action levels specified in the PPGWS (appendix 4). Detailed investigations of pesticide occurrence, seasonal change in concentrations related to changing water levels, and persistence in areas of special ground-water protection were done in Berks, Blair, and Lancaster Counties. Monitoring was done at and around three wells, referred to as hot-spot wells (BA 437, LN 1842, and BE 1370 are the USGS local well numbers for PDA-designated hot-spot wells, fig. 7). To evaluate concentration change related to changes in water levels and overall persistence of compounds, these three wells were sampled quarterly during 2003–06 and three times in 2007. Quarterly sampling was planned with one sample for each of the following criteria: 1) summer—declining water levels in wells (mid-growing season after application of herbicides), 2) fall—stable water levels after summer decline (harvest season), 3) winter—rising water levels in wells resulting from seasonal recharge, and 4) spring—rising water levels



State boundary from U.S. Geological Survey, 2005
County boundary from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Appalachian Mountain carbonate, Great Valley carbonate, and Piedmont carbonate hydrogeologic settings from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 7. Locations of hot-spot wells sampled in areas of special ground-water protection, Berks, Blair, and Lancaster Counties, Pennsylvania, March 2003 to August 2007. Ground-water samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory (NWQL) and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL).

resulting from spring or early summer storms. Water levels were estimated by use of the nearest USGS observation well. Sampling during a stable water-level period was the most problematic because of differences in water levels between settings and the quick change in water levels resulting from large storms.

To better understand persistence and possible degradation of parent compounds, a characterization of pesticide-degradation products in water from hot-spot wells BA 437, LN 1842, BE 1370 and neighboring water supplies was conducted. In 2005, hot-spot well BA 437 plus five neighboring wells and hot-spot well BE 1370 plus a spring and five neighboring wells were characterized. In 2006, hot-spot well LN 1842 plus five neighboring wells were characterized.

At hot-spot well BA 437 only, depth and yield characteristics of water-bearing zones and the depth that water with elevated pesticide concentrations entered the well were determined. A borehole video camera and a suite of borehole geophysical logs (caliper, gamma, temperature, and resistivity) were used to identify the zones where water entered the borehole. Heatpulse flowmetering was used to evaluate the rate and direction of vertical flow of ground water in the borehole to determine the depth that the water entered the well. An inflatable packer was used to isolate discrete water-bearing zones, and a submersible sampling pump was used to collect water samples in the shallow and deep water-bearing zones.

Evaluation of Water-Quality Conditions

Methods used for physical and chemical water-quality sampling, processing, and laboratory analyses are also described. Field-data collection, laboratory analyses, and statistical analyses were consistent with approved and published methods.

Physical Characteristics

Specific conductance, pH, dissolved oxygen, turbidity, and water temperature were measured with calibrated field meters or calibrated multi-parameter water-quality meters (table 4). Calibration followed procedures documented by Wilde (variously dated). Barometric pressure was recorded at most sites using a Thommen field barometer.

Chemical Sampling and Processing

Well-water sampling equipment was cleaned thoroughly prior to sample collection, following the USGS protocols for organic- and inorganic-compound sampling (Wilde, 2004). Collection of most well-water samples followed protocols documented by Wilde and others (1999) with several modifications: 1) brass fittings were used instead of Teflon to connect to plumbing at sampling points, 2) a flow manifold or processing chamber was not used, 3) Millipore filter holders with 0.45-micron filters were used instead of capsule filters for the filtration of nitrate/nitrite samples (years 2004 to 2007), and 4) pesticide samples were filtered if turbidity readings at the end of the well purge were greater than 4 Nephelometric Turbidity Units (NTU). Water with turbidity of 5 NTU or less does not have to be filtered for public supply (U.S. Environmental Protection Agency, 2008). This study did not include a comparison of results for filtered and non-filtered samples. Generally, there are no differences in results between filtered samples and unfiltered samples with low turbidity unless sufficient dissolved organic carbon is present; some dissolved organic carbon can pass through the filter in a filtered sample (Duane Wydoski, U.S. Geological Survey, oral commun., 2008). For the samples collected in the vicinity of hot-spot wells, 0.45-micron capsule filters were used for the filtration of nitrate samples, and all pesticide samples were filtered.

At most wells sampled, existing submersible pumps provided sample water to a tap either at the base of the pressure tank or at an outside faucet that by-passed any treatment. On several occasions, collections points were either at accessible locations on irrigation systems or public-water-supply lines. As the well was purged, measurements of pH, specific conductance, dissolved oxygen, water temperature, turbidity, and water level were recorded. When readings became stable (Wilde, variously dated), the well-water samples were collected.

Well-water samples were collected after volumetric purge criteria for each well were met. For processing of pesticide samples, if the turbidity readings were less than or equal to 4 NTU, water was collected directly into two 1-L amber glass bottles that were commercially cleaned and baked at 450°C to burn off all residual organic compounds. If turbidity readings were greater than 4 NTU, a pre-cleaned Savillex Teflon in-line filter holder with a baked, glass microfiber filter (47-mm diameter, 0.7-micron pore size) was used to filter the sample from the tap into two 1-L amber glass bottles. One bottle was shipped to the laboratory; the second bottle was held as an archive sample. For processing of well-water samples for total coliform and *E. coli* bacteria, water was collected directly into a pre-sterilized 125-mL bottle (sodium thiosulfate added to all bottles at the PADEPL as a chlorine neutralizer prior to sample collection). For nitrate/nitrite sample processing, well water was initially collected in a pre-cleaned bottle, then filtered to remove particles larger than 0.45 µg/L using a cleaned 50-mL syringe and either a pre-conditioned ground-water capsule filter or a Millipore filter unit with a 47-mm diameter mixed-cellulose-ester filter into a pre-rinsed 125-mL bottle. All bottles were immediately placed on ice and returned to the Pennsylvania Water Science Center (PA WSC) laboratory where they were either maintained at 4°C or shipped to the USGS NWQL or the PADEPL. The nitrate, nitrite, and bacteria samples were shipped the day of collection; pesticide samples were shipped within 2 days of sample collection via overnight delivery to the analytical laboratories.

Table 4. Physical characteristics, units, accuracies, and equipment types used for this study.

[NWIS, National Water Information System; °C, degrees Celsius; YSI, Yellow Springs Instrument Company; ICM, Industrial Chemical Measurement; µS/cm, microsiemens per centimeter at 25°C; mm, millimeters; mg/L, milligrams per liter; NTU, Nephelometric Turbidity Units]

Measurements	NWIS code	Reporting units	Reporting accuracy	Equipment/ sensor type
Water temperature	00010	°C	± 0.15 °C	YSI 556, precision thermister
	00010	°C	± 0.2 °C	Orion 122 specific conductivity meter thermister
	00010	°C	± 0.3 °C	YSI 58 dissolved oxygen meter thermister
pH	00400	standard units	± 0.2 pH	YSI 556, glass combination electrode
	00400	standard units	± 0.01 pH	Ross combination electrode, Beckman 210 pH meter
Specific conductivity	00095	µS/cm at 25°C	± 0.5 percent of the reading or ± 1 µS/cm; whichever is greater	YSI 556, 4-electrode cell with auto-ranging
	00095	µS/cm at 25°C	± 0.5 percent over meter's range	Orion 122, 012210 4-electrode cell
Dissolved oxygen	00300	mg/L	± 2 percent of reading or 0.2 mg/L; whichever is greater	YSI 556, steady state polarographic
	00300	mg/L	± 0.3 mg/L	YSI 58, polarographic
Barometric pressure	00025	mm mercury	± 0.75 to 1.5 mm mercury	Thommen Classic Altimeter Plus Barometer
Turbidity	63676	NTU	± 2 percent plus stray light (from debris on mirror, ampule, etc.)	Hach 2100P, 400-680 nm light source, 90 degree detection angle, multiple detectors with ratio compensation
	63675	NTU	0.1 percent or ± 1 count	ICM turbidity meter, Sensor Model 11520, 400-680 nm light source, 90 degree detection angle, one detector

Laboratory Analyses

Four laboratories were used for analytical work done during the project: the USGS Ohio Water Microbiology Laboratory (OWML), the USGS NWQL, the USGS Organic Geochemistry Research Laboratory (OGRL), and the PADEPL. Timeframes when samples were submitted to respective laboratories are found in table 5.

Bacteria were analyzed at the USGS OWML and the PADEPL. Both laboratories used Standard Method 9223B (Chromogenic Substrate Test) (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 2004), Idexx Colilert Quanti-Tray equipment, which gives results in Most Probable Number per 100 mL (MPN/100 mL) of total coliform and *E. coli* bacteria.

Nitrate and nitrite were analyzed at the PADEPL using the USEPA 353.2 method that uses cadmium reduction of nitrate to nitrite followed by colorimetry (on file at the PADEPL quality-assurance office [James Yoder, Pennsylvania Department of Environmental Protection Laboratory, Quality Assurance Section Chief, oral commun., February 4, 2008]).

At the NWQL, the concentration of nitrate plus nitrite nitrogen was determined using a method comparable to USEPA 353.2 (cadmium reduction of nitrate to nitrite followed by colorimetry), and nitrite concentration was determined using colorimetry (Fishman, 1993).

For pesticides analyzed at the PADEPL (table 6), a modification of USEPA Method 525.2 (Eichelberger and others, 1994) was used. Method 525.2 uses gas chromatography/mass spectroscopy (GCMS) with initial solid-phase extraction. The modification involved the extraction solvent; PADEPL used a 1:1 methylene chloride-acetone mix as the extraction solvent rather than a 1:1 methylene chloride-ethyl acetate mix because better extraction results have been obtained from the modified solvent mix (Michael Webb, Pennsylvania Department of Environmental Protection Laboratory, written commun.,

Table 5. Laboratories used for analytical work by analysis type and date of sample collection.

[USGS OWML, U.S. Geological Survey Ohio Water Microbiology Laboratory; USGS NWQL, U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; PADEPL, Pennsylvania Department of Environmental Protection Laboratory in Harrisburg, Pa.; USGS OGRL, U.S. Geological Survey Organic Geochemistry Research Laboratory in Lawrence, Kans.; *E. coli*, *Escherichia coli*; –, not applicable]

<table>
<tr><th rowspan="2">Laboratories</th><th>Pesticides</th><th>Nitrate plus nitrite and nitrite or nitrate and nitrite[1]</th><th>Total coliform and *E. coli*</th></tr>
<tr><th colspan="3">Month and year of sample collection</th></tr>
<tr><td>USGS OWML</td><td>–</td><td>–</td><td>March–May 2003</td></tr>
<tr><td>USGS NWQL</td><td>March–May 2003
May, June, Aug., Sept. 2005
Jan., May–Sept. 2006,
June–Sept. 2007</td><td>March–May 2003</td><td>–</td></tr>
<tr><td>PADEPL</td><td>Aug.–Oct., Dec. 2003,
May–Aug., Oct., Dec. 2004</td><td colspan="2">Aug.–Oct., Dec. 2003,
May–Aug., Oct., Dec. 2004
May, June, Aug., Sept. 2005
Jan., May–Sept. 2006
June–Sept. 2007</td></tr>
<tr><td>USGS OGRL</td><td>Aug., Sept. 2005,
June 2006</td><td colspan="2">–</td></tr>
</table>

[1] The PADEPL reported concentrations of nitrate as nitrogen and nitrite as nitrogen; the USGS NWQL reported concentrations of nitrate plus nitrite as nitrogen and nitrite as nitrogen.

2002). Several compounds analyzed (pendimethalin and acetochlor, for example) are not listed in this method; however, the PADEPL has run Minimum Detection Level and Demonstration of Capability studies for these compounds in water and has documented the results (available at PADEPL—Martina McGarvey, Pennsylvania Department of Environmental Protection Laboratory, oral commun., 2008).

Carbaryl, methomyl, and oxamyl were determined by USEPA Method 531.1 at the PADEPL (Munch, 1995); this method involves direct aqueous injection into a reverse phase high-performance liquid chromatography (HPLC) column with post-column derivatization and fluorescence detection.

Pesticides were analyzed at the NWQL using C-18 solid-phase extraction and capillary-column GCMS with selected-ion monitoring (table 7) (Zaugg and others, 1995; Madsen and others, 2003) (March to May 2003 and May 2005 to September 2007) or graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry (HPLCMS) (table 8) (Furlong and others, 2001) (May 2003). Pesticide samples collected in May 2003 were analyzed at the NWQL using two methods to measure concentrations of compounds of interest to PDA that could not be obtained through one method. Analytical methodology used at the USGS OGRL involved solid-phase extraction and HPLCMS (Lee and others, 2002; Lee and Strahan, 2003) (table 9). Ten compounds have not been formally approved for inclusion in the method (Michael Meyer, U.S. Geological Survey Organic Geochemistry Research Laboratory, oral commun., 2008) (table 9).

Table 6. Pesticides analyzed at the Pennsylvania Department of Environmental Protection Laboratory (PADEPL) in Harrisburg, Pennsylvania, from August 2003 to December 2004.

[NWIS, National Water Information System; USEPA, U.S. Environmental Protection Agency; MDL, method detection limit; MRL, minimum reporting level; µg/L, micrograms per liter; RPA, Rhone Poulenc Agro; NA, not available; NC, no code; FY04, fiscal year 2004]

Pesticides analyzed in samples collected for the baseline-assessment of the Blue Ridge crystalline and Triassic Lowland siliciclastic (10 of 20 samples) (2003) and the Eastern Lake surficial (20 samples) (2004) hydrogeologic settings				Pesticides analyzed in samples collected for the baseline-trends assessments (Great Valley carbonate, Piedmont carbonate, Appalachian Mountain carbonate, and Triassic Lowland siliciclastic) (2004) and trends assessments in areas of special ground-water protection (2004)			
Analyte	**NWIS parameter code**	**Minimum reporting level, in micrograms per liter**	**Method detection limit, in micrograms per liter**	**Analyte**	**NWIS parameter code**	**Minimum reporting level, in micrograms per liter**	**Method detection limit, in micrograms per liter**
USEPA 525.2 Method:				**USEPA 525.2 Method:**			
Acetochlor	49260	0.10–0.25	0.10	Acetochlor	49260	0.10–0.25	0.10
Alachlor	46342	0.10–0.25	.08	Alachlor	46342	0.10–0.25	.08
Atrazine	39632	0.10–0.25	.07	Atrazine	39632	0.10–0.25	.07
Azinphos-methyl[1]	82686	1.0	N/A	Chlorothalonil	49306	0.10–0.25	.08
Captan	61582	0.10–1.0	.10	Chlorpyriphos (Dursban)	38933	0.10–0.25	.09
Chlorothalonil	49306	0.10–0.25	.08	Dichlobenil[5]	63009	0.10	.06
Chlorpyriphos (Dursban)	38933	0.10–0.25	.09	Fenpropathrin[5]	64044	0.10	.08
Dichlobenil[2]	63009	0.10	.06	Hexachlorocyclopentadiene	34386	0.10–0.25	.09
Diuron[3]	49300	NA	NA	Metolachlor	39415	0.10–0.25	.10
Fenpropathrin[2]	64044	0.10	.08	Metribuzin	82630	0.10–0.25	.07
Hexachlorocyclopentadiene	34386	0.10–0.25	.09	Pendimethalin	82683	0.10–0.25	.06
Metolachlor	39415	0.10–0.25	.10	Phosmet[5]	61601	1.00	.09
Metribuzin	82630	0.10–0.25	.07	Simazine	04035	0.10–0.25	.10
Parathion-methyl	82667	0.10	.05				
Pendimethalin	82683	0.10–0.25	.06				
Phosmet[2]	61601	1.00	.09				
Phosphamidon[4]	63736	1.0	N/A				
Simazine	04035	0.10–0.25	.10				
Terbacil	82665	0.10–0.25	.10				
Trifluralin[2]	82661	0.10	.07				
1,3-dimethyl-2-nitrobenzene (surrogate)	NC	0.10	NA	1, 3-dimethyl-2-nitrobenzene (surrogate)	NC	0.10	NA
Pyrene-d10 (surrogate)	NC	0.10	NA	Pyrene-d10 (surrogate)	NC	0.10	NA
Triphenylphosphate (surrogate)	NC	0.10	NA	Triphenylphosphate (surrogate)	NC	0.10	NA
Perylene-d12 (surrogate)	NC	0.10	NA	Perylene-d 12 (surrogate)	NC	0.10	NA
USEPA 531.1 Method:				(October and December 2004 samples only at Hot-Spot Trend sites:)			
Carbaryl	82680	1.6–5.0	0.338–2.602	Isoxaflutole (RPA 201772)	62733	1.25	NA
Methomyl	49296	1.6–5.0	0.332–1.723	(RPA 203328) (terminal metabolite of isoxaflutole) [2-methanesulphonyl-4-trifluromethylbenzoic acid]	62656	1.25	NA
Oxamyl	38866	1.6–5.0	0.504–2.689	(RPA 202248) (primary metabolite of isoxaflutole) [2-cyclopropylcarbonyl-3-(2-methylsulphonyl-4-trifluoromethylpenyl)-3-oxopropanenitrile; diketonitrile]	63011	1.25	NA

[1] MRLs during project were reported as 0.10–0.50 µg/L. A PADEPL data review conducted in 2007 changed this level to 1.0 µg/L.

[2] FY04 addition.

[3] MRL during project was reported as 0.10 µg/L. A PADEPL data review conducted in 2007 could not verify acceptable recoveries and mass spectra during the period of sample submittal; therefore, acceptable MDLs and MRLs are not possible.

[4] MRLs during project were reported as 0.10–0.25 µg/L. A PADEPL data review conducted in 2007 changed this level to 1.0 µg/L.

[5] FY04 addition (July 2004) at the three hot-spot wells in the areas of special ground-water protection.

Table 7. Pesticides analyzed using C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado, from March to May 2003 and May 2005 to September 2007.

[NWIS, National Water Information System; **bolding** of compound names denotes all values are estimated because of low recoveries or high variability in lab reagent spikes; pct, percent; NA, not available]

Compound	NWIS parameter code	Minimum reporting level, in micrograms per liter	Method detection limit, in micrograms per liter
2,6-Diethylaniline	82660	0.002–0.006	0.001–0.003
alpha-HCH[1]	34253	0.002–0.005	0.001–0.002
alpha-HCH-d6 (surrogate)	91065	0.1 pct	NA
Acetochlor	49260	0.006	0.003
Alachlor	46342	0.005–0.006	0.002–0.003
Atrazine	39632	0.007	0.004
Deethylatrazine (CIAT)[2]	04040	0.006–0.014	0.003–0.007
Azinphos-methyl	82686	0.05–0.08	0.02–0.04
Benfluralin	82673	0.006–0.010	0.003–0.005
Butylate	04028	0.002–0.004	0.001–0.002
Carbaryl	82680	0.06–0.041	0.021–0.03
Carbofuran	82674	0.020–0.02	0.010–0.01
Chlorpyrifos	38933	0.005	0.003
cis-Permethrin	82687	0.006–0.01	0.003–0.005
Cyanazine	04041	0.018	0.009
Dacthal (DCPA)[3]	82682	0.0030–0.003	0.0015–0.002
Desulfinylfipronil	62170	0.004–0.012	0.006
Desulfinylfipronil amide	62169	0.009–0.029	0.015
Diazinon	39572	0.005	0.003
Diazinon-d10 (surrogate)	91063	0.1 pct	NA
Dieldrin	39381	0.0048–0.009	0.0024–0.004
Disulfoton	82677	0.02–0.021	0.01–0.011
EPTC[4]	82668	0.0020–0.004	0.0010–0.002
Ethalfluralin	82663	0.009	0.005
Ethoprop (Ethoprophos)	82672	0.005–0.012	0.002–0.006
Fipronil	62166	0.007–0.016	0.008
Fipronil sulfide	62167	0.005–0.013	0.006
Fipronil sulfone	62168	0.005–0.024	0.012
Fonofos	04095	0.0027–0.006	0.0013–0.003
Lindane	39341	0.0040–0.004	0.0020–0.002
Linuron	82666	0.035–0.06	0.018–0.03
Malathion	39532	0.016–0.027	0.008–0.014
Metolachlor	39415	0.006–0.013	0.003–0.006
Metribuzin	82630	0.006–0.028	0.003–0.014
Molinate	82671	0.0016–0.003	0.0008–0.002
Napropamide	82684	0.007–0.018	0.003–0.009
Parathion	39542	0.010	0.005
Parathion-methyl	82667	0.008–0.015	0.004–0.008
Pebulate	82669	0.004–0.0041	0.002–0.0021
Pendimethalin	82683	0.02–0.022	0.01–0.011
Phorate	82664	0.011–0.055	0.006–0.027
p,p’-DDE[5]	34653	0.0025–0.003	0.0013–0.001
Prometon	04037	0.005–0.015	0.002–0.007
Propachlor	04024	0.010–0.025	0.0048–0.012
Propanil	82679	0.011	0.005
Propargite	82685	0.02–0.023	0.01–0.011
Propyzamide	82676	0.004–0.0041	0.002–0.0021
Simazine	04035	0.005–0.006	0.002–0.003
Tebuthiuron	82670	0.016	0.008
Terbacil	82665	0.034–0.04	0.017–0.02
Terbufos	82675	0.012–0.017	0.006–0.009
Thiobencarb	82681	0.0048–0.01	0.0024–0.005
Triallate	82678	0.0023–0.006	0.0012–0.003
Trifluralin	82661	0.006–0.009	0.003–0.005

[1] Alpha hexachlorocyclohexane.

[2] 2-chloro-4-isopropylamino-6-amino-s-triazine.

[3] Dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid.

[4] S-ethyl dipropylthiocarbamate.

[5] p,p’-dichlorodiphenyldichloroethylene.

Table 8. Pesticides analyzed using graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado, in May 2003.

[NWIS, National Water Information System; **bolding** of compound names denotes permanently estimated values in May 2003 resulting from low recoveries or high variability in lab reagent spikes; pct, percent; NA, not available; these compounds were analyzed for 10 samples collected for the baseline assessment of the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting]

Compound	NWIS Parameter Code	Minimum reporting level, in micrograms per liter	Method detection limit, in micrograms per liter
2,4,5-T (surrogate)	99958	0.1 pct	0.1 pct
2,4-D[1]	39732	.0218	NA
2,4-D methyl ester	50470	.0086	NA
2,4-DB[2]	38746	.016	NA
3(4-Chlorophenyl)-1-methyl urea	61692	.0242	NA
Acifluorfen	49315	.0066	NA
Aldicarb	49312	.04	NA
Aldicarb sulfone	49313	.02	NA
Aldicarb sulfoxide	49314	.0082	NA
Atrazine	39632	.009	NA
2-Hydroxyatrazine (OIET)[3]	50355	.008	NA
Deethylatrazine (CIAT)[4]	04040	.0282	NA
Deethyldeisopropylatrazine (CAAT)[5]	04039	.01	NA
Deisopropylatrazine (CEAT)[6]	04038	.044	NA
Barban (surrogate)	90640	.1 pct	.1 pct
Bendiocarb	50299	.0252	NA
Benomyl	50300	.0038	NA
Bensulfuron-methyl	61693	.0158	NA
Bentazon	38711	.011	NA
Bromacil	04029	.033	NA
Bromoxynil	49311	.017	NA
Caffeine	50305	.0096	.0048
Caffeine-C13 (surrogate)	99959	.1 pct	.1 pct
Carbaryl	49310	.0284	.0142
Carbofuran	49309	.0056	NA
3-Hydroxycarbofuran	49308	.0058	NA
3-Ketocarbofuran	50295	1.5	NA
Chloramben, methyl ester	61188	.018	NA
Chlorimuron-ethyl	50306	.0096	NA
Chlorothalonil	49306	.035	.0173
Clopyralid	49305	.0138	N/A
Cycloate	04031	.013	NA
Dacthal monoacid	49304	.0116	NA
Dicamba	38442	.0128	NA
Dichlorprop	49302	.0138	NA
Dinoseb	49301	.012	NA
Diphenamid	04033	0.0264	NA
Diuron	49300	.015	NA
Fenuron	49297	.0316	NA
Flumetsulam	61694	.011	NA
Fluometuron	38811	.031	NA
Imazaquin	50356	.016	NA
Imazethapyr	50407	.017	NA
Imidacloprid	61695	.0068	NA
Linuron	38478	.0144	NA
MCPA[7]	38482	.0162	NA
MCPB[8]	38487	.015	NA
Metalaxyl	50359	.02	NA
Methiocarb	38501	.008	NA
Methomyl	49296	.0044	NA
Metsulfuron methyl	61697	.025	NA
Neburon	49294	.012	NA
Nicosulfuron	50364	.013	NA
Norflurazon	49293	.016	NA
Oryzalin	49292	.0176	NA
Oxamyl	38866	.0122	NA
Picloram	49291	.0198	NA
Propham	49236	.0096	NA
Propiconazole	50471	.021	NA
Propoxur	38538	.008	NA
Siduron	38548	.0168	NA
Sulfometuron-methyl	50337	.0088	NA
Tebuthiuron	82670	.0062	NA
Terbacil	04032	.0098	NA
Triclopyr	49235	.0224	NA

[1] (2,4-dichlorophenoxy) acetic acid.

[2] 4-(2,4-dichlorophenoxy) butyric acid.

[3] 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine.

[4] 2-chloro-4-isopropylamino-6-amino-s-triazine.

[5] Chloro-di-amino-s-triazine.

[6] 2-chloro-6-ethylamino-4-amino-s-traizine.

[7] 2-methyl-4-chlorophenoxyacetic acid.

[8] 4-(2-methyl-4-chlorophenoxy) butyric acid.

Table 9. Acetamide, triazine, and phenylurea pesticides and degradation products analyzed using solid-phase extraction and liquid chromatography/mass spectrometry at the U.S. Geological Survey Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kansas, from August to September 2005 and June 2006.

[NWIS, National Water Information System; *, degradation product; ESA, ethane sulfonic acid; OXA, oxanilic acid; SAA, sulfynil acetic acid]

Analyte	NWIS parameter code	Minimum reporting level, in micrograms per liter	Analyte	NWIS parameter code	Minimum reporting level, in micrograms per liter
Acetamide parents and degradation products:			**Triazine and phenylurea parents and degradation products:**		
Acetochlor	49260	0.02	Atrazine	39632	0.025
*Acetochlor ESA	61029	.02	Bromacil	04029	.025
*Acetochlor OXA	61030	.02	Cyanazine	04041	.025
*Acetochlor SAA	62847	.02	Prometon	04037	.025
*Acetochlor/metolachlor ESA – 2nd amide	62850	.02	Propazine	38535	.025
*Acetochlor/metolachlor – 2nd amide[1]	63782	.02	Simazine	04035	.025
*Acetochlor deschloro[1]	63778	.02	*Deethylatrazine (CIAT)[2]	04040	.025
*Acetochlor hydroxy[1]	63784	.02	*Deisopropylatrazine (CEAT)[3]	04038	.025
Alachlor	46342	.02	*Hydroxyatrazine or 2-hydroxyatrazine(OIET)[4]	50355	.025
*Alachlor ESA	50009	.02	*Hydroxysimazine	63154	.025
*Alachlor OXA	61031	.02	*Deethylhydroxyatrazine (OIAT)[5]	62676	.025
*Alachlor SAA	62848	.02	*Deisopropylhydroxyatrazine (OEAT)[6]	62678	.025
*Alachlor ESA – 2nd amide	62849	.02	*Deethyldeisopropylatrazine/ Didealkyatrazine (CAAT)[7]	04039	.025
*Alachlor – 2nd amide[1]	63781	.02	*Cyanazine acid	61745	.025
*Alachlor deschloro[1]	63777	.02	*Cyanazine amide	61709	.025
*Alachlor hydroxy[1]	63783	.02	*Deethylcyanazine acid	61750	.025
Dimethenamid	61588	.02	*Deethylcyanazine amide	61751	.025
*Dimethenamid ESA	61951	.02	*Deethylcyanazine	61749	.20
*Dimethenamid OXA	62482	.02	Diuron	50374	.20
*Dimethenamid deschloro[1]	63779	.02	Fluometuron	38811	.20
*Dimethenamid hydroxy[1]	64045	.02	*Demethylfluometuron (DMFM)	61755	.20
Flufenacet	62481	.02	Linuron	38478	.20
*Flufenacet ESA	61952	.02			
*Flufenacet OXA	62483	.02			
Metolachlor	39415	.02			
*Metolachlor ESA	61043	.02			
*Metolachlor OXA	61044	.02			
*Metolachlor deschloro[1]	63780	.02			
*Metolachlor hydroxy[1]	63785	.02			
Propachlor	04024	.02			
*Propachlor ESA	62766	.05			
*Propachlor OXA	62767	.02			

[1] Unapproved compound as of June 1, 2008 (Michael Meyer, U.S. Geological Survey Organic Geochemistry Research Laboratory, oral commun., 2008).

[2] 2-chloro-4-isopropylamino-6-amino-s-triazine.

[3] 2-chloro-6-ethylamino-4-amino-s-traizine.

[4] 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine.

[5] 2-hydroxy-4-isopropylamino-6-amino-s-triazine.

[6] 2-hydroxy-6-ethylamino-4-amino-s-triazine.

[7] Chlorodiamino-s-triazine.

Quality Assurance and Quality Control

A USEPA-approved Quality Assurance Project Plan (QAPP) (U.S. Environmental Protection Agency, 2000a) was implemented to obtain data of known and adequate quality specified by documented quality assurance (QA) objectives. The QAPP is on file at the PA WSC office of the USGS in New Cumberland, Pa.

Quality controls for field-instrument calibration as detailed in the QAPP (with the exception of barometric pressure and turbidity) are summarized in table 10. Instruments used to collect specific conductance, pH, dissolved oxygen, and turbidity were calibrated and checked for accuracy on the day of sampling by the use of certified standards and buffers; thermistors for field instruments were checked one time prior to each sampling season.

Quality-Assurance Objectives

For QC of water-quality samples, QA objectives were established as part of the QAPP to assure the

- Representativeness of samples to characterize the aquifer of interest using site-selection criteria combined with stability criteria for field measurements; the acceptance criteria for representativeness (percent of listed site-selection criteria being met for each well and percent of stability criteria for field measurements being met during well purge prior to sample collection) was not defined in the QAPP (QA objective 1),
- Bias resulting from sample contamination (resulting in false positives) from all processing sources (field processing, transport, and lab analysis) would be zero; the objective would, therefore, only be met if 100 percent of the blanks were without contamination (QA objective 2),
- Bias resulting from not detecting an analyte when the analyte was present would be less than 5 percent (resulting in false negatives) (QA objective 3),
- Bias in analyte recovery would be ± 25 percent of the ‘true’ (100-percent) recovery (QA objective 4), and
- Variability in results would be ± 25 percent (QA objective 5).

Table 10. Quality-control acceptance criteria for field-instrument calibration.

Measurements	Acceptance criteria
Water temperature	± 0.5 degrees Celsius
Specific conductance	± 5 percent
pH	± 0.05 units pH
Dissolved oxygen	± 5 percent
Barometric pressure	± 1 percent
Turbidity	± 2 percent

The five QA objectives were evaluated through methodology that involved either goals for adherence to well-selection criteria and well-purging stability indicators or QC samples to evaluate bias and (or) variability. QC samples submitted for the project included blanks, replicates, FSRW samples prepared in triplicate, nutrient SRWS, and 2-lab splits. QC data from lab reagent spikes (LRS) were used when data from field-submitted samples were not available. Blank samples help define the (false) positive bias that may be introduced into analytical results through sample contamination, either through improperly cleaned equipment, field processing, or lab processing. Data from replicates provided information on variability in analytical results. FSRW samples, SRWS, and internal laboratory-control data provided information for bias and (or) variability related to compound recovery. Therefore, if compound recoveries were above 100 percent, the results for the environmental samples would be biased high; alternately, if compound recoveries were less than 100 percent, the results for the environmental samples would be biased low. The numbers of QC samples and the respective laboratories used for analyses from 2003 through 2007 are summarized in table 11. Detailed information on methodology and the resulting analysis of QC data for each objective are presented in appendix 2. The following is a summary of the results:

QA objective 1

Representativeness in sampling: Water samples were considered representative of the aquifer being sampled because site-selection criteria combined with stability criteria for field measurements were met 75 to 100 percent of the time.

QA objective 2

False positives: There were no detections of pesticides above the method detection limit (MDL) for the three blank samples analyzed at the PADEPL; therefore, no PADEPL results for environmental samples analyzed had a positive bias because of sample contamination. For samples submitted to the NWQL, 1 field-blank pesticide sample of the 11 equipment and field blank samples submitted had an estimated (E) detection of p,p’-DDE (E 0.0009 µg/L), which was below the MDL (0.001 µg/L) and the MRL (0.003 µg/L) for this compound. It was unclear if the contamination was introduced from the air during sample collection or during analysis at the laboratory. Insufficient cleaning of equipment was discounted because p,p’-DDE was not detected in any of the wells sampled during the years of sample collection. For all intents and purposes, there was no contamination in blank samples for any pesticides analyzed at the NWQL except p,p’-DDE.

Of the 12 nitrate blank samples submitted to the PADEPL, only three had detections at or above the MRL

Table 11. Summary of the numbers of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.

[*E. coli*, *Escherichia coli*]

Quality-control sample type	Laboratory used	Number of samples
Equipment blanks		
Pesticides	PADEPL	1
	NWQL	4
Nitrate plus nitrite/ nitrate and (or) nitrite	PADEPL	2
	NWQL	1
Total coliform and *E. coli* bacteria	PADEPL	1
	OWML	1
Field blanks		
Pesticides	PADEPL	2
	NWQL	7
Nitrate plus nitrite/ nitrate and (or) nitrite	PADEPL	10
	NWQL	1
Total coliform and *E. coli* bacteria	PADEPL	6
	OWML	4
Trip blanks		
Nitrate plus nitrite/ nitrate and (or) nitrite	PADEPL	0
	NWQL	1
Total coliform and *E. coli* bacteria	PADEPL	0
	OWML	1
Replicates		
Nitrate plus nitrite/ nitrate and (or) nitrite	PADEPL	20
	NWQL	2
Total coliform and *E. coli* bacteria	PADEPL	34
	OWML	2
Field-spiked reagent water samples, prepared in triplicate		
Pesticides	PADEPL	18
	NWQL	36
	OGRL	4
Nitrate plus nitrite/ nitrate and (or) nitrite	PADEPL	12
	NWQL	3
Nutrient standard reference samples		
Nitrate and nitrite	PADEPL	6
2-lab split samples		
Pesticides	PADEPL	3
	NWQL	2
Nitrate plus nitrite/ nitrate and (or) nitrite	NWQL	5
Total coliform and *E. coli* bacteria	OWML	2

(0.04 mg/L). One field blank in 2004 had a concentration of 0.2 mg/L; the remaining two analyses (one collected in 2005 and one in 2006) reported nitrate concentrations at the MRL (0.04 mg/L). The 0.2 mg/L reported concentration in one blank was considered an isolated case where the equipment was not cleaned properly after one sample, because the sample collected the following day had no nitrate concentration above the MRL. Because of the three detections of nitrate above the MRL, reported concentrations of nitrate analyzed at the PADEPL may contain minimal positive bias (usually about 0.04 mg/L) resulting from sample contamination during collection, processing, or laboratory analysis. Nitrate was not detected above the MRL in the three blank samples analyzed at the NWQL; therefore, environmental results (April 2003–May 2003) do not have a positive bias because of sample contamination.

Bacteria were not detected in the seven blank samples submitted to the PADEPL or in the six blank samples submitted to the USGS OWML. Sterile buffered water with peptone is known to result in some false positives (Amie Brady, U.S. Geological Survey, oral commun., December 21, 2007); however, that result was not observed in this study. The goal of no false positives was met for the bacteria results.

QA objective 3

False negatives (spiked compounds that are not reported when the compounds are present should be less than 5 percent): There was a false negative for 1 (captan) of the 65 pesticides evaluated in FSRW samples and no false negatives for nitrate plus nitrite or total coliform/*E. coli* bacteria. Relative to the “less than 5 percent” goal for QA objective 3, captan had a bias of 100 percent because it was not reported in any spikes, and all other pesticides had zero bias. Nitrate and nitrite analyses and total coliform and *E. coli* bacteria results all met project goals (zero bias).

QA objective 4

Bias in recovery should be ± 25 percent of the ‘true’ value (at a 0.4 µg/L concentration for most pesticides evaluated).

Bias results for pesticide samples analyzed at the NWQL:

- Of the 60 pesticides included in triplicate FSRW samples analyzed at the NWQL (table 2-2, appendix 2) (surrogates not included in count), the following 17 compounds had low biases that did not meet project objectives: aldicarb, alicarb sulfone, aldicarb sulfoxide, deethylatrazine (CIAT), cis-permethrin, desulfinylfipronil amide, 2,6-diethylaniline, disulfoton, ethalfluralin, methiocarb, methomyl, metribuzin, oxamyl, p,p’-DDE, phorate, propargite, and terbacil. The compound 2, 6-diethylaniline also had poor median recovery (33 percent) in FSRW samples but excellent recovery and variability in LRS. The poor recoveries in FSRW samples could have been the result of methodology or equipment used in spike preparation because 2, 6-diethylaniline is very volatile (Lucinda Murtagh, U.S. Geological Survey, oral commun., December 19, 2007); therefore, this compound will not be qualified on the basis of the FSRW results. Median recoveries for these pesticides ranged from 11 to 74 percent.

- Of the 47 compounds not included in FSRW samples analyzed at the NWQL (table 2-2, appendix 2), 20 compounds did not meet project bias goals on the basis of the "long-term" median recoveries from LRS. Bensulfuron-methyl, chlorimuron-ethyl, flumetsulam, imazaquin, nicosulfuron, and sulfometuron-methyl had high biases ranging from 130 to 205 percent (table 2-2, appendix 2). The following 14 compounds had low biases in median recoveries ranging from 7 to 73 percent (table 2-2, appendix 2): 2,4-DB, deisopropylatrazine (CEAT), bendiocarb, bentazon, bromoxynil, 3-keto-carbofuran, chloramben methyl ester, deethyldeisopropylatrazine (CAAT), chlorothalonil, clopyralid, cycloate, dinoseb, metsulfuron-methyl, and MCPB.

Bias results for pesticide samples analyzed at the PADEPL:

- Of the 20 pesticides included in FSRW samples analyzed at the PADEPL (table 2-2, appendix 2) (surrogates not included in count), the following 3 compounds had low recoveries that did not meet project objectives: captan, hexachlorocyclopentadiene, and metribuzin. Median recoveries for these pesticides ranged from 0 to 72 percent.
- Three compounds analyzed at the PADEPL were not included in the FSRW samples—dichlobenil, fenpropathrin, and phosmet (table 2-2, appendix 2). For these compounds, median recoveries from LRS were used to evaluate bias; all lab median recoveries of LRS were within project goals for these compounds.

Bias results for pesticide samples analyzed at the OGRL laboratory:

- Of the 10 pesticides included in the FSRW samples sent to the USGS OGRL (acetochlor, alachlor, metolachlor, propachlor, atrazine, cyanazine, prometon, simazine, CIAT, and linuron), all compounds analyzed met project QA objective 4 goals except atrazine, prometon, simazine, and CIAT, which showed low biases in recoveries ranging from 62 to 74 percent (table 2-3).

Bias results for nitrate and nitrite samples analyzed at the NWQL and the PADEPL:

- Results were good at both laboratories: There was a negative bias of 1-2 percent for nitrate and 0-percent bias for nitrite. Therefore, bias was well within the ± 25 percent goal for both compounds.

Bias results for total coliform and E. coli results analyzed at the PADEPL:

- No total coliform or *E. coli* samples were submitted as spiked samples because of the wide confidence limits associated with the Colilert-tray methodology; therefore, bias was not evaluated.

QA objective 5

Variability in results would be ± 25 percent: For pesticides, two data sets were used to evaluate variability of pesticides included in spike mixes: 1) median relative standard deviations (RSDs), which were calculated using individual pesticides concentrations from triplicate sets, and 2) F-pseudosigma for FSRW and LRS recoveries. F-pseudosigma is a nonparametric statistic defined as the interquartile range of data divided by 1.349 (Hoaglin and others, 1983).

Variability results for pesticide samples analyzed at the NWQL:

- Using median RSDs calculated from concentrations of pesticides in triplicate FSRW samples for 60 pesticides analyzed at the NWQL (table 2-2, appendix 2) (surrogates not included in count), the goal of variability was met for all pesticides except the following: aldicarb, aldicarb sulfoxide, methiocarb, and methomyl. RSDs for these four compounds ranged from 26 to 93 percent. Using the F-pseudosigma results from aggregated compound recoveries from FSRW samples analyzed at the USGS NQWL, four compounds—azinphos-methyl, carbaryl, 2,6-diethylaniline, and fipronil—did not meet project objectives for variability. F-pseudosigmas for recoveries of these compounds ranged from 27 to 59 percent. The goal in variability was met for 93 percent of the compounds on the basis of RSD criteria and 93 percent on the basis of F-pseudosigmas of recoveries. Again, 2,6-diethylaniline results were not qualified due to the methodology or equipment used in spike preparation, which may have affected results.
- For the 47 pesticides not included in FSRW samples analyzed at the NWQL, the goal in variability was met for 70 percent of the compounds on the basis of F-pseudosigma of recoveries in LRS (table 2-2). Those 13 pesticides not meeting project objectives

for variability were bensulfuron-methyl, bentazon, bromacil, bromoxynil, chloramben methyl ester, chlorimuron-ethyl, cycloate, flumetsulam, imazaquin, imazethapyr, metsulfuron-methyl, nicosulfuron, and norflurazon. F-pseudosigmas on LRS recoveries ranged from 27 to 50 percent.

Variability results for pesticide samples analyzed at the PADEPL:

- Using the median RSDs calculated from concentrations of pesticides in triplicate FSRW samples for 20 pesticides analyzed at the PADEPL (table 2-2, appendix 2) (surrogates not included in count), the goal for variability was met for all pesticides analyzed that could be evaluated. The exception was captan—no concentrations were reported in the spiked samples above the MRL. Captan, therefore, was not qualified based on the variability in LRS (37 percent). Using the F-pseudosigma statistic calculated for samples analyzed at the PADEPL for individual compound recoveries, the goal was also met for all pesticides analyzed except azinphos-methyl (F-pseudosigma for this compound was 78 percent).
- For the three pesticides that were not included in FSRW samples analyzed at the PADEPL—dichlobenil, fenpropathrin, and phosmet. F-pseudosigmas for LRS recoveries for fenpropathrin (36 percent) and phosmet (47 percent) did not meet project objectives (table 2-2).

Variability results for pesticide samples analyzed at the OGRL:

- For the 10 pesticides in the triplicate FSRW samples sent to the USGS OGRL, only concentrations of linuron had a calculated RSD that did not meet QA objective 5 (44 percent). RSDs for all other compounds ranged from 0 to 24 percent.

Variability results for nitrate and nitrite samples analyzed at the NWQL and PADEPL:

- For nitrate and nitrite, the QA objective was met 100 percent of the time. Median RSDs of nitrate and nitrite replicate concentrations ranged from 0 to 2 percent and F-pseudosigmas of nitrate and nitrite recoveries ranged from 1 to 5 percent.

Variability results for total coliform and E. coli results analyzed at the PADEPL:

- For total coliform bacteria, a median RSD of 25 percent for well-water replicate samples met the QA objective for variability. Variability in *E. coli* results could not be evaluated because of infrequent detections in the samples submitted.

Qualifying Sample Results Based on Quality-Assurance Objectives

Estimates of bias and variability in reported concentrations (table 2-2) were used to ‘qualify’ selected results because QA objectives 4 and (or) 5 were not met. ‘Qualified’ concentrations may substantially differ from the true environmental concentrations because of poor performance of bias and variability using either field-submitted QC samples and (or) internally submitted laboratory QC samples. The effects of environmental-water chemistry in the respective well-water sample may increase or decrease bias and variability for individual compounds.

PADEPL—Twenty-three pesticides were analyzed at the PADEPL (table 6). Of these pesticide compounds, results for azinphos-methyl, captan, fenpropathrin, hexachlorocyclopentadiene, metribuzin, and phosmet were qualified on the basis of the results of six to nine project-submitted QC samples and (or) internally submitted QC samples. No reported concentrations in environmental samples were above the respective MRLs for any of these seven compounds when analyzed by the PADEPL, and it is possible, therefore, that some of the results reported as less than the MRLs are actually false negatives.

USGS NWQL—Of the 107 pesticide compounds analyzed at the NWQL, 48 compounds did not have results that met project QA objectives; the results for these compounds were qualified. Qualified compounds include those 39 compounds previously identified as permanently “Estimated” (one of several reasons concentrations are flagged with an “E” qualifier in the National Water Information System [NWIS] database) (based on internally submitted QC-sample results) (tables 7 and 8), and ethalfluralin, metribuzin, p,p’-DDE, and propargite were qualified as a result of 33 project-submitted QC-sample results. Results for five other pesticides were also qualified, 2,4-DB, bendiocarb, clopyralid, MCPB, and sulfometuron-methyl, which were not qualified as estimated in 2003 but which had internally submitted QC-sample results that did not meet project QA objectives. Of the 48 compounds, CIAT was reported above the MRL in 81 samples. Ten or fewer environmental samples had reported concentrations of terbacil, carbofuran, carbaryl, benomyl, deisopropylatrazine (CEAT), CAAT, dinoseb, norflurazon, and sulfometuron-methyl. The other qualified compounds were not reported above the respective MRLs in any of the samples analyzed; it is possible that some of the results were actually false negatives.

USGS OGRL—Of the 54 pesticide compounds analyzed at the USGS OGRL (table 9), 10 pesticide compounds (acetochlor, alachlor, metolachlor, propachlor, atrazine, cyanazine, prometon, simazine, CIAT, and linuron) were submitted in four project-submitted QC samples for evaluation of bias and variability (table 2-3). All compounds but linuron (RSD was 44 percent) met project QA goals for variability (no environmental samples had concentrations above the MRL), and all compounds but atrazine, prometon, simazine, and CIAT (low recoveries ranging from 62 to 74 percent) met project goals for bias (concentrations were reported above the MRLs). Linuron, atrazine, prometon, simazine, and CIAT results are noted as not meeting project QA goals but were not qualified because of the low numbers of project-submitted QC samples and the lack of long-term QC results for comparison.

Pesticides in Ground Water for the Baseline Assessment of Hydrogeologic Settings, 2003–07

Well-water samples were collected for the baseline assessment of hydrogeologic settings to identify occurrence and concentrations of pesticides in ground water from settings where few or no previous sample analyses for pesticides were available (Lindsey and Bickford, 1999). The following section describes the results from samples for 2003–07 (appendix 3).

Blue Ridge Crystalline and Triassic Lowland Siliciclastic

Twenty rural domestic wells were sampled in the Blue Ridge crystalline and Triassic Lowland siliciclastic setting in 2003. Of these 20 wells, 13 were in the Blue Ridge crystalline part of the setting, and 7 were in the western boundary of the Triassic Lowland siliciclastic part of the setting. Ten of the wells were randomly sampled in May 2003, and these samples were analyzed at the USGS NWQL (tables 7 and 8; MRLs ranged from 0.002 to 1.5 µg/L). The remaining 10 well samples were collected in August through September 2003; these samples were analyzed at the PADEPL (table 6; MRLs ranged from 0.10 to 1.6 µg/L). The MRLs are, therefore, higher for analyses completed at the PADEPL (table 6); fewer compounds were analyzed at the PADEPL than at the USGS NWQL (tables 7 and 8). The results presented for this setting should be considered relative to these two issues. No concentrations of pesticides were above 0.10 µg/L (1.6 µg/L for carbaryl, oxamyl, and methomyl) in samples analyzed at the PADEPL. The well locations in Cumberland County and Adams County, Pa., and laboratories used for analyses of respective samples are shown in figure 8. For the Blue Ridge crystalline and Triassic Lowland siliciclastic setting, the number of samples with pesticide detections are shown in table 12.

Concentrations of pesticides in samples collected in this setting are shown in table 13. Six wells had water with concentrations of one or more pesticides at or above the MRLs. Three well-water samples had only 1 pesticide with a concentration equal to or above the respective MRL (wells CU 951, AD 1160, and AD 1162); well AD 1159 had 2 co-occurring pesticides, well AD 1161 had 8 co-occurring pesticides, and well AD 1155 had 16 co-occurring pesticides. The herbicide 2,4-D had the greatest concentration in this setting (E 2.52 µg/L) followed by 2,4-D methyl ester (0.663 µg/L). CEAT and CAAT (degradation products of atrazine and simazine) were analyzed at the NWQL for 10 samples in the Triassic Lowland siliciclastic setting only; one sample had reported concentrations of CEAT of E 0.17 µg/L and CAAT of E 0.25 µg/L even though the concentration of atrazine and CIAT were both less than 0.10 µg/L (table 13). Atrazine and (or) degradates of atrazine and simazine were present in water from five of the six wells at concentrations above the MRLs.

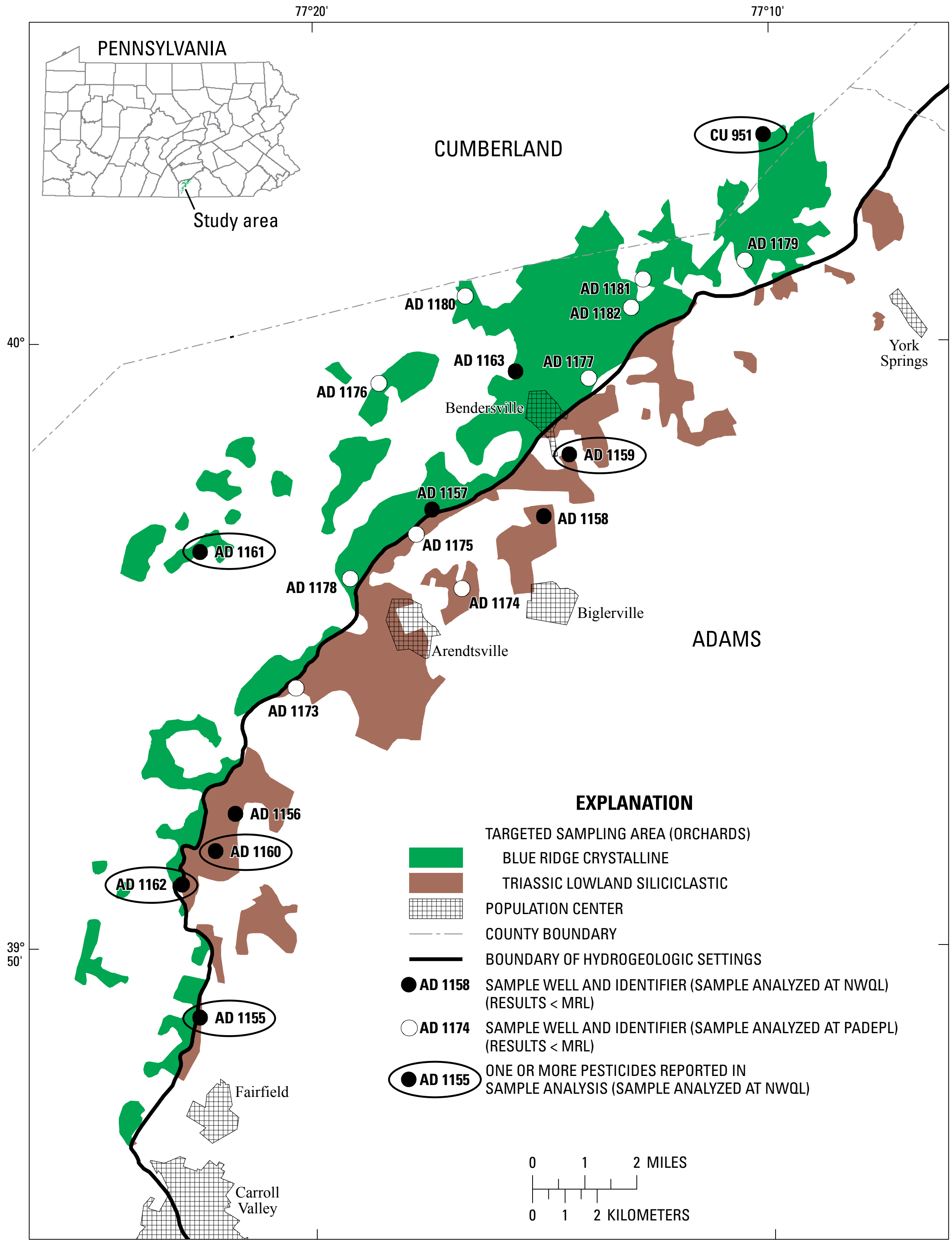
Eastern Lake Surficial

Twenty rural domestic wells were sampled in the Eastern Lake surficial setting (Erie County, Pa.) from May through August 2004 (fig. 9). Because of an analyst error, the sample extract for one sample (well ER 3506) was lost during preparation. This well was resampled in October 2004. The PADEPL in Harrisburg, Pa., analyzed all samples collected in 2004.

To test well water for pesticide compounds commonly used in grape-growing regions such as the Eastern Lake surficial setting, the PADEPL analyzed samples for four additional compounds (dichlobenil, fenpropathrin, and trifluralin, all with MRLs of 0.10 µg/L, and phosmet, MRL of 1.0 µg/L); therefore, each sample was analyzed for 23 pesticide compounds.

No concentrations of pesticides were above the MRLs (table 6) for any of the 20 well-water samples from the Eastern Lake surficial setting. The low number of reported concentrations may be at least partially explained by the greater PADEPL pesticide MRLs compared to those at the NWQL and the lower number of compounds analyzed at the PADEPL. Additionally, results from the QA samples submitted as FSRW samples in April and June 2004 indicated a negative bias in pesticide recoveries that may characterize the samples submitted the first month of sampling (May) and the entire month of June when samples were analyzed at the PADEPL. Whereas the April and June spikes showed an overall negative bias, the July spikes showed a positive bias with recoveries as high as 260 percent. No FSRW samples were submitted in August to evaluate PADEPL pesticide recoveries.

In addition to the variability bias in recovery, MRLs increased in 2004 for azinphos-methyl (from 0.10 to 0.50 µg/L), phosphamidon (from 0.10 to 0.25 µg/L), and the carbamates, carbaryl, oxamyl, and methomyl (from 1.6 to 2.0–5.0 µg/L). For well ER 3509, analyses for carbaryl, methomyl, and oxamyl were cancelled (per PADEPL report; unknown reason); therefore, no results are available for these compounds. The MRLs for phosphamidon and azinphos-methyl were later reevaluated by PADEPL and set at 1.0 µg/L (Martina McGarvey, Director, Pennsylvania Department



Population center and county boundary from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Targeted sampling area and boundary of hydrogeologic setting from Lindsey and Bickford, 1999
and USGS Multi-Resolution Land Characteristics Data, 2001

Albers Equal-Area Conic projection:
standard parallels 29°30'N and 45°30'N.
Central meridian 77°45'W, latitude of origin 23°00'N

Figure 8. Locations of wells sampled for pesticide analysis and wells with reported concentrations above the minimum reporting levels in the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting, Adams and Cumberland Counties, Pennsylvania, May and August 2003. Minimum reporting levels (MRLs) at the Pennsylvania Department of Environmental Protection Laboratory (PADEPL) ranged from 0.10 to 1.6 µg/L, and MRLs at the U.S. Geological Survey National Water Quality Laboratory (NWQL) ranged from 0.002 to 1.5 µg/L. The notation < MRL indicates no pesticides were reported at concentrations at or above the MRL.

Table 12. Numbers of samples with no pesticides detected below the minimum reporting level and with concentrations of pesticides detected in samples collected in subareas of the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting of Pennsylvania, 2003.

[NWIS, National Water Information System; NWQL, U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; PADEPL, Pennsylvania Department of Environmental Protection Laboratory in Harrisburg, Pa.; µg/L, micrograms per liter; MDL, method detection limit; MRL, minimum reporting level; E(1), estimated values reported for compound because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; –, pesticide concentrations not reported between or below this range; <, less than; ≥, greater than or equal to; NA, not available]

Compound	NWIS parameter code	Lab used	Number of samples sent to lab	MDL, in µg/L	MRL, in µg/L	Number of samples having concentrations			
						< MRL	Estimated < MRL	≥ MRL to < 0.01 µg/L	≥ 0.01 µg/L
Blue Ridge crystalline/Triassic Lowland siliciclastic (Year 1)									
Atrazine	39632	NWQL	10	0.004	0.007	7	0	1	2
	39632	PADEPL	10	.07	.10	10	–	–	0
CIAT[1], E(1)	04040	NWQL	10	.003	.006	7	0	2	1
CEAT[1], E(1)	04038	NWQL	10	NA	.044	8	0	0	2
CAAT[1], E(1)	04039	NWQL	10	NA	.01	6	0	0	4
Metolachlor	39415	NWQL	10	.006	.013	8	2	0	0
	39415	PADEPL	10	.10	.10	10	–	–	0
Diuron	49300	NWQL	10	NA	.015	7	1	0	2
Simazine	04035	NWQL	10	.002	.005	9	0	0	1
	04035	PADEPL	10	.10	.10	10	–	–	0
Benomyl, E(1)	50300	NWQL	10	NA	.004	8	0	1	1
2,4-D	39732	NWQL	10	NA	.022	9	0	0	1
2,4-D methyl ester	50470	NWQL	10	NA	.009	9	0	0	1
Carbaryl	49310	NWQL	10	.014	.028	9	1	0	0
	49310	PADEPL	10	.338	1.6	10	–	–	0
Dinoseb	49301	NWQL	10	NA	.012	9	1	0	0
Imidacloprid	61695	NWQL	10	NA	.007	9	1	0	0
Metalaxyl	50359	NWQL	10	NA	.02	9	1	0	0
Norflurazon, E(1)	49293	NWQL	10	NA	.016	9	0	0	1
Prometon	04037	NWQL	10	.007	.015	9	0	0	1
Sulfometuron-methyl	50337	NWQL	10	NA	.009	9	1	0	0

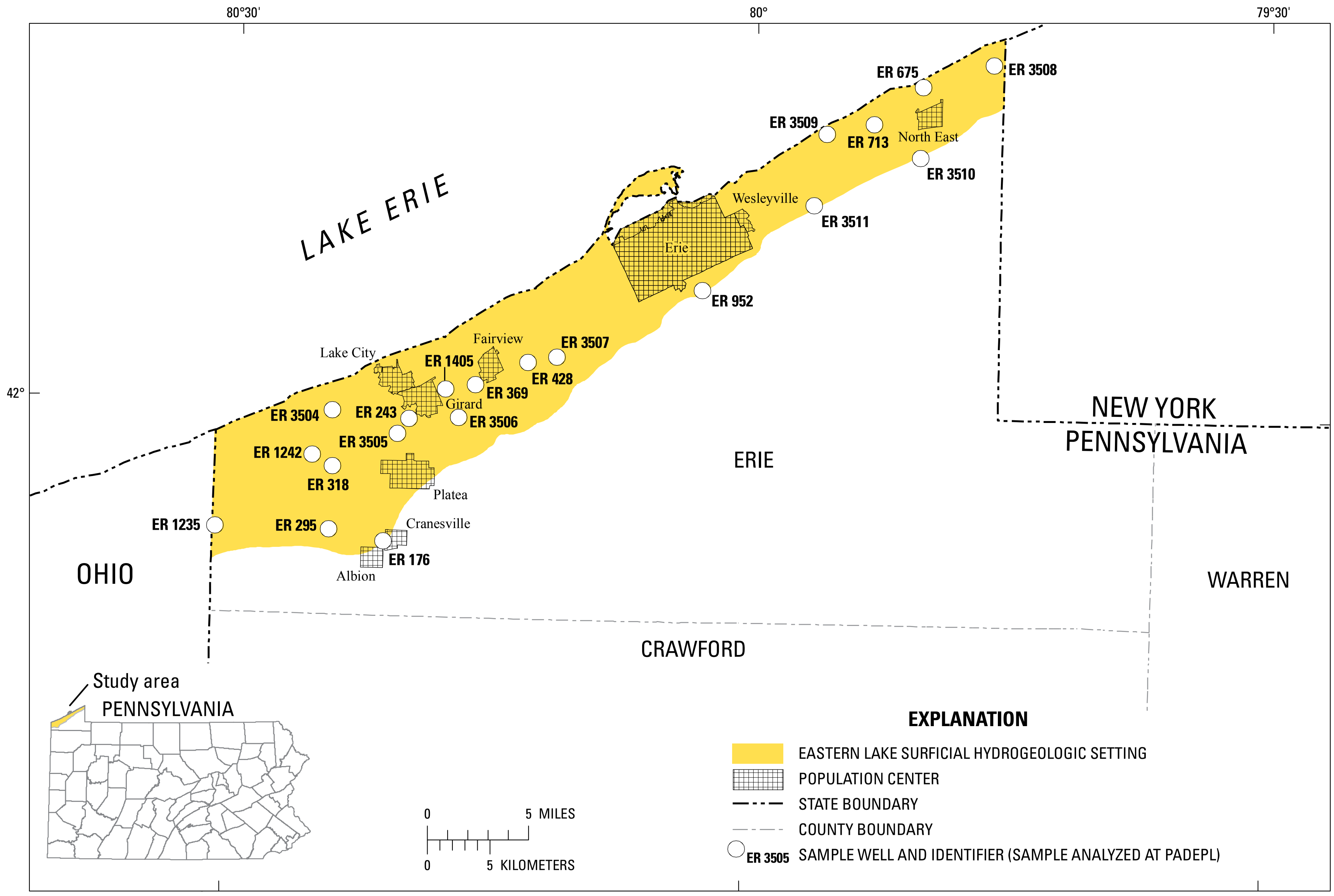
[1] Degradation products: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040); CEAT, 2-chloro-6-ethylamino-4-amino-s-triazine or deisopropylatrazine (NWIS parameter code 04038); CAAT, 2-chloro-4, 6-diamino-s-triazine or deethyldeisopropylatrazine (NWIS parameter code 04039).

Table 13. Local well numbers and concentrations of pesticides in samples collected in subareas of the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting of Pennsylvania, 2003.

[All pesticide results are from analyses completed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; samples for these wells were collected in May 2003; all concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit, if established, but less than the minimum reporting level; E(3), estimated because the value is below the long-term method detection limit; E(4), estimated because value was above highest calibration standard [1.0 µg/L]; <, less than; µg/L, micrograms per liter; MRL, minimum reporting level; –, concentration less than the MRL but not estimated; NWIS, National Water Information System]

Local well no.	Concentration, in µg/L																
	Atrazine	CIAT[1]	CEAT[1]	CAAT[1]	Metolachlor	Diuron	Simazine	Benomyl	2,4-D methyl ester	2,4-D	Carbaryl	Dinoseb	Imidacloprid	Metalaxyl	Norflurazon	Prometon	Sulfometuron-methyl
MRL	< 0.007	< 0.006	< 0.044	< 0.01	< 0.013	< 0.015	< 0.005	< 0.004	< 0.009	< 0.022	< 0.028	< 0.012	< 0.007	< 0.02	< 0.016	< 0.015	< 0.009
CU 951	–	–	–	–	–	**.03**	–	–	–	–		–	–	–	–	–	–
AD 1159	**.011**	**.007** E(1)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
AD 1161	**.007**	**.007** E(1)	**.17** E(1)	**.25** E(1)	**.004** E(3)	**.01** E(2)	**.151**	**.005** E(1)	–	–	–	–	–	–	–	–	–
AD 1160	–	–	–	**.01** E(1)	–	–	–	–	–	–	–	–	–	–	–	–	–
AD 1162	–	–	–	**.01** E(1)	–	–	–	–	–	–	–	–	–	–	–	–	–
AD 1155	**.040**	**.085** E(1)	**.11** E(1)	**.02** E(1)	**.008** E(2)	**.19**	–	**.026** E(1)	**.663**	**2.52** E(4)	**.007** E(3)	**.01** E(2)	**.006** E(2)	**.004** E(2)	**.15** E(2)	**.03**	**.006** E(2)

[1] Degradation products: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040); CEAT, 2-chloro-6-ethylamino-4-amino-s-triazine or deisopropylatrazine (NWIS parameter code 04038); CAAT, 2-chloro-4, 6-diamino-s-triazine or deethyldeisopropylatrazine (NWIS parameter code 04039).



State boundary from U.S. Geological Survey, 2005
Population centers, county and township boundaries from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Eastern Lake hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 9. Locations of wells sampled for pesticide analysis in the Eastern Lake surficial hydrogeologic setting, Erie County, Pennsylvania, May–October 2004. Minimum reporting levels at the Pennsylvania Department of Environmental Protection Laboratory (PADEPL) ranged from 0.10 to 5.0 µg/L. There were no reported concentrations above the minimum reporting levels.

of Environmental Protection Laboratory, written commun., 2007).

The results reported from the Eastern Lake surficial setting are, therefore, limited largely by the greater PADEPL MRLs (compared to those at the NWQL) and cannot be directly compared to numbers of samples with reported concentrations from the Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial hydrogeologic settings where analytical work was completed at the USGS NWQL.

Devonian-Silurian Carbonate

Well water was collected and analyzed from 28 rural domestic wells between June and August 2005 in the Devonian-Silurian carbonate setting. All well-water samples and most of the QC samples for pesticides were analyzed at the USGS NWQL for a suite of 52 pesticides (table 7). For the Devonian-Silurian carbonate setting, the numbers of samples with pesticide detections are shown in table 14. In this setting, only well JU 373 had a concentration below the MRL (atrazine, at E 0.004 µg/L); all other detections of compounds were above the respective MRLs. All the wells in this setting with concentrations above the MRLs had one or more pesticides with concentrations above 0.01 µg/L but less than 0.10 µg/L; 0.10 µg/L is the lowest MRL for pesticides analyzed at the PADEPL. Well locations and wells with concentrations of pesticides reported above and below the MRLs are shown in figure 10.

Sixteen wells had one or more pesticides reported in well-water samples (table 15). Fifteen of these wells showed co-occurrence of atrazine and CIAT, a degradate of atrazine. Three of these 15 wells also had measurable concentrations of simazine, and 1 of the 15 wells had a co-occurrence of metolachlor. Only one well (well JU 271) had a concentration of a single pesticide, acetochlor, at a concentration of 0.029 µg/L (table 15).

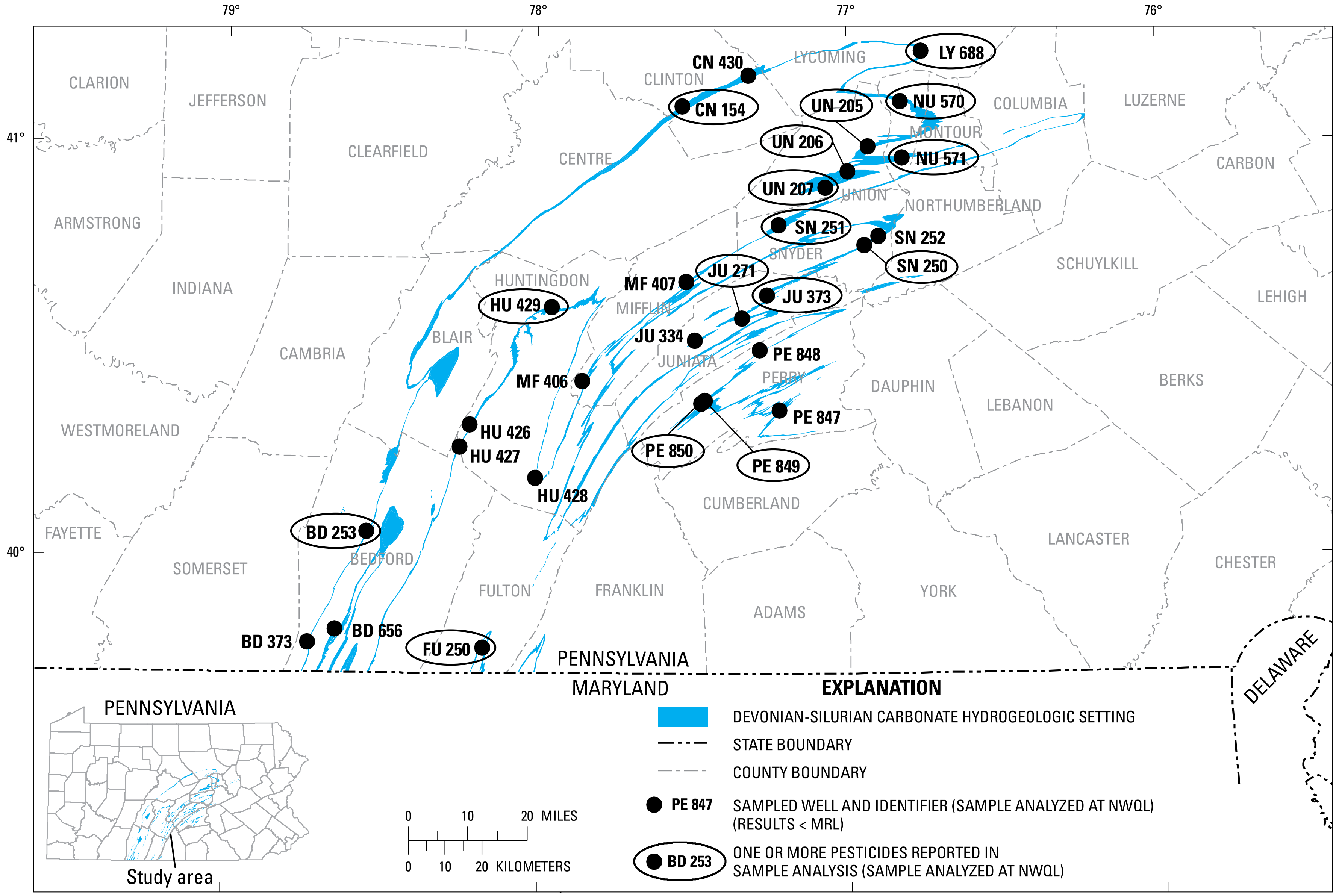
Maximum concentrations of atrazine and CIAT were 0.054 µg/L (well UN 205) and E 0.062 µg/L (well HU 429), respectively. Well HU 429 also had the maximum combined concentration of all pesticides reported (as mass per volume [µg/L] and not normalized to moles per volume)–0.114 µg/L, followed by well LY 688 (0.109 µg/L) and well UN 206 (0.104 µg/L). Median recoveries in LRS water samples in 2005 for atrazine (105 percent), metolachlor (103 percent), and simazine (99 percent) were ± 5 percent of the ‘true’ (100 percent) recovery; assuming negligible interferences from environmental-water chemistry, concentrations of these herbicides in well-water samples are accurate. CIAT, however, had a median recovery of 34 percent in a LRS sample in 2005; therefore, the actual concentrations could be greater than that reported in well-water samples.

Table 14. Number of samples with no pesticides detected below the minimum reporting levels and with concentrations of pesticides detected in samples collected in the Devonian-Silurian carbonate hydrogeologic setting of Pennsylvania, 2005.

[NWIS, National Water Information System; NWQL, U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; µg/L, micrograms per liter; MDL, method detection limit; MRL, minimum reporting level; E(1), estimated values reported for compound because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; <, less than; ≥, greater than or equal to]

	Compound				
	Atrazine	CIAT[1], E(1)	Metolachlor	Acetochlor	Simazine
NWIS parameter code	39632	04040	39415	49260	04035
Lab used	NWQL	NWQL	NWQL	NWQL	NWQL
Number of wells sampled	28	28	28	28	28
MDL, in µg/L	0.004	0.003	0.003	0.003	0.002
MRL, in µg/L	.007	.006	.006	.006	.005
Number of samples having concentrations					
< MRL	13	13	27	27	25
Estimated < MRL	1	0	0	0	0
≥ MRL to < 0.01 µg/L	1	1	1	0	1
≥ 0.01 µg/L	13	14	0	1	2

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).



State boundary from U.S. Geological Survey, 2005
County boundary from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Devonian-Silurian carbonate hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 10. Locations of wells sampled for pesticide analysis and wells with reported concentrations above the minimum reporting levels in the Devonian-Silurian carbonate hydrogeologic setting of Pennsylvania, June–August 2005. Minimum reporting levels (MRLs) at the U.S. Geological Survey National Water Quality Laboratory (NWQL) ranged from 0.003 to 0.05 µg/L. The notation < MRL indicates no pesticides were reported at concentrations at or above the MRL.

Table 15. Local well numbers and concentrations of pesticides in samples collected in the Devonian-Silurian carbonate hydrogeologic setting of Pennsylvania, 2005.

[All pesticide results are from analyses completed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; samples for these wells were collected in June–August 2005; all concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; µg/L, micrograms per liter; MRL, minimum reporting level; –, concentration less than the MRL but not estimated; <, less than; NWIS, National Water Information System]

Local well no.	Concentration, in µg/L				
	Atrazine	CIAT[1]	Metolachlor	Acetochlor	Simazine
MRL	< 0.007	< 0.006	< 0.006	< 0.006	< 0.005
BD 253	**.036**	**.035** E(1)	–	–	–
HU 429	**.052**	**.062** E(1)	–	–	–
FU 250	**.008**	**.014** E(1)	–	–	–
PE 850	**.017**	**.014** E(1)	–	–	–
PE 849	**.023**	**.056** E(1)	–	–	**.013**
CN 154	**.016**	**.021** E(1)	–	–	–
SN 251	**.024**	**.015** E(1)	–	–	**.008**
JU 373	**.004** E(2)	**.013** E(1)	–	–	–
JU 271	–	–	–	**.029**	–
SN 250	**.027**	**.033** E(1)	–	–	–
UN 207	**.045**	**.019** E(1)	–	–	–
UN 206	**.052**	**.052** E(1)	–	–	–
NU 571	**.014**	**.032** E(1)	–	–	–
UN 205	**.054**	**.009** E(1)	**.008**	–	–
NU 570	**.032**	**.034** E(1)	–	–	**.010**
LY 688	**.048**	**.061** E(1)	–	–	–

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).

Great Valley Siliciclastic

Thirty rural domestic wells were sampled in the Great Valley siliciclastic setting from June through August 2006. The samples were analyzed for 52 pesticides at the USGS NWQL. For the Great Valley siliciclastic setting, the numbers of samples with pesticide detections are shown in table 16. In this setting, only concentrations of atrazine, CIAT, and simazine were above the MRL (table 17). Simazine was reported at 0.007 µg/L in one sample. Three well-water samples had trace amounts of atrazine under the MRL (less than 0.007 µg/L), and two samples had concentrations above 0.01 µg/L (table 16). CIAT also was detected in three samples below the MRL (less than 0.014 µg/L) and in one sample above 0.01 µg/L. Both napronamide and metolachlor were reported at concentrations less than the respective MRLs. Locations of wells sampled and wells with concentrations of pesticides reported above and below the MRLs are shown in figure 11.

Five well-water samples had reported concentrations of pesticides (table 17). Four of the five wells showed co-occurrence of atrazine and CIAT, and two of these wells had water that included either napropamide or metolachlor and simazine. Maximum concentrations of atrazine and CIAT in the samples collected in the Great Valley siliciclastic setting were 0.025 and E 0.033 µg/L, respectively—both in one sample collected at well NP 828. The sample from this well also had the maximum combined concentration of all pesticides (as mass per volume [µg/L] and not normalized to moles per volume)—0.068 µg/L. Median recoveries in LRS samples for CIAT were low in 2006 (35 percent); therefore, the concentration of CIAT in well NP 828 may actually be greater than that reported.

Table 16. Number of samples with no pesticides detected below the minimum reporting levels and with concentrations of pesticides detected in samples collected in the Great Valley siliciclastic hydrogeologic setting of Pennsylvania, 2006.

[NWIS, National Water Information System; NWQL, U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; µg/L, micrograms per liter; MDL, method detection limit; MRL, minimum reporting level; E(1), estimated values reported for compound because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; –, range not applicable; <, less than; ≥, greater than or equal to]

	Compound				
	Atrazine	**CIAT[1], E(1)**	**Metolachlor**	**Napronamide**	**Simazine**
NWIS parameter code	39632	04040	39415	82684	04035
Lab used	NWQL	NWQL	NWQL	NWQL	NWQL
Number of wells sampled	30	30	30	30	30
MDL, in µg/L	0.004	0.007	0.003	0.003	0.002
MRL, in µg/L	.007	.014	.006	.007	.005
Number of samples having concentrations					
< MRL	25	26	28	29	29
Estimated < MRL	3	3	2	1	0
≥ MRL to < 0.01 µg/L	0	–	0	0	1
≥ 0.01 µg/L	2	1	0	0	0

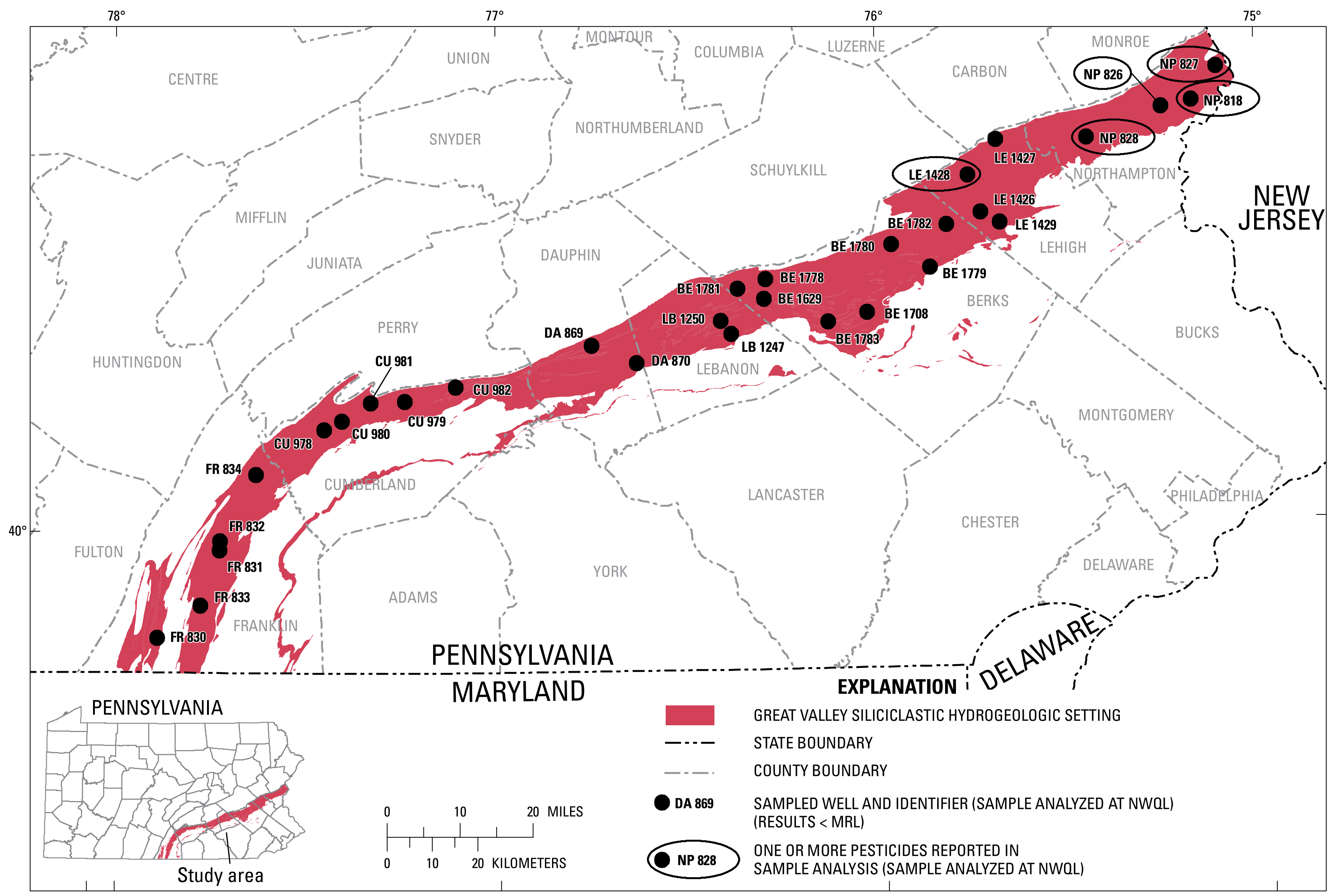
[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).

Table 17. Local well numbers and concentrations of pesticides in samples collected in the Great Valley siliciclastic hydrogeologic setting of Pennsylvania, 2006.

[All pesticide results are from analyses completed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; samples for these wells were collected from June through August 2006; all concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(3), estimated because the value is below the long-term method detection limit; MRL, minimum reporting level; –, concentration less than the MRL but not estimated; <, less than; NWIS, National Water Information System]

Local well no.	Concentration, in micrograms per liter				
	Atrazine	CIAT[1]	Metolachlor	Napronamide	Simazine
MRL	< 0.007	< 0.014	< 0.006	< 0.007	< 0.005
LE 1428	**.003** E(3)	**.002** E(1), E(3)	–	**.004** E(2)	–
NP 828	**.025**	**.033** E(1)	**.003** E(2)	–	**.007**
NP 826	**.002** E(3)	–	**.001** E(3)	–	–
NP 827	**.012**	**.008** E(1), E(2)	–	–	–
NP 818	**.002** E(3)	**.002** E(1), E(3)	–	–	–

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).



State boundary from U.S. Geological Survey, 2005
County boundary from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Great Valley siliciclastic hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 11. Locations of wells sampled for pesticide analysis and wells with reported concentrations above the minimum reporting levels in the Great Valley siliciclastic hydrogeologic setting of Pennsylvania, June–August 2006. Minimum reporting levels (MRLs) at the U.S. Geological Survey National Water Quality Laboratory (NWQL) ranged from 0.003 to 0.055 µg/L. The notation < MRL indicates no pesticides were reported at concentrations at or above the MRL.

Northeastern Glaciated Surficial

Twenty-eight wells were sampled in the Northeastern Glaciated surficial setting from May through September 2007. Of these wells, 7 were used for public-water supply, 3 were used for commercial supply, 1 was used for fire-protection supply, and 17 were used for rural domestic supply. The samples were analyzed for 52 pesticides at the USGS NWQL. The numbers of samples with pesticide detections are shown in table 18. In this setting, seven samples had concentrations above the MRL for atrazine, and three samples had concentrations above the MRL for CIAT. The remainder of the concentrations reported for atrazine, CIAT, metolachlor, and simazine were estimated values less than the MRL. Locations of wells sampled and wells with concentrations of pesticides reported above and below the MRLs are shown in figure 12.

Sixteen of the 28 well-water samples had reported concentrations of pesticides (table 19). Three wells (LY 691, LY 692, and WY 196) had estimated concentrations of only one pesticide—CIAT. Thirteen samples had co-occurrence of atrazine and CIAT; 5 of these samples also had concentrations of metolachlor and (or) simazine (table 19). Five of seven samples from production wells had co-occurrence of two or more pesticides; however, concentrations were 0.012 µg/L or less.

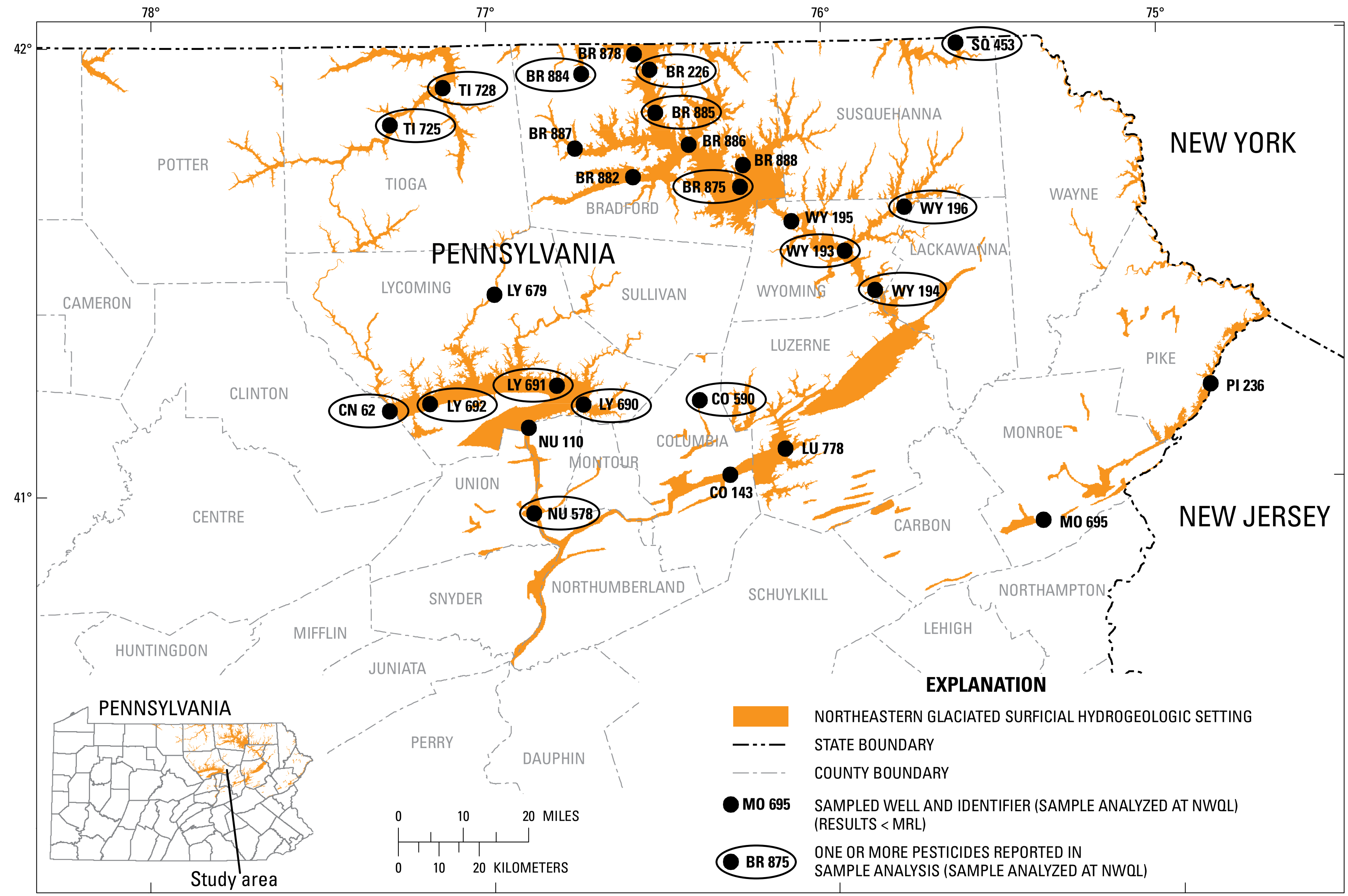
Maximum concentrations of atrazine and CIAT in the Northeastern Glaciated surficial setting were 0.064 µg/L (well LY 690) and E 0.025 µg/L (well BR 884), respectively (table 19). The sum of concentrations of all pesticides from these two wells were similar (as mass per volume [µg/L] and not normalized to moles per volume)—0.089 µg/L for well BR 884 and 0.085 µg/L for well LY 690. Combined reported concentrations for all other wells were 0.030 µg/L or less.

Table 18. Numbers of samples with no pesticides detected below the minimum reporting levels and with concentrations of pesticides detected in samples collected in the Northeastern Glaciated surficial hydrogeologic setting of Pennsylvania, 2007.

[NWIS, National Water Information System; NWQL, U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; samples for these wells were collected from May through September 2007; E(1), estimated values reported for compound because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; µg/L, micrograms per liter; MDL, method detection limit; MRL, minimum reporting level; –, range not applicable; <, less than; ≥, greater than or equal to]

	Compound			
	Atrazine	**CIAT[1], E(1)**	**Metolachlor**	**Simazine**
NWIS parameter code	39632	04040	39415	04035
Lab used	NWQL	NWQL	NWQL	NWQL
Number of wells sampled	28	28	28	28
MDL, in µg/L	0.004	0.007	0.005	0.003
MRL, in µg/L	.007	.014	.01	.006
Number of samples having concentrations				
< MRL	15	12	25	25
Estimated < MRL	6	13	3	3
≥ MRL to < 0.01 µg/L	3	–	–	0
≥ 0.01 µg/L	4	3	0	0

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).



State boundary from U.S. Geological Survey, 2005
County boundary from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Northeastern Glacial hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 12. Locations of wells sampled for pesticide analysis and wells with reported concentrations above the minimum reporting levels in the Northeastern Glaciated surficial hydrogeologic setting of Pennsylvania, May–September 2007. Minimum reporting levels (MRLs) at the U.S. Geological Survey National Water Quality Laboratory (NWQL) ranged from 0.003 to 0.08 µg/L. The notation < MRL indicates no pesticides were reported at concentrations at or above the MRL.

Table 19. Local well numbers and concentrations of pesticides in samples collected in the Northeastern Glaciated surficial hydrogeologic setting of Pennsylvania, 2007.

[All pesticide results are from analyses completed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colo.; samples for these wells were collected from May through September 2007; all concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(3), estimated because the value is below the long-term method detection limit; MRL, minimum reporting level; –, concentration less than the MRL but not estimated; <, less than; NWIS, National Water Information System]

Local well no.	Concentration, in micrograms per liter			
	Atrazine	CIAT[1]	Metolachlor	Simazine
MRL	< 0.007	< 0.014	< 0.010	< 0.006
[2]CN 62	**.007**	**.004** E(1), E(3)	**.003** E(3)	–
LY 692	–	**.003** E(1), E(3)	–	–
TI 725	**.004** E(2)	**.002** E(1), E(3)	–	–
[2]TI 728	**.002** E(3)	**.002** E(1), E(3)	–	**.004** E(2)
BR 884	**.061**	**.025** E(1)	**.003** E(3)	–
LY 691	–	**.006** E(1), E(3)	–	–
LY 690	**.064**	**.021** E(1)	–	–
[2]NU 578	**.002** E(3)	**.008** E(1), E(2)	–	–
CO 590	**.008**	**.006** E(1), E(3)	–	**.002** E(3)
[2]BR 885	**.012**	**.008** E(1), E(2)	–	–
[2]BR 226	**.008**	**.005** E(1), E(3)	**.002** E(3)	**.002** E(3)
BR 875	**.004** E(2)	**.011** E(1), E(2)		
WY 194	**.010**	**.020** E(1)	–	–
WY 193	**.003** E(3)	**.013** E(1), E(2)	–	–
WY 196	–	**.002** E(1), E(3)	–	–
SQ 453	**.004** E(2)	**.003** E(1), E(3)	–	–

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).

[2] Production well.

Correlating Pesticide Occurrence with Other Indicators of Water-Quality Degradation

Statistical analysis was used to investigate the strength of the relations among pesticide occurrence and two indicators of water-quality degradation—occurrence of bacteria and nitrate concentration.

To test the relation between pesticide and bacteria occurrence, a 2 × 2 contingency-table analysis was used to determine associations between the two nominal categorical variables (Helsel and Hirsch, 2002, p. 378). For this analysis, the categorical variables were the presence/absence of total coliform bacteria and the presence/absence of the pesticides atrazine or metolachlor above the MRLs in analyses of ground water by the USGS NWQL. In order for the standard chi-square test to be valid, each of the four categories of the contingency table must have an expected number of observations greater than one and at least 80 percent of the categories must have an expected number of observations greater than five (Helsel and Hirsch, 2002). These criteria were not met; hence, the Fisher's exact test (Uitenbroek, 1997) was used because the probability (p) value is accurate for all sample sizes. A significance level of 0.05 was used (p less than or equal to 0.05).

The results of the contingency-table analysis (fig. 13) indicated a significant relation between the presence or absence of atrazine or metolachlor and the presence or absence of bacteria in the Blue Ridge crystalline and Triassic Lowland siliciclastic setting ($p = 0.0333$). Relations for the Devonian-Silurian carbonate, Great Valley siliciclastic, or Northeastern Glaciated surficial settings were not significant ($p > 0.05$). The Eastern Lake surficial setting was excluded from testing because none of the 20 samples from the setting were analyzed for atrazine and metolachlor at the USGS NWQL.

To evaluate if there was a linear association between 1) number of pesticides above the MRLs and nitrate concentration, and 2) atrazine concentration and nitrate concentration (figs. 14 and 15, respectively), Spearman's rank correlation was used. Spearman's rank method can be used when both variables have a substantial number of non-detected values (Helsel and Hirsch, 2002) and involves ranking each variable separately and then calculating the Spearman's rank correlation coefficient for the ranks (Ott, 1993); all non-detected values are assigned the lowest rank value. Alpha levels and Spearman's rho statistics from the Spearman's rank correlation indicate the statistical significance of the association and the strength of the association, respectively. For this analysis, an alpha of 0.05 was used, and, therefore, if the probability generated from the Spearman's correlation is less than 0.05, there is a 95-percent chance that a mathematical association is present between the variables. Spearman's rho values can range from zero to one; the closer the Spearman's rho is to a value of one, the greater the strength of the association. The rank correlation used data from the Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial settings with SAS software (SAS Institute, 1990). Data from samples collected in the Eastern Lake surficial and Blue Ridge crystalline and Triassic Lowland siliciclastic settings were not analyzed because all or part of the samples were analyzed at the PADEPL where MRLs were greater than USGS NWQL MRLs. The greatest atrazine MRL used for collective work done in the Blue Ridge crystalline and Triassic Lowland siliciclastic setting was 0.10 µg/L where 10 samples were analyzed at the PADEPL (MRL for atrazine was < 0.10 µg/L; a suite of 18 pesticides analyzed) and 10 samples were analyzed at the NWQL (MRL for atrazine was < 0.007 µg/L; a suite of 115 pesticides analyzed).

Results of the Spearman's rank correlation showed strong correlations between the number of pesticides above the MRLs and nitrate concentration (rho = 0.85 and $p < 0.0001$) and between concentrations of atrazine and nitrate (rho = 0.88 and $p < 0.0001$) in the Devonian-Silurian carbonate setting. The relation between concentrations of atrazine and nitrate in the Great Valley siliciclastic setting was statistically significant (rho = 0.53 and $p = 0.0025$). There were no statistically significant relations in the Great Valley siliciclastic (rho = 0.35 and $p = 0.0597$) or Northeastern Glaciated surficial (rho = 0.06 and $p = 0.7672$) hydrogeologic settings between number of pesticides above the MRLs and nitrate concentration or in the Northeastern Glaciated surficial setting between concentrations of atrazine and nitrate (rho = 0.19 and $p = 0.3358$).

Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting, 2003		
N = 10	**One-sided p-value for p (Observed ≥ Expected) = 0.0333**	
	Number of samples with TC bacteria present	**Number of samples with TC bacteria absent**
Number of samples with Atrz or Metol present above the MRLs	3	0
Number of samples with Atrz or Metol absent above the MRLs	1	6

Devonian-Silurian carbonate hydrogeologic setting, 2005		
N = 27	**One-sided p-value for p (Observed ≥ Expected) = 0.2928**	
	Number of samples with TC bacteria present	**Number of samples with TC bacteria absent**
Number of samples with Atrz or Metol present above the MRLs	11	3
Number of samples with Atrz or Metol absent above the MRLs	8	5

Great Valley siliciclastic hydrogeologic setting, 2006		
N = 30	**One-sided p-value for p (Observed ≥ Expected) = 0.6483**	
	Number of samples with TC bacteria present	**Number of samples with TC bacteria absent**
Number of samples with Atrz or Metol present above the MRLs	1	1
Number of samples with Atrz or Metol absent above the MRLs	11	17

Northeastern Glaciated surficial hydrogeologic setting, 2007		
N = 28	**One-sided p-value for p (Observed ≥ Expected) = 0.8077**	
	Number of samples with TC bacteria present	**Number of samples with TC bacteria absent**
Number of samples with Atrz or Metol present above the MRLs	3	4
Number of samples with Atrz or Metol absent above the MRLs	11	10

EXPLANATION

TC, Total Coliform; Atrz, Atrazine; Metol, Metolachlor; MRL, minimum reporting level; N, number of samples.

p-value is the test statistic, and a p-value of 0.05 or less is significant at the 95 percent confidence level.

Atrazine MRL is less than 0.007 micrograms per liter

Metolachlor MRL is less than 0.006 to 0.013 micrograms per liter

Figure 13. Contingency table (2 × 2) and one-sided p-values resulting from Fischer's Exact Test for the same or stronger associations (Uitenbroek, 1997) from four hydrogeologic settings, Pennsylvania, 2003 and 2005–07, to determine relation of presence or absence of pesticides (by use of occurrence of atrazine or metolachlor in ground-water samples at or above the minimum reporting level concentrations as measured by the USGS National Water Quality Laboratory) and presence or absence of total coliform bacteria in ground-water samples.

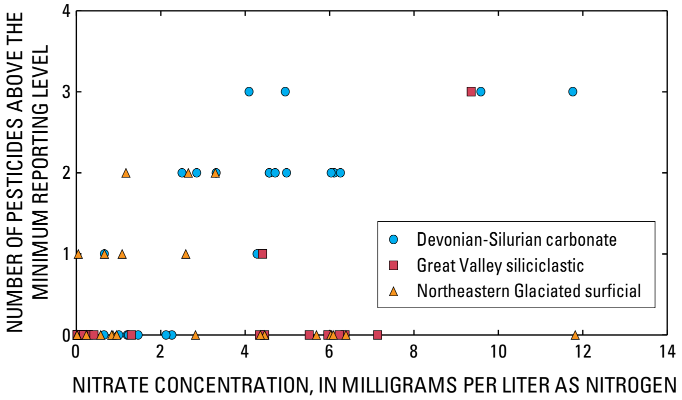


Figure 14. The relation between numbers of pesticides above the minimum reporting level and nitrate concentration in well-water samples collected in the Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial hydrogeologic settings of Pennsylvania. Pesticide analyses for these settings were completed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL). Data from the Eastern Lake surficial and Blue Ridge crystalline and Triassic Lowland siliciclastic settings are not shown because all or part of the samples were analyzed at the Pennsylvania Department of Environmental Protection Laboratory where minimum reporting levels (MRLs) were greater than MRLs at the USGS NWQL.

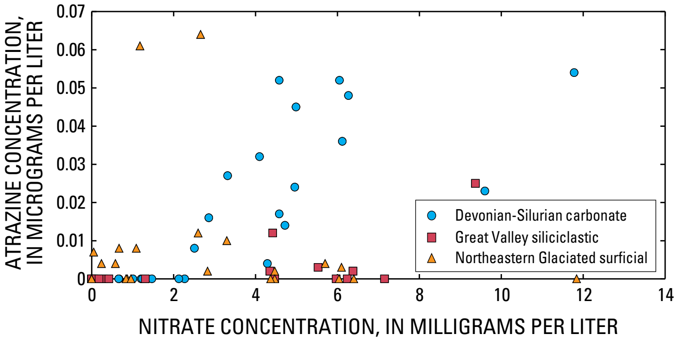


Figure 15. The relation between concentrations of atrazine and nitrate in well-water samples collected in the Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial hydrogeologic settings of Pennsylvania. Pesticide analyses for these settings were completed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL). Data from the Eastern Lake surficial and Blue Ridge crystalline and Triassic Lowland siliciclastic settings are not shown because all or part of the samples were analyzed at the Pennsylvania Department of Environmental Protection Laboratory where minimum reporting levels (MRLs) were greater than MRLs at the USGS NWQL.

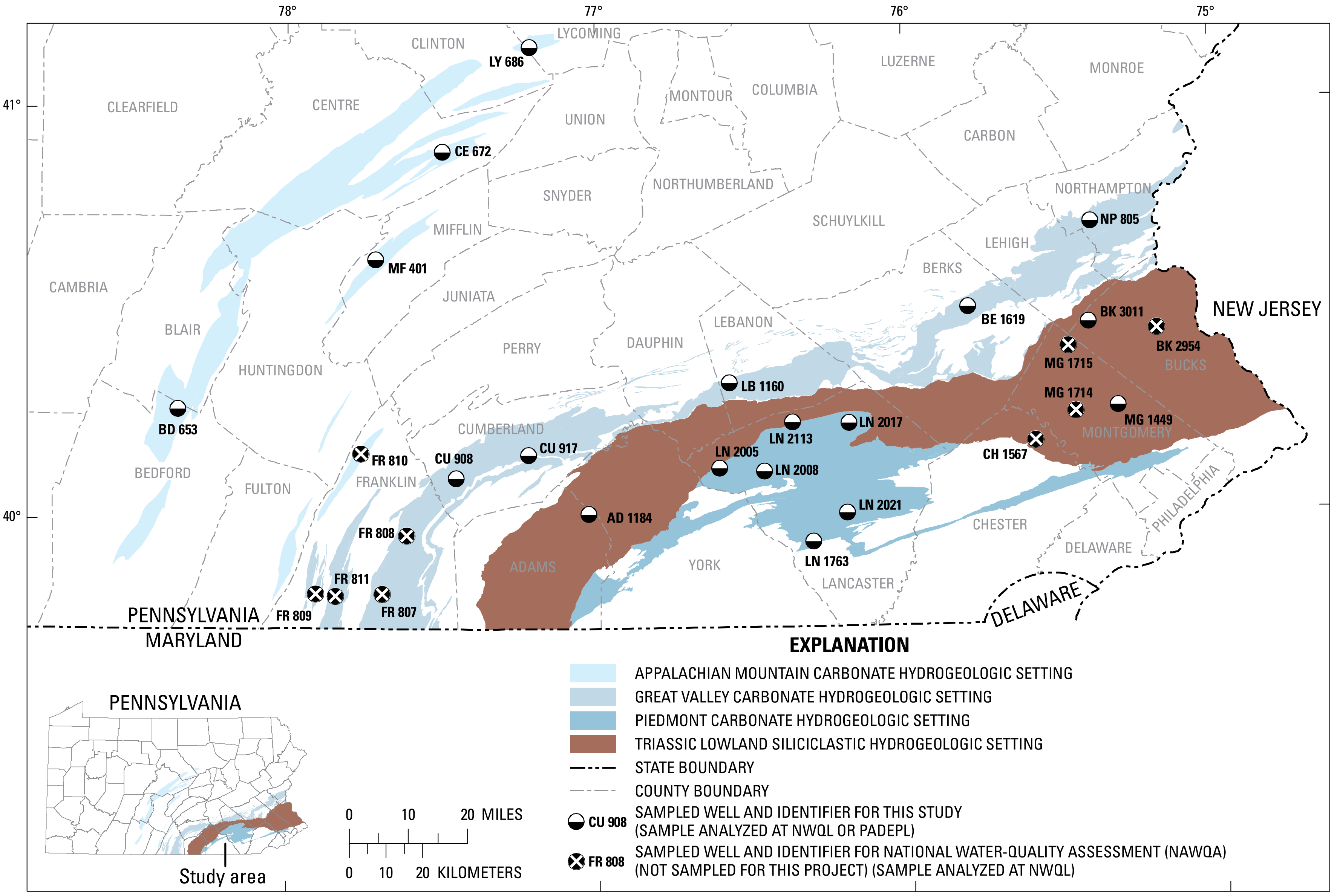
Trend Assessments

Pesticide Concentration Changes for Selected Wells in Baseline-Assessment Areas

Several wells have been sampled in Pennsylvania as part of this project and as part of the National Water-Quality Assessment (NAWQA) Program (Delaware, Lower Susquehanna, and Potomac River Basins) to assess ground-water quality and how it is changing over time (fig. 16). Wells selected for a trend network in baseline-assessment areas to evaluate long-term changes in pesticide concentration were previously sampled for USGS (Lower Susquehanna or Delaware NAWQA programs), PDA, or Pennsylvania Department of Environmental Protection programs (table 20). Sixteen wells initially were chosen for inclusion in this network because available data from 1993 to 2001 indicated measureable concentrations of one or more pesticides in ground water. Water from these wells had one or more concentrations of pesticides above an arbitrary value of 0.20 µg/L. A minimum concentration of 0.20 µg/L was chosen to evaluate change from initial concentrations reported in the 1993 to 2001 samples. Because of difficulties locating wells with reported historical concentrations of pesticides in the Triassic Lowland siliciclastic setting, well AD 1184 was located through a referral; previous concentrations of pesticides for a sample collected by Groundwater Sciences Corporation in February 1997 were stored in the Agway Andgrow (East Berlin, Pa.) Chemistry Database and were available from the well owner. In 2004, one replacement well had to be located in each of the Great Valley carbonate and Piedmont carbonate settings. Of the 18 wells (appendix 3), 4 wells were in each of the Appalachian Mountain carbonate and Triassic Lowland siliciclastic settings, and 5 wells were in each of the Great Valley carbonate and Piedmont carbonate settings (fig. 16) (table 20). These four settings were ranked ‘high’ or ‘moderate/high’ in relative vulnerability to pesticide contamination (Lindsey and Bickford, 1999). Pesticide samples were analyzed at the USGS NWQL in 2003, and the PADEPL was used for pesticide analyses in 2004.

Most of the well-water samples collected from 1993 to 2001 were analyzed either at the NWQL (GCMS methodology) or the PADEPL (USEPA 525.2, GCMS methodology). There were two exceptions—water for well LN 1763 was analyzed at the PDA laboratory in 1995 using an immunoassay method, and water for well AD 1184 was analyzed at EnviroTest Laboratories, Inc. using the USEPA 608 wastewater method (gas chromatography [GC]).

The wells selected for a trend network in baseline-assessment areas originally were sampled for programs with their own respective timelines for sample collection. For the majority of wells sampled, the initial sample was collected during the post-emergent pesticide-application period (June–August) (table 20). Fifteen of the selected wells were resampled in



State boundary from U.S. Geological Survey, 2005
County boundary from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Appalachian Mountain carbonate, Great Valley carbonate, and Piedmont carbonate,
Triassic Lowland hydrogeologic settings from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 16. Locations of wells sampled for this project and the National Water-Quality Assessment (NAWQA) project. Ground-water samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory (NWQL) or the Pennsylvania Department of Environmental Protection Laboratory (PADEPL).

Table 20. Wells selected for a trend network in baseline-assessment areas.

[NS, not sampled; –, no analysis done; NWQL, U.S. Geological Survey (USGS) National Water Quality Laboratory; PADEPL, Pennsylvania Department of Environmental Protection Laboratory; shading indicates wells selected for paired-sample analysis; PDA, Pennsylvania Department of Agriculture; LSUS NAWQA, Lower Susquehanna River Basin National Water Quality Assessment project; DELR, Delaware River Basin]

Local well number	Hydrogeologic setting	Initial sample				2003 sample		2004 sample	
		Agency/program associated with sample collection	Year	Month	Laboratory	Month	Laboratory	Month	Laboratory
BD 653	Appalachian Mountain carbonate	USGS LSUS NAWQA	1994	August	NWQL	April	NWQL	April	PADEPL
CE 672	Appalachian Mountain carbonate	USGS LSUS NAWQA	1994	August	NWQL	April	NWQL	April	PADEPL
LY 686	Appalachian Mountain carbonate	PDA, Ground-water monitoring program	2001	June	PADEPL	April	NWQL	April	PADEPL
MF 401	Appalachian Mountain carbonate	USGS LSUS NAWQA	1994	July	NWQL	April	NWQL	April	PADEPL
BE 1619	Great Valley carbonate	USGS/PDA cooperative study	1998	April	PADEPL	April	NWQL	April	PADEPL
CU 908	Great Valley carbonate	USGS LSUS NAWQA	1995	June	NWQL	April	NWQL	April	PADEPL
CU 917	Great Valley carbonate	USGS LSUS NAWQA	1995	July	NWQL	NS (Replacement well for NP 805 in 2004)	NWQL	April	PADEPL
LB 1160	Great Valley carbonate	USGS LSUS NAWQA	1995	July	NWQL	April	NWQL	April	PADEPL
NP 805	Great Valley carbonate	USGS/PDA cooperative study	1998	January	PADEPL	April	NWQL	NS	–
LN 1763	Piedmont carbonate	PDA, Ground-water monitoring program	1995	April	PDA	NS (Replacement well for LN 2008 in 2004)	NWQL	March	PADEPL
LN 2005	Piedmont carbonate	USGS LSUS NAWQA	1993	July	NWQL	April	NWQL	March	PADEPL
LN 2008	Piedmont carbonate	USGS LSUS NAWQA	1993	July	NWQL	April	NWQL	NS	–
LN 2017	Piedmont carbonate	USGS LSUS NAWQA	1993	July	NWQL	April	NWQL	April	PADEPL
LN 2021	Piedmont carbonate	USGS LSUS NAWQA	1993	July	NWQL	April	NWQL	March	PADEPL
AD 1184	Triassic Lowland	PADEP	1995	December	EnviroTest Laboratories, Inc.	October	PADEPL	April	PADEPL
BK 3011	Triassic Lowland	PDA, Ground-water monitoring program	1999	March	PADEPL	April	NWQL	April	PADEPL
MG 1449	Triassic Lowland	USGS DELR NAWQA	1999	October	NWQL	April	NWQL	April	PADEPL
LN 2113	Triassic Lowland	PDA, Ground-water monitoring program	1999	March	PADEPL	April	NWQL	April	PADEPL

April 2003, and these samples were analyzed at the NWQL for 52 pesticides with MRLs ranging from 0.002 to 0.05 µg/L; well AD 1184 was resampled in October 2003, and this sample was analyzed at the PADEPL for 10 pesticides with MRLs ranging from 0.10 to 0.12 µg/L. The following year (2004), samples were collected March 30–April 29 and analyzed for 10 pesticides at the PADEPL with MRLs of 0.10 to 0.25 µg/L.

Nine of the wells chosen as trend wells in baseline-assessment areas were used to determine changes in long-term pesticide concentrations. The nine wells were selected because the NWQL was the analyzing laboratory for one-time samples collected in 1993, 1994, or 1995 as part of the NAWQA project in Pennsylvania and again for samples collected as part of this project (2003). Pesticides reported in the initial sample (1993, 1994, or 1995) generally were still present in samples collected in 2003; however, the concentrations generally were lower than in the previous samples. Changes in concentration from 1993 to 2003 are shown by well, using atrazine and its breakdown product CIAT as examples, in figure 17. Water-level changes in the wells ranging from 2.5 to nearly 40 ft (fig. 17) indicate high water levels in 2003 compared to 1993–95 could be a factor in the concentration changes observed. Water-level rises attributed to recharge could dilute the concentration of pesticides in ground water or could carry pesticides to ground water thereby increasing the concentrations. If breakdown processes alone were responsible for the drop in atrazine concentration, a systematic increase in CIAT concentration might be expected; however, this was not observed. Hence, water-level change is one factor that, along with land-use change and pesticide-use change, needs to be considered in explaining the lower concentrations in 2003 compared to 1993–95.

Nonparametric statistical analyses were used to determine long-term changes in pesticide concentrations at the nine trend wells in baseline-assessment areas. The Kruskal-Wallis test is a rank-transform test used as a screening tool to examine for significant differences in the medians of two or more groups of data (Helsel and Hirsch, 2002). In this study, concentrations of atrazine and metolachlor in samples from the nine wells sampled one time in 1993, 1994, or 1995 and one time again in 2003 were ranked from lowest to highest; all censored data (values less than the reporting limits) were assigned the lowest rank. The test compared the rank-transformed pesticide data to the categorical variable sample date (group 1—pesticide data 1993, 1994, or 1995; group 2—pesticide data 2003). If results of the Kruskal-Wallis test showed statistically significant differences in the ranked concentrations grouped by sample date at a significance level of 0.05, the Tukey-Kramer multiple-comparison test was used to determine which groups differed from each other. The groups with the highest medians were assigned a letter "A," the groups with the next highest medians were assigned a letter "B," or an "AB" combination, and so on. Any groups assigned the same letter (or combination of letters) designations were not statistically different from each other.

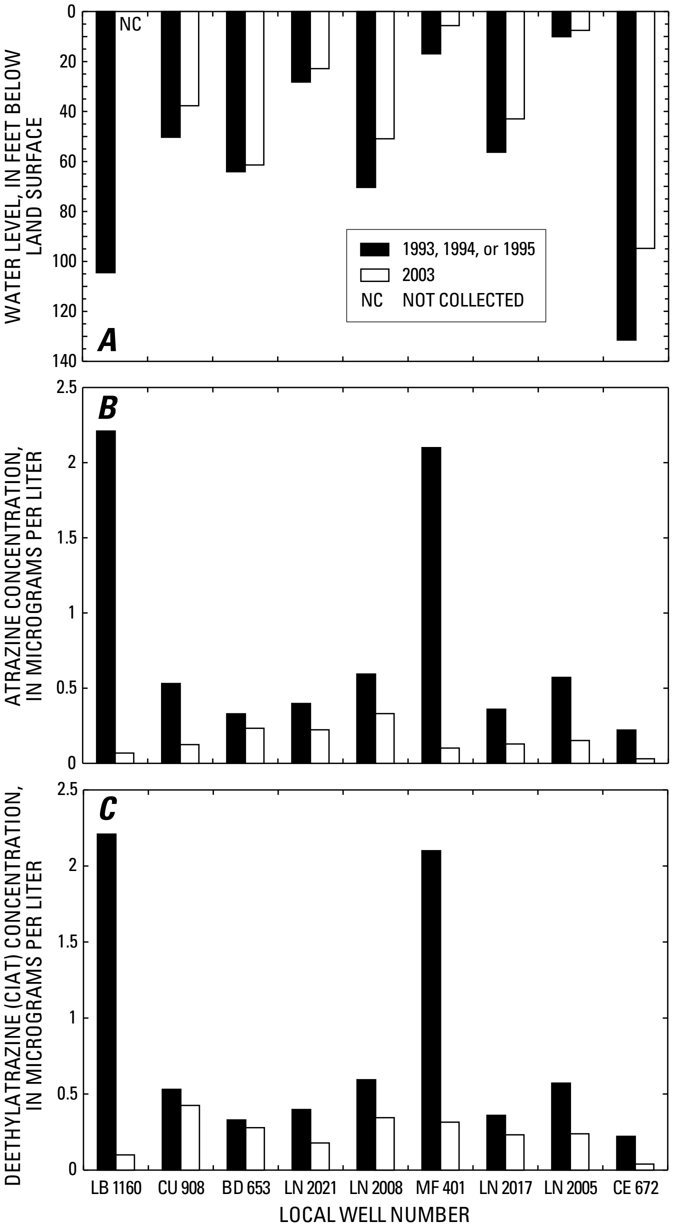


Figure 17. Data for nine wells in agricultural row-crop settings underlain by carbonate bedrock, Lower Susquehanna River Basin, Pennsylvania, from a one-time sample from those wells in 1993–95 and a sample in 2003 for *A*) water level, *B*) concentration of atrazine, and *C*) concentration of CIAT (deethylatrazine), a breakdown product of atrazine.

Using the Kruskal-Wallis and Tukey-Kramer multiple-comparison tests, significantly lower median concentrations of atrazine were observed in the samples collected from the nine trend wells in baseline-assessment areas during 2003 than during 1993–95 (fig. 18a). No significant change was observed in median concentrations of metolachlor between sample dates.

Because of the availability of paired observations from the nine trend wells in baseline-assessment areas, the Wilcoxon signed-rank test (Helsel and Hirsch, 2002) was used to test for temporal changes in median concentrations at a 0.05 significance level. Censored pesticide concentrations (values below the reporting limit, or non-detects) were assigned a common value lower than the lowest quantified pesticide concentration. Therefore, all values below the reporting limit for a single pesticide compound were tied at the lowest rank. Pesticide concentrations from the nine sites sampled once in 2003 were subtracted from the pesticide concentrations from each of the same wells in 1993, 1994, or 1995. Examining these differences in paired-observation data, a significant decrease in atrazine concentration was identified (p = 0.004, fig. 18b). The pattern of decline in atrazine concentrations for this study is consistent with results of other ground-water studies. For example, Kolpin and others (1997) reported decreasing concentrations of atrazine in ground-water samples collected from selected municipal wells in Iowa over time (1982–95). Conversely, Kolpin and others (1997) reported increasing concentrations of metolachlor in the Iowa wells over that same time period (1982–95). The decreasing trend for atrazine and the increasing trend for metolachlor were reported to be consistent with changes in statewide chemical use and application rates for the two pesticides; there were no apparent relations between precipitation and temporal patterns in atrazine and metolachlor (Kolpin and others, 1997). A study of ground-water quality in agricultural areas of the Mid-Atlantic region (Potomac NAWQA), including carbonate rocks in the Great Valley, reported significantly decreasing concentrations of atrazine, CIAT, and prometon in 2002 compared to 1993 (Debrewer and others, 2008). The decreasing trend in pesticide concentrations was reported by Debrewer and others (2008) to be related to hydrogeology, climate, changes in land use, and changes in chemical applications. As explained previously, water-level change, land-use change, pesticide-use change, and date of sample collection are all factors for this study that need to be considered in explaining the lower atrazine concentrations in 2003 compared to 1993–95. From 1993–95 to 2003, the amount of land used for row-crop agriculture decreased (table 1), atrazine pesticide application (fig. 5) decreased in many counties in Pennsylvania over the past 10 years, and water levels increased (fig. 17). Similar findings for metolachlor were not observed for this study. Applications of metolachlor/S-metolachlor increased from 1996 to 2004–05 in many counties (fig. 6), but the Wilcoxon signed-rank test did not identify a significant temporal change in concentrations for the nine trend wells in baseline-assessment areas (p = 0.625).

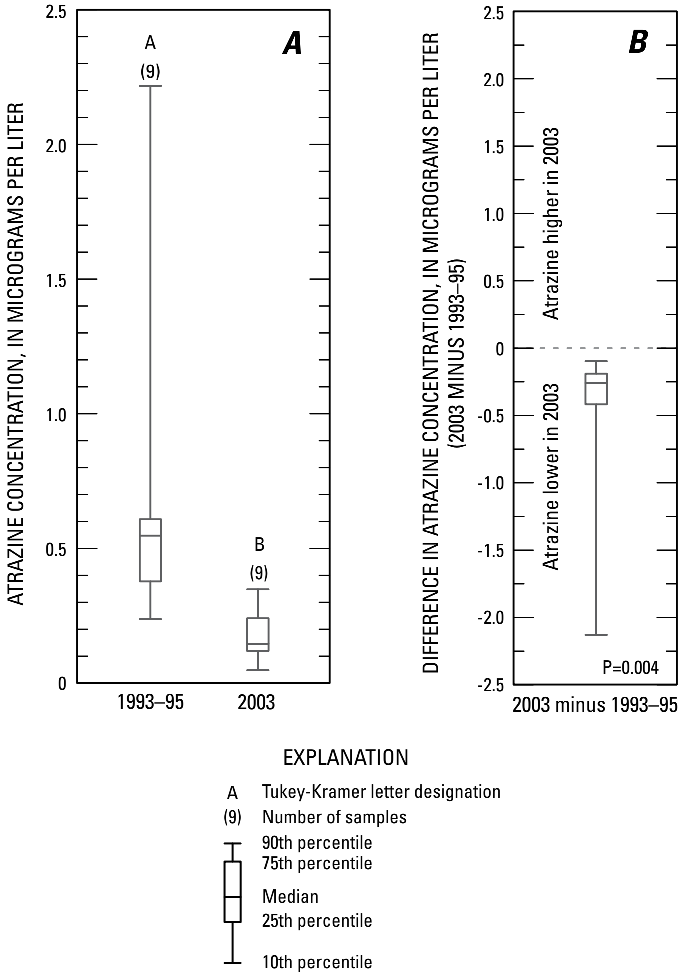


Figure 18. Range of *A*) atrazine concentrations 1993–95 (one-time sample) compared to 2003 with results of Tukey-Kramer multiple-comparison test and *B*) paired differences in atrazine concentrations 2003 minus 1993–95 for nine wells in agricultural row-crop setting underlain by carbonate bedrock, Lower Susquehanna River Basin, Pennsylvania. P-value indicates result of the Wilcoxon signed-rank test.

Because the 2003 data showed that pesticide concentrations had dropped below the action levels set for the PDA PPGWS (appendix 4) and that further sample collection would only serve to confirm the trend to low concentrations with a large added cost to the project, the collection of samples at these baseline-assessment-area wells was discontinued before the field season in 2005.

Pesticide and Nitrate Concentration Changes for Three Hot-Spot Wells in Areas of Special Ground-Water Protection

The three hot-spot wells in areas of special ground-water protection are in the Great Valley carbonate, Appalachian Mountain carbonate, and Piedmont carbonate hydrogeologic settings (fig. 7), areas known for high percentages of land in row crop and high pesticide usage (Lindsey and Bickford, 1999). These areas are also known to have high concentrations of nitrate in ground water (Lindsey and others, 1997). The wells frequently had one or more pesticide concentrations at or above the PPGWS action levels (invoked by the PDA at fractions of the USEPA MCLs or Lifetime Health Advisories [LHAs], appendix 4) prior to when this project began in 2003.

The Berks County hot-spot well (BE 1370) is on a farm in the Great Valley carbonate setting. The initial sample collected in 1998 from this well had an alachlor concentration of 14 µg/L, which was above the USEPA MCL of 2 µg/L. Thus, hot-spot monitoring was initiated in 1998. Water from well BE 1370 historically had nitrate concentrations one to two times the USEPA MCL of 10 mg/L as N (nitrogen) (U.S. Environmental Protection Agency, 2008).

The Blair County hot-spot well (BA 437), in the Appalachian Mountain carbonate setting, is at a building housing municipal offices and the highway department. The building is in an agricultural area and is adjacent to a property historically used for pesticide mixing and handling. When the first sample was collected in 1984, concentrations of atrazine and alachlor were 11 and 20 µg/L, respectively. The nitrate concentration of 100 mg/L as N was 10 times the USEPA MCL of 10 mg/L as N. From 2003 to 2006, four samples collected at well BA 437 exceeded the PPGWS action level for metolachlor prior to the USEPA LHA change from 100 to 700 µg/L in 2006, and one sample (August 2003) exceeded the PPGWS action level for atrazine (1.0 µg/L).

The Lancaster County hot-spot well (LN 1842) is on a farm in the Piedmont carbonate setting. The barnyard area near the well is also used for handling and mixing of pesticides. When the first sample was collected in 1991, the well water had reported concentrations for atrazine and alachlor of 1.8 and 2.8 µg/L, respectively. With the exception of the August 2007 sample, all samples collected at well LN 1842 from 2003 to 2007 exceeded the PPGWS action level of 0.66 µg/L for alachlor. Samples collected between 1996 and 2005 frequently had reported concentrations of metolachlor near to or above the 2004 USEPA LHA (100 µg/L) (U.S. Environmental Protection Agency, 2004). The USEPA LHA was changed in 2006 to 700 µg/L (U.S. Environmental Protection Agency, 2006); no sample concentrations exceeded the 2006 USEPA LHA for metolachlor between 2006 and 2007. Nitrate concentrations have historically been two to four times the USEPA MCL at this site.

Samples were collected seasonally at hot spots to examine pesticide concentrations in well water in the summer, fall, winter, and spring (appendix 3). The change from season to season usually results in predictable changes in water levels in wells. For example, water levels usually decline during summer and early fall months because of increased rates of evaporation and transpiration by plants; water levels usually rise in winter and early spring months because low rates of evaporation and transpiration allow recharge water to reach the aquifer. Timing for sampling was estimated by referencing on-line, real-time data (U.S. Geological Survey, 2008) for USGS wells in the county ground-water-level network (Lancaster, LN 1351; Berks, BE 623; and Blair, BA 74). Spring samples were collected from April through May, summer samples from June through early August, fall samples from late August through October, and winter samples from December through March. The timing of the fall sample collection was occasionally missed because of multiple major precipitation events that quickly changed water-level conditions before samples could be collected.

Evaluation of the hot-spot data to determine trends was done in two steps—exploratory data analysis and trend testing. For the exploratory data analysis, scatterplots were used to analyze the data graphically. LOWESS smooth curves derived by the data were added to the scatterplots, a smoothing technique that has no simple equation or significance test associated with it that is used to visually highlight patterns through the middle of the data (Helsel and Hirsch, 2002). Boxplots also were used to analyze the data graphically. After graphical analysis of the data, the Kruskal-Wallis test was used as a screening tool to examine for significant seasonality in the data sets for the hot-spot wells and the Tukey-Kramer multiple-comparison test was used to determine which seasonal groups differed from each other. Kruskal-Wallis and Tukey-Kramer tests can indicate whether or not seasonality may be an issue but do not account for trends in concentrations over time; therefore, if seasonality was observed with those tests, use of seasonal trend tests to analyze the data was warranted. For the trend testing, the Mann-Kendall and the Seasonal Kendall tests were used to analyze concentration data for temporal trends.

For hot-spot well BE 1370, historical alachlor concentrations were above the USEPA MCL of 2 µg/L until June 2001 (table 21); metolachlor and atrazine also were detected above the MRLs in the majority of samples collected from 1998 to 2007. Only one sample collected from 2003 to 2007 at hot-spot well BE 1370 had an alachlor concentration that exceeded the PPGWS action level. When samples were analyzed at the NWQL (March and May 2003 and May 2005–May 2007), CIAT concentrations were greater than atrazine concentrations. Concentrations of alachlor, metolachlor, and atrazine in well water from BE 1370 decreased over time (fig. 19); the compounds with the largest initial concentrations (alachlor and metolachlor) showed the greatest decreases. During the periods of time when the NWQL was used for analytical work and CIAT was included in the analytical schedules, CIAT regularly co-occurred with reported concentrations of alachlor, metolachlor, and atrazine. CIAT concentrations also decreased over time.

For hot-spot well BA 437, alachlor, metolachlor, and atrazine had the greatest concentrations, but dieldrin, s-ethyl dipropylthiocarebamate (EPTC), prometon, CIAT, cyanazine, simazine, butylate, and carbofuran also had reported concentrations from 1996 to 2007 (table 22). Atrazine and alachlor showed slight decreases in concentration over time since the initial sample in 1996 (fig. 20). The concentration of

Table 21. Pesticide co-occurrence in ground water collected at well BE 1370, Oley Township, Berks County, Pennsylvania, from 1998 to 2007. Concentrations of alachlor, metolachlor, and atrazine are shown in figure 19.

[All concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; NWIS, National Water Informtion System; <, less than; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(3), estimated because the value is below the long-term method detection limit; na, not analyzed; nad, not analyzed because of sample damage at laboratory]

Sample date	Concentration, in micrograms per liter									
	Acetochlor	Alachlor	Metolachlor	Atrazine	CIAT[1]	2,6 diethylaniline	Chlorothalonil	Prometon	Simazine	Trifluralin
2/3/1998	na	**14**	**6.3**	**0.40**	na	na	< 0.30	na	< 0.30	na
4/7/1998	na	**2.3**	**1.9**	**.38**	na	na	< .30	na	< .30	na
1/26/1999	na	**9.4**	**4.5**	**.45**	na	na	< .10	na	< .10	na
4/6/1999	na	**5.5**	**3.0**	**.29**	na	na	< .10	na	< .10	na
3/6/2000	na	**9.5**	**6.2**	**.31**	na	na	< .10	na	< .10	na
2/7/2001	na	**2.2**	**.76**	**.20**	na	na	< .10	na	< .10	na
6/7/2001	na	**3.7**	**1.4**	**.61**	na	na	**.34**	na	< .10	na
10/11/2001	na	**1.8**	**.87**	**.30**	na	na	< .25	na	< .50	na
3/26/2003	< 0.006	**.396**	**1.06**	**.164**	**0.318** E(1)	< 0.006	na	< 0.015	< .005	**0.006** E(2)
5/15/2003	< .006	**.260**	**.461**	**.154**	**.234** E(1)	**.001** E(3)	na	**.006** E(3)	**.006**	**.003** E(3)
8/13/2003	< .10	**.15**	**.37**	**.10**	na	na	< .10	na	< .10	na
10/8/2003	< .10	<.10	**.86**	<.10	na	na	< .10	na	< .10	na
12/3/2003	< .11	<.11	**.73**	<.11	na	na	< .11	na	< .11	na
4/19/2004	< .10	<.10	**.22**	<.10	na	na	< .10	na	< .10	na
7/21/2004	< .10	**.98**	**2.02**	**.26**	na	na	< .10	na	< .10	na
10/6/2004	nad	nad	nad	nad	na	na	nad	na	nad	na
12/15/2004	< .10	<.10	**.48**	**.18**	na	na	< .10	na	< .10	na
5/24/2005	< .006	**.046**	**.216**	**.154**	**.194** E(1)	< .006	na	< .010	< .005	< .009
5/30/2006	**.015**	<.005	**.157**	**.108**	**.183**	< .006	na	< .010	**.005** E(2)	< .009
5/17/2007	< .006	**.024**	**.325**	**.123**	**.157** E(1)	< .002	na	< .008	< .006	**.002** E(3)

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).

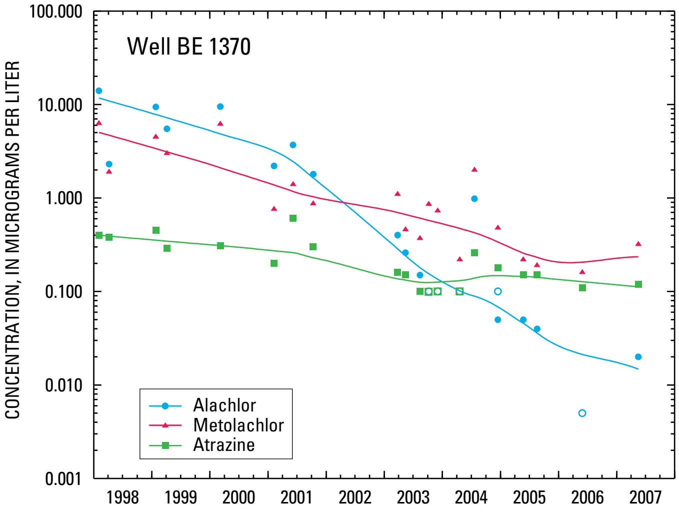


Figure 19. Concentrations of alachlor, metolachlor, and atrazine in samples collected from 1998 to 2007 at well BE 1370, Oley Township, Berks County, Pennsylvania. Lines fitted through the data are LOWESS smooth curves. Concentrations less than minimum reporting levels (MRLs) were plotted as open symbols at concentrations equal to the respective MRLs (these concentrations were included in the formulation of LOWESS smooth curves).

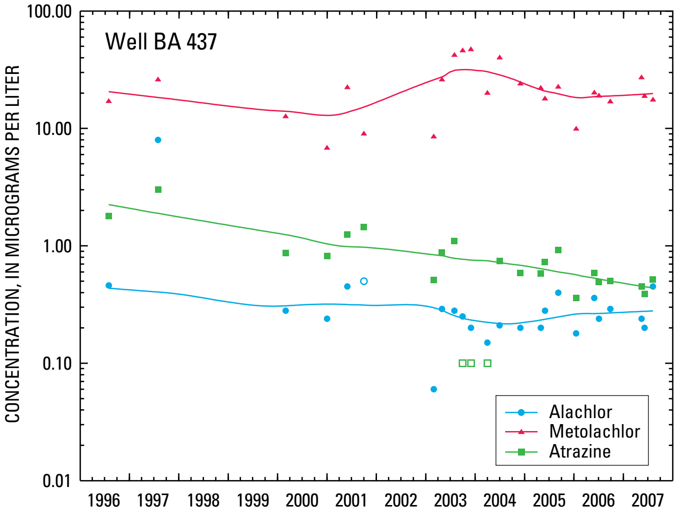


Figure 20. Concentrations of alachlor, metolachlor, and atrazine in samples collected from 1996 to 2007 at well BA 437, North Woodbury Township, Blair County, Pennsylvania. Lines fitted through the data are LOWESS smooth curves. Concentrations less than minimum reporting levels (MRLs) were plotted as open symbols at concentrations equal to the respective MRLs (these concentrations were included in the formulation of LOWESS smooth curves).

Table 22. Pesticide co-occurrence in ground water collected at well BA 437, North Woodbury Township, Blair County, Pennsylvania, from 1996 to 2007. Concentrations of alachlor, metolachlor, and atrazine are shown in figure 20.

[All concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; NWIS, National Water Information System; <, less than; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(3), estimated because the value is below the long-term method detection limit; E(4), estimated because of failure in some aspect of lab quality control; E(5), estimated because result exceeds largest calibration standard; na, not analyzed; nad, not analyzed because of sample damage at lab]

Sample date	Concentration, in micrograms per liter											
	Alachlor	Metolachlor	Atrazine	CIAT[1]	Cyanazine	Simazine	Dieldrin	EPTC[2]	Prometon	Butylate	Carbofuran	Pendimethalin
8/7/1996	**0.46** E(2)	**17.0**	**1.8**	na	**0.26** E(2)	**0.32** E(2)	na	na	na	na	na	**0.11** E(2)
8/27/1997	**8.0**	**26.0**	**3.0**	na	< .1	< .1	na	na	na	na	na	< .1
3/8/2000	**.28**	**12.6** E(5)	**.87**	na	**.30**	< .10	na	na	na	na	na	< .10
1/31/2001	**.24**	**6.8** E(5)	**.82**	na	**.34**	< .10	na	na	na	na	na	< .10
6/4/2001	**.45**	**22.3** E(5)	**1.25**	na	**.42**	**.34**	na	na	na	na	na	< .10
10/2/2001	< .50	**8.99**	**1.44**	na	**.28**	< .50	na	na	na	na	na	< .25
3/25/2003	**.060**	**8.50**	**.511**	**0.177** E(1)	< .018	**.055**	< 0.005	< 0.002	**0.13**	< 0.002	< 0.02	< .022
5/12/2003	**.292**	**25.9**	**.881**	**.201** E(1)	**.131** E(4)	**.126**	**.034**	**.013**	**.26**	**.006**	**.011** E(1) E(2)	< .022
8/14/2003	**.28**	**41.9** E(5)	**1.11**	na	na	**.260**	na	na	na	na	na	< .100
10/7/2003	**.25**	**46.0**	< .10	na	na	< .10	na	na	na	na	na	< .11
12/2/2003	**.20**	**47.1**	< .11	na	na	< .11	na	na	na	na	na	< .11
4/20/2004	**.15**	**19.6** E(5)	< .10	na	na	< .10	na	na	na	na	na	< .10
7/20/2004	**.21**	**39.7** E(5)	**.74**	na	na	< .10	na	na	na	na	na	< .10
10/5/2004	nad	nad	nad	na	na	nad	na	na	na	na	na	nad
12/16/2004	**.20**	**23.6** E(5)	**.59**	na	na	**.10**	na	na	na	na	na	< .100
5/25/2005	**.200**	**22.0** E(5)	**.578**	**.133** E(1)	< .14	**.100**	**.026**	**.009**	**.16**	**.004** E(2)	**.015** E(1) E(2)	< .022

Table 22. Pesticide co-occurrence in ground water collected at well BA 437, North Woodbury Township, Blair County, Pennsylvania, from 1996 to 2007.—Continued
Concentrations of alachlor, metolachlor, and atrazine are shown in figure 20.

[All concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; NWIS, National Water Information System; <, less than; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated value because the concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(3), estimated because the value is below the long-term method detection limit; E(4), estimated because of failure in some aspect of lab quality control; E(5), estimated because result exceeds largest calibration standard; na, not analyzed; nad, not analyzed because of sample damage at lab]

Sample date	Concentration, in micrograms per liter											
	Alachlor	Metola-chlor	Atrazine	CIAT[1]	Cyanazine	Simazine	Dieldrin	EPTC[2]	Prometon	Butylate	Carbofuran	Pendi-methalin
6/28/2005	**0.280**	**17.9**	**0.734**	**0.146** E(1)	< 0.22	**0.123**	**0.029**	**0.014**	**0.23**	**0.006**	**0.014** E(1) E(2)	<0 .022
9/7/2005	**.397**	**22.5** E(5)	**.917**	**.121** E(1)	**.084** E(4)	**.110**	**.025**	**.016**	**.27**	**.009**	< .02	< .022
1/18/2006	**.176**	**9.89**	**.361**	**.10** E(1)	**.085** E(4)	**.057**	**.014**	**.006**	**.10**	**.004** E(2)	**.008** E(1) E(3)	< .022
5/31/2006	**.355**	**20.1**	**.592**	**.136** E(1)	**.131** E(4)	**.115**	**.026**	**.017**	**.25**	**.008**	**.015** E(2)	< .022
7/5/2006	**.240**	**18.9**	**.487**	**.128** E(1)	< .103	**.108**	**.027**	**.011**	**.18**	< .004	< .02	< .022
9/27/2006	**.290**	**16.9**	**.498**	**.118** E(1)	< .018	**.103**	**.033**	**.013**	**.19**	< .004	< .02	< .022
5/15/2007	**.245**	**27.1** E(5)	**.450**	**.134** E(1)	**.088**	**.105**	**.033**	**.010**	**.17**	**.005**	**.019** E(1) E(2)	< .02
6/7/2007	**.203**	**18.8** E(5)	**.389**	**.135** E(1)	**.082**	**.089**	**.036**	**.008**	**.13**	< .002	< .02	< .02
8/8/2007	**.446**	**17.5**	**.521**	**.138** E(1)	**.111**	**.085**	**.018**	**.015**	**.21**	**.007**	< .02	< .02

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).

[2] EPTC, S-ethyl dipropyl(thiocarbamate) (NWIS parameter code 82668).

metolachlor ranged from 6.8 to 47.1 µg/L from 1996 to 2007 (table 22) with periods of decreasing and increasing concentration resulting in little overall change (fig. 20). Concentrations of cyanazine, simazine, and the atrazine degradate CIAT have slight but generally steady declines over their respective periods of record; the concentrations of dieldrin, EPTC, butylate, carbofuran, and prometon remained fairly constant (table 22).

For hot-spot well LN 1842, reported concentrations of acetochlor, alachlor, metolachlor, and atrazine from 1995 to 2007 are shown in figure 21. CIAT, cyanazine, simazine, butylate, EPTC, linuron, napropamide, prometon, terbacil, and tebuthiuron also had reported concentrations (table 23). Of these pesticides, atrazine concentrations decreased over time (fig. 21); acetochlor, alachlor, and metolachlor concentrations remained fairly constant.

Nitrate concentrations over time are shown in figure 22 for hot-spot wells BA 437, LN 1842, and BE 1370. Nitrate concentrations at BA 437 showed the greatest fluctuations and the greatest decreases over the period of record (1996–2007) compared to nitrate concentrations at wells LN 1842 and BE 1370.

Nonparametric statistical techniques were used in exploratory data analysis and in determining trends in concentration at the three hot-spot wells using a 5-yr (2003–07) data set and the long-term data sets. In addition to scatterplots described previously for the exploratory data analysis, boxplots also were used to analyze the data graphically. After graphical analysis of the data, the Kruskal-Wallis test was used as a screening tool to examine for significant seasonality in the data sets for the hot-spot wells. For this study, data were collected quarterly, and "season" was defined by four categories (winter season, generally December, January, February, and March; spring season, generally April and May; summer season, generally June, July, and early August; and fall season, generally late August, September, October, and November). Concentrations of acetochlor, alachlor, atrazine, metolachlor, and nitrate in samples collected from 2003 to 2007 were ranked from lowest to highest; all censored data (values less than the detection limits) were assigned the lowest rank. The test compared the rank-transformed data to the categorical variable for seasonal groups (winter, spring, summer, and fall groups). If results of the Kruskal-Wallis test showed statistically significant differences in the ranked concentrations grouped by season at a significance level of 0.05, the Tukey-Kramer multiple-comparison test was used to determine which seasonal groups differed from each other.

The Kruskal-Wallis and Tukey-Kramer tests showed significantly higher median concentrations of alachlor in BA 437 during the fall than during the winter (fig. 23); however, seasonality was not evident in any of the other constituents analyzed in this exploratory phase of data analysis. Because seasonality was observed for alachlor, more rigorous statistical analysis methods to test for seasonal trends (Seasonal Kendall test) were considered valid.

Contaminant concentration data were analyzed for trends in ground-water quality over time by use of the Mann-Kendall trend test and the Seasonal Kendall trend test with the level of significance set at 0.05 (p equal to 0.05 or less) (Helsel and others, 2005). The nonparametric Mann-Kendall statistic is a test for whether concentrations tend to increase or decrease with time (monotonic change) (Helsel and Hirsch, 2002, p. 326). The nonparametric Seasonal Kendall test is a modified Mann-Kendall test (Helsel and Hirsch, 2002, p. 338) that determines whether concentrations increase or decrease with time and compares relative ranks of data values from the same season. Censored data were assigned a common value lower than the lowest quantified value before ranking (all values below the reporting limit for a single pesticide compound were tied at the lowest rank). In the Seasonal Kendall test, winter data were only compared with winter data, spring data were only compared with spring data, etc. The Seasonal Kendall test statistic is the summation of all Mann-Kendall test results on the individual seasons.

Trends of selected pesticides (acetochlor, alachlor, atrazine, and metolachlor) and nitrate were determined for the hot-spot wells. Prior to 2003, data generally were collected at least annually. A change in program emphasis in 2003 resulted in quarterly sampling for the selected constituents (an increase in sampling frequency) to determine if there were any seasonal trends in the hot-spot wells. The 5-year data sets (2003–07) for wells BA 437 and LN 1842 were analyzed using the Mann-Kendall test for overall trend and the Seasonal Kendall trend test. Because of low concentrations in hot-spot well BE 1370 after the first 2 years of quarterly sampling (2003 and 2004), quarterly sampling was discontinued. As a result, well BE 1370 had an insufficient number of samples to analyze for trend using the Seasonal Kendall trend test; the 5-year data set (2003–07) for well BE 1370 was analyzed using the Mann-Kendall trend test only. The trend tests also were conducted using additional data that included samples collected before 2003, hereafter termed "long-term data," for the hot-spot wells. The long-term data for hot-spot well BA 437 covers 1996–2007, the long-term data for hot-spot well LN 1842 covers 1991–2007, and the long-term data for hot-spot well BE 1370 covers 1998–2007. As with the 5-year data sets, the long-term data sets were analyzed using the Mann-Kendall and Seasonal Kendall trend tests. Results of the trend analyses for the 5-year and long-term data sets are presented in table 24.

The Mann-Kendall test for overall trend and the Seasonal Kendall trend test indicated a statistically significant trend for nitrate in hot-spot well BA 437 for the 5-year data set. Concentrations of nitrate had a significant downward trend indicating an improvement in water quality since 2003. Seasonal Kendall results indicate that nitrate decreased by 25 mg/L over the 2003–07 timeframe. This same result (downward trend) was not observed when the long-term data set (1996–2007) was analyzed; there was no statistically significant trend for nitrate in the long-term data set. According to Helsel and Hirsch (2002), the fact that no trend was found does not "prove" that no trend exists; rather, there is not sufficient evidence to conclude that there is a trend in existing data at the

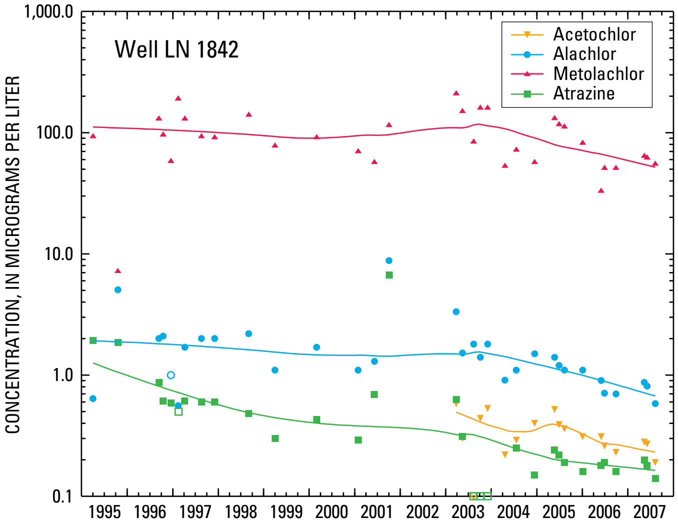


Figure 21. Concentrations of acetochlor, alachlor, metolachlor, and atrazine in samples collected from 1995 to 2007 at well LN 1842, Earl Township, Lancaster County, Pennsylvania. Lines fitted through the data are LOWESS smooth curves. Concentrations less than minimum reporting levels (MRLs) were plotted as open symbols at concentrations equal to the respective MRLs (these concentrations were included in the formulation of LOWESS smooth curves).

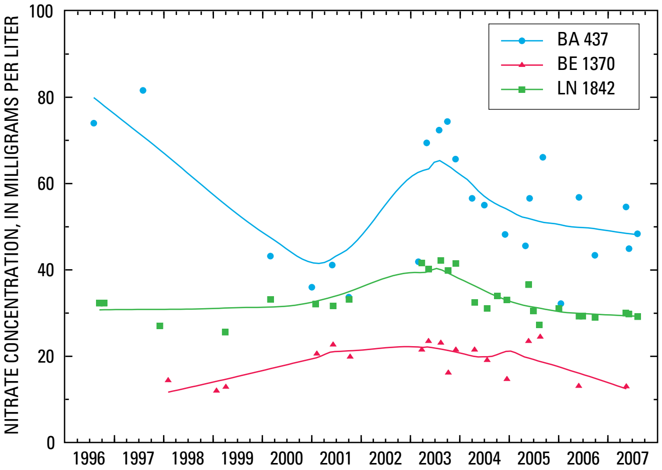


Figure 22. Nitrate concentrations in 1996–2007 for samples collected at wells BA 437, LN 1842, and BE 1370 in Pennsylvania. Lines fitted through the data are LOWESS smooth curves.

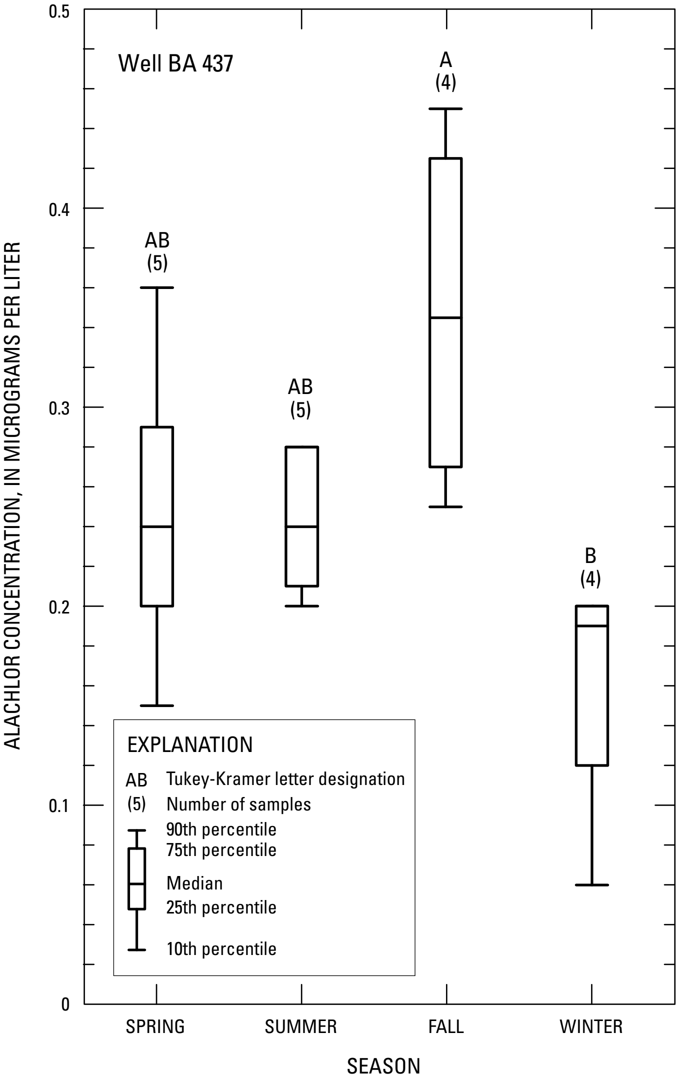


Figure 23. Range of alachlor concentrations from 2003 to 2007 by season at well BA 437, North Woodbury Township, Blair County, Pennsylvania, and results of Tukey-Kramer multiple-comparison test.

Table 23. Pesticide co-occurrence in ground water collected at well LN 1842, Earl Township, Lancaster County, Pennsylvania, from 1995 to 2007. Concentrations of acetochlor, alachlor, metolachlor, and atrazine are shown in figure 21.

[All concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; NWIS, National Water Information System; <, less than; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated because concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(4), estimated because of failure in some aspect of lab quality control; E(5), estimated because result exceeds largest calibration standard; na, not analyzed; na, not analyzed; nad, not analyzed because of sample damage at lab; ud, unable to determine because of matrix interference]

Sample date	Concentration, in micrograms per liter														
	Aceto-chlor	Alachlor	Metola-chlor	Atrazine	Chlorpy-rifos	CIAT[1]	Cyan-azine	Simazine	Butylate	EPTC[2]	Prome-ton	Linuron	Napron-amide	Terbacil	Tebuthi-uron
4/2/1995	na	**0.64**	**93**	**1.9**	na	na	**1.40**	nd	na	na	na	na	na	na	na
10/19/1995	na	**5.0**	**7.2**	**1.9**	**0.12**	na	na	na	na	na	na	na	na	na	na
9/12/1996	na	**2**	**130**	**.87**	< .5	na	**1.4**	**0.31** E(2)	na	na	na	na	na	na	na
10/16/1996	na	**2.1**	**96**	**.61**	< .5	na	**1.1**	<.5	na	na	na	na	na	na	na
12/18/1996	na	< 1.0	**58**	**.59** E(2)	< 1.0	na	**.65** E(2)	<1.0	na	na	na	na	na	na	na
2/13/1997	na	**.56**	**190**	< .5	< .5	na	<.5	<.5	na	na	na	na	na	na	na
4/8/1997	na	**1.7**	**130**	**.61**	na	na	**.98**	na	na	na	na	na	na	na	na
8/19/1997	na	**2**	**93**	**.6**	< .1	na	<.1	<.10	na	na	na	na	na	na	na
12/3/1997	na	**2**	**91**	**.6**	< .3	na	<.3	<.3	na	na	na	na	na	na	na
9/3/1998	na	**2.2**	**140**	**.48**	< .10	na	<.1	<.10	na	na	na	na	na	na	na
4/1/1999	na	**1.1**	**78** E(5)	**.3**	< .10	na	**.25**	**.08** E(2)	na	na	na	na	na	na	na
3/1/2000	na	**1.7**	**91** E(5)	**.43**	< .10	na	<.1	<.10	na	na	na	na	na	na	na
1/29/2001	na	**1.1**	**70** E(5)	**.29**	**.19**	na	**.41**	<.10	na	na	na	na	na	na	na
6/7/2001	na	**1.3**	**57** E(5)	**.69**	< .10	na	**.37**	<.10	na	na	na	na	na	na	na
10/3/2001	na	**8.8**	**115**	**6.7** E(2)	< 12.5	na	<.25	<25.00	na	na	na	na	na	na	na
3/26/2003	**0.577**	**3.33**	**210** E(5)	**.627**	< .005	**.542** E(1)	ud	**.074**	**.030**	**.232**	**.06**	<.035	**.044**	**.280** E(1)	<.02
5/15/2003	**.298**	**1.52**	**150** E(5)	**.31**	< .005	**.345** E(1)	**.414**	**.049**	**.022**	**.227**	**.04**	**.127**	**.033**	**.233** E(1)	**.01** E(2)
8/13/2003	< .10	**1.79**	**83.8** E(5)	< .10	< .10	na	na	<.10	na	na	na	na	na	na	na
10/6/2003	**.44**	**1.40**	**160**	< .10	< .10	na	na	<.10	na	na	na	na	na	na	na
12/3/2003	**.53**	**1.76**	**159**	< .10	< .10	na	na	<.10	na	na	na	na	na	na	na

Table 23. Pesticide co-occurrence in ground water collected at well LN 1842, Earl Township, Lancaster County, Pennsylvania, from 1995 to 2007.—Continued Concentrations of acetochlor, alachlor, metolachlor, and atrazine are shown in figure 21.

[All concentrations reported are in **bold** font; if concentration reported is estimated, a notation is located under the reported value; NWIS, National Water Information System; <, less than; E(1), estimated value because the median long-term recovery in lab reagent spikes (LRS) is between 30 and 60 percent and (or) the F-pseudosigma of recoveries in LRS is greater than 25 percent; E(2), estimated because concentration is greater than or equal to the long-term method detection limit but less than the minimum reporting level; E(4), estimated because of failure in some aspect of lab quality control; E(5), estimated because result exceeds largest calibration standard; na, not analyzed; na, not analyzed; nad, not analyzed because of sample damage at lab; ud, unable to determine because of matrix interference]

Sample date	Concentration, in micrograms per liter														
	Aceto-chlor	Alachlor	Metola-chlor	Atrazine	Chlorpy-rifos	CIAT[1]	Cyan-azine	Simazine	Butylate	EPTC[2]	Prome-ton	Linuron	Napron-amide	Terbacil	Tebuthi-uron
4/21/2004	**0.22**	**0.91**	**53.5** E(5)	< 0.10	< 0.10	na	na	<0.10	na	na	na	na	na	na	na
7/21/2004	**.29**	**1.05**	**72.3** E(5)	**.25**	< .10	na	na	<.10	na	na	na	na	na	na	na
10/6/2004	nad	nad	nad	nad	nad	na	na	nad	na	na	na	na	na	na	na
12/15/2004	**.40**	**1.50**	**56.7** E(5)	**.15**	< .10	na	na	<.10	na	na	na	na	na	na	na
5/24/2005	**.515**	**1.43**	**131** E(5)	**.244**	< .005	**0.184** E(1)	**0.413**	**.067**	**0.026**	**0.148**	**0.03**	**0.082**	**0.038**	**0.155** E(1)	**0.01** E(2)
6/29/2005	**.393**	**1.16**	**117** E(5)	**.219**	< .005	**.242** E(1)	<.68	**.054**	**.018**	**.139**	**.03**	**.108**	**.040**	**.214** E(1)	**.01** E(2)
8/11/2005	**.364**	**1.13**	**112** E(5)	**.187**	<.156	**.173** E(1)	<.337	**.031**	<.016	**.108**	**.02** E(4)	**.117** E(4)	**.029** E(4)	**.118** E(1)	<.08
1/4/2006	**.307**	**1.1**	**82.0** E(5)	**.160**	< .005	**.235** E(1)	<.442	**.029**	**.013**	**.100**	**.03**	**.060**	**.034**	**.181** E(1)	**.01** E(2)
6/1/2006	**.306**	**.902**	**33.1** E(5)	**.185**	< .005	**.236** E(1)	**.220** E(4)	**.039**	**.013**	**.115**	**.03**	**.111**	**.048** E(4)	**.212** E(1)	**.01** E(2)
6/29/2006	**.264**	**.714**	**51.1** E(5)	**.188**	< .005	**.256** E(1)	**.299** E(4)	**.037**	**.010**	**.092**	**.03**	**.097**	**.038** E(4)	**.157** E(1)	< .02
9/28/2006	**.234**	**.702**	**50.8** E(5)	**.162**	< .005	**.198** E(1)	<.018	**.031**	<.004	**.083**	**.03**	**.070**	**.042**	<.034	**.01** E(2)
5/14/2007	**.285**	**.872**	**64.0** E(5)	**.205**	< .005	**.234** E(1)	**.208**	**.056**	**.011** E(4)	**.063** E(4)	**.04**	**.081**	**.043** E(4)	**.13** E(1)	**.03** E(4)
6/6/2007	**.271**	**.810**	**61.8** E(5)	**.185**	< .005	**.254** E(1)	**.183**	**.044**	**.011**	**.093**	**.03**	**.074**	**.039**	**.153** E(1)	**.02**
8/9/2007	**.188**	**.582**	**54.7** E(5)	**.138**	< .005	**.188** E(1)	**.16**	**.027**	**.008**	**.076**	**.02**	**.060**	**.037**	<.04	**.02** E(4)

[1] Degradation product: CIAT, 2-chloro-4-isopropylamino-6-amino-s-triazine or deethylatrazine (NWIS parameter code 04040).

[2] EPTC, S-ethyl dipropyl(thiocarbamate) [NWIS parameter code 82668].

Table 24. Trends in concentrations of selected pesticides and nitrate in hot-spot wells BA 437, LN 1842, and BE 1370 in Pennsylvania.

[n, number of samples; down, downward trend; NT, no trend; –, not analyzed for trend; K_{tau}, Kendall correlation coefficient; statistically significant trends in **bold**]

Compound	Data set	BA 437				LN 1842				BE 1370			
		Trend[1]	Seasonal Kendall p-value (K_{tau}) n	Trend[1]	Mann Kendall p-value (K_{tau}) n	Trend[1]	Seasonal Kendall p-value (K_{tau}) n	Trend[1]	Mann Kendall p-value (K_{tau}) n	Trend[1]	Seasonal Kendall p-value (K_{tau}) n	Trend[1]	Mann Kendall p-value (K_{tau}) n
Acetochlor[2]	5-yr[3]	–	–	–	–	NT	0.206 (-0.312) 18	NT	0.120 (-0.268) 18	–	–	–	–
	Long term	–	–	–	–	–	–	–	–	–	–	–	–
Alachlor	5-yr[3]	NT	0.886 (0.062) 18	NT	0.398 (0.150) 18	**down**	**.000** **(-.812)** **18**	**down**	**.000** **(-.621)** **18**	–	–	NT	0.253 (-0.258) 12
	Long term	NT	0.130 (-.286) 25	NT	0.276 (-.154) 26	**down**	**.002** **(-.460)** **33**	**down**	**.001** **(-.436)** **33**	**down**	**.001** **(-.698)** **20**	**down**	**.000** **(-.653)** **20**
Atrazine	5-yr[3]	NT	.206 (-.312) 18	NT	.226 (-.209) 18	NT	.673 (-.125) 18	NT	.787 (-.052) 18	–	–	NT	.721 (.091) 12
	Long term	**down**	**.001** **(-.619)** **25**	**down**	**.000** **(-.511)** **26**	**down**	**.000** **(-.558)** **33**	**down**	**.000** **(-.564)** **33**	**down**	**.006** **(-.605)** **20**	**down**	**.003** **(-.489)** **20**
Metolachlor	5-yr[3]	NT	.325 (-.250) 18	NT	.074 (-.307) 18	NT	.068 (-.438) 18	**down**	**.020** **(-.399)** **18**	–	–	**down**	**.041** **(-.439)** **12**
	Long term	NT	1.00 (-.016) 25	NT	.705 (.055) 26	NT	.358 (-.142) 34	NT	.216 (-.150) 34	**down**	**.006** **(-.605)** **20**	**down**	**.000** **(-.653)** **20**
Nitrate	5-yr[3]	**down**	**.047** **(-.500)** **17**	**down**	**.047** **(-.353)** **17**	**down**	**.001** **(-.750)** **19**	**down**	**.000** **(-.573)** **19**	–	–	NT	.402 (-.179) 13
	Long term	NT	.207 (-.250) 29	NT	.143 (-.210) 25	NT	.063 (-.306) 29	NT	.076 (-.234) 29	NT	.594 (.147) 19	NT	.317 (0.170) 19

[1] The NT (no trend) designation indicates that the evidence available is not sufficient to conclude that there is a trend at the 0.05 significance level (p-value > 0.05).

[2] Acetochlor was not analyzed prior to 2003 for this study and was not found in concentrations above the reporting level in any water sample from hot-spot well BA 437 collected 2003–07 and in only one sample (concentration of 0.01 µg/L) from BE 1370 collected 2003–07. Five-year trend analyses for acetochlor were done for hot-spot well LN 1842 only.

[3] Hot-spot well BE 1370 was sampled quarterly 2003–04 and annually 2005–07. Therefore, there were too few samples to analyze for trend using the Seasonal-Kendall trend test on the 5-year data set.

chosen level of significance. A significant downward trend was observed when analyzing the long-term data set for atrazine from hot-spot well BA 437. Seasonal Kendall results indicated concentrations of atrazine decreased by 1.43 µg/L over the 1996–2007 timeframe.

Concentrations of alachlor and nitrate in hot-spot well LN 1842 had statistically significant downward trends when analyzing the 5-year data set (2003–07) using the Mann-Kendall and Seasonal Kendall trend tests. Seasonal Kendall results indicate alachlor and nitrate concentrations decreased by 1.1 and 9.1 mg/L, respectively, over the 2003–07 timeframe. A significant downward trend for metolachlor also was observed using the Mann-Kendall trend test. Concentrations of metolachlor decreased by 65 µg/L over the 2003–07 timeframe. Additional downward trends in alachlor and atrazine were observed when the long-term data set from hot-spot well LN 1842 was analyzed. Seasonal Kendall results indicated concentrations of alachlor and atrazine decreased by 1.8 and 0.80 µg/L, respectively, over the 1991–2007 timeframe. These downward trends in contaminant concentrations in hot-spot well LN 1842 indicate improvement in water quality.

The Mann-Kendall test for overall trend indicated statistically significant trends for metolachlor in hot-spot well BE 1370 when analyzing the 5-year data set. Mann-Kendall results indicate that metolachlor decreased by 0.26 µg/L over the 2003–07 timeframe, indicating an improvement in water quality. The results of the Mann-Kendall trend test on concentrations of alachlor and atrazine indicated no significant trends over the 2003–07 timeframe. However, the percentages of non-detects (data below the MRL) for the alachlor and atrazine data sets were 25 percent or greater, which decreases the statistical power of the trend test for these two constituents. Significant downward trends were observed in alachlor, atrazine, and metolachlor when analyzing the long-term data set. Seasonal Kendall results indicated concentrations of alachlor, atrazine, and metolachlor decreased by 6.6, 0.33, and 2.16 µg/L, respectively, over the 1998–2007 timeframe in hot-spot well BE 1370. The metolachlor data set for hot-spot well BE 1370 did not contain any non-detects, so the decreasing trend indicates an improvement in water quality with respect to this compound. Similar to the 5-year data sets for alachlor and atrazine, the long-term data sets had high percentages of non-detected values (40 and 15 percent, respectively), so the trend results for these two compounds are less certain.

The long-term data sets were tested to determine differences between seasons that would not be apparent using the trends tests, which assume a single monotonic pattern of trend across all seasons. This is called testing for homogeneity of trend (van Belle and Hughes, 1984; Helsel and Hirsh, 2002), which will uncover, for example, if trends for a particular constituent were due entirely to trends in one season (and no trends in the other seasons). Testing for homogeneity of trend also will uncover whether or not a constituent that was observed to have no statistically significant trends really had trends in the different seasons (upward and downward) that negated each other. The results of the within-season analysis are presented in table 25. Analyzing the long-term data from each season individually using the Mann-Kendall test for trend showed that the downward trend (Seasonal Kendall trend test results) observed for atrazine in hot-spot well BA 437 (table 24) was due entirely to a significant downward trend in the summer (table 25). The trend test for homogeneity also indicated a downward trend in alachlor concentrations in the summer (table 25); however, a trend was not observed for alachlor in that well using the Seasonal Kendall trend test (table 24). The fact that no trend was observed for alachlor using the Seasonal Kendall trend test indicates the downward trend was likely weak. The downward trend for alachlor in well LN 1842 (table 24) was due to significant downward trends in the summer and fall (table 25). Similarly, the downward trend observed using the Seasonal Kendall test on the long-term data for atrazine in well LN 1842 (table 24) was the result of significant downward trends in the spring and fall (table 25). Finally, the results of the Seasonal Kendall test indicating downward trends in the long-term data set for atrazine and metolachlor in hot-spot well BE 1370 (table 24) were due entirely to significant downward trends in the winter samples (table 25). The downward trend for alachlor in hot-spot well BE 1370 (table 24) was the result of significant downward trends in the winter and spring (table 25).

Table 25. Within-season analysis of long-term trends in concentrations of selected pesticides and nitrate in hot-spot wells BA 437, LN 1842, and BE 1370 in Pennsylvania using the Mann-Kendall test for trend.
(Table continued on next page)

[n, number of samples; down, downward trend; NT, no trend (at the 0.05 significance level); K_{tau}, Kendall correlation coefficient; statistically significant trends in **bold**]

Compound[1]	BA 437	
	Summer	
	Trend	*p*-value (K_{tau}) n
Alachlor	**down**	**0.004** **(-0.733)** **10**
Atrazine	**down**	**.0002** **(-.933)** **10**
Metolachlor	NT	0.928 (0.044) 10
Nitrate	NT	0.059 (-0.528) 9

[1] Acetochlor was not analyzed prior to 2003 for this study and was not included in the within-season analysis of long-term data.

Table 25. Within-season analysis of long-term trends in concentrations of selected pesticides and nitrate in hot-spot wells BA 437, LN 1842, and BE 1370 in Pennsylvania using the Mann-Kendall test for trend.—Continued

[n, number of samples; down, downward trend; NT, no trend (at the 0.05 significance level); K_{tau}, Kendall correlation coefficient; statistically significant trends in **bold**]

Compound[1]	LN 1842						BE 1370			
	Spring		Summer		Fall		Winter		Spring	
	Trend	p-value (K_{tau}) n	Trend	p-value (K_{tau}) n	Trend	p-value (K_{tau}) n	Trend	p-value (K_{tau}) n	Trend	p-value (K_{tau}) n
Alachlor	NT	0.118 (-0.444) 9	**down**	**0.036** **(-0.714)** **7**	**down**	**0.036** **(-0.583)** **9**	**down**	**0.015** **(-0.810)** **7**	**down**	**0.044** **(-0.619)** **7**
Atrazine	**down**	**0.016** **(-.667)** **9**	NT	0.133 (-0.524) 7	**down**	**.036** **(-.583)** **9**	**down**	**.048** **(-.667)** **7**	NT	0.095 (-0.571) 7
Metolachlor	NT	1.00 (0.000) 9	NT	0.548 (-0.238) 7	NT	0.834 (-0.083) 9	**down**	**.023** **(-.762)** **7**	NT	0.095 (-0.571) 7
Nitrate	NT	0.548 (-0.238) 7	NT	0.060 (-0.733) 6	NT	0.598 (-0.167) 9	NT	0.339 (0.400) 6	NT	0.848 (-0.133) 6

[1] Acetochlor was not analyzed prior to 2003 for this study and was not included in the within-season analysis of long-term data.

Pesticides and Pesticide-Degradation Products in Ground Water near Hot-Spot Wells

Hot-spot wells yield water with concentrations of pesticides greater than or equal to at least one action level specified in the PPGWS (appendix 4). PDA has designated three areas of special ground-water protection in Berks, Blair, and Lancaster Counties (a hot-spot well is located in each of these areas). Descriptions of the hot-spot wells and the occurrence of pesticide compounds in well water were presented earlier. This section describes the results of sampling conducted to understand the co-occurrence of pesticides and pesticide-degradation products in ground water near the hot-spot wells.

Pesticides are applied as the “parent” chemical. As pesticides age in the soil and in water, they are biologically degraded and chemically transformed into chemical compounds different than the parent. As the breakdown takes place, typically in the soil zone, the concentrations of the “degradation products” increase and the concentrations of the parent pesticides decrease. To understand the extent of natural breakdown of pesticides, it is important to analyze for parent pesticides and degradation products. A total of 16 sites (15 wells and 1 spring) were sampled once to characterize the distribution of 15 pesticides, 39 pesticide breakdown products (degradates), and other indicators of water-quality degradation, such as bromide, chloride, and nitrate (appendix 3).

Berks County, Oley Township

In August 2005, hot-spot well BE 1370, BE SP20 (a spring adjacent to the farmhouse supplied by well BE 1370), and five rural domestic wells at neighboring residences were sampled (table 3, fig. 24). For this study, acetamide pesticides include parent compounds and degradates of acetochlor, alachlor, dimethenamid, metolachlor, and propachlor; triazine and phenylurea pesticides include parent compounds and degradates of atrazine, bromacil, cyanazine, prometon, propazine, simazine, diuron, fluometuron, and linuron (table 9). Results of the analyses of ground-water samples are summarized in tables 26, 27, and 28.

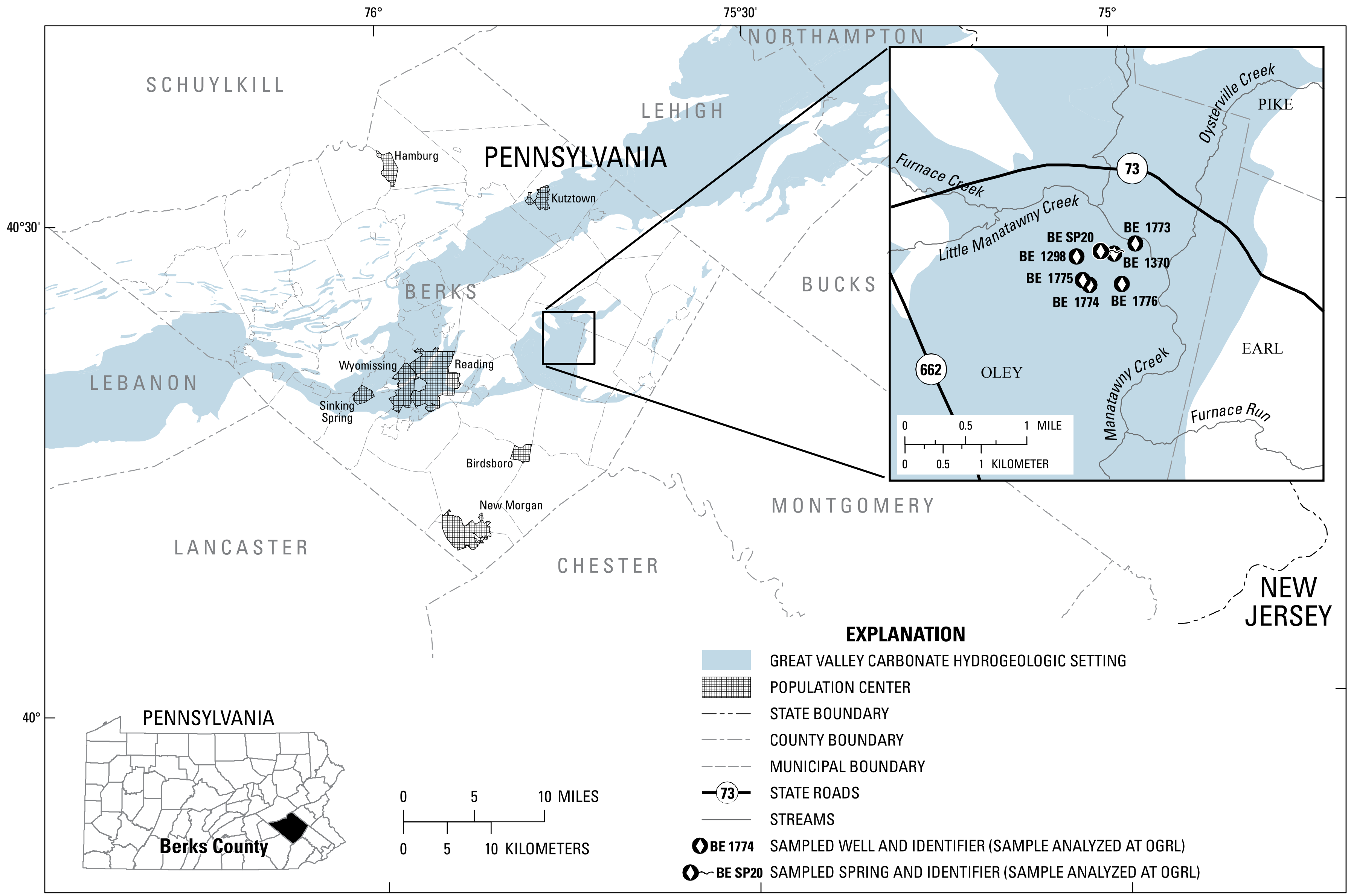
The water from hot-spot well BE 1370 and spring BE SP20 have similar concentrations of parent compounds and degradation products from the acetamide and triazine and phenylurea pesticide groupings. There are 3 to 4 times as many degradation products with up to 10 times the concentrations of the alachlor and metolachlor parent compounds in water from hot-spot well BE 1370 and spring BE SP20 compared to the neighboring wells sampled.

Waters from wells near the hot-spot well have variable water-quality characteristics. To the southwest of BE 1370, waters from wells completed in shallow and deeper parts of the aquifer (wells BE 1298 and BE 1775) have concentrations of pesticides most similar to the hot-spot well; the difference is that the acetamide parent compounds were not detected in samples from BE 1298 and BE 1775. Well BE 1774, the deepest well sampled, and well BE 1776, both to the south of the well BE 1370, had similarities in ground-water quality. Water from these two wells had no parent compounds at the OGRL reporting levels of 0.02 to 0.05 µg/L, concentrations of degradation products at least a factor of two less than the hot spot, and acetamide degradation products more prevalent in number and higher in concentration than triazine and phenylurea degradation products in the same water samples. A trace of acetamide degradation products was reported above the MRL in water from well BE 1773, adjacent to the Little Manatawny Creek.

Table 26. Summary of selected well and water-quality characteristics with associated numbers of pesticide parent compounds and numbers of pesticide degradates in water from well BE 1370, five neighboring wells, and a spring, Oley Township, Berks County, Pennsylvania, August 18–23, 2005.

[Water use: R, residence; L, Livestock; N, nitrogen; D.O., dissolved oxygen; Cl, chloride; Cl:Br, mass (weight) ratio of chloride and bromide concentrations; µg/L, micrograms per liter; < , less than; RL, reporting level; –, no data]

Well or spring (SP) number	Water use	Well depth, in feet	Concentration, in milligrams per liter			Cl:Br	Triazines; 0.025–0.2 µg/L reporting level		Acetamides; 0.02–0.05 µg/L reporting level		Total number of pesticide compounds at or above RL
			Nitrate as N	D.O.	Cl		Number of parent compounds at or above RL	Number of degradate compounds at or above RL	Number of parent compounds at or above RL	Number of degradate compounds at or above RL	
BE 1370	R	110	24.5	8.7	5.2	38	1	3	2	8	14
BE 1298	R	62	15.3	8.4	21	121	1	3	0	4	8
BE 1773	R	–	< .06	.1	7.7	39	0	0	0	2	2
BE 1774	R	397	.6	.1	17	97	0	1	0	2	3
BE 1775	R	320	6.4	.1	41	199	1	3	0	3	7
BE 1776	R	180	2.8	1.7	37	191	0	1	0	3	4
BE SP20	L	–	12.5	5.2	12	69	1	4	1	7	13



State boundary and streams from U.S. Geological Survey, 2005
Roads, population centers, county and municipal boundaries from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Piedmont carbonate hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 24. Locations of well BE 1370, five neighboring wells, and a spring, Oley Township, Berks County, Pennsylvania. Samples were analyzed at the U.S. Geological Survey Organic Geochemistry Research Laboratory (OGRL).

Table 27. Concentrations of acetamide pesticides and degradation products in water from well BE 1370, five neighboring wells, and a spring, Oley Township, Berks County, Pennsylvania, August 18–23, 2005.

[Asterisks denote compounds that are degradation products of the parent pesticide. < , less than; RL, reporting level; SP, spring. Shaded cells are concentrations at or above the reporting level]

Chemical name	Concentration, in micrograms per liter						
	BE 1370	BE 1298	BE 1773	BE 1774	BE 1775	BE 1776	BE SP20
Acetochlor	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
*Acetochlor ESA (ethane sulfonic acid)	.03	< .02	< .02	< .02	< .02	< .02	.03
*Acetochlor OXA (oxanilic acid)	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor SAA (sulfynil acetic acid)	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor/metolachlor ESA – 2nd amide	.08	.02	< .02	< .02	< .02	< .02	.08
*Acetochlor/metolachlor – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor deschloro	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Alachlor	.04	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor ESA	.31	.08	.02	.13	.92	.12	.26
*Alachlor OXA	.99	< .02	< .02	< .02	< .02	< .02	.05
*Alachlor SAA	.03	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor ESA – 2nd amide	< .02	< .02	< .02	< .02	< .02	.03	< .02
*Alachlor – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor deschloro	.02	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Dimethenamid	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid ESA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid deschloro	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Flufenacet	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Flufenacet ESA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Flufenacet OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Metolachlor	.19	< .02	< .02	< .02	< .02	< .02	.16
*Metolachlor ESA	.63	2.29	.04	.19	1.05	.22	1.92
*Metolachlor OXA	.41	.02	< .02	< .02	.03	< .02	.25
*Metolachlor deschloro	< .02	< .02	< .02	< .02	< .02	< .02	.05
*Metolachlor hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Propachlor	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
*Propachlor ESA	< .05	< .05	< .05	< .05	< .05	< .05	< .05
*Propachlor OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Total number of parent acetamide compounds at or above RL	2	0	0	0	0	0	1
Total number of acetamide degradation products at or above RL	8	4	2	2	3	3	7
Total number of acetamide compounds at or above RL	10	4	2	2	3	3	8

Table 28. Concentrations of triazine and phenylurea pesticides and degradation products in water from well BE 1370, five neighboring wells, and a spring, Oley Township, Berks County, Pennsylvania, August 18–23, 2005.

[Asterisks denote compounds that are degradation products of the parent pesticide. <, less than; RL, reporting level. Shaded cells are concentrations at or above the reporting level]

Chemical name	Concentration, in micrograms per liter						
	BE 1370	BE 1298	BE 1773	BE 1774	BE 1775	BE 1776	BE SP20
Atrazine	0.15	0.11	< 0.025	< 0.025	0.08	< 0.025	0.10
*Deethylatrazine (CIAT)	.36	.47	< .025	< .025	.26	.04	.37
*Deisopropylatrazine (CEAT)	< .025	.03	< .025	< .025	< .025	< .025	.03
*Hydroxyatrazine (HA)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylhydroxyatrazine (DEHA)	.04	< .025	< .025	< .025	.03	< .025	.03
*Deisopropylhydroxyatrazine (DIHA)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethyldeisopropylatrazine/Didealkyatrazine (CAAT)	.21	.27	< .025	.03	.15	< .025	.21
Bromacil	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Cyanazine	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Cyanazine acid (CAC)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Cyanazine amide (CAM)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine acid (DCAC)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine amide (DCAM)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine (DEC)	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Prometon	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Propazine	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Simazine	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Hydroxysimazine	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Diuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Fluometuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20
*DMFM (demethylfluometuron)	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Linuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Total number of parent triazine and phenylurea compounds at or above RL	1	1	0	0	1	0	1
Total number of triazine and phenylurea degradates at or above RL	3	3	0	1	3	1	4
Total number of triazine and phenylurea compounds at or above RL	4	4	0	1	4	1	5

Blair County, North Woodbury Township

Concentrations of nitrate and pesticides in water from well BA 437 have exceeded MCLs for years. The following includes a brief history of monitoring, a description and summary of the major findings from the borehole testing, and a description and summary of the water-quality results.

In 1984, USGS conducted a regional assessment of well yields and ground-water quality in an area that included Blair County (Becher, 1996). The assessment showed that water from well BA 437 had high concentrations of chloride (470 mg/L), nitrate (100 mg/L as nitrogen), and pesticides (20 μg/L of alachlor and 11 μg/L of atrazine). In 1996, PDA initiated a surveillance program of the ground water at well BA 437 to monitor long-term changes in the concentration of nitrate and pesticides. Because of concerns over the concentrations of nitrate in ground water by communities neighboring North Woodbury Township, USGS conducted an investigation of water sources and nitrate origin for the Borough of Martinsburg (Lindsey and Koch, 2004). Lindsey and Koch (2004, p. 35) reported that well BA 437 was near the southern extent of the zone of contribution of ground water to the supply wells for Martinsburg. Surveillance results at well BA 437 indicated the persistence of high concentrations of pesticides; hence, PDA requested in early 2005 that USGS investigate the occurrence of pesticide breakdown products and conduct detailed borehole tests to determine whether the high concentrations were present only in shallow parts of the aquifer.

In August 2005, borehole testing at well BA 437 included video, caliper, flowmeter, and geophysical logging to identify water-bearing fractures in the rock. The total well depth is 106 ft below land surface (bls), and the well is cased to 21 ft bls with a 6-in. diameter steel casing. The static water level at the start of testing was 33 ft bls. The testing showed major fractures at 43, 45, and 48 ft bls and numerous smaller fractures at 68, 74, and 97–99 ft bls. The fractures in the 43–48 ft interval were termed the shallow water-bearing zone, and the fractures between 68 and 99 ft were termed the deep water-bearing zone. Water conductivity showed a sudden increase at 101 ft bls, indicating an increase in dissolved solids content and correspondingly higher water density. Bedding surfaces had an average orientation (strike) of N.26°E. and a dip of 61°NW. On August 30, 2005, an inflatable barrier (packer) was set at 65 ft bls to separate the shallow and deep water-bearing zones. A submersible pump positioned above the barrier showed the seal between the zones was tight. Pumping data showed a yield for the shallow zone of about 2 gal/min. After purging over three volumes of water from the shallow zone, a water-quality sample was collected. On August 31, 2005, the submersible sampling pump was positioned below the inflatable barrier. Pumping data indicated a yield of less than 0.25 gal/min for the deep zone. After 6 hours of purging, a water-quality sample was collected from the deep zone.

To summarize the borehole logging of well BA 437:

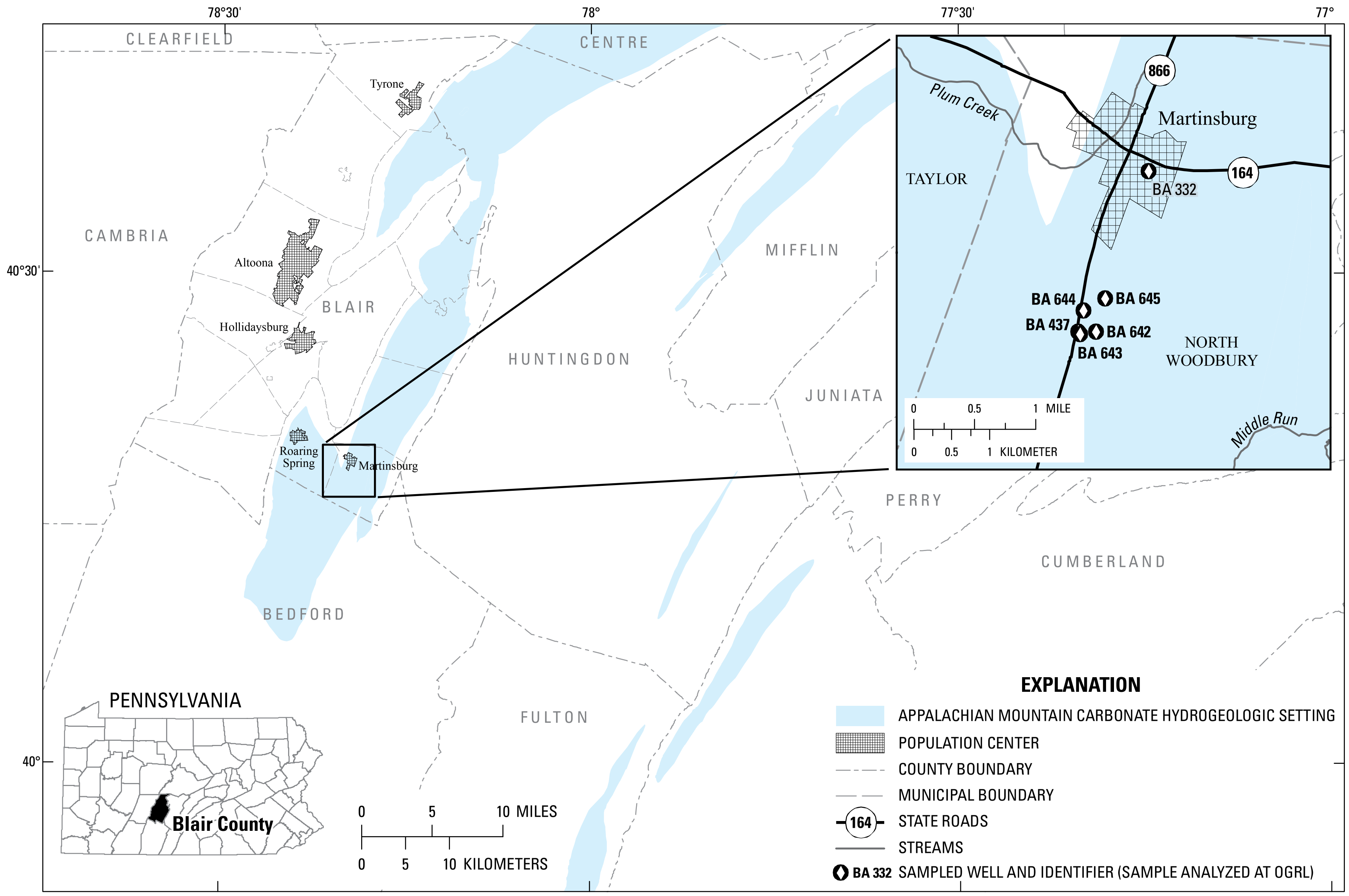
1. The casing appears intact. Minor amounts of water seep into the borehole above the static water level and below the base of the casing.
2. The well yield is chiefly from a shallow water-bearing zone at 43–48 ft bls where fractures and other openings in the rock connect with the borehole. A deep water-bearing zone at 68–99 ft is a source of minor amounts of water.
3. Sustained well yield, without significant drawdown of water level, is about 2 gal/min. The deep zone yields less than 0.25 gal/min.
4. Water at the base of the borehole has relatively high dissolved solids content.

The detailed water-quality sampling and testing at well BA 437 was used to compare concentrations of chloride, nitrate, and pesticides in water from the shallow and deep zones. On September 7, 2005, a composite sample was collected from the open borehole of well BA 437 to compare to the samples from the shallow and deep zones of well BA 437 and to samples from neighboring wells. The neighboring wells included a commercial well (BA 643) historically used for pesticide mixing and handling; three rural domestic wells at residences (BA 642, BA 644, and BA 645); and the nearest production well for the Borough of Martinsburg (BA 332) (table 3, fig. 25). Results of the analyses of ground-water samples are summarized in tables 29, 30, and 31.

At well BA 437, the nitrate concentrations in the shallow and deep zones were 61.7 mg/L and 28.8 mg/L, respectively. The composite sample, with a nitrate concentration of 66.1 mg/L, is further evidence that most of the water yield originates in the shallow zone, and the nitrate contamination is greatest in that zone. The concentration in composite samples has remained in the 35–75 mg/L as N range since 1996 (the USEPA MCL for nitrate in public drinking water is 10 mg/L as N).

The chloride concentration in the shallow zone at well BA 437 was 196 mg/L. The deep zone was only slightly more enriched in chloride (228 mg/L). Although the chloride concentrations were high, the magnitude was about one half the concentration measured by USGS in 1984. The USEPA secondary MCL for drinking water for chloride of 250 mg/L was not exceeded. The ratio of chloride to bromide (Cl:Br) is an indicator of whether the chloride is from (a) halite (NaCl—either naturally occurring in the rock or from road salt), (b) sewage, or (c) a mixture of sewage and halite. The relatively large Cl:Br value of about 4,000 in the deep-zone sample indicates a halite source. The Cl:Br value of about 700 in the shallow zone suggests a mixture of halite and sewage sources for the chloride in ground water. It is possible that the halite source is, at least in part, from road salt stored adjacent to the well. The high conductance water noted at the bottom of the well is consistent with the water-quality results.

The triazine herbicides (atrazine, bromacil, and prometon) and the acetamide herbicides (metolachlor and alachlor)



State boundary and streams from U.S. Geological Survey, 2005
Roads, population centers, county and municipal boundaries from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Piedmont carbonate hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30′N and 45°30′N.
Central meridian 77°45′W, latitude of origin 23°00′N

Figure 25. Locations of well BA 437 and five neighboring wells, North Woodbury Township and Borough of Martinsburg, Blair County, Pennsylvania. Samples were analyzed at the U.S. Geological Survey Organic Geochemistry Research Laboratory (OGRL).

Table 29. Summary of selected well and water-quality characteristics with associated numbers of pesticide parent compounds and numbers of pesticide degradates in water from well BA 437 and five neighboring wells, North Woodbury Township and Borough of Martinsburg, Blair County, Pennsylvania, August 30 through September 8, 2005.

[RL, reporting level; µg/L, micrograms per liter; D.O., dissolved oxygen; Cl, chloride; Cl:Br, mass (weight) ratio of chloride and bromide concentrations; N, nitrogen; < , less than. Flow-path location: Up, Upgradient of hot spot; Down, Downgradient of hot spot. Water use: R, residence; NC, non-consumptive; P, public supply. Sample interval: S, shallow; D, deep; M, mixture of shallow and deep; –, no data]

Well number	Flow-path location	Water use	Well depth, in feet	Sample interval	Concentration, in milligrams per liter			Cl:Br	Triazines; 0.025–0.2 µg/L reporting level		Acetamides; 0.02–0.05 µg/L reporting level		Total number of pesticide compounds at or above RL
					Nitrate as N	D.O.	Cl		Number of parent compounds at or above RL	Number of degradate compounds at or above RL	Number of parent compounds at or above RL	Number of degradate compounds at or above RL	
BA 437	Hot spot	NC	< 65	S	61.7	0.3	196	723	4	6	2	12	24
BA 437	Hot spot	NC	105	D	28.8	–	228	4,071	4	10	3	10	27
BA 437	Hot spot	NC	105	M	66.1	.5	206	3,029	5	6	2	11	24
BA 332[1]	Down	P	100	–	8.8	7.0	34	1,789	1	2	1	5	9
BA 642	Up	R	300	–	1.1	1.8	270	5,625	1	4	0	3	8
BA 643	Hot spot	NC	330	–	64.3	.1	106	328	6	6	1	11	24
BA 644	Down	R	150	–	2.2	.1	64	2,065	6	7	2	9	24
BA 645	Down	R	207	–	11.7	5.3	76	2,000	1	2	1	6	10

[1] Production well for Borough of Martinsburg, Pa.

Table 30. Concentrations of acetamide pesticides and degradation products in water from well BA 437 and five neighboring wells, North Woodbury Township and Borough of Martinsburg, Blair County, Pennsylvania, August 30 through September 8, 2005.

[Asterisks denote compounds that are degradation products of the parent pesticide. < , less than; RL, reporting level; Sample interval: S, shallow; D, deep; M, mixture of shallow and deep. Shaded cells are concentrations at or above the RL.]

Chemical name	Concentration, in micrograms per liter							
	BA 437 S	BA 437 D	BA 437 M	BA 332	BA 642	BA 643	BA 644	BA 645
Acetochlor	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
*Acetochlor ESA (ethane sulfonic acid)	.19	.46	.19	.05	< .02	.09	< .02	.37
*Acetochlor OXA (oxanilic acid)	.05	.68	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor SAA (sulfynil acetic acid)	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor/metolachlor ESA – 2nd amide	.10	.08	.15	.06	< .02	.17	< .02	.09
*Acetochlor/metolachlor – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor deschloro	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Alachlor	.34	.09	.36	< .02	< .02	.82	.83	< .02
*Alachlor ESA	.84	1.99	.99	.09	.04	1.44	.51	.57
*Alachlor OXA	3.10	3.74	3.96	< .02	< .02	4.27	4.14	< .02
*Alachlor SAA	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor ESA – 2nd amide	.02	< .02	.02	< .02	< .02	.03	.03	< .02
*Alachlor – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor deschloro	.25	.29	.26	< .02	< .02	.36	.11	< .02
*Alachlor hydroxy	.53	< .02	.51	< .02	< .02	.83	.75	< .02
Dimethenamid	< .02	.02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid ESA	< .02	< .02	< .02	< .02	< .02	< .02	< .02	.04
*Dimethenamid OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid deschloro	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Flufenacet	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Flufenacet ESA	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Flufenacet OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Metolachlor	18.	6.57	20.	.14	< .02	< .02	2.20	.03
*Metolachlor ESA	2.93	3.30	3.36	1.27	.40	3.17	.35	1.91
*Metolachlor OXA	6.76	6.93	7.29	.11	.05	7.53	.36	.37
*Metolachlor deschloro	.26	.16	.22	< .02	< .02	.24	.02	< .02
*Metolachlor hydroxyl	.32	.08	.30	< .02	< .02	.37	.03	< .02
Propachlor	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
*Propachlor ESA	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05
*Propachlor OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Total number of parent acetamide compounds at or above RL	2	3	2	1	0	1	2	1
Total number of acetamide degradation products at or above RL	12	10	11	5	3	11	9	6
Total number of acetamide compounds at or above RL	14	13	13	6	3	12	11	7

Table 31. Concentrations of triazine and phenylurea pesticides and degradation products in water from well BA 437 and five neighboring wells, North Woodbury Township and Borough of Martinsburg, Blair County, Pennsylvania, August 30 through September 8, 2005.

[Asterisks denote compounds that are degradation products of the parent pesticide. < , less than; RL, reporting level; Sample interval: S, shallow; D, deep; M, mixture of shallow and deep. Shaded cells are concentrations at or above the reporting level.]

Chemical name	Concentration, in micrograms per liter							
	BA 437 S	BA 437 D	BA 437 M	BA 332	BA 642	BA 643	BA 644	BA 645
Atrazine	0.60	0.11	0.51	< 0.025	0.03	1.18	0.19	0.07
*Deethylatrazine (CIAT)	.07	.29	.27	.12	.03	.26	.08	.12
*Deisopropylatrazine (CEAT)	.06	.16	.12	< .025	.04	.10	.03	< .025
*Hydroxyatrazine (HA)	< .025	.04	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylhydroxyatrazine (DEHA)	< .025	.03	< .025	< .025	.04	< .025	< .025	< .025
*Deisopropylhydroxyatrazine (DIHA)	1.03	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethyldeisopropylatrazine/Didealkyatrazine (CAAT)	< .025	.20	.80	.20	.14	.40	.06	.10
Bromacil	1.74	.22	1.41	< .025	< .025	2.59	.14	< .025
Cyanazine	.06	.10	.08	< .025	< .025	.21	.11	< .025
*Cyanazine acid (CAC)	.08	.62	.09	< .025	< .025	.25	.16	< .025
*Cyanazine amide (CAM)	.10	.66	.12	< .025	< .025	.35	.23	< .025
*Deethylcyanazine acid (DCAC)	.33	.30	.20	< .025	< .025	.38	.09	< .025
*Deethylcyanazine amide (DCAM)	< .025	.03	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine (DEC)	< .20	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Prometon	.21	.03	.19	.03	< .025	.39	.04	< .025
Propazine	< .025	< .025	< .025	< .025	< .025	.04	.04	< .025
Simazine	< .025	< .025	.09	< .025	< .025	.10	< .025	< .025
*Hydroxysimazine	< .025	.03	< .025	< .025	< .025	< .025	.03	< .025
Diuron	< .20	< .20	< .20	< .20	< .20	< .20	.35	< .20
Fluometuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20	< .20
*DMFM (demethylfluometuron)	< .20	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Linuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Total number of parent triazine and phenylurea compounds at or above RL	4	4	5	1	1	6	6	1
Total number of triazine and phenylurea degradates at or above RL	6	10	6	2	4	6	7	2
Total number of triazine and phenylurea compounds at or above RL	10	14	11	3	5	12	13	3

were present primarily in water from the shallow zone at well BA 437. Numerous triazine degradation products were present in the waters; cyanazine and its degradation products were prevalent in the deep zone. The atrazine concentration has remained below 1 µg/L (table 22), the action concentration set by the PDA (appendix 4); however, the atrazine concentration in 1984 was 11 µg/L. Alachlor concentrations (0.34 to 0.36 µg/L) were about one half the PDA action concentration (appendix 4) and up to five alachlor degradation products were present with concentrations ranging from about 0.02 to nearly 4 µg/L in the shallow and deep zones. The 20 µg/L of metolachlor in the composite sample collected on September 7, 2005, is consistent with results since 1997 (see fig. 20). Metolachlor concentrations were 18 µg/L in the shallow zone and 6.57 µg/L in the deep zone. The concentrations of metolachlor degradation products were nearly identical in the shallow and deep zones.

BA 642, a rural domestic well considered "upgradient" of the hot spot on the basis of the location and relative concentration of nitrate and pesticides, is one of the deepest wells but had the highest concentration of chloride (270 mg/L) of the five wells sampled. The Cl:Br value near 5,000 indicates a halite mineral in the aquifer or road salt as possible sources of the chloride and bromide. Although relatively low in concentration, atrazine and four triazine degradation products were reported (table 31) along with acetamide degradation products of alachlor and metolachlor. BA 642 well water has the lowest measured concentrations of pesticides in the vicinity of well BA 437.

At BA 643, atrazine, alachlor, and bromacil are present in water at concentrations nearly double the concentrations in water from well BA 437 (tables 30 and 31). The historical use of well BA 643 to supply water for a commercial pesticide mixing facility may indicate a potential source for the alachlor, atrazine, and bromacil in ground water; however, the concentration of metolachlor below reporting levels in BA 643 well water is confounding. With a measured total depth of 330 ft, well BA 643 is the deepest of the wells sampled. Little is known about the construction of well BA 643 or the depth and nature of water-bearing zones to the well.

Wells BA 644 and BA 645 are north of well BA 437 along the simulated line of northward ground-water flow towards well BA 332 (Lindsey and Koch, 2004). The concentrations of pesticides in these wells are intermediate between the hot spot area and well BA 332. Well BA 644 has the same set of parent pesticides and degradation products, although at lower concentrations, as those observed at well BA 437. The nitrate concentration in well BA 644 is relatively low and suggests a possible connection to a fracture system that intersects well BA 642.

The borehole investigation at well BA 437 underscores the complex nature of the fractured carbonate-rock aquifers in the vicinity. The directions and rates of ground-water flow are not well characterized in this area. Additional hydrogeologic measurements and water-quality sampling are required to yield more insight into the occurrence of pesticides, nitrate, and chloride in this complex flow system.

The pesticide concentrations in well BA 437 or in neighboring wells sampled do not exceed USEPA health advisories (U.S. Environmental Protection Agency, 2006, 2008). No USEPA MCLs or health advisories currently exist for degradation products and for combinations of pesticides and pesticide degradation products.

Lancaster County, Earl Township

In June 2006, well LN 1842, four wells used for farmyard, livestock, and rural domestic purposes at neighboring residences, and a production well for the Borough of New Holland were sampled (table 3, fig. 26). Results of the analyses of ground-water samples are summarized in tables 32, 33, and 34.

The pesticide compounds in ground water from well LN 1842 were primarily acetamide compounds (dominated by metolachlor) with lesser concentrations of triazine herbicides. The presence of degradation products indicates the degradation of metolachlor, alachlor, and acetochlor parent compounds is occurring. The concentrations of selected degradation products of alachlor and acetochlor exceeded the concentration of parent compounds. The alachlor concentration in water from well LN 1842 was 2.8 µg/L in 1991 (Durlin and Schaffstall, 1993, p. 307), which triggered the hot-spot status for the well. The sum of concentrations of alachlor degradation products and parent compounds averaged for the two June 2006 samples from well LN 1842 (0.0109 micromoles per liter [µM/L]) was about equal to the historic concentration of alachlor alone (0.0104 µM/L). In the June 2006 samples, the combined concentration of metolachlor degradation products is to about 0.07 µM/L (or about 20 µg/L), one third of the 0.21 µM/L concentration of the metolachlor parent compound (about 60 µg/L) (table 33). The newly proposed "ambient water-quality human-health criteria" for metolachlor is 69 µg/L (Pennsylvania Department of Environmental Protection, 2008).

Wells neighboring well LN 1842 were chosen for sampling in an attempt to represent three possible components of the ground-water flow system in the carbonate-rock aquifers of Cambrian age underlying Earl Township and the Borough of New Holland. The first component was deep flow discharging as pumpage from the municipal wells at the north side of New Holland (fig. 26). Well LN 1291 was sampled to represent this discharge area. The second component was flow towards the southeast and Mill Creek, which represents another possible discharge point for ground water. This component was represented by wells LN 2118 and LN 2119. The third component of flow was along the axis of an anticlinal rock structure striking approximately east-west near well LN 1842. Well LN 2000 was along the axial strike to the east. Well LN 1998 was chosen to represent a plausible upgradient location in the flow system.

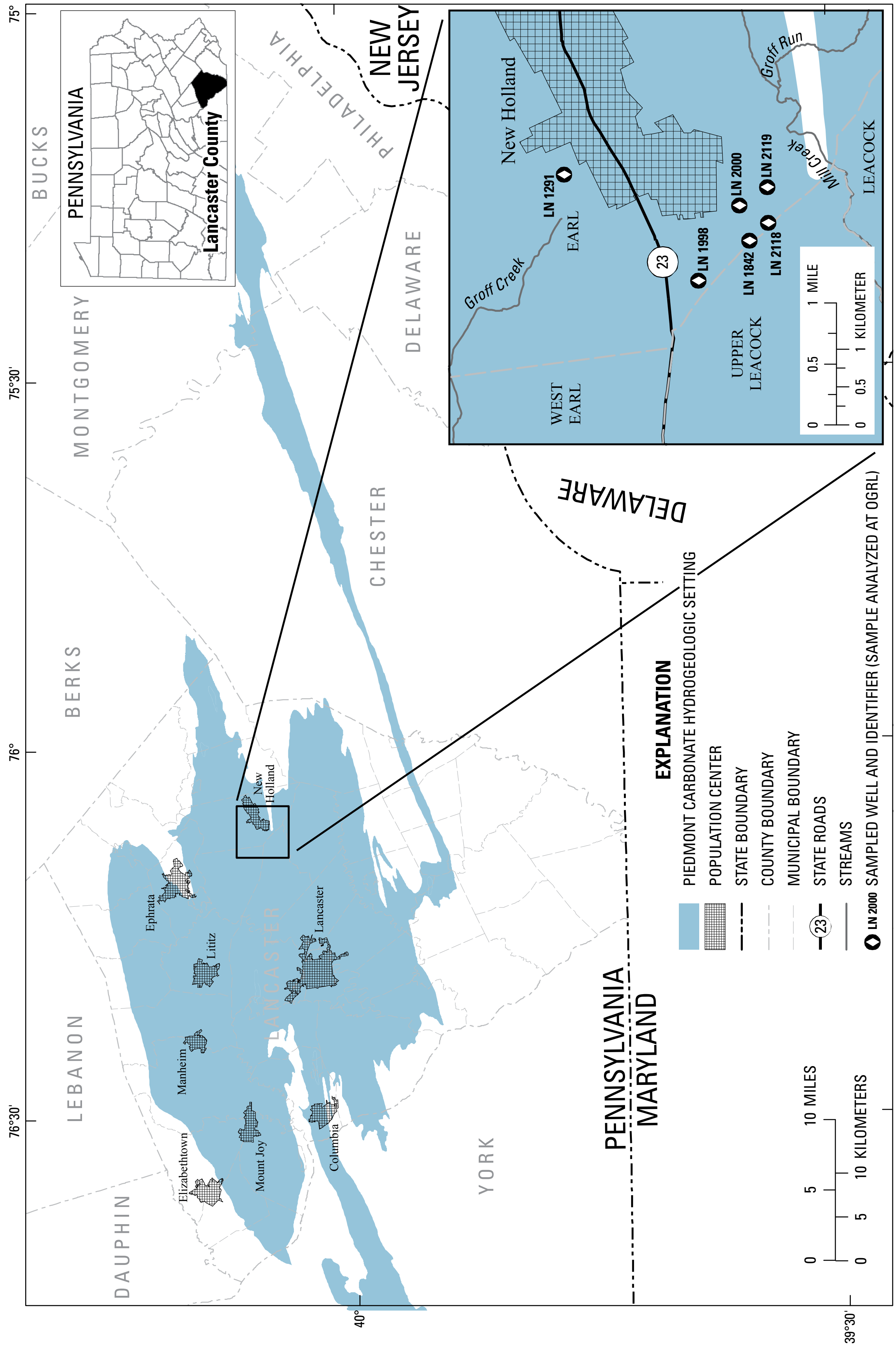
All well-water samples had reported concentrations of nitrate and pesticides. Nitrate concentration was above 10 mg/L as N in samples from wells along the southeast and axial east flow components. Nitrate was lowest in the samples from wells LN 1998 and LN 1291 with concentrations of 7.6 and 4.3 mg/L, respectively (table 32). Pesticide occurrence was dominated by acetamide degradation products (table 33); however, wells LN 2118 and LN 2119 had a higher number of triazine degradation products than the other neighboring wells (table 34). The four triazine degradation products in samples from wells LN 2118 and LN 2119 were among the seven triazine degradation products reported in samples from the hot-spot well LN 1842. Water samples from well LN 2119 appear to have the same set of pesticide compounds as well LN 1842 except the acetochlor group in LN 1842 sample water was not present in well LN 2119 or the other wells (tables 33 and 34). The flow component to the discharge point at the New Holland supply well (LN 1291) has atrazine and one degradation product each of atrazine and metolachlor in ground water at concentrations of 0.03 to 0.05 µg/L. These concentrations are nearly an order of magnitude less than in waters from wells LN 1998 and LN 2000.

Table 32. Summary of selected well and water-quality characteristics with associated numbers of pesticide parent compounds and numbers of pesticide degradates in water from well LN 1842 and five neighboring wells, Earl Township and Borough of New Holland, Lancaster County, Pennsylvania, June 1 through June 29, 2006.

[Water use: R, residence; L, Livestock; P, public supply. D.O., dissolved oxygen; Cl, chloride; Cl:Br, mass (weight) ratio of chloride and bromide concentrations; N, nitrogen; µg/L, micrograms per liter; RL, reporting level; –, no data]

Well number (date sample collected)	Water use	Well depth, in feet	Concentration, in milligrams per liter			Cl:Br	Triazines; 0.025–0.2 µg/L Reporting level		Acetamides; 0.02–0.05 µg/L Reporting level		Total number of pesticide compounds at or above RL
			Nitrate as N	D.O.	Cl		Number of parent compounds at or above RL	Number of degradate compounds at or above RL	Number of parent compounds at or above RL	Number of degradate compounds at or above RL	
LN 1842 (6/1/06)	R, L	65	33.3	9.7	45	1,154	2	7	3	11	23
LN 1842 (6/29/06)	R, L	65	32.1	8.3	44	1,222	4	6	3	12	25
LN 1291[1] (6/5/06)	P	232	4.3	4.6	32	1,000	1	1	0	1	3
LN 1998 (6/6/06)	R	60	7.6	.2	54	2,700	1	2	0	3	6
LN 2000 (6/1/06)	R, L	120	14.8	6.9	4.2	210	0	1	1	3	5
LN 2118 (6/6/06)	R, L	–	23.8	5.7	28	1,474	1	4	1	4	10
LN 2119 (6/6/06)	R, L	175	38.9	1.5	27	1,800	1	4	0	7	12

[1] Production well for Borough of New Holland, Pa.



State boundary and streams from U.S. Geological Survey, 2005
Roads, population centers, county and municipal boundaries from Commonwealth of Pennsylvania, 2008; 1:100,000 scale
Piedmont carbonate hydrogeologic setting from Lindsey and Bickford, 1999

Albers Equal-Area Conic projection: standard parallels 29°30'N and 45°30'N.
Central meridian 77°45'W, latitude of origin 23°00'N

Figure 26. Locations of well LN 1842 and five neighboring wells, Earl Township and Borough of New Holland, Lancaster County, Pennsylvania. Samples were analyzed at the U.S. Geological Survey Organic Geochemistry Research Laboratory (OGRL).

Table 33. Concentrations of acetamide pesticides and degradation products in water from well LN 1842 and five neighboring wells, Earl Township and Borough of New Holland, Lancaster County, Pennsylvania, June 1 through June 29, 2006.

[Asterisks denote compounds that are degradation products of the parent pesticide. <, less than; RL, reporting level. Shaded cells are concentrations at or above the RL.]

Chemical name	Concentration, in micrograms per liter						
	LN 1842 (6/1/06)	LN 1842 (6/29/06)	LN 1291	LN 1998	LN 2000	LN 2118	LN 2119
Acetochlor	0.34	0.28	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
*Acetochlor ESA (ethane sulfonic acid)	.23	.18	< .02	< .02	< .02	< .02	< .02
*Acetochlor OXA (oxanilic acid)	.40	.30	< .02	< .02	< .02	< .02	< .02
*Acetochlor SAA (sulfynil acetic acid)	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor/metolachlor ESA – 2nd amide	.24	.32	< .02	.05	.08	.13	.45
*Acetochlor/metolachlor – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor deschloro	.04	< .02	< .02	< .02	< .02	< .02	< .02
*Acetochlor hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Alachlor	.99	.75	< .02	< .02	< .02	< .02	< .02
*Alachlor ESA	.75	.61	< .02	< .02	< .02	.07	.91
*Alachlor OXA	1.76	1.17	< .02	< .02	< .02	< .02	.73
*Alachlor SAA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor ESA – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	.14
*Alachlor – 2nd amide	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Alachlor deschloro	.15	.14	< .02	< .02	< .02	< .02	.13
*Alachlor hydroxy	< .02	.05	< .02	< .02	< .02	< .02	< .02
Dimethenamid	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid ESA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid deschloro	< .02	.02	< .02	< .02	< .02	< .02	< .02
*Dimethenamid hydroxy	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Flufenacet	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Flufenacet ESA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Flufenacet OXA	< .02	< .02	< .02	< .02	< .02	< .02	< .02
Metolachlor	56.	60.	< .02	< .02	.43	.37	< .02
*Metolachlor ESA	9.30	7.21	.05	.78	.56	2.30	1.88
*Metolachlor OXA	9.10	13.	< .02	.07	.12	.65	1.11
*Metolachlor deschloro	< .02	.49	< .02	< .02	< .02	< .02	< .02
*Metolachlor hydroxyl	.49	< .02	< .02	< .02	< .02	< .02	< .02
Propachlor	< .02	< .02	< .02	< .02	< .02	< .02	< .02
*Propachlor ESA	< .05	< .05	< .05	< .05	< .05	< .05	< .05
*Propachlor OXA	.03	.03	< .02	< .02	< .02	< .02	< .02
Total number of parent acetamide compounds at or above RL	3	3	0	0	1	1	0
Total number of acetamide degradation products at or above RL	11	12	1	3	3	4	7
Total number of acetamide compounds at or above RL	14	15	1	3	4	5	7

Table 34. Concentrations of triazine and phenylurea pesticides and degradation products in water from well LN 1842 and five neighboring wells, Earl Township and Borough of New Holland, Lancaster County, Pennsylvania, June 1 through June 29, 2006.

[Asterisks denote compounds that are degradation products of the parent pesticide. <, less than; RL, reporting level. Shaded cells are concentrations at or above the reporting level.]

Chemical name	Concentration, in micrograms per liter						
	LN 1842 (6/1/06)	LN 1842 (6/29/06)	LN 1291	LN 1998	LN 2000	LN 2118	LN 2119
Atrazine	0.14	0.12	0.03	0.03	< .025	0.07	0.07
*Deethylatrazine (CIAT)	.31	.37	.03	.07	.03	.16	.13
*Deisopropylatrazine (CEAT)	.15	.14	< .025	< .025	< .025	.04	.03
*Hydroxyatrazine (HA)	.10	< .025	< .025	< .025	< .025	.03	.28
*Deethylhydroxyatrazine (DEHA)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deisopropylhydroxyatrazine (DIHA)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethyldeisopropylatrazine/Didealkyatrazine (CAAT)	.28	.20	< .025	.08	< .025	.20	.21
Bromacil	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Cyanazine	.19	.20	< .025	< .025	< .025	< .025	< .025
*Cyanazine acid (CAC)	.71	.51	< .025	< .025	< .025	< .025	< .025
*Cyanazine amide (CAM)	.53	.46	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine acid (DCAC)	.33	.29	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine amide (DCAM)	< .025	< .025	< .025	< .025	< .025	< .025	< .025
*Deethylcyanazine (DEC)	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Prometon	< .025	.04	< .025	< .025	< .025	< .025	< .025
Propazine	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Simazine	< .025	.04	< .025	< .025	< .025	< .025	< .025
*Hydroxysimazine	< .025	< .025	< .025	< .025	< .025	< .025	< .025
Diuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Fluometuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20
*DMFM (demethylfluometuron)	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Linuron	< .20	< .20	< .20	< .20	< .20	< .20	< .20
Total number of parent triazine and phenylurea compounds at or above RL	2	4	1	1	0	1	1
Total number of triazine and phenylurea degradates at or above RL	7	6	1	2	1	4	4
Total number of triazine and phenylurea compounds at or above RL	9	10	2	3	1	5	5

Summary and Conclusions

This report was prepared by the U.S. Geological Survey (USGS) in cooperation with the Pennsylvania Department of Agriculture (PDA) to evaluate the occurrence of pesticides in ground water as part of the Pennsylvania Pesticides and Ground Water Strategy (PPGWS). Overall, the major findings reported herein are:

- ***Evaluating occurrence and trends of pesticides in ground water required laboratory methods capable of measuring small concentrations***—
  Pesticide concentrations in ground water are small enough that monitoring for and comparing pesticide concentrations in ground waters in several hydrogeologic settings required the use of consistent laboratory methods that reported a common set of pesticide compounds at minimum reporting levels (MRLs) that were less than 0.05 micrograms per liter (µg/L) and were supported by extensive quality assurance (QA). These attributes allowed for evaluation of concentrations among settings and over time. Analytical methods developed and used by USGS laboratories and the resulting data were a critical first step in evaluating occurrence and trends in pesticide concentrations.

- ***Co-occurrence of pesticides was common***—
  In at least 50 percent of well samples with pesticides, multiple pesticides were detected; however, many concentrations were less than 0.01 µg/L. Atrazine was the pesticide most reported in ground water. Commonly, deethylatrazine (CIAT) co-occurred with atrazine. Metolachlor and (or) simazine, although rare in occurrence, were the only other compounds to co-occur with atrazine in four of the five hydrogeologic settings.

- ***Pesticide-degradation products exhibited co-occurrence with parent pesticide compounds***—
  Pesticide-degradation products were detected with parent compounds often at concentrations greater than the parent compounds. Analyzing for pesticide degradation products along with the parent compounds would be an important component of a comprehensive monitoring strategy for pesticides in ground water.

- ***Monitoring since 2003 has shown no exceedances of maximum contaminant or health advisory levels (MCLs or LHAs) for pesticides in ground water***—
  Assessment of newly collected (2003 and 2005–07) monitoring data for pesticide concentrations in ground water from four hydrogeologic settings previously unassessed or assessed to a limited extent in baseline assessment and special-protection areas and extensive QA data for pesticides shows the MCLs and LHAs were not exceeded.

- ***The number of pesticides in ground water, the magnitude of the concentrations, and the spatial patterns of occurrence have shown distinct variations among the five hydrogeologic settings***—
  Widespread occurrence patterns, with pesticides at measurable concentrations in waters from over 50 percent of wells sampled, characterized the Devonian-Silurian carbonate and Northeastern Glaciated surficial settings. The carbonate setting, with a median atrazine concentration five times larger than the glaciated surficial setting, was the more vulnerable of the two. In contrast, a localized occurrence pattern with pesticides at measurable concentrations in waters from 20 percent of wells sampled, characterized the Great Valley siliciclastic setting with a median atrazine concentration similar to the glaciated surficial setting and five times lower than the carbonate setting. This supports earlier studies that identified carbonate settings as the most vulnerable for pesticide contamination of ground water.

- ***Nitrate concentration testing showed some promise as a way to prioritize well samples for pesticide analyses***—
  Relatively inexpensive test results for nitrate correlated directly with the number of pesticides above the MRLs in the Devonian-Silurian carbonate setting and with atrazine concentrations in the Devonian-Silurian carbonate and the Great Valley siliciclastic settings. Accordingly, elevated nitrate results from wells in these two settings could be used to prioritize wells selected for future sample collection for pesticide analyses.

- ***Preliminary testing for trends in pesticide concentrations indicates a decline in concentration for atrazine but no change for metolachlor in ground water***—
  In carbonate settings known to be vulnerable to pesticide contamination, initial results on changes in pesticide concentrations in 2003 compared to 1993–95 showed waters from nine wells sampled twice having lower atrazine concentrations in 2003.

- ***Monitoring in three areas of special ground-water protection led to improved understanding of pesticide occurrence in the vicinity of hot-spot wells***—
  Samples from wells neighboring the hot-spot wells showed the same sets of pesticides as the hot-spot wells. Concentrations at or in the vicinity of hot-spot wells BA 437 and LN 1842 qualified for continued monitoring as part of the PPGWS.

Details of the findings are presented below. Subheadings developed from the main scope elements and sections of this report are used to organize the summary material.

Changing Patterns of Pesticide Use Related to Land-Use Changes

Agricultural pesticide use was estimated using application-rate and crop-acreage data; atrazine and metolachlor, with 1,314,000 and 895,000 lb/yr, respectively, were the most heavily used agricultural pesticides statewide in 2004–05. Atrazine and metolachlor were used predominantly on corn crops. On the basis of statewide pesticide-use data for corn, atrazine use decreased and metolachlor/S-metolachlor use increased in 2004–05 (2004 data were for field corn and 2005 data were for sweet corn) compared to 1996 (field corn and sweet corn data were combined). Counties where agricultural lands are predominant make up a large fraction of the total use of pesticides; Lancaster County had the greatest amounts of use for 1996 and 2004–05, followed by York, Franklin, and Berks Counties. Of 66 counties statewide, these four counties accounted for atrazine and metolachlor use in 2004–05 of 360,000 and 236,000 lb/yr, respectively. To explain changes in agricultural pesticide use, changes in forest, agriculture, and urban land covers were evaluated in nine major hydrogeologic settings using the National Land Cover Database (NLCD) 1992 and NLCD 2001. A comparison of 1992 county data and 2001 county data showed decreases of agricultural land up to 12 percent (median decrease 7.2 percent), decreases of forested land up to 10 percent (median decrease 4.5 percent), and a corresponding increase of urban land up to 11 percent (median increase 2 percent).

Investigations of Pesticides in Pennsylvania Ground Water, 1997–2002

A retrospective summary of investigations of pesticides in Pennsylvania ground water through 1998 compiled in an earlier study documented that five of the nine hydrogeologic settings identified as vulnerable to pesticide contamination had inadequate monitoring data for the PPGWS. An updated retrospective through 2002 added six new data sources from previous USGS investigations and identified a data gap in the five hydrogeologic settings; filling this data gap was the impetus for the 2003–07 data-collection efforts in the baseline-assessment areas.

Quality Assurance and Quality Control

Quality-control (QC) analyses of representativeness of sampling in the hydrogeologic settings, false positives, false negatives, and bias and variability in results for pesticides, nitrate, nitrite, total coliform, and *E. coli* bacteria were used to qualify the data from the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), the USGS National Water Quality Laboratory (NWQL), and the USGS Organic Geochemistry Research Laboratory (OGRL). Results of these analyses indicated 1) waters sampled were considered representative of the aquifers sampled because site-selection criteria combined with stability criteria for field measurements were met 75 to 100 percent of the time; 2) false positives were not a problem in most cases—sampling procedures, sample equipment and containers, cleaning procedures, and analytical processes were not contributing contamination bias to samples; 3) false negatives (spiked compounds not reported) were less than 5 percent; and 4) bias in recovery and variability varied by compound and laboratory used for pesticides, were excellent for nitrate and nitrite, and could not be adequately evaluated for bacteria because of the methodology used.

Biases in recovery and variability for pesticides were determined from field-spiked reagent water (FSRW) or lab-reagent-spiked (LRS) water samples; selected pesticide results were ‘qualified’ where QA objectives for bias (recovery within ± 25 percent of the true value) and variability (replicate results within ± 25 percent of each other) were not met. The effects of matrix environmental water on recoveries were not evaluated during this study. Reported recoveries of the qualified compounds should be interpreted with the ground-water results because of the potential for 1) actual concentrations to be higher or lower than reported or 2) false negatives. The qualified compounds by laboratory are as follows:

- *PADEPL*—Azinphos-methyl, captan, fenpropathrin, hexachlorocyclopentadiene, metribuzin, and phosmet results were qualified on the basis of the results of six to nine field QC samples and (or) internally submitted QC samples. No reported concentrations in environmental samples were above the respective minimum reporting levels (MRLs) for any of these seven compounds when analyzed by thePADEPL, and it is possible, therefore, that some of the results reported as less than the MRLs are actually false negatives.

- *USGS NWQL*—Of the 107 pesticide compounds analyzed at the NWQL, results for 48 compounds did not meet QA objectives. Qualified compounds include those 39 compounds identified from internal NWQL QC as “estimated,” 4 compounds qualified as a result of 33 field QC samples (ethalfluralin, metribuzin, p,p’-DDE, and propargite), and 5 additional compounds (2,4-DB, bendiocarb, clopyralid, MCPB, and sulfometuron-methyl) that were not qualified as estimated in 2003 but had NWQL QC results (LRS) that did not meet study QA objectives. Of the 48 compounds, deethylatrazine (CIAT) was reported above the MRL in 81 samples. Ten or fewer samples had reported concentrations of terbacil, carbofuran, carbaryl, benomyl, deisopropylatrazine (CEAT), deethyldeisopropylatrazine (CAAT), dinoseb, norflurazon, and sulfometuron-methyl. The remaining qualified compounds were not reported at, above, or below the MRLs in any of the samples analyzed; it is possible that some of the results are actually false negatives.

- *USGS OGRL*—Of the 54 pesticide compounds analyzed at the OGRL, bias and variability were evaluated for acetochlor, alachlor, atrazine, cyanazine, CIAT, linuron, metolachlor, propachlor, prometon, and simazine in field QC samples. All compounds but linuron met study QA goals for variability, and all compounds but atrazine, prometon, simazine, and CIAT met study QA goals for bias. Linuron was not detected above the MRL; however, atrazine, prometon, simazine, and CIAT were detected above the respective MRLs. Linuron, atrazine, prometon, simazine, and CIAT results are noted as not meeting study QA goals but were not qualified because of the low numbers of field QC samples and the lack of long-term QC results that could be used for comparison.

Monitoring Data for Pesticide Occurrence, 2003–07

A total of 126 wells were monitored for pesticides, nitrate, nitrite, and most probable numbers of total coliform and *E. coli* bacteria for the baseline assessment of five hydrogeologic settings previously unassessed or assessed to a limited extent. Between 20 and 30 wells per setting were sampled in the following hydrogeologic settings: Blue Ridge crystalline and Triassic Lowland siliciclastic, Eastern Lake surficial, Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial. Of the 126 well waters analyzed, 43 had concentrations of one or more pesticides above the respective MRLs or estimated below the MRLs. All reported concentrations from 15 of these 43 wells were estimated below the MRL or estimated because of unacceptable bias in recovery and (or) variability. Well samples with one or more estimated pesticide concentrations were analyzed at the NWQL; the majority of these wells were in the Northeastern Glaciated surficial hydrogeologic setting (9 wells), followed by the Great Valley siliciclastic (3 wells), the Blue Ridge crystalline and Triassic Lowland siliciclastic (2 wells), and the Devonian-Silurian carbonate (1 well) settings. Occurrence of pesticides varied by setting. In terms of laboratory used and total number of wells sampled per setting, the number of well waters with reported concentrations (above the MRLs or estimated below the MRLs) was: Blue Ridge crystalline and Traissic Lowland (NWQL—6 of 10 wells; PADEPL—0 of 10 wells), Eastern Lake surficial (PADEPL—0 of 20 wells), Devonian-Silurian carbonate (NWQL—16 of 28 wells), Great Valley siliciclastic (NWQL—5 of 30 wells), and Northeastern Glaciated surficial (NWQL—16 of 28 wells). At the PADEPL, at least 19 pesticide compounds were analyzed at MRLs of 0.10 to 1.6 µg/L; at the NWQL, at least 52 pesticide compounds were analyzed at MRLs of 0.002 to 1.5 µg/L. No pesticide concentration in samples collected in the five hydrogeologic settings exceeded the USEPA maximum contaminant levels (MCLs) or PPGWS action levels, although the pesticide results in the Eastern Lake surficial and sections of the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic settings (samples analyzed at the PADEPL) can not be directly compared with the pesticide results in the Devonian-Silurian carbonate, Great Valley siliciclastic, and Northeastern Glaciated surficial hydrogeologic settings (samples analyzed at the NWQL) because of the analytical differences for the two laboratories.

Opportunities to evaluate co-occurrence of pesticides in well water sampled varied by year because of the differences in the number and respective MRLs of the pesticides analyzed at the PADEPL and the NWQL. Co-occurrence of pesticides was common (50 to 100 percent) in well samples, but many concentrations were at estimated levels; metolachlor and (or) simazine co-occurred with atrazine, and frequently CIAT, in one or more well-water samples in the following hydrogeologic settings: Blue Ridge crystalline and Triassic Lowland siliciclastic, the Devonian-Silurian carbonate, the Great Valley siliciclastic, and the Northeastern Glaciated surficial. Only one concentration of simazine (0.151 µg/L) was above 0.10 µg/L.

Statistical-correlation analysis, using the NWQL analytical results, was used to investigate the strength of the relations between pesticide occurrence and two indicators of water-quality degradation—occurrence of total coliform bacteria and nitrate concentration. The results of a 2 × 2 contingency-table test showed a significant relation between presence or absence of atrazine or metolachlor and presence or absence of total coliform bacteria only for the 10 wells representing the Blue Ridge crystalline and Triassic Lowland siliciclastic setting. The Eastern Lake surficial setting was excluded from testing because none of the 20 samples from the setting were analyzed at the NWQL. Therefore, although bacteria were commonly found in samples of well water, statistical testing indicated bacteria in well water were not a significant indicator of the presence of pesticides, and bacteria results could not be used to prioritize selection of wells for pesticide analyses. Spearman's rank-test correlations were done using pesticide and nitrogen results in the following hydrogeologic settings: Devonian-Silurian carbonate, the Great Valley siliciclastic, and the Northeastern Glaciated surficial. Results suggest that a direct correlation exists between nitrate concentration and the number of pesticides above the MRLs in the Devonian-Silurian carbonate setting and between nitrate and atrazine concentrations in the Devonian-Silurian carbonate and the Great Valley siliciclastic settings. Accordingly, elevated nitrate results from wells in these two settings could be used to prioritize wells selected for future sample collection for pesticide analyses. The pesticide results from the Blue Ridge crystalline and Triassic Lowland siliciclastic and the Eastern Lake surficial settings were not included in these statistical tests because of the MRL differences in all or part of these data sets where samples were analyzed at the PADEPL. Therefore, for future monitoring that involves comparison of pesticide concentrations in ground waters in several hydrogeologic settings, the use of a consistent set of laboratory methods and reporting a consistent set of pesticide compounds at MRLs less than

0.05 µg/L is essential for evaluation of concentrations among settings and over time.

Patterns of Pesticide Concentration Change, 1993–2004

Changes in pesticide concentrations were evaluated for 18 wells sampled twice during the decade 1993–2004 in the Appalachian Mountain carbonate, Triassic Lowland siliciclastic, Great Valley carbonate, and Piedmont carbonate hydrogeologic settings. Nine of the 18 wells were chosen for further analysis because the NWQL was used consistently for analyses of the pairs of samples. Pesticides reported in the initial sample from each well in the mid-1990s were generally still present in samples collected in 2003 but at lower concentrations. Two nonparametric statistical analyses, the Kruskal-Wallis and Tukey-Kramer tests, were used to determine if there were statistically significant correlations between atrazine and metolachlor concentrations and a categorical 'date' variable for the nine wells. These tests indicated significantly lower median concentrations of atrazine in the samples collected during 2003 than during 1993–95; however, significant changes in the median concentrations of metolachlor were not observed between the sample dates. The Wilcoxon signed-rank test also was used to test for temporal changes in median concentrations for atrazine and metolachlor using differences in paired-observation data (1993, 1994, or 1995 and 2003) for the nine baseline-assessment wells. Results from this test showed a significant decrease in atrazine concentration but did not identify a significant temporal change in metolachlor concentration. For the nine wells, a comparison of changes in concentration of atrazine and its degradation product CIAT to changes in water levels and land-use practices indicated that higher water levels, decreases in agricultural land use, and decreases in atrazine application in 2003 compared to 1993–95 could all be factors in the decreased concentrations observed.

Pesticides in Ground Waters Representing Three Areas of Special Ground-Water Protection

At three pesticide hot-spot wells (wells BA 437, LN 1842, and BE 1370 in areas of special ground-water protection), changes in concentration of parent pesticide compounds and the co-occurrence of pesticide-degradation products with parent compounds in ground water were evaluated. During exploratory data analysis, scatterplots and boxplots were used to analyze the data graphically; the Kruskal-Wallis and Tukey-Kramer tests were used as screening tools to examine for significant seasonality and to determine which seasonal groups differed from each other but did not account for trend over time. These exploratory statistical tests indicated seasonality was likely a factor for well BA 437; significantly higher median concentrations of alachlor were observed at BA 437 during the fall than during the winter. During trend testing, seasonality was observed at all three hot-spot wells.

Nonparametric statistical analyses were used to determine monotonic trends in pesticide and nitrate concentration data at the three hot-spot wells using a 5-year (2003–07) data set and a long-term data set (dates varied). Trends in concentrations of alachlor, atrazine, metolachlor, and nitrate from wells BA 437 and LN 1842 were analyzed with the Mann-Kendall (overall trend) and Seasonal Kendall trend tests with a p-value of 0.05. Acetochlor concentrations in well LN 1842 also were analyzed using the same data sets and trend tests mentioned above. Acetochlor was not analyzed for trends at wells BA 437 or BE 1370 because of insufficient data.

At well BA 437, statistically significant downward trends were observed in results from both trend tests in the long-term data set for atrazine and in the 5-year data set for nitrate. These trends indicate improvements in water quality.

At well LN 1842, alachlor was the only pesticide that had statistically significant downward trends in concentration for both the 5-year and long-term data sets. Atrazine had a significant downward trend in concentrations only in the long-term data set, and a downward trend was observed for nitrate only in the 5-year data set. Metolachlor showed a downward trend using the Mann-Kendall test for the 5-year data set even though a downward trend for metolachlor was not observed in the 5-year data set at a 0.05 significance level (p equal to 0.05 or less) using the Seasonal Kendall trend test. Metolachlor had the most dramatic decrease in concentrations evaluated for trends at well LN 1842 using the 2003–07 data set—approximately 65 µg/L. Overall, the downward trends observed in well LN 1842 indicated improvements in water quality.

At well BE 1370, the 5-year data (2003–07) were analyzed using the Mann-Kendall trend test only; the number of samples was insufficient to analyze for trend using the Seasonal Kendall trend test. The results of the Mann-Kendall trend test indicated concentrations of metolachlor had significant downward trends in 2003–07, but concentrations of alachlor, atrazine, and nitrate had no significant trends. The long-term data set for well BE 1370 was analyzed for trends with the Mann-Kendall and Seasonal Kendall trend tests (p-value equal to 0.05 or less); significant downward trends were observed in alachlor, atrazine, and metolachlor. The 5-year and long-term data sets for well BE 1370 had high percentages of censored (less-than) values for alachlor and atrazine, and trend results for these two compounds are less certain. As observed for wells BA 437 and LN 1842, the downward trends in pesticide concentration in well BE 1370 indicated improvements in water quality.

Testing for homogeneity of trend was done on the long-term data sets to evaluate seasonal differences in pesticide concentrations that would not be apparent using the tests for trend that assume a single pattern of trend across all seasons. Results of these analyses showed that the downward trend for atrazine at well BA 437 was due entirely to a significant downward trend in the summer. The homogeneity of trend test also indicated a downward trend for alachlor concentrations in the summer in well BA 437; however, the trend was weak because the results from the Seasonal Kendall trend test indicated no trend. At well LN 1842, the downward trend in alachlor was due to statistically significant downward trends in the summer and fall, but for atrazine, the downward trend was due to statistically significant downward trends in the spring and fall. Finally, the homogeneity of trend test indicated that the downward trends in the long-term data set for atrazine and metolachlor in well BE 1370 were entirely due to significant downward trends in the winter samples, and the downward trends in the long-term data for alachlor were the result of significant downward trends in the winter and spring.

Additional sampling near the three hot-spot wells, BE 1370, BA 437, and LN 1842, was conducted in 2005 and 2006 to better understand the occurrence of pesticides and pesticide degradation products in ground water and to enhance monitoring in areas of special ground-water protection. To understand the extent of natural breakdown of the pesticides, parent pesticides and their degradation products were analyzed. A total of 16 sites (15 wells and 1 spring) in addition to the three hot-spot wells were sampled one time to characterize the distribution of 15 pesticides, 39 pesticide degradation products, and other water-quality indicators, such as bromide, chloride, and nitrate. Pesticide occurrence in water from wells in all three areas of special ground-water protection was highly variable, but no pesticide concentrations exceeded current USEPA MCLs or lifetime health advisories (LHAs).

Near well BE 1370, pesticides present in the hot-spot well also were present in the five neighboring wells tested (BE 1775, BE 1298, BE 1776, BE 1774, and BE 1773) and in a spring (BE SP20) on the same property as the hot-spot well. The spring and well BE 1370 both had three to four times as many degradation products as parent compounds; concentrations of parent compounds and degradation products were similar. Acetamide degradation products were more common than the triazine and phenylurea degradation products at all wells, except BE 1775.

At well BA 437, a shallow water-bearing zone at 43–48 ft below land surface supplied most of the water to the well, and a deeper water-bearing zone at 68–99 ft was only a minor source of water. Pesticide parent compounds and degradation products were present in both the shallow and deep zones. Water in the shallow zone had greater concentrations of nitrate, metolachlor, alachlor, and the triazine herbicide parents than the deeper zone. Cyanazine degradates were mostly in the deep zone, and the shallow zone had more alachlor degradates than the deep zone. Degradates of metolachlor had similar concentrations in the deep and shallow zones.

Near well BA 437, the same sets of pesticides in the hot-spot well were present in select wells of the five neighboring wells tested (BA 642, BA 643, BA 644, BA 645, and BA 332). Water from well BA 643 had concentrations of atrazine, alachlor, and bromacil nearly double the concentrations measured in well BA 437. All neighboring wells sampled had reported concentrations of one or more pesticide parents and degradation products in well water. The samples collected from wells BA 643 and BA 644 each had 24 pesticide compounds (parent and degrades combined), which were comparable to that reported from hot-spot well BA 437. The production well (BA 332) had reported concentrations of nine pesticide compounds—the maximum concentration of these compounds was for metolachlor ethane sulfonic acid (ESA) (1.27 µg/L). For four of the five neighboring wells, nitrate concentrations ranged from 1.1 to 11.7 mg/L as N. For BA 643, the nitrate concentration was 64 mg/L as N, which was similar to the concentration at the hot-spot well (66 mg/L as N).

At well LN 1842, pesticides in water were primarily acetamide compounds dominated by metolachlor. Five wells neighboring LN 1842 (LN 1291, LN 2118, LN 2119, LN 1998, and LN 2000) had measured concentrations for one or more pesticide parents and degradates; the number of degradates was greater than the number of parent compounds in most samples. Pesticide occurrence in the five wells was also dominated by acetamide degradation products—up to a maximum number of seven degradates in well LN 2119; however, wells LN 2118 and LN 2119 had a higher number (4) of triazine degradation products than the other wells. One degradate of acetochlor was measured in four of the neighboring wells. Supply well LN 1291 had reported concentrations of atrazine, CIAT, and metolachlor ESA, all at concentrations of 0.05 µg/L or less. Nitrate concentrations were less than 10 mg/L (USEPA MCL for nitrate) in water from only two neighboring wells—LN 1998 and LN 1291.

Exceedances of the PPGWS action levels were assessed at the three pesticide hot-spot wells and the neighboring wells. For alachlor, the PPGWS action level of 0.66 µg/L was exceeded at well LN 1842 in all samples collected from 2003 to 2007, with the exception of the August 2007 sample; at well BE 1370, one sample collected in July 2004 exceeded the alachlor action level, and near well BA 437, the alachlor action level was exceeded at wells BA 643 and BA 644. For metolachlor, the PPGWS action level of 33 µg/L was exceeded in all samples from well LN 1842 and in four samples from well BA 437. For atrazine, the PPGWS action level of 1.0 µg/L was exceeded at well BA 437 (August 2003) and a neighboring well (BA 643 in September 2005). For simazine, the PPGWS action level of 1.3 µg/L was not exceeded. Therefore, continued monitoring of alachlor, metolachlor, and atrazine concentrations as part of the PPGWS would be needed at wells LN 1842 and near BA 437.

As part of the PPGWS, continued monitoring in the area of wells LN 1842 and BA 437 would be needed to further define the occurrence and persistence of pesticide parent compounds and degradation products, especially for wells with pesticide concentrations exceeding action levels. The occurrence of pesticide parent compounds and degradation products in well water was not limited to the three hot-spot wells summarized herein because all wells sampled near the pesticide hot spots had one or more reported concentrations of pesticides and (or) degradation products. Concentrations of some degradation products were significantly greater than concentrations of the respective parent compound. No USEPA

MCLs or LHAs exist for pesticide degradation products or for combinations of pesticides and pesticide degradation products; therefore, the human-health effects (cancer risk, effects on human organs, etc.) of concentrations of these compounds in well water are not established.

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References Cited

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 2004, Standard methods for the analysis of water and wastewater (21st ed.): Washington, D.C., American Public Health Association, Section 9223.

Becher, A.E., 1996, Ground-water resources of Cambrian and Ordovician carbonate rocks in the Valley and Ridge Physiographic Province of Pennsylvania: U.S. Geological Survey Open-File Report 90-109, 134 p.

Bexfield, L.M., 2008, Decadal-scale changes of pesticides in ground water of the United States, 1993–2003: Journal of Environmental Quality, v. 37, p. S-226–S-239.

Breen, K.J., 2000, Quality-assurance design applied to an assessment of agricultural pesticides in ground water from carbonate bedrock aquifers in the Great Valley of eastern Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 00-4104, 31 p.

Coll, M.B., Jr., and Siwicki, R.W., 1999, Water resources data, Pennsylvania, water year 1998, vol. 3, Ohio River and St. Lawrence River Basins: U.S. Geological Survey Water-Data Report PA-98-3, 352 p.

Commonwealth of Pennsylvania, 2008, Roads, population centers, county and municipal boundaries: accessed February 22, 2008, at *http://www.pasda.psu.edu/.*

Debrewer, L.M., Ator, S.W., and Denver, J.M., 2008, Temporal trends in nitrate and selected pesticides in Mid-Atlantic ground water: Journal of Environmental Quality, v. 37, p. S-296–S-308.

Durlin, R.R., and Schaffstall, W.P., 1993, Water resources data, Pennsylvania, water year 1992, vol. 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Report PA-92-2, p. 279-337.

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

Durlin, R.R., and Schaffstall, W.P., 1999b, Water resources data, Pennsylvania, water year 1998, vol. 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Report PA-98-2, 456 p.

Durlin, R.R., and Schaffstall, W.P., 2001, Water resources data, Pennsylvania, water year 2000, vol. 1, Delaware River Basin: U.S. Geological Survey Water-Data Report PA-00-1, 652 p.

Durlin, R.R., and Schaffstall, W.P., 2002, Water resources data, Pennsylvania, water year 2001, vol. 1, Delaware River Basin: U.S. Geological Survey Water-Data Report PA-01-1, 529 p.

Durlin, R.R., and Schaffstall, W.P., 2003, Water resources data, Pennsylvania, water year 2002, vol. 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Report PA-02-2, 536 p.

Eichelberger, J.W., Munch, J.W., and Shoemaker, J.A., 1994, Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/mass spectrometry: U.S. Environmental Protection Agency Method 525.2, 60 p.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Furlong, E.T., Anderson, B.D., Werner, S.L., Soliven, P.P., Coffey, L.J., and Burkhardt, M.R., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4134, 73 p.

Helsel, D.R., and Hirsch, R.M., 2002, Statistical methods in water resources: U.S. Geological Survey Techniques of Water-Resources Investigations, book 4, chap. A3, 510 p.

Helsel, D.R., Mueller, D.K., and Slack, J.R., 2005, Computer program for the Kendall family of trend tests: U.S. Geological Survey Scientific Investigations Report 2005-5275, 4 p.

Hoaglin, D.C., Mosteller, F., and Tukey, J.S., 1983, Understanding robust and exploratory data analysis: New York, John Wiley and Sons, 447 p.

Kolpin, D.W., Schnoebelen, D.J., and Thurman, E.M., 2004, Degradates provide insight to spatial and temporal trends of herbicides in ground water: Ground Water, v. 42, no. 4, p. 601-608.

Kolpin, D.W., Sneck-Fahrer, D., Hallberg, G.R., and Libra, R.D., 1997, Temporal trends of selected agricultural chemicals in Iowa's groundwater, 1982–1995—Are things getting better?: Journal of Environmental Quality, v. 26, p. 1,007-1,017.

Lee, E.A., and Strahan, A.P., 2003, Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of acetamide herbicides and their degradation products in water using online solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 03-173, 17 p.

Lee, E.A., Strahan, A.P., and Thurman, E.M., 2002, Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of triazine and phenylurea herbicides and their degradation products in water using solid-phase extraction and liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02-436, 19 p.

Lietman, P.L., 1997, Evaluation of agricultural best-management practices in the Conestoga River headwaters, Pennsylvania—A summary report, 1982-90: U.S. Geological Survey Water-Supply Paper 2493, 69 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.

Lindsey, B.D., Breen, K.J., Bilger, M.D., and Brightbill, R.A., 1998, Water quality in the lower Susquehanna River Basin, Pennsylvania and Maryland, 1992-95: U.S. Geological Survey Circular 1168, 38 p.

Lindsey, B.D., and Koch, M.L., 2004, Determining sources of water and contaminants to wells in a carbonate aquifer near Martinsburg, Blair County, Pennsylvania, by use of geochemical indicators, analysis of anthropogenic contaminants, and simulation of ground water flow: U.S. Geological Survey Scientific Investigations Report 2004-5124, 46 p., available at *http://pubs.usgs.gov/sir/2004/5124/.*

Lindsey, B.D., Loper, C.A., and Hainly, R.A., 1997, Nitrate in ground water and stream base flow in the Lower Susquehanna River Basin, Pennsylvania and Maryland: U.S. Geological Survey Water-Resources Investigations Report 97-4146, 66 p.

Low, D.J., Chichester, D.C., and Zarr, L.F., 2008, Selected ground-water-quality data in Pennsylvania—1979–2006: U.S. Geological Survey Data Series 314, 22 p., available at *http://pubs.usgs.gov/ds/314/.*

Low, D.J., and Conger, R.W., 2002, Ground-water availability in part of the Borough of Carroll Valley, Adams County, Pennsylvania, and the establishment of a drought monitor well: U.S. Geological Survey Water-Resources Investigations Report 02-4273, 78 p.

Madsen, J.E., Sandstrom, M.W., and Zaugg, S.D., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—-A method supplement for the determination of fipronil and degradates in water by gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02-462, 11 p.

Multi-Resolution Land Characteristics, 1992, National land cover database 1992: accessed January 2008 at *http://www.mrlc.gov/landcover.usgs.gov/natlandcover.php*

Multi-Resolution Land Characteristics, 2001, National land cover database 2001: accessed January 2008 at *http://www.mrlc.gov/mrlc2k_nlcd.asp*

Munch, J.W., ed., 1995, Measurement of N-methyl carbamoyloximes and n-methyl-carabamates in water by direct aqueous injection HPLC with post column derivatization: U.S. Environmental Protection Agency Method 531.1, 23 p.

Ott, R.L., 1993, An introduction to statistical methods and data analysis: Belmont, Calif., Duxbury Press, 1,051 p.

Pennsylvania Department of Agriculture, 1997, Pennsylvania Agricultural Statistics 1996-1997: Harrisburg, Pa., p. 71-73.

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

Pennsylvania Department of Agriculture, 2004, Pennsylvania Agricultural Statistics 2003-2004: Harrisburg, Pa., p. 13.

Pennsylvania Department of Agriculture, 2005, Pennsylvania Agricultural Statistics 2004-2005: Harrisburg, Pa., p. 3.

Pennsylvania Department of Agriculture, 2006, Pennsylvania Agricultural Statistics 2005-2006: Harrisburg, Pa., 3 p.

Pennsylvania Department of Agriculture, 2007, Pennsylvania Agricultural Statistics 2006-2007: Harrisburg, Pa., 3 p.

Pennsylvania Department of Environmental Protection, 2008, Triennial review of water quality standards: Pennsylvania Bulletin, v. 38, no. 2 (January 12, 2008), p. 241.

SAS Institute, 1990, SAS user's guide–The CORR procedure–Version 6 (3rd ed.): Cary, N.C., SAS Institute Pub., p. 209-235.

Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90-4101, 109 p.

Uitenbroek, D.G., 1997, Fisher exact SISA: accessed April 17, 2009, at *http://www.quantitativeskills.com/sisa/statistics/fisher.htm*

U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, Agricultural chemical usage 1996 vegetable summary: accessed December 28, 2008, at *http://usda.mannlib.cornell.edu/usda/nass/AgriChemUsVeg/1990s/1997/AgriChemUsVeg-07-15-1997.txt*

U.S. Department of Agriculture National Agricultural Statistics Service, 1997b, Pennsylvania Statistics: accessed December 28, 2008, at *http://www.nass.usda.gov/Statistics_by_State/Pennsylvania/index.asp*

U.S. Department of Agriculture National Agricultural Statistics Service, 2004, Agricultural chemical usage 2003 field crops summary: Washington, D.C., p. 70.

U.S. Department of Agriculture National Agricultural Statistics Service, 2005a, Agricultural chemical usage 2004 vegetables summary: Washington, D.C., p. 77, 155.

U.S. Department of Agriculture National Agricultural Statistics Service, 2005b, Pennsylvania Statistics: accessed December 28, 2008, at *http://www.nass.usda.gov/Statistics_by_State/Pennsylvania/index.asp*

U.S. Department of Agriculture National Agricultural Statistics Service, 2006a, Agricultural chemical usage 2005 field crops summary: Washington, D.C., p. 33, 68.

U.S. Department of Agriculture National Agricultural Statistics Service, 2006b, Agricultural chemical usage 2005 fruit summary: Washington, D.C., p. 32-34, 102, 156-157.

U.S. Department of Agriculture National Agricultural Statistics Service, 2006c, Pennsylvania Statistics: accessed December 28, 2008, at *http://www.nass.usda.gov/Statistics_by_State/Pennsylvania/index.asp*

U.S. Department of Agriculture National Agricultural Statistics Service, 2007a, Agricultural chemical usage 2006 field crops summary: Washington, D.C., p. 38, 70.

U.S. Department of Agriculture National Agricultural Statistics Service, 2007b, Agricultural chemical usage 2006 vegetables summary: Washington, D.C., p. 37,100.

U.S. Environmental Protection Agency, 2000a, Policy and program requirements for the mandatory agency-wide quality system: USEPA Order 5360.1 A2, May 5, 2000, 13 p.

U.S. Environmental Protection Agency, 2000b, Cyanazine cancellation order: Federal Register Environmental Documents, v. 65, no. 4, January 6, 2000.

U.S. Environmental Protection Agency, 2004, 2004 Edition of the Drinking Water Standards and Health Advisories: accessed March 4, 2009, at *http://www.epa.gov/waterscience/criteria/drinking/#dw-standards/dwstandards2004[1].pdf*

U.S. Environmental Protection Agency, 2006, Ground water & drinking water, Drinking water contaminants: accessed October 8, 2008, at *http://www.epa.gov/safewater/hfacts.html*

U.S. Environmental Protection Agency, 2008, Water Quality Criteria, Drinking Water Health Advisories: accessed October 8, 2008, at *http://epa.gov/waterscience/criteria/drinking/.*

U.S. Geological Survey, 2005, State boundary and stream GIS data: accessed February 14, 2008, at *http://www.nationalatlas.gov/atlasftp.html/.*

U.S. Geological Survey, 2008, USGS ground-water data for Pennsylvania from National Water Information System-Web Interface: accessed December 15, 2008, at *http://waterdata.usgs.gov/pa/nwis/gw*

van Belle, G., and Hughes, J.P., 1984, Nonparametric tests for trend in water quality: Water Resources Research, v. 20, p. 127-136.

Wilde, F.D., ed., variously dated, Field measurements (ver. 1.2: pH, 7/2003; specific conductance, 8/2005; temperature, 4/2004; ver. 2.1: dissolved oxygen 6/2006; turbidity 9/2005): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, accessed June 17, 2008, at *http://pubs.water.usgs.gov/twri9A6/*.

Wilde, F.D., ed., April 2004, Cleaning of equipment for water sampling (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A3, accessed August 9, 2007, at *http://pubs.water.usgs.gov/twri9A3*

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., September 1999, National field manual for the collection of water-quality data—Collection of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, variously paged.

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., April 2004, Processing of water samples (version 2.1): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A5, accessed March 15, 2007, at *http://pubs.water.usgs.gov/twri9A5*

Williams, J.H., Taylor, L.E., and Low, D.J., 1998, Hydrogeology and groundwater quality of the glaciated valleys of Bradford, Tioga, and Potter Counties, Pennsylvania: Pennsylvania Geological Survey, 4th ser., Water Resource Report 68, 89 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, 60 p.

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.

[–, not available; ft, feet; gal/min, gallons per minute]

Local well number:	The number that is assigned to identify the well. It is prefixed by a two-letter abbreviation of the county.	
Well location:	Latitude and longitude datum is North American Datum 1927 (NAD 27).	
Aquifer code:	000MBSL	METABASALT
	000MTRL	METARHYOLITE
	112ALVM	ALLUVIUM
	112BECH	BEACH DEPOSITS
	112ICCC	ICE CONTACT DEPOSITS
	112LAKE	LAKE DEPOSITS
	112OTSH	OUTWASH
	112SFDF	STRATIFIED DRIFT
	112TILL	TILL
	231BRCK	BRUNSWICK FORMATION
	231GBRG	GETTYSBURG SHALE
	231NOXF	NEW OXFORD FORMATION
	344HMLN	HAMILTON GROUP
	347KRTL	KEYSER, TONOLOWAY FORMATIONS UNDIFFERENTIATED
	347KTWM	KEYSER,TONOLOWAY,WILLS CREEK,BLOOMSBURG,MIFFLINTOWN FORMATIONS, UNDIFFERENTIATED
	347KYSR	KEYSER LIMESTONE
	351TNLY	TONOLOWAY LIMESTONE
	351WLCK	WILLS CREEK FORMATION
	351WLCKL	WILLS CREEK FORMATION, LOWER MEMBER
	361BSKL	BUSHKILL MEMBER OF MARTINSBURG FORMATION
	361MRBG	MARTINSBURG SHALE
	361MRBGL	MARTINSBURG SHALE, LOWER MEMBER
	361RMBG	RAMSEYBURG MEMBER OF MARTINSBURG SHALE
	364BKMN	BEEKMANTOWN GROUP
	364CSNL	COBURN, SALONA, NEALMONT, BENNER, SNYDER, HATTER, LOYSBURG FMS. UNDIFFERENTIATED
	364HMBG	HAMBURG SEQUENCE
	367BFAX	AXEMANN, BELLEFONTE FORMATIONS
	367BLFN	BELLEFONTE FORMATION
	367CNSG	CONESTOGA FORMATION
	367EPLR	EPLER FORMATION
	367LBRG	LOYSBURG FORMATION
	367NNLK	NITTANY LARKE FORMATIONS
	367NTTN	NITTANY FORMATION
	371ALNN	ALLENTOWN FORMATION
	371ELBK	ELBROOK FORMATION
	371MDCK	MAIDEN CREEK MEMBER OF ALLENTOWN FORMATION
	371MLBC	MILBACH FORMATION
	371SDGV	SHADYGROVE FORMATION
	374LSVL	LEITHSVILLE FORMATION
	374ZKCR	ZOOKS CORNER FORMATION
	377LDGR	LEDGER FORMATION
Casing material:	S, steel; P, PVC, fiberglass, or other plastic; D, copper.	
Type of seal:	N, no seal; G, grouted; B, bentonite; C, clay or cuttings.	
Water level:	A, artesian; n, number of water-level measurements.	

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Latitude	Longitude	Aquifer code	Depth to top of water-bearing unit (ft)	Depth of well (ft)	Casing length	Casing material	Type of seal
Baseline-assessment areas								
Blue Ridge and Triassic Lowland hydrogeologic setting, 2003								
AD 1155	394849.8	772233.7	364BKMN	–	202	34	S	–
AD 1156	395212	772146.8	231GBRG	55	220	60	S	N
AD 1157	395713.3	771727.3	000MTRL	30	260	42	S	G
AD 1158	395706	771500	231GBRG	55	220	60	S	–
AD 1159	395807	771426	231GBRG	–	160	–	S	–
AD 1160	395135	772213	231GBRG	10	200	20	S	G
AD 1161	395632	772232	000MTRL	33	180	63	S	B
AD 1162	395102	772257	000MTRL	50	180	60	S	B
AD 1163	395930	771536	000MTRL	49	190	53	S	–
AD 1173	395417.1	772025.6	231GBRG	–	99	99	S	–
AD 1174	395554.7	771647.8	231GBRG	–	225	–	S	–
AD 1175	395648.8	771747.7	231GBRG	–	155	26	S	–
AD 1176	395919.4	771836	000MBSL	–	175	55	S	–
AD 1177	395923	771400.4	000MTRL	30	120	44	S	G
AD 1178	395605.1	771914.7	000MTRL	30	140	–	S	N
AD 1179	400119	771034	000MBSL	25	200	63	S	–
AD 1180	400045.2	771642	000MTRL	28	180	–	S	–
AD 1181	400101	771248.4	000MTRL	56	140	60	S	–
AD 1182	400032.6	771304	000MTRL	32	210	40	S	–
CU 951	400324	771009	000MTRL	16	90	21	S	–
Eastern Lake surficial hydrogeologic setting, 2004								
ER 176	415409	802112	112TILL	–	30	30	S	–
ER 243	415924	801953	112OTSH	–	88	88	S	–
ER 295	415437	802423	112OTSH	–	80	78	S	–
ER 318	415718	802415	112TILL	–	86	86	S	–
ER 369	420055	801605	112OTSH	–	49	49	S	–
ER 428	420156	801305	112OTSH	–	41	41	S	–
ER 675	421403	795029	112OTSH	–	94	94	S	–
ER 713	421225	795317	112TILL	–	32	32	–	–
ER 952	420511	800304	112OTSH	–	40	40	S	–
ER 1235	415438	803058	112OTSH	–	52	52	–	–
ER 1242	415746	802527	112BECH	–	34	34	–	–
ER 1405	420042	801749	112BECH	–	45	45	–	–
ER 3504	415941.3	802421.4	112BECH	–	18	–	S	–
ER 3505	415845.2	802033.3	112OTSH	–	89	97	S	–
ER 3506	415931.9	801701.9	112LAKE	–	111.8	111.8	S	–
ER 3507	420210.6	801125.4	112ALVM	–	33	33	S	–
ER 3508	421503.4	794622	112OTSH	–	20	20	S	–
ER 3509	421158.1	795600.7	112OTSH	–	80	80	S	–
ER 3510	421102.2	795033.1	112OTSH	–	15	15	–	–
ER 3511	420853.5	795640	112ALVM	–	39	19.8	S	–

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Date well constructed	Elevation of land surface (ft)	Range of date for water level	Water level[1] (ft)		Well yield (gal/min)
				Min	Max	
Baseline-assessment areas						
Blue Ridge and Triassic Lowland hydrogeologic setting, 2003						
AD 1155	1/30/1970	670	1/30/71, 5/5/03	23.6	28.0	24
AD 1156	9/1989	720	9/89, 5/5/03	13.0	14.1	10
AD 1157	4/15/1997	920	4/15/97, 5/8/03	9.0	40.0	2.5
AD 1158	10/23/1990	690	10/23/90, 5/7/03	24.7	30.0	40
AD 1159	1981	630	5/7/2003	12.6		33
AD 1160	8/5/1991	710	5/6/2003	2.6		4
AD 1161	12/27/1996	1,300	12/27/96, 5/14/03	47.0	60.0	5
AD 1162	8/14/2001	860	8/14/01, 5/14/03	15.9	40.0	7
AD 1163	10/3/1980	730	10/3/80, 5/13/03	5.0	5.1	5
AD 1173	7/1999	760	8/20/2003	10.4		50
AD 1174	6/1995	735	8/28/2003	16.6		–
AD 1175	7/19/1971	780	8/20/2003	32.2		–
AD 1176	9/1983	1,145	9/1983	43.6		4
AD 1177	10/12/1994	750	1/12/94, 8/26/03	40.0	50.1	12
AD 1178	4/1999	660	4/94–8/27/03	16.0	37.5	15
AD 1179	9/20/2001	835	8/19/2003	11.4		3
AD 1180	10/1991	970	10/91–8/21/03	4.0	4.8	15
AD 1181	3/6/1986	760	3/6/86–8/28/03	40.0	43.6	15
AD 1182	3/31/1986	890	3/31/1986	36.0		2
CU 951	10/1988	940	5/13/2003	24.0		30
Eastern Lake surficial hydrogeologic setting, 2004						
ER 176	8/23/77	895	8/23/76	20.0		3
ER 243	8/22/73	826	8/22/73, 7/21/04	45.0	61.0	30
ER 295	6/3/68	915	6/3/68, 7/29/04	15.0	26.8	3
ER 318	7/70	790	7/70, 7/29/04	55.0	59.1	10
ER 369	3/11/77	840	3/11/77, 6/22/04	7.0	12.9	40
ER 428	9/1/72	826	9/1/72	23.0		18
ER 675	6/14/73	710	6/14/73	60.0		10
ER 713	8/9/72	740	8/9/72–6/8/04	8.0	8.2	20
ER 952	5/18/72	970	5/18/72–6/8/04	24.5	28.0	30
ER 1235	12/4/56	850	12/4/56, 7/22/04	38.0	38.2	20
ER 1242	12/31/56	735	12/31/56	11.0		10
ER 1405	12/31/57	784	12/31/57, 6/23/04	23.2	35.0	7
ER 3504	2004	720	8/5/04	4.8		–
ER 3505	9/90	840	9/90, 8/4/04	37.0	37.1	8.75
ER 3506	3/31/98	875	3/31/98, 8/19/04	74.0	77.3	1
ER 3507	5/10/85	860	5/10/85–6/24/04	7.9	8.0	2.7
ER 3508	1/92	710	8/5/04	12.5		8
ER 3509	2000	673	5/19/04	15.4		3.33
ER 3510	2004	1,040	2004, 8/4/2004	7.5	8.0	15
ER 3511	3/88	885	8/18/04	4.9		3

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Latitude	Longitude	Aquifer code	Depth to top of water-bearing unit (ft)	Depth of well (ft)	Casing length	Casing material	Type of seal
Devonian-Silurian carbonate hydrogeologic setting, 2005								
BD 253	400350	783244.1	347KYSR	10	223	21	S	–
BD 373	394744	784354	347KYSR	8	224	42	S	–
BD 656	394938.2	783838.7	351WLCK	30	125	40	S	G
CN 154	410528.7	773151.9	347KTWM	160	200	167	S	–
CN 430	410955.4	771901.8	347KTWM	70	125	80	S	N
FU 250	394703.1	781020.5	351WLCK	–	–	–	S	–
HU 426	401919.8	781300.6	347KRTL	14	247	21	S	N
HU 427	401606.9	781455.4	344HMLN	15	80	20	P	–
HU 428	401138.6	780019.8	351WLCK	18	140	42	S	N
HU 429	403623	775709	351WLCK	3	160	100	S	N
JU 334	403130	772936	351TNLY	15	150	30	S	–
JU 373	403801.3	771536.8	351TNLY	50	150	56	S	–
JU 271	403443	772029	347KRTL	48	160	60	S	N
LY 688	411319.2	764524	351TNLY	124	124	124	S	N
MF 406	402538.8	775116.5	347KRTL	53	129	84	S	N
MF 407	403958.9	773111	347KRTL	35	100	35	S	N
NU 570	410604.2	764934.1	347KRTL	9	147	59	S	C
NU 571	405753.8	764915.6	347KRTL	6	123	60.8	S	N
PE 689	402223	772825	351TNLY	–	240	63	S	–
PE 686	402121.9	771315.7	351TNLY	8	240	102	S	–
PE 687	403005.4	771702	351WLCKL	38	180	60	S	B
PE 688	402247.8	772739.9	351TNLY	55	120	83	S	N
SN 252	404633.5	765357.2	347KRTL	30	126	63	S	N
SN 250	404516	765641	347KRTL	37	201	41	S	–
SN 251	404809.5	771316.3	347KTWM	27	176	84	S	N
UN 205	405931.3	765555.6	347KRTL	21	147	42	S	G
UN 206	405557.1	765954.2	347KRTL	17	95	40	S	N
UN 207	405332.9	770407.8	347KRTL	14	180	103	S	N
Great Valley siliciclastic hydrogeologic setting, 2006								
BE 1629	402700	761801	364HMBG	–	197	81.5	S	–
BE 1708	402516.56	760147.42	364HMBG	46.28	175	46.28	S	–
BE 1778	402919.3	761745.2	364HMBG	16	225	40	S	G
BE 1779	403026.3	755146.6	364HMBG	70	250	85	S	G
BE 1780	403312.7	755751	364HMBG	23	160	63	S	–
BE 1781	402814	762207.6	364HMBG	50	140	60	S	–
BE 1782	403528	754904.3	364HMBG	87	150	93	S	–
BE 1783	402413.3	760758.1	364HMBG	–	40	–	S	–
CU 978	401158	772714	361MRBG	20	148	80	S	–
CU 979	401515.9	771435.3	361MRBG	8	52	20	S	–
CU 980	401257.4	772427.7	361MRBG	8	142	40	S	B

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Date well constructed	Elevation of land surface (ft)	Range of date for water level	Water level[1] (ft)		Well yield (gal/min)
				Min	Max	
Devonian-Silurian carbonate hydrogeologic setting, 2005						
BD 253	5/15/79	1,291	5/15/79, 8/12/80	152.8	170.0	12
BD 373	2/78	1,125	8/29/80	98.3		10
BD 656	11/20/03	1,160	11/20/03, 8/1/05	-.8	.0	20
CN 154	10/80	620	10/1/80, 8/10/05	55.9	60.0	60
CN 430	12/21/98	560	12/21/98, 8/9/05	20.0	20.8	12
FU 250	1999	600	8/2/05	39.0		–
HU 426	10/22/99	920	6/28/05	15.5		30
HU 427	4/28/82	980	4/28/82, 6/28/05	22.0	25.5	15
HU 428	9/91	760	9/91, 8/2/05	15.2	18.0	12
HU 429	6/16/02	900	6/16/02, 8/29/05	40.0	43.9	30
JU 334	9/12/78	610	6/1/05	22.5		12
JU 373	5/24/83	700	5/24/83, 8/8/05	33.8	80.0	20
JU 271	10/25/96	540	10/25/96–8/30/05	38.6	50.0	15
LY 688	9/85	530	8/9/05	28.8		30
MF 406	2/12/01	660	2/12/01–8/2/05	4.9	8.0	20
MF 407	9/4/03	620	8/15/05	8.4		30
NU 570	11/6/01	570	6/21/05	34.6		30
NU 571	9/95	460	6/20/05	16.3		60
PE 689	8/16/04	830	8/31/05	47.2		15
PE 686	1/11/92	610	6/8/05	83.8		15
PE 687	8/91	630	8/91, 6/22/05	14.0	40.0	12
PE 688	8/8/86	780	8/8/86, 6/1/05	34.6	45.0	15
SN 252	9/86	550	9/86, 6/8/05	15.0	18.7	25
SN 250	9/87	590	9/87, 6/8/05	66.1	70.0	22
SN 251	8/4/99	780	8/4/99, 6/22/05	45.0	45.4	50
UN 205	1/91	485	6/21/05	38.8		20
UN 206	10/5/93	580	10/5/93, 6/20/05	22.0	23.9	45
UN 207	11/90	340	6/20/05	47.1		40
Great Valley siliciclastic hydrogeologic setting, 2006						
BE 1629	10/96	540	7/21/98, 6/7/06	22.0	26.0	–
BE 1708	5/9/83	400	6/22/00	15.3		30
BE 1778	1/4/01	640	1/4/01, 6/7/06	22.7	45.0	20
BE 1779	9/10/02	520	9/10/02, 6/29/06	46.2	90.0	25
BE 1780	7/9/03	540	6/13/06	47.3		35
BE 1781	9/17/04	550	9/17/04, 6/28/06	18.6	30.0	20
BE 1782	1/23/80	700	1/23/80, 8/2/06	25.4	35.0	20
BE 1783	1/72	440	8/7/06	15.3		–
CU 978	3/31/97	640	6/21/2006	14.8		50
CU 979	10/86	555	10/86, 8/8/06	15.0	16.9	30
CU 980	10/21/00	575	10/21/00	30.0		100

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Latitude	Longitude	Aquifer code	Depth to top of water-bearing unit (ft)	Depth of well (ft)	Casing length	Casing material	Type of seal
Great Valley siliciclastic hydrogeologic setting, 2006—Continued								
CU 981	401505.6	771956.5	361MRBG	–	190	65	S	–
CU 982	401652.5	770634.4	361MRBG	–	223	40	S	–
DA 869	402140.5	764512.9	364HMBG	20	175	85	S	–
DA 870	401936.6	763808.6	364HMBG	40	200	60	S	–
FR 830	394727.3	775320.9	361MRBG	30	225	42	S	N
FR 831	395746	774337	361MRBG	39	220	63	S	G
FR 833	395117.4	774640.3	361MRBG	22	198	42	S	N
FR 832	395853	774335	361MRBGL	15	123	42	S	N
FR 834	400641	773754	361MRBG	–	96	–	S	–
LB 1247	402254.5	762310.7	364HMBG	76	225	121	S	–
LB 1250	402425.9	762452.2	364HMBG	16	150	81	S	G
LE 1426	403651.8	754339	364HMBG	55	250	75	S	G
LE 1427	404523.5	754106.1	361MRBG	67	224	76	S	G
LE 1428	404113.7	754535.9	361MRBG	12	100	26	S	G
LE 1429	403534.5	754037.5	361MRBG	35	200	40	S	G
NP 818	404934.68	751001.77	361MRBG	33.18	260	33.08	S	–
NP 826	404852	751450	361BSKL	18	190	30	S	N
NP 827	405328.1	750602	361RMBG	69	94	71	S	–
NP 828	404522.7	752645.3	361MRBG	48	165	58	D	G
Northeastern Glaciated surficial hydrogeologic setting, 2007								
BR 226	–	–	112OTSH	–	88	68	S	–
BR 875	414039.5	761457.8	112OTSH	–	36	36	S	G
BR 878	415838.8	763326	112SFDF	88	88	88	S	–
BR 882	414213	763400.8	112SFDF	50	62	62	S	–
BR 884	415608	764259	112ALVM	–	40	40	S	–
BR 885	–	–	112ALVM	–	–	–	S	–
BR 886	414625	762359	112ALVM	–	71	71	S	–
BR 887	414612	764418	112SFDF	–	108	108	S	–
BR 888	414326	761411	112ALVM	–	36	36	S	–
CN 62	–	–	112SFDF	–	47	41	–	–
CO 143	–	–	112OTSH	–	62	57	P	–
CO 590	411216.7	762251	112ALVM	–	46	46	S	–
LU 778	410532	760752	112ALVM	–	–	–	S	–
LY 679	412647	765856	112ALVM	–	40	40	S	–
LY 690	411155	764325	112ALVM	–	40	40	S	–
LY 691	411431	764804	112ALVM	–	–	–	S	–
LY 692	411213	771034	112ALVM	–	60	60	S	–
MO 695	405508	752239	112ALVM	–	143	143	S	–
NU 110	410854	765309	112ALVM	–	41	–	–	–
NU 578	–	–	112ALVM	–	50	–	S	–
PI 236	–	–	112ICCC	–	165	165	–	–

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Date well constructed	Elevation of land surface (ft)	Range of date for water level	Water level[1] (ft)		Well yield (gal/min)
				Min	Max	
Great Valley siliciclastic hydrogeologic setting, 2006—Continued						
CU 981	6/11/86	580	7/27/06	23.0		–
CU 982	8/23/89	470	7/31/06	13.2		–
DA 869	4/2/96	490	6/6/06	29.6		20
DA 870	5/14/98	430	6/6/06	12.4		40
FR 830	6/19/95	600	6/19/95, 6/20/06	25.0	150.0	10
FR 831	3/13/03	600	3/10/03, 6/14/06	18.0	20.7	17
FR 833	2/14/94	570	2/14/94, 6/20/06	20.0	35.9	25
FR 832	10/26/98	660	10/26/98, 6/14/06	30.0	47.3	50
FR 834	1967	680	6/21/06	27.4		–
LB 1247	4/8/99	600	6/8/06	26.8		45
LB 1250	12/19/97	435	6/22/06	18.2		30
LE 1426	2/21/96	805	2/21/1996	60.0		18
LE 1427	11/3/00	700	11/3/00, 7/18/06	21.6	39.0	12
LE 1428	8/30/00	580	8/30/00, 7/24/06	25.0		16
LE 1429	6/26/98	710	6/26/98, 8/7/06	18.2	40.0	8
NP 818	7/91	740	6/14/00, 8/1/06	47.0	56.3	5
NP 826	6/95	700	6/95, 7/19/06	40.0	40.4	6
NP 827	3/7/73	620	3/7/73	30.0		25
NP 828	7/03	720	7/03, 7/6/06	31.9	55.0	11
Northeastern Glaciated surficial hydrogeologic setting, 2007						
BR 226	4/72	765	4/1/72, 4/17/72	17	17	1683
BR 875	7/04	680	7/04, 8/16/07	8	14.2	10
BR 878	7/02	780	7/02–8/15/07	19	25	15
BR 882	1988	910	8/15/07	19.4		–
BR 884	1977	1,090	–	–	–	–
BR 885	1980	730	–	–	–	–
BR 886	5/21/04	710	5/21/04, 7/25/07	26.7	32	30
BR 887	9/15/64	970	9/15/64	2.0		32
BR 888	1973	740	–	–	–	–
CN 62	1940	550	11/1/42	15.0		350
CO 143	8/16/79	490	6/10/80–4/30/81	21.57	26.4	–
CO 590	8/5/75	785	8/5/75, 8/14/07	20	20	10
LU 778	1955	510	5/29/07	28.6		–
LY 679	1998	750	8/9/07–8/22/07	14.8	16.28	–
LY 690	1970	650	5/30/07	23.8		–
LY 691	1998	540	5/24/07	11.6		–
LY 692	1970	545	–	–	–	–
MO 695	8/02	750	8/27/07	35.4		45
NU 110	–	485	11/7/75–8/23/07	16.75	19	30
NU 578	1980	440	8/23/07	20.5		–
PI 236	5/15/69	410	5/15/69	40.0		20

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Latitude	Longitude	Aquifer code	Depth to top of water-bearing unit (ft)	Depth of well (ft)	Casing length	Casing material	Type of seal
Northeastern Glaciated surficial hydrogeologic setting, 2007—Continued								
SQ 453	415915.3	753550.7	112SFDF	–	68	68	S	N
TI 725	414934.1	771716.5	112SFDF	–	45	45	S	N
TI 728	–	–	112ALVM	–	20	17	S	B
WY 193	413152	755634	112ALVM	–	48	48	S	–
WY 194	412632	755120	112ALVM	–	55	55	S	–
WY 195	413558	760556	112ALVM	–	74	74	S	N
WY 196	413733	754549	112ALVM	–	30	20	S	–
Great Valley carbonate hydrogeologic setting, 2003 and (or) 2004								
BE 1619	402934	754818	371MDCK	25	150	120	S	N
CU 908	400513.3	772747.1	371SDGV	42	182	120	S	–
CU 917	400834.2	771344.4	371ELBK	40	200	60	S	N
LB 1160	401856.3	763450	367EPLR	40	180	95	S	–
NP 805	404144	752415	367EPLR	115	140	114	S	G
Appalachian Mountain carbonate hydrogeologic setting, 2003 and 2004								
BD 653	401524.9	782135.2	367NNLK	30	170	84	S	N
CE 672	405251.6	773015.4	364CSNL	–	200	125	S	–
LY 686	410805	771314	367LBRG	120	175	134.5	S	N
MF 401	403712.2	774320.1	367BLFN	–	120	40	S	–
Piedmont carbonate hydrogeologic setting, 2003 and (or) 2004								
LN 1763	395542	761853	367CNSG	–	250	46	S	–
LN 2005	400629.5	763652.5	371MLBC	11	100	40	S	–
LN 2008	400557.7	762812.7	371MLBC	40	175	102	S	–
LN 2017	401255.1	761147.3	367EPLR	20	160	42	S	–
LN 2021	395952.3	761221.4	367CNSG	27	150	41	S	N
Triassic Lowland hydrogeologic setting, 2003 and 2004								
AD 1184	395955.1	770207.7	231GBRG	–	180	101	S	G
BK 3011	402704	752457	231BRCK	–	100	–	–	–
LN 2113	401307	762243	231NOXF	75	200	103	S	–
MG 1449	401447.71	751935.18	231BRCK	–	114.5	30	S	–
Selected areas of special ground-water protection								
Blair County, North Woodbury Township								
BA 332	–	–	367NTTN	–	100	–	–	–
BA 437[2]	401724	781958	367BFAX	7	105	21	S	–
BA 642	401724	781948	367NNLK	–	325	–	P	–
BA 643	401723	781957	367BFAX	–	330	–	S	–
BA 644	401733	781955	367BFAX	–	145	–	S	–
BA 645	401738	781943	367BFAX	15	207	60	S	N

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Date well constructed	Elevation of land surface (ft)	Range of date for water level	Water level[1] (ft)		Well yield (gal/min)
				Min	Max	
Northeastern Glaciated surficial hydrogeologic setting, 2007—Continued						
SQ 453	11/3/71	1,030	11/3/71, 7/5/07	30	32	6
TI 725	8/90	1,190	6/27/07	10.6		18
TI 728	5/28/90	1,040	5/28/90, 6/28/07	8.74	10.42	100
WY 193	3/28/95	605	3/28/95, 7/5/07	25	31.8	20
WY 194	1/90	580	1/90, 6/20/07	22	26.5	20
WY 195	6/2/00	760	6/21/07	52.8		20
WY 196	1/24/01	730	1/24/01, 9/4/07	6	7.6	30
Great Valley carbonate hydrogeologic setting, 2003 and (or) 2004						
BE 1619	6/26/89	400	11/13/97–4/14/04 (n = 3)	27.02	37.71	–
CU 908	3/22/91	650	2/7/95–4/15/04 (n = 5)	28.12	50.30	4.52
CU 917	3/9/89	585	3/1/95–4/28/04 (n = 4)	35.25	59.70	4.36
LB 1160	5/5/80	440	5/5/80–7/19/95 (n = 4)	86.00	104.49	4.3
NP 805	5/1/95	400	1/14/98, 4/1/03 (n = 2)	66.30	78.52	–
Appalachian Mountain carbonate hydrogeologic setting, 2003 and 2004						
BD 653	6/19/90	1,370	5/26/94–4/26/04 (n = 5)	47.42	64.10	4.80
CE 672	1988	1,190	4/19/94–4/29/04 (n = 5)	84.24	131.50	6.82
LY 686	7/13/88	765	7/13/88–4/27/04 (n = 3)	82.20	110.00	60
MF 401	1991	870	6/21/94–4/13/04 (n = 4)	3.47	16.90	9
Piedmont carbonate hydrogeologic setting, 2003 and (or) 2004						
LN 1763	3/28/81	435	5/24/91–3/31/04 (n = 3)	36.00	40.85	8.5
LN 2005	1975	390	3/12/93–3/31/04 (n = 5)	7.50	10.04	6.4
LN 2008	8/91	370	5/14/93–4/9/03 (n = 3)	48.70	70.40	4.3
LN 2017	7/92	410	7/92–4/1/04 (n = 6)	20.00	56.30	12
LN 2021	8/8/89	370	3/29/93–3/30/04 (n = 5)	22.10	28.20	8.41
Triassic Lowland hydrogeologic setting, 2003 and 2004						
AD 1184	9/20/95	500	9/20/95–4/8/04 (n = 3)	11.18	40.00	10
BK 3011	10/21/92	550	4/15/03, 4/7/04 (n = 2)	A	A	–
LN 2113	10/10/92	500	4/2/03, 4/6/04 (n = 2)	32.60	36.50	100
MG 1449	1971	265	6/21/96–6/12/07 (n = 7)	10.49	11.24	55
Selected areas of special ground-water protection						
Blair County, North Woodbury Township						
BA 332	1945	1,440	–	–	–	20.00
BA 437[2]	6/10/80	1,435	5/7/84–8/8/07 (n = 22)	14.8	37.1	6.6
BA 642	1994	1,455	8/25/05–9/6/05 (n = 2)	41.7	44.4	–
BA 643	1960	1,445	8/25/05–9/1/05 (n = 2)	39.1	39.1	–
BA 644	2005	1,440	9/1/05 (n = 1)	46.7		–
BA 645	10/25/04	1,420	9/1/05 (n = 1)	37.4		15

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Latitude	Longitude	Aquifer code	Depth to top of water-bearing unit (ft)	Depth of well (ft)	Casing length	Casing material	Type of seal
				Berks County, Oley Township				
BE 1298	402237	754455	371ALNN	8	62	41	S	–
BE 1370[2,3]	402238	754434	371ALNN	–	110	–	–	–
BE 1773	402242	754422	374LSVL	–	–	–	–	–
BE 1774	402225	754448	371ALNN	50	397	60	S	N
BE 1775	402227	754452	371ALNN	–	320	64	S	–
BE 1776	402225	754430	371ALNN	15	180	42	S	–
				Lancaster County, Earl Township				
LN 1291	–	–	371ELBK	–	232	25	–	–
LN 1842[2]	400456	760657	374ZKCR	–	65	40	S	–
LN 1998	400518	760719	374ZKCR	–	60	–	S	–
LN 2000	400500	760637	374ZKCR	–	120	–	S	–
LN 2118	400448	760647	377LDGR	–	–	–	S	–
LN 2119	400448	760627	377LDGR	4	175	126	S	G

[1] Single water level indicates only a single measurement is on record.

[2] Detailed investigations of pesticide occurrence, concentration change related to water-level condition, and persistence done at these sites, 2003–07.

[3] Additional reference water levels for BE 1370 where taken at BE 1774.

BE 1774 402225 754448 371ALNN 50 397 60 S N

Table 3. Records of wells sampled for assessments of pesticides in ground water from baseline-assessment areas and areas of special ground-water protection, 2003–07, Pennsylvania.—Continued

Local well number	Date well constructed	Elevation of land surface (ft)	Range of date for water level	Water level[1] (ft)		Well yield (gal/min)
				Min	Max	
			Berks County, Oley Township			
BE 1298	10/81	330	12/31/81–8/23/05 (n = 32)	13.9	23.3	60
BE 1370[2,3]	–	330	8/18/05, 5/17/07 (n = 2)	15.5	17.8	–
BE 1773	1980	310	–	–	–	–
BE 1774	6/5/97	356	6/5/97–5/17/05 (n = 15)	31.0	41.8	8
BE 1775	6/05	360	8/15/05–8/23/05 (n = 4)	33.8	37.2	–
BE 1776	8/82	345	8/0/82–8/23/05 (n = 2)	20.0	27.2	35
			Lancaster County, Earl Township			
LN 1291		500	5/9/59 (n = 1)	60.0		240
LN 1842[2]	1940	440	5/21/91–8/9/07 (n = 23)	31.1	39.9	25
LN 1998	1992	470	8/20/92 (n = 1)	45.0		–
LN 2000	1992	440	–	–	–	–
LN 2118	1970	410	6/6/06 (n = 1)	14.5		–
LN 2119	6/23/97	440	6/5/06 (n = 1)	45.6		50

BE 1774 6/5/1997 356 6/5/97–5/17/07 (n = 15) 31.0 41.8 8

Appendixes 1–4

Appendix 1. Methods for Estimating Pesticide Use

Data for estimating pesticide use were obtained through U.S. Department of Agriculture Chemical Use Reports (U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, 1997b, 2004, 2005a, 2005b, 2006a, 2006b, 2006c, 2007a, 2007b) and the Pennsylvania Agricultural Statistics published by Pennsylvania Department of Agriculture (1997). The Census of Agriculture provides accurate pesticide-use information, but these data were not used; direct comparison between past and present census surveys could not be made because the 2007 survey, which would best represent the 2003–07 study period, was not completed at the time this report was developed.

A U.S. Geological Survey method for estimating pesticide use (Thelin, 2000) was modified to use the best data available for the mid 1990s and the study period of 2003-07 for Pennsylvania and its counties. Statewide and county agricultural production and pesticide use are related as follows:

$$P_{County} = A_{County} T_{PA} k_{PA} n, \qquad (1)$$

where

P_{County} is pesticide total applied for county, in pounds,

A_{County} is area of crop commodity harvested for county, in acres,

T_{PA} is treated-area fraction for pesticide applied in Pennsylvania, in percent,

k_{PA} is rate of annual application for Pennsylvania, in pounds per acre per year, and

n is number of applications.

Area Harvested

Values for A_{County} were from data published in Pennsylvania Agricultural Statistics Bulletins available for the study period (Pennsylvania Department of Agriculture, 2004, 2005, 2006, 2007). The total area harvested for Pennsylvania, A_{PA}, is equivalent to the summation of A_{County} for 66 counties[1]:

$$A_{PA} = \sum_{i=1}^{66} A_{County} \qquad (2)$$

Pesticide Applied

Data for pesticide use were not available for every crop for every year for every state in the United States. Values for pesticide use were based on the best available data that could be attained for the past and current study period. The data were obtained for representative years available during the study period for each crop commodity for Pennsylvania or representative pesticide-use data interpolated from adjacent states.

Values for n, T_{PA}, and k_{PA} were taken directly from data published in the Agricultural Chemical Usage Summary Reports for Field Crops, Vegetables or Fruit (U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, 1997b, 2004, 2005a, 2005b, 2006a, 2006b, 2006c, 2007a, 2007b) and are shown in table 1-1. The comparisons made for 21 of the 134 pesticides used statewide are based on area of crop commodity planted acres (not on acres harvested) for Pennsylvania (U.S. Department of Agriculture National Agricultural Statistics Service, 2004, 2005a, 2006a, 2006b, 2007a, 2007b). All other figures including countywide comparisons contain calculated data based on A_{County}.

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[1] No data for Philadelphia County.

Table 1-1. Factors in computations of pesticide use.

[–, no data; Pennsylvania Department of Agriculture, 1997; U.S. Departmenof Agriculture, 1997a, 1997b, 2005a, 2005b, 2006a, 2006c]

Pesticide	Area applied factor, percent		Application rate factor, pounds per acre per year		Number of applications factor	
	1996	2004–05	1996	2004–05	1996	2004–05
			Corn (Grain and Silage)			
Acetochlor	17	11	2.07	1.610	1	1
Atrazine	91	87	1.14	1.096	1	1
Metolachlor	28	3	1.76	1.217	1	1
S-Metolachlor	–	48	–	1.220	–	1
			Sweet Corn			
Acetochlor	–	–	–	–	–	–
Atrazine	[1]45	90	[1]1.23	1.41	1.1	1
Metolachlor	[1]40	–	[1]1.93	–	1	–
S-Metolachlor	–	71	–	1.80	–	1

[1] Data interpolated for the same year from New Jersey chemical-use data.

References Cited

Pennsylvania Department of Agriculture, 1997, Pennsylvania Agricultural Statistics 1996-1997: Harrisburg, Pa., p. 71-73.

Pennsylvania Department of Agriculture, 2004, Pennsylvania Agricultural Statistics 2003-2004: Harrisburg, Pa., p. 13, 126.

Pennsylvania Department of Agriculture, 2005, Pennsylvania Agricultural Statistics 2004-2005: Harrisburg, Pa., p. 3, 25, 26.

Pennsylvania Department of Agriculture, 2006, Pennsylvania ‘Ag Snapshot’ 2005: Pennsylvania Agricultural Statistics 2005-2006, Harrisburg, Pa., 3 p.

Pennsylvania Department of Agriculture, 2007, Pennsylvania ‘Ag Snapshot’ 2006: Pennsylvania Agricultural Statistics 2006-2007, Harrisburg, Pa., 3 p.

Thelin, G.P., 2000, Method for estimating pesticide use for county areas of conterminous United States: U.S. Geological Survey Open-File Report 00-250, p. 6-16.

U.S. Department of Agriculture National Agricultural Statistics Service, 1997a, Agricultural chemical usage 1996 vegetable summary: accessed December 28, 2008, at *http://usda.mannlib.cornell.edu/usda/nass/AgriChemUsVeg/1990s/1997/AgriChemUsVeg-07-15-1997.txt*

U.S. Department of Agriculture National Agricultural Statistics Service, 1997b, Pennsylvania Statistics: accessed December 28, 2008, at *http://www.nass.usda.gov/Statistics_by_State/Pennsylvania/index.asp*

U.S. Department of Agriculture National Agricultural Statistics Service, 2004, Agricultural chemical usage 2003 field crops summary: Washington, D.C., p. 70.

U.S. Department of Agriculture National Agricultural Statistics Service, 2005a, Agricultural chemical usage 2004 vegetables summary: Washington, D.C., p. 77, 155.

U.S. Department of Agriculture National Agricultural Statistics Service, 2005b, Pennsylvania Statistics: accessed December 28, 2008, at *http://www.nass.usda.gov/Statistics_by_State/Pennsylvania/index.asp*

U.S. Department of Agriculture National Agricultural Statistics Service, 2006a, Agricultural chemical usage 2005 field crops summary: Washington, D.C., p. 33, 68.

U.S. Department of Agriculture National Agricultural Statistics Service, 2006b, Agricultural chemical usage 2005 fruit summary: Washington, D.C., p. 32-34, 102, 156-157.

U.S. Department of Agriculture National Agricultural Statistics Service, 2006c, Pennsylvania Statistics: accessed December 28, 2008, at *http://www.nass.usda.gov/Statistics_by_State/Pennsylvania/index.asp*

U.S. Department of Agriculture National Agricultural Statistics Service, 2007a, Agricultural chemical usage 2006 field crops summary: Washington, D.C., p. 38, 70.

U.S. Department of Agriculture National Agricultural Statistics Service, 2007b, Agricultural chemical usage 2006 vegetables summary: Washington, D.C., p. 37, 100.

Appendix 2. Detailed Description of Quality-Control Methods and Data Analyses

This appendix provides detailed information on quality-control methods, the analysis of quality-control sample results, and how the analyses were used to evaluate project quality-assurance (QA) objectives. For QA objectives related to bias and variability, data were presented separately for pesticides, nitrate and nitrite, and total coliform and *Escherichia coli* (*E. coli*) bacteria.

Quality-control samples were submitted to the Pennsylvania Department of Environmental Protection Laboratory (PADEPL) and three U.S. Geological Survey (USGS) laboratories—Ohio Water Microbiology Laboratory (OWML), Organic Geochemistry Research Laboratory (OGRL), and National Water Quality Laboratory (NWQL)—for QA of analytical results for well-water samples (table 2-1); the results from these samples were used to evaluate additional QA objectives.

Representativeness of Sampling of Hydrogeologic Settings

QA objective 1 (representativeness of samples) was met by adhering to well-selection criteria and USGS protocols for stability of field measurements (U.S. Geological Survey, variously dated) during well purging prior to sampling. QA goals for well selection were established using the following criteria: the wells 1) were used on a daily basis, 2) had available detailed driller information (records on file with the homeowner or Pennsylvania Topographic and Geologic Survey that would provide confirmation of well depth and aquifer lithology), 3) were not affected by point sources of contamination, 4) were not influenced by surface-water sources, 5) had storage and treatment systems that could be by-passed during well purge and sample collection, 6) were used for household or farm-water supply in an area of row crop, orchard, or vineyard land use, 7) had sufficient yield to obtain a sample representative of the aquifer, and 8) had depths of 250 ft or less (100 ft or less for the Eastern Lake surficial setting) or had all the water-bearing zones less than 250 ft (100 ft for the Eastern Lake surficial setting) and were cased to the primary aquifer. In 2007, the last year of the study, commercial and production wells also were considered for sampling if the land near the wells was used for row-crop agriculture. The criteria for water-use type were expanded for several reasons: 1) to improve the number of possible wells meeting lithology criteria—wells drilled in recent years are drilled through unconsolidated sand and gravel into bedrock to improve water quality and this limited the number of household or farm wells completed in sand and gravel, 2) to improve the number of wells meeting the land-use criteria—field observations indicated that many row-crop areas were fallow, and 3) to more accurately reflect the water quality in the setting because of the higher yield of commercial and production wells.

Locating wells that would meet all eight well-selection criteria was not practical; between six and eight criteria were met for each well that was selected for sample collection. Stability criteria for field measurements were met approximately 95 percent of the time. Most wells were used every day; therefore, flushing of the well for daily household processes (bathing, laundry, etc.) was routine, and the stability of all indicators usually could be reached within 30 minutes. During the well purge at several low-yielding wells, the stability of all indicators was not reached in 30 minutes, and the sample was collected with only three to four indicators being stable.

False Positives

QA objective 2 (bias resulting from sample contamination) was evaluated through the use of equipment, trip, and field blanks. A ‘blank’ is a water sample intended to be free of the analytes of interest. Approximately 18 percent of the number of environmental samples were submitted as QA blanks.

Equipment blanks were collected in the Pennsylvania Water Science Center (PA WSC) laboratory by pouring blank water through the equipment used for sample collection. Certified inorganic-free blank water was used for nitrate and nitrite, organic-free blank water was used for pesticides, and autoclaved deionized water (years 2005 and 2006) or sterile phosphate buffer with peptone (years 2003 and 2004) was used for bacteria. Autoclaved deionized water, used for bacteria blanks after 2004, was the blank solution used for the Colilert-tray method. During the 5-year study, five equipment blanks were analyzed for pesticides, three equipment blanks were analyzed for nitrate and nitrite, and two equipment blanks were analyzed for total coliform and *E. coli* bacteria.

Trip blanks were prepared to evaluate if contamination was introduced in the transportation of samples and containers. Two trip blanks—one for nitrate and nitrite and one for total coliform and *E. coli* bacteria—were analyzed.

Field blanks were prepared at the well site to demonstrate that (1) equipment was adequately cleaned to remove contamination introduced by samples collected at previous sites, (2) sample collection and processing did not produce artificial contamination, and (3) sample handling and transport did not introduce contamination. In addition, because the field blank was treated like an environmental sample at the analytical laboratory, field blanks could help to identify potential contamination introduced during laboratory handling and analysis. Nine field blanks were analyzed for pesticides, 11 field blanks were analyzed for nitrate and nitrite, and 10 field blanks were analyzed for total coliform and *E. coli* bacteria.

Table 2-1. Summary of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.

[Pesticides analyzed using C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (GCMS) at the USGS NWQL are listed in table 7; pesticides analyzed using graphitized carbon-based SPE and high-performance liquid chromatography/mass spectrometry (HPLCMS) at the USGS NWQL are listed in table 8; U.S. Environmental Protection Agency (USEPA) 525.2-method USEPA 531.1-method pesticides (baseline-assessment and trends listings) are listed on table 6; pesticides analyzed by SPE and HPLCMS at the OGRL are listed on table 9; 2-lab split samples are split samples analyzed at two laboratories; *E. coli*, *Escherichia coli*]

Quality-control sample type	Station name	U.S. Geological Survey station identification number	Date	Time(s)	Laboratory analyzing sample	
					PADEPL[1]	USGS X(1)=NWQL[2] X(2)=OWML[3] X(3)=OGRL[4]
Equipment blanks						
Pesticides	Lemoyne Station	401435076540910	03/24/03	2010		X(1)
	Lemoyne Station	401435076540910	04/15/03	1115		X(1)
	Lemoyne Station	401435076540910	05/06/03	1300		X(1)
	Lemoyne Station	401435076540910	05/06/03	1305		X(1)
	Lemoyne Station	401435076540910	03/02/04	1210	X	
Nitrate plus nitrite/ nitrate and (or) nitrite	Lemoyne Station	401435076540910	03/24/03	2015		X(1)
	Lemoyne Station	401435076540910	03/02/04	1130	X	
	Lemoyne Station	401435076540910	05/10/04	1530	X	
Total coliform and *E. coli* bacteria	Lemoyne Station	401435076540910	03/24/03	2000		X(2)
	Lemoyne Station	401435076540910	03/02/04	1100	X	
Field blanks						
Pesticides	ER 295	415437080242301	07/29/04	1035	X	
	ER 3505	415845080203301	08/04/04	1121	X	
	PE 848	403005077170201	06/22/05	1200		X(1)
	BA 437	401724078195801	06/28/05	1137		X(1)
	MF 407	403959077311101	08/15/05	1100		X(1)
	FR 834	400641077375401	06/21/06	1000		X(1)
	NP 827	405328075060201	07/20/06	1250		X(1)
	LN 1842	400456076065701	06/06/07	1110		X(1)
	BR 884	415608076425901	07/26/07	1100		X(1)
Nitrate plus nitrite/ nitrate and (or) nitrite	BK 3011	402704075245701	04/15/03	1129		X(1)
	LN 2021	395951076122301	03/30/04	1130	X	
	ER 1405	420042080174901	06/23/04	0841	X	
	ER 3511	420854079564001	08/18/04	1226	X	
	SN 250	404516076564101	06/08/05	1136	X	
	BA 437	401724078195801	06/28/05	1136	X	
	FR 831	395746077433701	06/14/06	1121	X	
	LE 1427	404523075410601	07/18/06	1245	X	
	BE 1782	403528075490401	08/02/06	1030	X	
	BE 1370	402238075443401	05/17/07	1115	X	
	BR 886	414625076235901	07/25/07	1110	X	
Total coliform and *E. coli* bacteria	LN 2113	401307076224301	04/02/03	1605		X(2)
	BD 653	401525078213801	04/08/03	1450		X(2)
	AD 1155	394850077223401	05/05/03	0720		X(2)
	BK 1370	402238075443401	05/15/03	1144		X(2
	LN 2021	395951076122301	03/30/04	1000	X	
	ER 3508	421503079462201	08/05/04	0701	X	
	BD 656	394938078383901	08/01/05	1021	X	
	CU 980	401257077242801	07/13/06	0930	X	
	BA 437	401724078195801	06/07/07	1030	X	
	CO 590	411217076225101	08/14/07	1213	X	

Table 2-1. Summary of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.—Continued

[Pesticides analyzed using C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (GCMS) at the USGS NWQL are listed in table 7; pesticides analyzed using graphitized carbon-based SPE and high-performance liquid chromatography/mass spectrometry (HPLCMS) at the USGS NWQL are listed in table 8; U.S. Environmental Protection Agency (USEPA) 525.2-method USEPA 531.1-method pesticides (baseline-assessment and trends listings) are listed on table 6; pesticides analyzed by SPE and HPLCMS at the OGRL are listed on table 9; 2-lab split samples are split samples analyzed at two laboratories; *E. coli*, *Escherichia coli*]

Quality-control sample type	Station name	U.S. Geological Survey station identification number	Date	Time(s)	Laboratory analyzing sample	
					PADEPL[1]	USGS X(1)=NWQL[2] X(2)=OWML[3] X(3)=OGRL[4]
Trip blanks						
Nitrate plus nitrite/ nitrate and (or) nitrite	AD 1156	395212077214701	05/05/03	0745		X(1)
Total coliform and *E. coli* bacteria	AD 1155	394850077223401	05/05/03	1100		X(2)
Replicates						
Nitrate plus nitrite/ nitrate and (or) nitrite	LY 686	410805077131401	04/30/03	1211 1212		X(1)
	BE 1619	402934075481801	04/14/04	1116 1117	X	
	ER 369	402055080160501	06/22/04	1121 1122	X	
	PE 847	402122077131601	06/08/05	0841 0842	X	
	NU 570	410604076493401	06/21/05	0946 0947	X	
	FR 833	395117077464001	06/20/06	1123 1124	X	
	CU 981	401506077195701	07/27/06	1150 1155	X	
	BA 437	401724078195801	05/15/07	1208 1209	X	
	LY 690	411155076432501	05/30/07	1421 1422	X	
	BR 886	414625076235901	07/25/07	1256 1257	X	
	NU 110	410854076530901	08/23/07	0851 0852	X	

Table 2-1. Summary of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.—Continued

[Pesticides analyzed using C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (GCMS) at the USGS NWQL are listed in table 7; pesticides analyzed using graphitized carbon-based SPE and high-performance liquid chromatography/mass spectrometry (HPLCMS) at the USGS NWQL are listed in table 8; U.S. Environmental Protection Agency (USEPA) 525.2-method USEPA 531.1-method pesticides (baseline-assessment and trends listings) are listed on table 6; pesticides analyzed by SPE and HPLCMS at the OGRL are listed on table 9; 2-lab split samples are split samples analyzed at two laboratories; *E. coli*, *Escherichia coli*]

Quality-control sample type	Station name	U.S. Geological Survey station identification number	Date	Time(s)	Laboratory analyzing sample	
					PADEPL[1]	USGS X(1)=NWQL[2] X(2)=OWML[3] X(3)=OGRL[4]
Replicates—Continued						
Total coliform and *E. coli* bacteria	LN 2017	401254076114701	04/16/03	1033 1034		X(2)
	BA 437	401724078195801	04/20/04	0911 0912	X	
	ER 3510	421102079503301	08/04/04	0821 0822	X	
	ER 3504	415941080242101	08/05/04	0946 0947	X	
	UN 205	405931076555601	06/21/05	1131 1132	X	
	FU 250	394703078102102	08/02/05	0821 0822	X	
	[5]MF 407	403959077311101	08/15/05	1051 1052	X	
	[5]BA 437	401724078195801	09/07/05	0950 0955	X	
	FR 833	395117077464001	06/20/06	1121 1122	X	
	LN 1842	400456076065701	06/29/06	0915 0920	X	
	CU 980	401257077242801	07/13/06	1040 1045	X	
	NP 818	404935075100201	08/01/06	1150 1155	X	
	BA 437	401724078195801	05/15/07	1206 1207	X	
	LU 778	410532076075201	05/29/07	1631 1632	X	
	BR 886	414625076235901	07/25/07	1256 1257	X	
	BA 437	401724078195801	08/08/07	1116 1117	X	
	CO 590	411217076225101	08/14/07	1211 1212	X	
	NU 110	410854076530901	08/23/07	0851 0852	X	

Table 2-1. Summary of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.—Continued

[Pesticides analyzed using C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (GCMS) at the USGS NWQL are listed in table 7; pesticides analyzed using graphitized carbon-based SPE and high-performance liquid chromatography/mass spectrometry (HPLCMS) at the USGS NWQL are listed in table 8; U.S. Environmental Protection Agency (USEPA) 525.2-method USEPA 531.1-method pesticides (baseline-assessment and trends listings) are listed on table 6; pesticides analyzed by SPE and HPLCMS at the OGRL are listed on table 9; 2-lab split samples are split samples analyzed at two laboratories; *E. coli*, *Escherichia coli*]

Quality-control sample type	Station name	U.S. Geological Survey station identification number	Date	Time(s)	Laboratory analyzing sample: PADEPL[1]	Laboratory analyzing sample: USGS X(1)=NWQL[2] X(2)=OWML[3] X(3)=OGRL[4]
Field-spiked (pesticides) reagent water samples, prepared in triplicate						
	Lemoyne Station	401435076540910	04/15/03	1120 1121 1122		X(1)
	Lemoyne Station	401435076540910	05/06/03	1240 1241 1242		X(1)
	Lemoyne Station	401435076540910	05/06/03	1243 1244 1245		X(1)
	Lemoyne Station	401435076540910	08/27/03	1100 1105 1110	X	
	Lemoyne Station	401435076540910	04/21/04	0900 0905 0910	X	
	Lemoyne Station[6]	401435076540910	06/08/04	1300 1305 1310 1315 1320 1325	X	
	Lemoyne Station[6]	401435076540910	07/21/04	1250 1255 1300 1305 1310 1315	X	
	Lemoyne Station[6]	401435076540910	05/24/05	1030 1040 1050		X(1)
	Lemoyne Station	401435076540910	06/21/05	1020 1030 1040		X(1)
	Lemoyne Station	401435076540910	08/08/05	1100 1105 1110		X(1)

Table 2-1. Summary of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.—Continued

[Pesticides analyzed using C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (GCMS) at the USGS NWQL are listed in table 7; pesticides analyzed using graphitized carbon-based SPE and high-performance liquid chromatography/mass spectrometry (HPLCMS) at the USGS NWQL are listed in table 8; U.S. Environmental Protection Agency (USEPA) 525.2-method USEPA 531.1-method pesticides (baseline-assessment and trends listings) are listed on table 6; pesticides analyzed by SPE and HPLCMS at the OGRL are listed on table 9; 2-lab split samples are split samples analyzed at two laboratories; *E. coli*, *Escherichia coli*]

Quality-control sample type	Station name	U.S. Geological Survey station identification number	Date	Time(s)	Laboratory analyzing sample	
					PADEPL[1]	USGS X(1)=NWQL[2] X(2)=OWML[3] X(3)=OGRL[4]
Field-spiked (pesticides) reagent water samples, prepared in triplicate—Continued						
	Lemoyne Station	401435076540910	06/01/06	0730 (single sample)		X(3)
	Lemoyne Station	401435076540910	06/28/06	1610 1620 1640		X(3)
	Lemoyne Station	401435076540910	06/28/06	1500 1510 1520		X(1)
	Lemoyne Station[6]	401435076540910	07/27/06	1100 1105 1110		X(1)
	Lemoyne Station[6]	401435076540910	08/07/06	1110 1115 1120		X(1)
	Lemoyne Station	401435076540910	06/28/07	0930 0935 0940		X(1)
	Lemoyne Station	401435076540910	07/26/07	0830 0835 0840		X(1)
	Lemoyne Station	401435076540910	08/27/07	1110 1120 1130		X(1)
Field-spiked (nitrate, nitrite) reagent water samples, prepared in triplicate						
	Lemoyne Station	401435076540910	05/13/03	1130 1131 1132		X(1)
	Lemoyne Station	401435076540910	04/07/04	1130 1131 1132	X	
	Lemoyne Station[7]	401435076540910	08/08/05	0850 0900 0910	X	
	Lemoyne Station[7]	401435076540910	06/05/06	1710 1720 1730	X	
	Lemoyne Station[7]	401435076540910	08/27/07	0930 0935 0940	X	

Table 2-1. Summary of quality-control samples analyzed at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL), USGS Ohio Water Microbiology Laboratory (OWML), the USGS Organic Geochemistry Research Laboratory (OGRL), and the Pennsylvania Department of Environmental Protection Laboratory (PADEPL), 2003–07.—Continued

[Pesticides analyzed using C-18 solid-phase extraction (SPE) and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (GCMS) at the USGS NWQL are listed in table 7; pesticides analyzed using graphitized carbon-based SPE and high-performance liquid chromatography/mass spectrometry (HPLCMS) at the USGS NWQL are listed in table 8; U.S. Environmental Protection Agency (USEPA) 525.2-method USEPA 531.1-method pesticides (baseline-assessment and trends listings) are listed on table 6; pesticides analyzed by SPE and HPLCMS at the OGRL are listed on table 9; 2-lab split samples are split samples analyzed at two laboratories; *E. coli*, *Escherichia coli*]

Quality-control sample type	Station name	U.S. Geological Survey station identification number	Date	Time(s)	Laboratory analyzing sample	
					PADEPL[1]	USGS X(1)=NWQL[2] X(2)=OWML[3] X(3)=OGRL[4]
Nutrient standard reference samples						
	Lemoyne Station	401435076540910	08/27/03	1000	X	
	Lemoyne Station	401435076540910	04/14/04	0900	X	
	Lemoyne Station	401435076540910	06/21/05	1200	X	
	Lemoyne Station	401435076540910	07/20/06	0715	X	
	Lemoyne Station	401435076540910	05/14/07	0700	X	
	Lemoyne Station	401435076540910	05/14/07	0710	X	
2-lab split samples (see footnotes 5 and 8)						
Pesticides	Lemoyne Station	401435076540910	06/08/04	1245		X(1)
	Lemoyne Station	401435076540910	07/21/04	1320		X(1)
	Lemoyne Station	401435076540910	05/24/05	1100	X	
	Lemoyne Station	401435076540910	07/27/06	1115	X	
	Lemoyne Station	401435076540910	08/07/06	1125	X	
Nitrate plus nitrite/ nitrate and (or) nitrite	Lemoyne Station	401435076540910	08/08/05	0920		X(1)
	LN 1842[8]	400456076065701	06/01/06	1115		X(1)
	Lemoyne Station	401435076540910	06/05/06	1740		X(1)
	LN 1842[8]	400456076065701	06/29/06	0930		X(1)
	Lemoyne Station	401435076540910	08/27/07	0945		X(1)
Total coliform and *E. coli* bacteria	MF 407	403959077311101	08/15/05	1053		X(2)
	BA 437	401724078195801	09/07/05	0945		X(2)

[1] Methodologies used at the PADEPL: nitrate and nitrite, cadmium reduction of nitrate to nitrite followed by colorimetry (nitrate-N and nitrite-N); pesticides, USEPA 525.2 method, SPE and GCMS (listing analyzed for trends assessments) or USEPA 525.2 method, SPE and GCMS and USEPA 531.1 method, direct aqueous injection into a reverse phase high-performance liquid chromatography (HPLC) column with post column derivitazation and fluorescence detection (listing analyzed for baseline-assessments); bacteria, Colilert tray.

[2] Methodologies used at the USGS NWQL: nitrate plus nitrite, Cadmium reduction of nitrate to nitrite followed by colorimetry (nitrate plus nitrite- nitrogen (N) and nitrite-N); pesticides, C-18 SPE and capillary-column GCMS with selected-ion monitoring; May 6, 2003 @ 1305 sample only, graphitized carbon-based SPE and high-performance HPLCMS.

[3] Methodology used at USGS OWML: bacteria, Colilert tray.

[4] Methodology used at USGS OGRL: pesticides, SPE and HPLCMS.

[5] An additional split-environmental sample was collected and submitted to the OWML to verify reported values received from PADEPL; this sample is listed under the 2-lab-split sample heading of this table (same station name and date, different time).

[6] An additional field-spiked reagent water sample was prepared and submitted to either the PADEPL or the NWQL to verify reported values received from the primary laboratory (see table 5) at the time of sample collection; this sample is listed under the 2-lab-split sample heading of this table (same station name and date, different time).

[7] An additional field-spiked reagent water sample was prepared and submitted to the NWQL to verify reported values for samples analyzed at the PADEPL; this sample is listed under the 2-lab-split sample heading of this table (same station name and date, different time).

[8] A split-environmental sample sent to the NWQL to verify reported values for samples analyzed at the PADEPL.

False Negatives

False negatives (QA objective 3) occur when known concentrations of analytes are not detected. Potential false-negative results were evaluated mainly through the use of field-spiked reagent water (FSRW) samples (pesticides and nitrate and nitrite), USGS Branch of Quality Systems standard reference water samples (SRWS) (used for nitrate and nitrite only), and, to a lesser degree, samples analyzed at two laboratories (2-lab splits). Approximately 33 percent of the number of environmental samples were submitted as spikes. A spike is a sample prepared from either environmental or reagent-grade water fortified with a known mass of the analyte of interest; for this study, only reagent-water spikes were used.

For pesticides, no false negatives were reported for 64 of the 65 compounds (surrogates not included in count) in 58 FSRW samples and five 2-lab splits. Sixty of the 65 pesticides were included in FSRW samples analyzed at the NWQL; 15 of the 60 pesticides analyzed at the NWQL in FSRW samples were also submitted in QC samples analyzed at the PADEPL. Five additional pesticides—captan, hexachlorocyclopentadiene, phosphamidon, chlorothalonil, and diuron—were included in FSRW samples analyzed only at the PADEPL. Captan was the only compound in two sets of triplicate spikes submitted to the PADEPL that was not reported in any of the six samples. The internal QC sample recoveries at the PADEPL were evaluated and found to be within an acceptable range. The manufacturer of the spike solution was contacted to determine if captan was mistakenly not included in the spike solution; all internal records indicated that captan was included in the spike mixture as requested. The source of the problem (false negatives for captan) was not apparent through any communications with the spike manufacturer or the laboratory. The false negatives for captan could not be verified with 2-lab splits because samples analyzed at the NWQL did not include captan. Captan was not detected in any environmental samples analyzed at the PADEPL.

Bias and Variability

Estimates of bias and variability in reported concentrations using field-submitted and laboratory QC samples for analyses of nitrate, nitrite, total coliform and E. coli bacteria, and pesticides analyzed at the PADEPL, USGS NWQL, and the USGS OWML are shown in table 2-2 (at back of appendix). Pesticide-recovery results for a single FSRW sample and a set of triplicate FSRW samples sent to the USGS OGRL in June 2006 using a USGS-certified spike mixture of pesticides and herbicides are shown in table 2-3.

Magnitude of the departure from a ‘true’ or known sample concentrations (called ‘bias’) was estimated from spiked-sample results by calculating the percentage of the added analyte recovered in the sample (Friedman and Erdmann, 1982). Recovery can be either greater than or less than 100 percent, so the bias can be either positive or negative. Recovery results from SRWS and triplicate FSRW samples (nitrate and nitrite) and triplicate FSRW samples (pesticides) were used primarily to evaluate QA objective 4 goals; however, if compounds were not included in SRWS or FSRW samples, lab-reagent spike (LRS) data were used for estimates of bias in recoveries. The bias estimates (table 2-2) do not include the effect of environmental water matrices, which were not evaluated during this project.

Variability is the degree of random error in independent measurements of the same quantity, or more simply stated, how “tightly” concentrations of compounds can be reported for identical samples whether they are environmental samples, spikes, or reference samples. Information on variability can be used to estimate the reproducibility of individual measurements, the concentration needed to be assured of exceeding a water-quality standard, and the likelihood that two measurements of water quality are different. One method to estimate variability related to FSRW, SRWS, and LRS recoveries used a nonparametric statistic termed F-pseudosigma. F-pseudosigma is defined as the interquartile range of data divided by 1.349 (Hoaglin and others, 1983). F-pseudosigmas were calculated using aggregated recoveries of individual compounds in field-submitted SRWS and triplicate FSRW samples (nitrate and nitrite) and triplicate FSRW samples (pesticides) over the course of the project. For those pesticides not included in FSRW samples, F-pseudosigmas were calculated using recoveries from LRS to provide an estimate of analytical variability.

Variability also was determined using a second method that included the calculation of Relative Standard Deviation (RSD) (Friedman and Erdmann, 1982). RSD measures differences between concentrations of triplicate samples and is computed as follows:

$$RSD = \frac{SD\ of\ triplicate\ concentrations}{mean\ concentration\ of\ triplicate\ results} \times 100$$

where

RSD is relative standard deviaion, in percent, and

SD is standard deviation.

RSDs were first calculated using concentrations from individual sets of quality-control samples: results from triplicate environmental replicates and FSRW samples (nitrate and nitrite), triplicate environmental replicates (total coliform and *E. coli* bacteria), and triplicate FSRW samples (pesticides) were used. The median RSD was then calculated using the RSDs from individual sets of triplicate results for each compound. Results for F-pseudosigma from aggregated compound recoveries (method 1) and also median RSDs from concentrations in triplicate field-submitted samples (method 2) were primarily used to evaluate if variability in reported data was within 25 percent (QA objective 5). The variability estimates in pesticide results noted in table 2-2 do not include the effect of environmental water matrices, which were not evaluated during this project.

Table 2-3 Quality-assurance test results for spiked samples of pesticide-free water (field-spiked reagent water) submitted to the U.S. Geological Survey Organic Geochemistry Research Laboratory in 2006.

[*, degradation product; Conc., concentrations; RSD, relative standard deviation; <, less than; N, number of recoveries used in mean or median calculations; all concentrations reported are in **bold** font]

Chemical name, short	Concentration, in micrograms per liter						Recovery percentages and summary statistics						RSD in concentrations of triplicate spikes, in percent
	Spiked Conc. (6/1/06)	Lemoyne Station (6/1/06 @ 0730)	Spiked Conc. (6/28/06)	Lemoyne Station (6/28/06 @ 1610)	Lemoyne Station (6/28/06 @ 1620)	Lemoyne Station (6/28/06 @ 1640)	6/1/06 @ 0730	6/28/06 @ 1610	6/28/06 @ 1620	6/28/06 @ 1640	June Mean (N=4)	June Median (N=4)	
Acetochlor	0.40	**0.36**	0.40	**0.35**	**0.37**	**0.35**	90.0	87.5	92.5	87.5	89.4	89.7	3
*Acetochlor ESA (ethane sulfonic acid)		< .02		< .02	< .02	< .02							
*Acetochlor OXA (oxanilic acid)		< .02		< .02	< .02	< .02							
*Acetochlor SAA (sulfynil acetic acid)		< .02		< .02	< .02	< .02							
*Acetochlor/metolachlor ESA–2nd amide		< .02		< .02	< .02	< .02							
*Acetochlor/metolachlor–2nd amide		**.35**		**.39**	**.38**	**.35**							
*Acetochlor deschloro		< .02		< .02	< .02	< .02							
*Acetochlor hydroxy		< .02		< .02	< .02	< .02							
Alachlor	.40	**.31**	.40	**.31**	**.31**	**.31**	77.5	77.5	77.5	77.5	77.5	77.5	0
*Alachlor ESA		< .02		< .02	< .02	< .02							
*Alachlor OXA		< .02		< .02	< .02	< .02							
*Alachlor SAA		< .02		< .02	< .02	< .02							
*Alachlor ESA–2nd amide		< .02		< .02	< .02	< .02							
*Alachlor–2nd amide		< .02		< .02	< .02	< .02							
*Alachlor deschloro		< .02		< .02	< .02	< .02							
*Alachlor hydroxy		< .02		< .02	< .02	< .02							
Dimethenamid		< .02		< .02	< .02	< .02							
*Dimethenamid ESA		< .02		< .02	< .02	< .02							
*Dimethenamid OXA		< .02		< .02	< .02	< .02							
*Dimethenamid deschloro		< .02		< .02	< .02	< .02							
*Dimethenamid hydroxy		< .02		< .02	< .02	< .02							
Flufenacet		< .02		< .02	< .02	< .02							
*Flufenacet ESA		< .02		< .02	< .02	< .02							
*Flufenacet OXA		< .02		< .02	< .02	< .02							
Metolachlor	.40	**.33**	.40	**.34**	**.33**	**.31**	82.5	85.0	82.5	77.5	81.9	82.5	5
*Metolachlor ESA		< .02		< .02	< .02	< .02							
*Metolachlor OXA		< .02		< .02	< .02	< .02							
*Metolachlor deschloro		< .02		< .02	< .02	< .02							
*Metolachlor hydroxyl		< .02		< .02	< .02	< .02							

Table 2-3 Quality-assurance test results for spiked samples of pesticide-free water (field-spiked reagent water) submitted to the U.S. Geological Survey Organic Geochemistry Research Laboratory in 2006.—Continued

[*, degradation product; Conc., concentrations; RSD, relative standard deviation; <, less than; N, number of recoveries used in mean or median calculations; all concentrations reported are in **bold** font]

Chemical name, short	Concentration, in micrograms per liter						Recovery percentages and summary statistics						RSD in concentrations of triplicate spikes, in percent
	Spiked Conc. (6/1/06)	Lemoyne Station (6/1/06 @ 0730)	Spiked Conc. (6/28/06)	Lemoyne Station (6/28/06 @ 1610)	Lemoyne Station (6/28/06 @ 1620)	Lemoyne Station (6/28/06 @ 1640)	6/1/06 @ 0730	6/28/06 @ 1610	6/28/06 @ 1620	6/28/06 @ 1640	June Mean (N=4)	June Median (N=4)	
Propachlor	0.40	**0.37**	0.40	**0.34**	**0.34**	**0.33**	92.5	85.0	85.0	82.5	86.3	85.6	2
*Propachlor ESA		< .05		< .05	< .05	< .05							
*Propachlor OXA		< .02		< .02	< .02	< .02							
Atrazine	.40	**.40**	.40	**.23**	**.29**	**.24**	100.0	57.5	72.5	60.0	72.5	72.5	13
Bromacil		< .025		< .025	< .025	< .025							
Cyanazine	.40	**.40**	.40	**.34**	**.31**	**.28**	100.0	85.0	77.5	70.0	83.1	84.1	10
Prometon	.40	**.28**	.40	**.28**	**.34**	**.26**	70.0	70.0	85.0	65.0	72.5	71.3	14
Propazine		< .025		< .025	.030	< .025							
Simazine	.40	**.26**	.40	**.30**	**.32**	**.29**	65.0	75.0	80.0	72.5	73.1	74.1	5
*Deethylatrazine (DEA)	.40	**.26**	.40	**.26**	**.17**	**.27**	65.0	65.0	42.5	67.5	60.0	62.5	24
*Deisopropylatrazine (DIA)		< .025		< .025	< .025	< .025							
*Hydroxyatrazine (HA)		< .025		< .025	< .025	< .025							
*Hydroxysimazine		< .025		< .025	< .025	< .025							
*Deethylhydroxyatrazine (DEHA)		< .025		< .025	< .025	< .025							
*Deisopropylhydroxyatrazine (DIHA)		< .025		< .025	< .025	< .025							
*Deethyldeisopropylatrazine/Didealkyatrazine (DDA)		< .025		< .025	< .025	< .025							
*Cyanazine acid (CAC)		< .025		< .025	< .025	< .025							
*Cyanazine amide (CAM)		< .025		< .025	< .025	< .025							
*Deethylcyanazine acid (DCAC)		< .025		< .025	< .025	< .025							
*Deethylcyanazine amide (DCAM)		< .025		< .025	< .025	< .025							
*Deethylcyanazine (DEC)		< .20		< .20	< .20	< .20							
Diuron		< .20		< .20	< .20	< .20							
Fluometuron		< .20		< .20	< .20	< .20							
*DMFM (demethylfluometuron)		< .20		< .20	< .20	< .20							
Linuron	.40	**.26**	.40	**.51**	**.31**	**.21**	65.0	127.5	77.5	52.5	80.6	79.1	44

Pesticides

Most of the FSRW samples were submitted in triplicate so that bias and variability of results could be determined with each set of quality-control samples. For May 2003 and 2005–07, the pesticide-spike solutions used were Supelco or NWQL-prepared, USGS-certified mixtures of pesticides and herbicides. ULTRA Scientific custom-spike mixtures were used August 2003 and during 2004 to evaluate compounds not available in USGS-certified spike solutions. Spike solutions were prepared in the PA WSC laboratory using a micropipette to create solutions with concentrations of 0.4 µg/L for the targeted analytes, except for carbaryl, oxamyl, and methomyl spikes analyzed in 2003 and 2004. During this time, separate triplicate pesticide-spiked samples for carbaryl, oxamyl, and methomyl were prepared using a commercially available mixture of pesticides diluted to a concentration of 3.2 µg/L. These samples were intended to be analyzed at the PADEPL where the minimum reporting levels (MRLs) for these compounds were 2.0 µg/L, but they were actually analyzed at both the PADEPL and the NWQL.

The pesticide-spike concentration of 0.4 µg/L was selected to evaluate bias near action levels defined by Pennsylvania Pesticides and Ground Water Strategy (Pennsylvania Department of Agriculture, 1998) and to approximate concentrations in ground water analyzed in previous studies, summarized in Lindsey and Bickford (1999). Action levels for pesticides (Pennsylvania Department of Agriculture, 1998) are invoked by the PDA at fractions of the U.S. Environmental Protection Agency (USEPA) maximum contaminant levels (MCLs) or lifetime health advisories (LHAs) (appendix 4).

Analysis of recovery of pesticides spiked into water was used to assess bias of results. Pesticide recoveries, in percent, were calculated using the following formula:

$$\frac{\mathit{Lab\text{-}reported\ concentration}}{\mathit{Known\ concentration}} \times 100$$

where,

Lab-reported concentration is the concentration that the NWQL or PADEPL measured for each pesticide in the FSRW sample in micrograms per liter, and

Known concentration is the spike concentration prepared at the PA WSC laboratory, in micrograms per liter.

Methodology for determining the known concentration of each compound in the spike solution is available from the NWQL (U.S. Geological Survey, 1996). Because certified, analyte-free (reagent) water was used for all spikes, it was assumed that no analytes of interest were contributed from the water used to make the spike solution.

To evaluate bias in recovery for pesticides, median recoveries (in percent) from two data sets were used: 1) triplicate FSRW samples, and 2) lab internal quality-control samples. For the 65 pesticides included in spike mixtures used for this project (table 2-2), median recoveries of pesticides in FSRW samples were calculated from recovery results from samples analyzed at the USGS NWQL and separately for samples analyzed at the PADEPL. Median pesticide recoveries were calculated using recoveries from 3 to 33 samples depending on the compound and laboratory.

Using lab internal quality-control sample data, median recoveries from LRS recovery data were used in two ways: 1) for comparison only—to FSRW sample median recoveries (calculated for 65 pesticides), and 2) as the sole indicator of the performance in recovery of the compound, if the pesticide was not included in the spikes submitted (50 pesticides, table 2-2). USGS LRS median recoveries (table 2-2) are based on data compiled from 2002 to 2006 for a suite of pesticides (table 2-4); statistics were based on 968 to 1,417 spike results, depending on the specific compound. USGS LRS median recoveries for another suite of pesticides (table 2-5) were based on data compiled from February 2002 to February 2003 using approximately 235 spike results. PADEPL LRS median recoveries for compounds analyzed by USEPA 525.2 method (table 2-6) were calculated from recovery information from between 5 and 17 LRS. Because LRS samples were not analyzed for the USEPA 531.1 method (table 2-6) at the PADEPL, carbaryl, oxamyl, and methomyl recoveries from lab-spiked environmental samples were used as estimates of method performance, assuming LRS would give recoveries closer to 100 percent in the absence of the effects of environmental water.

Additional detail on internal quality control at the USGS NWQL and OGRL can be found in Zaugg and others (1995), Madsen and others (2003), Furlong and others (2001), Lee and others (2002), and Lee and Strahan (2003). Detail on internal quality control for methods USEPA 531.1 (carbamates) and USEPA 525.2 (semi-volatiles and pesticides) is available as Standard Operating Procedures on file at the PADEPL QA office (James Yoder, Pennsylvania Department of Environmental Protection Laboratory, QA Section Chief, oral commun., February 4, 2008).

Nitrate and Nitrite

For nitrate and nitrite, analytical laboratories have established internal quality-control samples to monitor method performance. Results from internal spiked samples are compared to acceptance criteria to decide if the spiked sample should be re-analyzed or if a comment should be added to the result noting that the quality-control criteria were not met. Details on internal quality control for the nitrate and nitrite methodology used at the NWQL are found in Fishman (1993). Similar detail for internal control for methodology used at the PADEPL is available as a Standard Operating Procedure (USEPA 353.2–Automated Colorimetry) on file at the PADEPL QA office (James Yoder, Pennsylvania Department of Environmental Protection Laboratory, QA Section Chief, oral commun., February 4, 2008).

To evaluate bias in reported data, 15 FSRW samples for nitrate and nitrite were prepared using Spex CertiPrep

Table 2-4. Pesticides analyzed using C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring at the U.S. Geological Survey National Water-Quality Laboratory in Denver, Colorado, from March to May 2003 and May 2005 to September 2007.

[NWIS, National Water Information System; bolding of compound names denotes all values are estimated because of low recoveries or high variability in lab reagent spikes; pct, percent; NA, not available]

Compound	NWIS parameter code	Minimum reporting level, in micrograms per liter	Method detection limit, in micrograms per liter
2,6-Diethylaniline	82660	0.002–0.006	0.001–0.003
alpha-HCH[1]	34253	0.002–0.005	0.001–0.002
alpha-HCH-d6 (surrogate)	91065	.1 pct	NA
Acetochlor	49260	0.006	0.003
Alachlor	46342	0.005–0.006	0.002–0.003
Atrazine	39632	0.007	0.004
Deethylatrazine (CIAT)[2]	04040	0.006–0.014	0.003–0.007
Azinphos-methyl	82686	0.05–0.08	0.02–0.04
Benfluralin	82673	0.006–0.010	0.003–0.005
Butylate	04028	0.002–0.004	0.001–0.002
Carbaryl	82680	0.06–0.041	0.021–0.03
Carbofuran	82674	0.020–0.02	0.010–0.01
Chlorpyrifos	38933	0.005	0.003
cis-Permethrin	82687	0.006–0.01	0.003–0.005
Cyanazine	04041	0.018	0.009
Dacthal (DCPA)[3]	82682	0.0030–0.003	0.0015–0.002
Desulfinylfipronil	62170	0.004–0.012	0.006
Desulfinylfipronil amide	62169	0.009–0.029	0.015
Diazinon	39572	0.005	0.003
Diazinon-d10 (surrogate)	91063	0.1 pct	NA
Dieldrin	39381	0.0048–0.009	0.0024–0.004
Disulfoton	82677	0.02–0.021	0.01–0.011
EPTC[4]	82668	0.0020–0.004	0.0010–0.002
Ethalfluralin	82663	0.009	0.005
Ethoprop (Ethoprophos)	82672	0.005–0.012	0.002–0.006
Fipronil	62166	0.007–0.016	0.008
Fipronil sulfide	62167	0.005–0.013	0.006
Fipronil sulfone	62168	0.005–0.024	0.012
Fonofos	04095	0.0027–0.006	0.0013–0.003
Lindane	39341	0.0040–0.004	0.0020–0.002
Linuron	82666	0.035–0.06	0.018–0.03
Malathion	39532	0.016–0.027	0.008–0.014
Metolachlor	39415	0.006–0.013	0.003–0.006
Metribuzin	82630	0.006–0.028	0.003–0.014
Molinate	82671	0.0016–0.003	0.0008–0.002
Napropamide	82684	0.007–0.018	0.003–0.009
Parathion	39542	0.010	0.005
Parathion-methyl	82667	0.008–0.015	0.004–0.008
Pebulate	82669	0.004–0.0041	0.002–0.0021
Pendimethalin	82683	0.02–0.022	0.01–0.011
Phorate	82664	0.011–0.055	0.006–0.027
p,p'-DDE[5]	34653	0.0025–0.003	0.0013–0.001
Prometon	04037	0.005–0.015	0.002–0.007
Propachlor	04024	0.010–0.025	0.0048–0.012
Propanil	82679	0.011	0.005
Propargite	82685	0.02–0.023	0.01–0.011
Propyzamide	82676	0.004–0.0041	0.002–0.0021
Simazine	04035	0.005–0.006	0.002–0.003
Tebuthiuron	82670	0.016	0.008
Terbacil	82665	0.034–0.04	0.017–0.02
Terbufos	82675	0.012–0.017	0.006–0.009
Thiobencarb	82681	0.0048–0.01	0.0024–0.005
Triallate	82678	0.0023–0.006	0.0012–0.003
Trifluralin	82661	0.006–0.009	0.003–0.005

[1] Alpha hexachlorocyclohexane.

[2] 2-chloro-4-isopropylamino-6-amino-s-triazine.

[3] Dimethyl-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid.

[4] S-ethyl dipropylthiocarbamate.

[5] p,p'-dichlorodiphenyldichloroethylene.

Table 2-5. Pesticides analyzed using graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry at the U.S. Geological Survey National Water-Quality Laboratory in Denver, Colorado, in May 2003.

[NWIS, National Water Information System; bolding of compound names denotes permanently estimated values in May 2003 resulting from low recoveries or high variability in lab reagent spikes; pct, percent; NA, not available; these compounds were analyzed for 10 samples collected for the baseline assessment of the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting]

Compound	NWIS Parameter Code	Minimum reporting level, in micrograms per liter	Method detection limit, in micrograms per liter
2,4,5-T (surrogate)	99958	0.1 pct	0.1 pct
2,4-D[1]	39732	.0218	NA
2,4-D methyl ester	50470	.0086	NA
2,4-DB[2]	38746	.016	NA
3(4-Chlorophenyl)-1-methyl urea	61692	.0242	NA
Acifluorfen	49315	.0066	NA
Aldicarb	49312	.04	NA
Aldicarb sulfone	49313	.02	NA
Aldicarb sulfoxide	49314	.0082	NA
Atrazine	39632	.009	NA
2-Hydroxyatrazine (OIET)[3]	50355	.008	NA
Deethylatrazine (CIAT)[4]	04040	.0282	NA
Deethyldeisopropylatrazine (CAAT)[5]	04039	.01	NA
Deisopropylatrazine (CEAT)[6]	04038	.044	NA
Barban (surrogate)	90640	.1 pct	.1 pct
Bendiocarb	50299	.0252	NA
Benomyl	50300	.0038	NA
Bensulfuron-methyl	61693	.0158	NA
Bentazon	38711	.011	NA
Bromacil	04029	.033	NA
Bromoxynil	49311	.017	NA
Caffeine	50305	.0096	.0048
Caffeine-C13 (surrogate)	99959	.1 pct	.1 pct
Carbaryl	49310	.0284	.0142
Carbofuran	49309	.0056	NA
3-Hydroxycarbofuran	49308	.0058	NA
3-Ketocarbofuran	50295	1.5	NA
Chloramben, methyl ester	61188	.018	NA
Chlorimuron-ethyl	50306	.0096	NA
Chlorothalonil	49306	.035	.0173
Clopyralid	49305	.0138	N/A
Cycloate	04031	.013	NA
Dacthal monoacid	49304	.0116	NA
Dicamba	38442	.0128	NA
Dichlorprop	49302	.0138	NA
Dinoseb	49301	.012	NA
Diphenamid	04033	0.0264	NA
Diuron	49300	.015	NA
Fenuron	49297	.0316	NA
Flumetsulam	61694	.011	NA
Fluometuron	38811	.031	NA
Imazaquin	50356	.016	NA
Imazethapyr	50407	.017	NA
Imidacloprid	61695	.0068	NA
Linuron	38478	.0144	NA
MCPA[7]	38482	.0162	NA
MCPB[8]	38487	.015	NA
Metalaxyl	50359	.02	NA
Methiocarb	38501	.008	NA
Methomyl	49296	.0044	NA
Metsulfuron methyl	61697	.025	NA
Neburon	49294	.012	NA
Nicosulfuron	50364	.013	NA
Norflurazon	49293	.016	NA
Oryzalin	49292	.0176	NA
Oxamyl	38866	.0122	NA
Picloram	49291	.0198	NA
Propham	49236	.0096	NA
Propiconazole	50471	.021	NA
Propoxur	38538	.008	NA
Siduron	38548	.0168	NA
Sulfometuron-methyl	50337	.0088	NA
Tebuthiuron	82670	.0062	NA
Terbacil	04032	.0098	NA
Triclopyr	49235	.0224	NA

[1] (2,4-dichlorophenoxy) acetic acid.

[2] 4-(2,4-dichlorophenoxy) butyric acid.

[3] 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine.

[4] 2-chloro-4-isopropylamino-6-amino-s-triazine.

[5] Chloro-di-amino-s-triazine.

[6] 2-chloro-6-ethylamino-4-amino-s-traizine.

[7] 2-methyl-4-chlorophenoxyacetic acid.

[8] 4-(2-methyl-4-chlorophenoxy) butyric acid.

Table 2-6. Pesticides analyzed at the Pennsylvania Department of Environmental Protection Laboratory (PADEPL) in Harrisburg, Pennsylvania, from August 2003 to December 2004.

[NWIS, National Water Information System; USEPA, U.S. Environmental Protection Agency; MDL, method detection limit; MRL, minimum reporting level; µg/L, micrograms per liter; RPA, Rhone Poulenc Agro; NA, not available; NC, no code; FY04, fiscal year 2004]

Pesticides analyzed in samples collected for the baseline-assessment of the Blue Ridge crystalline and Triassic Lowland siliciclastic (10 of 20 samples) (2003) and the Eastern Lake surficial (20 samples) (2004) hydrogeologic settings				Pesticide analyzed in samples collected for the baseline-trends assessments (Great Valley carbonate, Piedmont carbonate, Appalachian Mountain carbonate, and Triassic Lowland siliciclastic) (2004) and trends assessments in areas of special ground-water protection (2004)			
Analyte	**NWIS parameter code**	**Minimum reporting level, in micrograms per liter**	**Method detection limit, in micrograms per liter**	**Analyte**	**NWIS parameter code**	**Minimum reporting level, in micrograms per liter**	**Method detection limit, in micrograms per liter**
USEPA 525.2 Method:				**USEPA 525.2 Method:**			
Acetochlor	49260	0.10–0.25	0.10	Acetochlor	49260	0.10–0.25	0.10
Alachlor	46342	0.10–0.25	.08	Alachlor	46342	0.10–0.25	.08
Atrazine	39632	0.10–0.25	.07	Atrazine	39632	0.10–0.25	.07
Azinphos-methyl[1]	82686	1.0	N/A	Chlorothalonil	49306	0.10–0.25	.08
Captan	61582	0.10–1.0	.10	Chlorpyriphos (Dursban)	38933	0.10–0.25	.09
Chlorothalonil	49306	0.10–0.25	.08	Dichlobenil[5]	63009	0.10	.06
Chlorpyriphos (Dursban)	38933	0.10–0.25	.09	Fenpropathrin[5]	64044	0.10	.08
Dichlobenil[2]	63009	0.10	.06	Hexachlorocyclopentadiene	34386	0.10–0.25	.09
Diuron[3]	49300	NA	NA	Metolachlor	39415	0.10–0.25	.10
Fenpropathrin[2]	64044	0.10	.08	Metribuzin	82630	0.10–0.25	.07
Hexachlorocyclopentadiene	34386	0.10–0.25	.09	Pendimethalin	82683	0.10–0.25	.06
Metolachlor	39415	0.10–0.25	.10	Phosmet[5]	61601	1.00	.09
Metribuzin	82630	0.10–0.25	.07	Simazine	04035	0.10–0.25	.10
Parathion-methyl	82667	0.10	.05				
Pendimethalin	82683	0.10–0.25	.06				
Phosmet[2]	61601	1.00	.09				
Phosphamidon[4]	63736	1.0	N/A				
Simazine	04035	0.10–0.25	.10				
Terbacil	82665	0.10–0.25	.10				
Trifluralin[2]	82661	0.10	.07				
1,3-dimethyl-2-nitrobenzene (surrogate)	NC	0.10	NA	1, 3-dimethyl-2-nitrobenzene (surrogate)	NC	0.10	NA
Pyrene-d10 (surrogate)	NC	0.10	NA	Pyrene-d10 (surrogate)	NC	0.10	NA
Triphenylphosphate (surrogate)	NC	0.10	NA	Triphenylphosphate (surrogate)	NC	0.10	NA
Perylene-d12 (surrogate)	NC	0.10	NA	Perylene-d 12 (surrogate)	NC	0.10	NA
USEPA 531.1 Method:				(October and December 2004 samples only at Hot-Spot Trend sites:)			
Carbaryl	82680	1.6–5.0	0.338–2.602	Isoxaflutole (RPA 201772)	62733	1.25	NA
Methomyl	49296	1.6–5.0	0.332–1.723	(RPA 203328) (terminal metabolite of isoxaflutole) [2-methanesulphonyl-4-trifluromethylbenzoic acid]	62656	1.25	NA
Oxamyl	38866	1.6–5.0	0.504–2.689	(RPA 202248) (primary metabolite of isoxaflutole) [2-cyclopropylcarbonyl-3-(2-methylsulphonyl-4-trifluoromethylpenyl)-3-oxopropanenitrile; diketonitrile]	63011	1.25	NA

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[1] MRLs during project were reported as 0.10–0.50 µg/L. A PADEPL data review conducted in 2007 changed this level to 1.0 µg/L.

[2] FY04 addition.

[3] MRL during project was reported as 0.10 µg/L. A PADEPL data review conducted in 2007 could not verify acceptable recoveries and mass spectra during the period of sample submittal; therefore, acceptable MDLs and MRLs are not possible.

[4] MRLs during project were reported as 0.10–0.25 µg/L. A PADEPL data review conducted in 2007 changed this level to 1.0 µg/L.

[5] FY04 addition (July 2004) at the three hot-spot wells in the areas of special ground-water protection.

quality-controlled spike solutions with nitrate concentrations ranging from 3.81 to 8.68 mg/L and nitrite concentrations ranging from 0.75 to 1.83 mg/L. All nitrate and nitrite spikes were prepared using a pipet to transfer 10 mL of quality-control concentrate into a 1-L volumetric flask and diluting to volume with inorganic-blank water.

Six SRWS (N78, N82, N86, N90, N91, and N92) were submitted to the PADEPL to determine bias in recovery of nitrate and nitrite. SRWS are samples of known concentration prepared by the USGS Branch of Quality Systems in Denver, Colo. Recoveries of nitrate and nitrite reported for the SRWS were combined with recoveries calculated from triplicate FSRW samples to determine median recoveries.

To evaluate variability in nitrate and nitrite concentrations, RSDs were calculated from five triplicate field-spike sets and additional results from 11 well-water triplicate-set results (replicates). A median RSD from all triplicate-set results for nitrate and nitrite was then calculated.

Bacteria

For total coliform and *E. coli* bacteria, both the PADEPL and the OWML employ all method-required internal quality-control samples to quality assure reported results. Both labs used the Colilert tray methodology; detail on internal quality-control samples is found in SM 9223 (Enzyme Substrate Test) (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 2004).

No total coliform or *E. coli* samples were submitted as spiked samples for analysis of bias. Eighteen sets of well-water triplicate sets were submitted for analysis of variability in bacteria results. There were no replicate sets for *E. coli* analyses where both samples had counts of bacteria, so estimates of variability could not be determined; however, 9 out of 18 sets of replicates for total coliform bacteria provided results for estimates of variability

References Cited

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 2004, Standard methods for the analysis of water and wastewater (21st ed.): Washington, D.C., American Public Health Association, Section 9223.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory–Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Friedman, L.C., and Erdmann, D.E., 1982, Quality assurance practices for the chemical and biological analyses of water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A6, 181 p.

Furlong, E.T., Anderson, B.D., Werner, S.L., Soliven, P.P., Coffey, L.J., and Burkhardt, M.R., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—-Determination of pesticides in water by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4134, 73 p.

Hoaglin, D.C., Mosteller, F., and Tukey, J.S., 1983, Understanding robust and exploratory data analysis: New York, John Wiley and Sons, 447 p.

Lee, E.A., and Strahan, A.P., 2003, Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of acetamide herbicides and their degradation productions in water using online solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 03-173, 17 p.

Lee, E.A., Strahan, A.P., and Thurman, E.M., 2002, Methods of analysis by the U.S. Geological Survey Organic Geochemistry Research Group—Determination of triazine and phenylurea herbicides and their degradation products in water using solid-phase extraction and liquid chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02-436, 19 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.

Madsen, J.E., Sandstrom, M.W., and Zaugg, S.D., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—-A method supplement for the determination of fipronil and degradates in water by gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 02-462, 11 p.

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

U.S. Geological Survey, variously dated, National field manual for the collection of water quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at *http://pubs.water.usgs.gov/twri9A*

U.S. Geological Survey, 1996, National Water Quality Laboratory, Calculation of matrix spike recovery: accessed June 16, 2008, at *http://wwwnwql.cr.usgs.gov/USGS/SpikeCalc.html*

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, 60 p.

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli*) bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.

[Samples were analyzed at the Pennsylvania Department of Environmental Protection Laboratory, the U.S. Geological Survey National Water-Quality Laboratory, and the U.S. Geologidal Survey Ohio Water Microbiology Laboratory. B_N, number of blanks (equipment, trip, and field combined); B_{ND}, number of blanks in which compound was detected; S_N, number of samples; R_N, number of replicate sets; $R_{SETDECT}$, number of replicate sets within which compound was consistently detected; LRS, lab reagent spikes; SRWS, U.S. Geological Survey Standard Reference Water Sample; FSRW samples, field-spiked reagent water samples; ND, no detections NC, could not be calculated; env. reps, environmental replicates; CNBD, could not be determined; mg/L, miligrams per liter; µg/L, micrograms per liter; E, estimated; –, no data; GCMS, gas chromatography/mass spectrometry; HPLCMS, high-performance liquid chromatography/mass spectrometry; QC, quality control; NWIS, National Water Information System. **Bolded** compounds are currently reported as permanently estimated concentrations at the USGS NWQL due to poor recovery, bias, and (or) high variability in laboratory reagent water spikes; these compounds are reviewed annually, and if performance improves or degrades, the list of permanently estimated compounds may change; USGS(1), U.S. Geolgical Survey (USGS) National Water Quality Laboratory (NWQL) in Denver, Colo.; USGS(1), bias and variability evaluated using results from field-spiked reagent water samples; USGS(1), bias and variability evaluated using results from lab-reagent spikes; USGS(2), USGS Ohio Water Microbiology Laboratory in Columbus, Ohio [bacteria]; PADEPL, Pennsylvania Department of Environmental Protection Laboratory in Harrisburg, Pa.; PADEPL, bias and variability evaluated using results from field-spiked reagent water samples; PADEPL, bias and variability evaluated using results from lab-reagent spikes; NAV, not able to verify acceptable recovery; **bolded black** numbers indicate percents of bias or variability that did not meet project quality-assurance objectives]

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of bias					
		Data sets used					
		Field-submitted samples					LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		Blank samples			SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides) (Spike concentrations and SRWS identifiers found in footnote 1)		
		Bias, using concentration (detections result in false positives due to contamination)			Bias, using recoveries, in percent		Bias, using recoveries, in percent
		B_N	B_{ND}	Maximum reported concentration in blanks	S_N	Median recovery, in percent	Median recovery, in percent
Nitrate[1]	PADEPL	12	3	0.2 mg/L	18	98	–
	USGS(1)	3	0	ND	3	99	–
Nitrite[1]	PADEPL	12	0	ND	18	100	–
	USGS(1)	3	0	ND	3	100	–
Total coliform	PADEPL	7	0	ND	4	NC	–
	USGS(2)	6	0	ND	4	NC	–
E. coli	PADEPL	7	0	ND	4	NC	–
	USGS(2)	6	0	ND	4	NC	–
Acetochlor	PADEPL	3	0	–	12	84	98
	USGS(1)	10	0	–	33	117	106
Acifluorfen	USGS(1)	1	0	–	0	–	92
Alachlor	PADEPL	3	0	–	12	95	102
	USGS(1)	10	0	–	33	119	105
Aldicarb	USGS(1)	1	0	–	3	**11**	**9**
Aldicarb sulfone	USGS(1)	1	0	–	3	**63**	**58**
Aldicarb sulfoxide	USGS(1)	1	0	–	3	**25**	**42**
2,4-D	USGS(1)	1	0	–	0	–	114
2,4-D methyl ester	USGS(1)	1	0	–	0	–	76
2,4-DB	USGS(1)	1	0	–	0	–	**72**
2-chloro-6-ethylamino-4-amino-s-triazine (CEAT, deisopropylatrazine)	USGS(1)	1	0	–	0	–	**62**
2-hydroxyatrazine	USGS(1)	1	0	–	0	–	102
3-(4-chlorophenyl)-1-methyl urea	USGS(1)	1	0	–	0	–	95
Alpha -HCH	USGS(1)	10	0	–	33	96	98
Alpha-HCH-d6 (surrogate)	USGS(1)	10	–	–	33	93	94
Atrazine	PADEPL	3	0	–	12	85	94
	USGS(1)	11	0	–	33	112	106 (79)
2-chloro-4-isopropylamino-6-amino-s-triazine (deethylatrazine; CIAT) (permanent 'E' only for GCMS method)	USGS(1)	11	0	–	33	**26**	**44** (72)
Azinphos-methyl	PADEPL	2	0	–	9	122	121
	USGS(1)	10	0	–	33	90	87
Barban (positive ion surrogate)	USGS(1)	1	–	–	3	86	96
Bendiocarb	USGS(1)	1	0	–	0	–	**71**
Benfluralin	USGS(1)	10	0	–	33	78	**72**
Benomyl	USGS(1)	1	0	–	0	–	90
Bensulfuron-methyl	USGS(1)	1	0	–	0	–	**136**
Bentazon	USGS(1)	1	0	–	0	–	**57**
Bromacil	USGS(1)	1	0	–	0	–	85
Bromoxynil	USGS(1)	1	0	–	0	–	**58**
Butylate	USGS(1)	10	0	–	33	96	93
2,4,5-T (negative ion surrogate)	USGS(1)	1	–	–	3	**66**	83
Caffeine	USGS(1)	1	0	–	0	–	96
Caffeine-13C (positive ion surrogate)	USGS(1)	1	–	–	3	102	98

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of variability				
		Data sets used				
		Field-submitted samples				LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides)	Triplicate env. reps. and triplicate FSRW (nitrate and nitrite); triplicate env. reps (total coliform bacteria); triplicate FSRW samples (pesticides)			
		Variabiliy, using F-pseudosigma of recoveries, in percent.	Variability, using median relative standard deviation (RSD) of concentrations in triplicate sets[3]			Variabiliy, using F-pseudosigma of recoveries, in percent.
		F-pseudo-sigma, in percent	R_N	$R_{SETDECT}$	Median RSD, in percent	F-pseudosigma, in percent
Nitrate	PADEPL	5	14	10	2	–
	USGS(1)	2	2	2	2	–
Nitrite	PADEPL	4	14	6	0	–
	USGS(1)	1	2	1	1	–
Total coliform	PADEPL	NC	17	9	25	–
	USGS(2)	NC	1	0	NC	–
E. coli	PADEPL	NC	17	0	NC	–
	USGS(2)	NC	1	0	NC	–
Acetochlor	PADEPL	20	4	4	10	22
	USGS(1)	11	11	11	2	15
Acifluorfen	USGS(1)	–	0	–	–	15
Alachlor	PADEPL	18	4	4	8	**27**
	USGS(1)	7	11	11	2	14
Aldicarb	USGS(1)	13	1	1	**89**	**33**
Aldicarb sulfone	USGS(1)	7	1	1	17	24
Aldicarb sulfoxide	USGS(1)	5	1	1	**26**	16
2,4-D	USGS(1)	–	0	–	–	17
2,4-D methyl ester	USGS(1)	–	0	–	–	13
2,4-DB	USGS(1)	–	0	–	–	11
2-chloro-6-ethylamino-4-amino-s-triazine (CEAT, deisopropylatrazine)	USGS(1)	–	0	–	–	14
2-hydroxyatrazine	USGS(1)	–	0	–	–	20
3-(4-chlorophenyl)-1-methyl urea	USGS(1)	–	0	–	–	12
Alpha -HCH	USGS(1)	12	11	11	2	10
Alpha-HCH-d6 (surrogate)	USGS(1)	10	11	11	3	8
Atrazine	PADEPL	6	4	4	12	25
	USGS(1)	7	11	11	2	13 (13)
2-chloro-4-isopropylamino-6-amino-s-triazine (deethylatrazine; CIAT) (permanent 'E' only for GCMS method)	USGS(1)	6	11	11	2	17 (19)
Azinphos-methyl	PADEPL	**78**	3	3	7	**54**
	USGS(1)	**41**	11	11	4	**35**
Barban (positive ion surrogate)	USGS(1)	13	1	1	19	14
Bendiocarb	USGS(1)	–	0	–	–	12
Benfluralin	USGS(1)	8	11	11	4	12
Benomyl	USGS(1)	–	0	–	–	24
Bensulfuron-methyl	USGS(1)	–	0	–	–	**35**
Bentazon	USGS(1)	–	0	–	–	**48**
Bromacil	USGS(1)	–	0	–	–	**35**
Bromoxynil	USGS(1)	–	0	–	–	**44**
Butylate	USGS(1)	8	11	11	1	10
2,4,5-T (negative ion surrogate)	USGS(1)	3	1	1	7	14
Caffeine	USGS(1)	–	0	–	–	12
Caffeine-13C (positive ion surrogate)	USGS(1)	7	1	1	10	16

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of bias					
		Data sets used					
		Field-submitted samples					LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		Blank samples			SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides) (Spike concentrations and SRWS identifiers found in footnote 1)		
		Bias, using concentration (detections result in false positives due to contamination)			Bias, using recoveries, in percent		Bias, using recoveries, in percent
		B_N	B_{ND}	Maximum reported concentration in blanks	S_N	Median recovery, in percent	Median recovery, in percent
Captan	PADEPL	2	0	–	6	**0**	95
Carbaryl	PADEPL	2	0	–	9	87	103
	USGS(1)	11	0	–	33	108	111(87)
Carbofuran	USGS(1)	11	0	–	33	96	113 (86)
3-Hydroxy carbofuran	USGS(1)	3	0	–	3	78	85
3-keto-carbofuran	USGS(1)	1	0	–	0	–	**32**
Chloramben methyl ester	USGS(1)	1	0	–	0	–	**64**
Chlordiamino-s-triazine (CAAT, desethyl desisopropyl atrazine)	USGS(1)	1	0	–	0	–	**47**
Chlorimuron-ethyl	USGS(1)	1	0	–	0	–	**205**
Chlorothalonil	USGS(1)	1	0	–	0	–	**7**
	PADEPL	3	0	–	9	75	97
Clopyralid	USGS(1)	1	0	–	0	–	**69**
Chlorpyrifos (Dursban)	PADEPL	3	0	–	12	82	95
	USGS(1)	10	0	–	33	99	98
cis-Permethrin	USGS(1)	10	0	–	33	**54**	**42**
Cyanazine	USGS(1)	10	0	–	33	100	108
Cycloate	USGS(1)	1	0	–	0	–	**42**
Dacthal (DCPA)	USGS(1)	10	0	–	33	111	106
Dacthal monoacid	USGS(1)	1	0	–	0	–	94
Desulfinylfipronil	USGS(1)	10	0	–	27	118	112
Desulfinylfipronil amide	USGS(1)	10	0	–	27	**64**	112
Diazanon	USGS(1)	10	0	–	33	102	103
Diazinon-d10(surrogate)	USGS(1)	10	–	–	33	111	103
Dicambia	USGS(1)	1	0	–	0	–	97
Dichlobenil	PADEPL	2	0	–	0	–	100
Dichlorprop	USGS(1)	1	0	–	0	–	89
Dieldrin	USGS(1)	10	0	–	33	93	94
2,6–Diethylaniline[4]	USGS(1)	10	0	–	33	**(33)**	94
1,3-dimethyl-2-nitrobenzene (surrogate)	PADEPL	3	–	–	12	93	93
Dinoseb	USGS(1)	1	0	–	0	–	**73**
Diphenamid	USGS(1)	1	0	–	0	–	84
Disulfoton	USGS(1)	10	0	–	33	**50**	**43**
Diuron	USGS(1)	1	0	–	0	–	92
	PADEPL	2	0	–	6	101	NAV
EPTC	USGS(1)	10	0	–	33	94	93
Ethalfluralin	USGS(1)	10	0	–	33	**73**	87
Ethoprop	USGS(1)	10	0	–	33	94	90
Fenpropathrin	PADEPL	2	0	–	0	–	87
Fenuron	USGS(1)	1	0		0	–	86
Fipronil	USGS(1)	10	0	–	27	106	119
Fipronil sulfide	USGS(1)	10	0	–	27	109	103
Fipronil sulfone	USGS(1)	10	0	–	27	84	89

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli*) bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of variability				
		Data sets used				
		Field-submitted samples				LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides)	Triplicate env. reps. and triplicate FSRW (nitrate and nitrite); triplicate env. reps (total coliform bacteria); triplicate FSRW samples (pesticides)			
		Variabiliy, using F-pseudosigma of recoveries, in percent.	Variability, using median relative standard deviation (RSD) of concentrations in triplicate sets[3]			Variabiliy, using F-pseudosigma of recoveries, in percent.
		F-pseudo-sigma, in percent	R_N	$R_{SETDECT}$	Median RSD, in percent	F-pseudosigma, in percent
Captan	PADEPL	NC	2	0	NC	**37**
Carbaryl	PADEPL	8	3	3	6	12
	USGS(1)	**44**	11	11	6	**35** (11)
Carbofuran	USGS(1)	17	11	11	7	**27** (12)
3-Hydroxy carbofuran	USGS(1)	9	1	1	15	**30**
3-keto-carbofuran	USGS(1)	–	0	–	–	12
Chloramben methyl ester	USGS(1)	–	0	–	–	**38**
Chlordiamino-s-triazine (CAAT, desethyl desisopropyl atrazine)	USGS(1)	–	0	–	–	21
Chlorimuron-ethyl	USGS(1)	–	0	–	–	**46**
Chlorothalonil	USGS(1)	–	0	–	–	11
	PADEPL	15	3	3	8	17
Clopyralid	USGS(1)	–	0	–	–	21
Chlorpyrifos (Dursban)	PADEPL	11	4	4	9	18
	USGS(1)	13	11	11	4	11
cis-Permethrin	USGS(1)	10	11	11	6	17
Cyanazine	USGS(1)	18	11	11	3	20
Cycloate	USGS(1)	–	0	–	–	**45**
Dacthal (DCPA)	USGS(1)	13	11	11	1	10
Dacthal monoacid	USGS(1)	–	0	–	–	15
Desulfinylfipronil	USGS(1)	17	9	9	3	17
Desulfinylfipronil amide	USGS(1)	11	9	9	6	**34**
Diazanon	USGS(1)	10	11	11	2	12
Diazinon-d10(surrogate)	USGS(1)	9	11	11	2	12
Dicambia	USGS(1)	–	0	–	–	11
Dichlobenil	PADEPL	–	0	–	–	18
Dichlorprop	USGS(1)	–	0	–	–	9
Dieldrin	USGS(1)	22	11	11	3	13
2,6–Diethylaniline[4]	USGS(1)	**(59)**	11	11	5	11
1,3-dimethyl-2-nitrobenzene (surrogate)	PADEPL	7	4	4	2	10
Dinoseb	USGS(1)	–	0	–	–	20
Diphenamid	USGS(1)	–	0	–	–	12
Disulfoton	USGS(1)	14	11	11	4	**38**
Diuron	USGS(1)	–	0	–	–	10
	PADEPL	16	2	2	11	NAV
EPTC	USGS(1)	9	11	11	2	8
Ethalfluralin	USGS(1)	12	11	11	3	14
Ethoprop	USGS(1)	14	11	11	2	13
Fenpropathrin	PADEPL	–	0	–	–	**36**
Fenuron	USGS(1)	–	0	–	–	21
Fipronil	USGS(1)	**27**	9	9	5	**31**
Fipronil sulfide	USGS(1)	13	9	9	5	17
Fipronil sulfone	USGS(1)	11	9	9	4	20

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of bias					
		Data sets used					
		Field-submitted samples					LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		Blank samples			SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides) (Spike concentrations and SRWS identifiers found in footnote 1)		
		Bias, using concentration (detections result in false positives due to contamination)			Bias, using recoveries, in percent		Bias, using recoveries, in percent
		B_N	B_{ND}	Maximum reported concentration in blanks	S_N	Median recovery, in percent	Median recovery, in percent
Fonofos	USGS(1)	10	0	–	33	106	94
Flumetsulam	USGS(1)	1	0	–	0	–	**136**
Fluometuron	USGS(1)	1	0	–	0	–	87
Hexachlorocyclopentadiene	PADEPL	3	0	–	9	**30**	87
Imazaquin	USGS(1)	1	0	–	0	–	**133**
Imazethapyr	USGS(1)	1	0	–	0	–	116
Imidacloprid	USGS(1)	1	0	–	0	–	122
Lindane	USGS(1)	10	0	–	33	100	102
Linuron	USGS(1)	11	0	–	33	122	101 (86)
Malathion	USGS(1)	10	0	–	33	108	104
Metalaxyl	USGS(1)	1	0	–	0	–	81
Methiocarb	USGS(1)	1	0	–	3	**16**	**62**
Methomyl	PADEPL	2	0	–	9	98	100
	USGS(1)	1	0	–	3	**29**	**71**
Metolachlor	PADEPL	3	0	–	12	90	99
	USGS(1)	10	0	–	33	119	104
Metribuzin	PADEPL	3	0	–	12	**72**	78
	USGS(1)	10	0	–	33	**65**	84
Metsulfuron-methyl	USGS(1)	1	0	–	0	–	**40**
MCPA	USGS(1)	1	0	–	0	–	84
MCPB	USGS(1)	1	0	–	0	–	**73**
Molinate	USGS(1)	10	0	–	33	100	95
Napropamide	USGS(1)	10	0	–	33	108	94
Neburon	USGS(1)	1	0	–	0	–	92
Nicosulfuron	USGS(1)	1	0	–	0	–	**184**
Norflurazon	USGS(1)	1	0	–	0	–	88
Oryzalin	USGS(1)	1	0	–	0	–	77
Oxamyl	PADEPL	2	0	–	9	94	107
	USGS(1)	1	0	–	3	**49**	**70**
p,p'-DDE	USGS(1)	10	1	E 0.0009	33	**60**	**61**
Parathion	USGS(1)	10	0	–	33	105	99
Parathion-methyl	PADEPL	2	0	–	9	94	90
	USGS(1)	10	0	–	33	95	93
Pebulate	USGS(1)	10	0	–	33	98	94
Pendimethalin	PADEPL	3	0	–	12	94	87
	USGS(1)	10	0	–	33	90	79
Perylene-d12 (surrogate)	PADEPL	3	–	–	12	103	98
Phorate	USGS(1)	10	0	–	33	**74**	**64**
Phosphamidon	PADEPL	2	0	–	6	121	99
Phosmet	PADEPL	2	0	–	0	–	115
Picloram	USGS(1)	1	0	–	0	–	88
Prometon	USGS(1)	10	0	–	33	105	105
Propachlor	USGS(1)	10	0	–	33	111	106

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of variability				
		Data sets used				
		Field-submitted samples				LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides)	Triplicate env. reps. and triplicate FSRW (nitrate and nitrite); triplicate env. reps (total coliform bacteria); triplicate FSRW samples (pesticides)			
		Variabiliy, using F-pseudosigma of recoveries, in percent.	Variability, using median relative standard deviation (RSD) of concentrations in triplicate sets[3]			Variabiliy, using F-pseudosigma of recoveries, in percent.
		F-pseudo-sigma, in percent	R_N	$R_{SETDECT}$	Median RSD, in percent	F-pseudosigma, in percent
Fonofos	USGS(1)	11	11	11	2	14
Flumetsulam	USGS(1)	–	0	–	–	**28**
Fluometuron	USGS(1)	–	0	–	–	10
Hexachlorocyclopentadiene	PADEPL	25	3	3	6	**29**
Imazaquin	USGS(1)	–	0	–	–	**27**
Imazethapyr	USGS(1)	–	0	–	–	**28**
Imidacloprid	USGS(1)	–	0	–	–	24
Lindane	USGS(1)	13	11	11	2	11
Linuron	USGS(1)	24	11	11	4	**31** (8)
Malathion	USGS(1)	19	11	11	3	17
Metalaxyl	USGS(1)	–	0	–	–	11
Methiocarb	USGS(1)	21	1	1	**93**	**60**
Methomyl	PADEPL	9	3	3	7	5
	USGS(1)	14	1	1	**52**	**50**
Metolachlor	PADEPL	20	4	4	6	15
	USGS(1)	12	11	11	2	15
Metribuzin	PADEPL	15	4	4	5	9
	USGS(1)	9	11	11	3	16
Metsulfuron-methyl	USGS(1)	–	0	–	–	**35**
MCPA	USGS(1)	–	0	–	–	12
MCPB	USGS(1)	–	0	–	–	12
Molinate	USGS(1)	12	11	11	1	10
Napropamide	USGS(1)	20	11	11	3	15
Neburon	USGS(1)	–	0	–	–	12
Nicosulfuron	USGS(1)	–	0	–	–	**50**
Norflurazon	USGS(1)	–	0	–	–	**32**
Oryzalin	USGS(1)	–	0	–	–	16
Oxamyl	PADEPL	10	3	3	6	7
	USGS(1)	5	1	1	14	20
p,p’-DDE	USGS(1)	8	11	11	3	11
Parathion	USGS(1)	11	11	11	4	23
Parathion-methyl	PADEPL	13	3	3	5	23
	USGS(1)	10	11	11	4	20
Pebulate	USGS(1)	10	11	11	2	8
Pendimethalin	PADEPL	22	4	4	9	8
	USGS(1)	19	11	11	5	16
Perylene-d12 (surrogate)	PADEPL	4	4	4	2	16
Phorate	USGS(1)	20	11	11	3	**33**
Phosphamidon	PADEPL	17	2	2	8	17
Phosmet	PADEPL	–	0	–	–	**47**
Picloram	USGS(1)	–	0	–	–	15
Prometon	USGS(1)	8	11	11	2	16
Propachlor	USGS(1)	14	11	11	2	15

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of bias					
		Data sets used					
		Field-submitted samples					LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		Blank samples			SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides) (Spike concentrations and SRWS identifiers found in footnote 1)		
		Bias, using concentration (detections result in false positives due to contamination)			Bias, using recoveries, in percent		Bias, using recoveries, in percent
		B_N	B_{ND}	Maximum reported concentration in blanks	S_N	Median recovery, in percent	Median recovery, in percent
Propanil	USGS(1)	10	0	–	33	108	106
Propargite	USGS(1)	10	0	–	33	**69**	78
Propham	USGS(1)	1	0	–	0	–	88
Propiconazole	USGS(1)	1	0	–	0	–	94
Propoxur	USGS(1)	1	0	–	3	79	85
Propyzamide (pronamide in 2003)	USGS(1)	10	0	–	33	106	98
Pyrene-d10 (surrogate)	PADEPL	3	–	–	12	104	103
Siduron	USGS(1)	1	0	–	0	–	93
Simazine	PADEPL	3	0	–	12	100	97
	USGS(1)	10	0	–	33	104	91
Sulfometuron-methyl	USGS(1)	1	0	–	0	–	**130**
Tebuthiuron	USGS(1)	11	0	–	33	102	118 (97)
Terbacil	PADEPL	2	0	–	9	105	101
	USGS(1)	11	0	–	33	**63**	88 (90)
Terbufos	USGS(1)	10	0	–	33	79	75
Thiobencarb	USGS(1)	10	0	–	33	118	103
Triallate	USGS(1)	10	0	–	33	101	95
Triphenylphosphate (surrogate)	PADEPL	3	–	–	12	125	121
Triclopyr	USGS(1)	1	0	–	0	–	94
Trifluralin	PADEPL	2	0	–	6	86	79
	USGS(1)	10	0	–	33	75	76

[1] Recoveries of nitrate and nitrite used from SRWS N78 (2003), SRWS N82 (2004), SRWS N86 (2005), SRWS N90 (2006), and SRWS N91 (2007) and also recoveries of nitrate and nitrite in FSRW samples; spike concentrations of nitrate/nitrite in triplicate FSRW samples: 5.61 mg/L/0.95 mg/L (2003); 7.50 mg/L/0.75 mg/L (2004); 8.68 mg/L/1.83 mg/L (2005); 8.41 mg/L/1.01 mg/L (2006); and 3.81 mg/L/1.67 mg/L (2007). Pesticide FSRW samples analyzed at the USGS NWQL were spiked to a concentration of 0.4 µg/L for samples using the GCMS method (33 samples). Three pesticide FSRW samples, spiked at 3.2 µg/L for carbaryl and carbofuran, were also analyzed at the NWQL using the HPLCMS method; bias and variability data for these three samples were not included in the statistics presented in this table. Pesticide FSRW samples analyzed at the PADEPL were spiked to a concentration of 0.4 µg/L for compounds analyzed using USEPA 525.2 method and 3.2 µg/L for carbaryl, methomyl, and oxamyl compounds analyzed using USEPA 531.1.

[2] USGS NWQL LRS median recoveries and associated F-pseudosigmas data are based on data compiled for 2002–06 pesticide compounds analyzed by GCMS methodology (table 2-4); data statistics are based on between 968–1,417 spike results. LRS are spiked to a concentration of 0.1 µg/L for the GCMS method. USGS(1) LRS median recoveries and associated F-pseudosigmas for pesticide compounds analyzed by HPLCMS methodology (table 2-5) are based on data compiled from 2/7/02–2/7/03, approximately 235 spike results, at a concentration of 0.25 µg/L (Sonja Abney, U.S. Geological Survey, written commun., December, 2008). When common pesticide compounds were analyzed using the GCMS and LCMS methodologies, parentheses are used to denote the recoveries for the HPLCMS method. PADEP LRS median recoveries for compounds analyzed by USEPA method 525.2 were calculated from recovery information for batch-set lab-reagent-spikes; the number of spike recoveries used to calculate medians and F-pseudosigmas ranged from 5 to 17, depending on the compound, and spiked to concentrations of 0.5 µg/L or 1.0 µg/L. Laboratory reagent-spike samples are not analyzed for method USEPA 531.1 at the PADEPL as internal QC samples. Carbaryl, oxymyl, and methomyl batch matrix spike recoveries are used as estimates of method performance, assuming LRS data would give recoveries closer to 100 percent in the absence of matrix effects; calculations of lab median recoveries and F-pseudosigmas were done using all matrix spike-recovery data for batches which included project samples for PADEPL results for carbaryl, oxymyl, and methomyl, spiked at a concentration of 20 µg/L.

[3] Surrogate recoveries were used for RSD calculations instead of concentrations.

[4] Compound not qualified due to possible error in field-spiked reagent water sample preparation—recoveries, therefore, are shown in parentheses.

Table 2-2. Estimates of bias and variability in reported concentrations of nitrate, nitrite, total coliform and *Escherichia coli* (*E. coli)* bacteria, and pesticides using results from field-submitted and laboratory quality-control samples.—Continued

Compound	Lab used	Evaluation of variability				
		Data sets used				
		Field-submitted samples				LRS samples (Numbers of spikes, period of record, and spike concentrations found in footnote 2)
		SRWS and triplicate FSRW samples (nitrate and nitrite); triplicate FSRW samples (pesticides)	Triplicate env. reps. and triplicate FSRW (nitrate and nitrite); triplicate env. reps (total coliform bacteria); triplicate FSRW samples (pesticides)			
		Variabiliy, using F-pseudosigma of recoveries, in percent.	Variability, using median relative standard deviation (RSD) of concentrations in triplicate sets[3]			Variabiliy, using F-pseudosigma of recoveries, in percent.
		F-pseudo-sigma, in percent	R_N	$R_{SETDECT}$	Median RSD, in percent	F-pseudosigma, in percent
Propanil	USGS(1)	17	11	11	3	17
Propargite	USGS(1)	10	11	11	6	20
Propham	USGS(1)	–	0	–	–	10
Propiconazole	USGS(1)	–	0	–	–	12
Propoxur	USGS(1)	7	1	1	12	11
Propyzamide (pronamide in 2003)	USGS(1)	10	11	11	2	11
Pyrene-d10 (surrogate)	PADEPL	11	4	4	6	10
Siduron	USGS(1)	–	0	–	–	22
Simazine	PADEPL	11	4	4	9	24
	USGS(1)	11	11	11	2	**27**
Sulfometuron-methyl	USGS(1)	–	0	–	–	21
Tebuthiuron	USGS(1)	17	11	11	9	**26** (13)
Terbacil	PADEPL	9	3	3	8	**26**
	USGS(1)	20	11	11	6	**26 (42)**
Terbufos	USGS(1)	10	11	11	2	21
Thiobencarb	USGS(1)	16	11	11	2	13
Triallate	USGS(1)	16	11	11	2	12
Triphenylphosphate (surrogate)	PADEPL	12	4	4	1	18
Triclopyr	USGS(1)	–	0	–	–	9
Trifluralin	PADEPL	16	2	2	12	**28**
	USGS(1)	9	11	11	3	13

Appendix 3. List of Electronic Databases Used in This Report

Description of contents of database	Database name
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for wells sampled for the Blue Ridge crystalline and Triassic Lowland siliciclastic hydrogeologic setting baseline-assessment area, 2003	BASELINE_OCCURRENCE2003a.Monitoring.xls BASELINE_OCCURRENCE2003bMonitoring.xls (because of MicroSoft Excel space limitations, two files were needed to provide results for all compounds analyzed)
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for wells sampled for the Eastern Lake surficial hydrogeologic setting baseline-assessment area, 2004	BASELINE_OCCURRENCE2004Monitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for wells sampled for the Devonian-Silurian carbonate hydrogeologic setting baseline-assessment area, 2005	BASELINE_OCCURRENCE2005Monitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for wells sampled for the Great Valley siliciclastic hydrogeologic setting baseline-assessment area, 2006	BASELINE_OCCURRENCE2006Monitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for wells sampled for the Northeastern Glaciated surficial hydrogeologic setting baseline-assessment area, 2007	BASELINE_OCCURRENCE2007Monitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for wells in baseline-assessment areas (four settings vulnerable to pesticide contamination), 2003 and 2004	CHANGEMonitoring_VulnerableSettings.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for hot-spot well BA 437, 2003 to 2007	HOT-SPOTWellBA437SeasonalMonitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for hot-spot well LN 1842, 2003 to 2007	HOT-SPOTWellLN1842SeasonalMonitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for hot-spot well BE 1370, 2003 to 2007	HOT-SPOTWellBE1370SeasonalMonitoring.xls
Local number, station number, dates and times of sample collection, depth of well, depth to water level, and field parameter and water-quality results for three hot-spot and neighboring wells, 2005 and 2006.	HOT-SPOTWellsandNeighborWells.xls

Appendix 4. Regulatory Information for Compounds Measured in This Study

[Concentrations are in micrograms per liter unless otherwise noted. USEPA, U.S.Environmental Protection Agency; MCL, maximum contaminant level; LHA, lifetime health advisory; PDA, Pennsylvania Department of Agriculture; –, no standard; *http://www.epa.gov/waterscience/criteria/drinking/dwstandards.html*, accessed June 23, 2008; bolding indicates standard used to calculate action level]

Compound	Concentration		
	USEPA MCL	USEPA LHA	PDA action level 1/3 of USEPA MCL or LHA
Alachlor	**2**	–	0.66
Aldicarb	**3**	7	.99
Aldicarb sulfone	**2**	7	.66
Aldicarb sulfoxide	**4**	7	1.3
Atrazine	**3**	–	1.0
Bentazon	–	**200**	66
Bromacil	–	**70**	23
Carbofuran	**40**	–	13
Chlorpyrifos	–	**2**	.66
Cyanazine	–	**1**	.33
2,4-D	**70**	–	23
Dacthal (DCPA)	–	**70**	23
Diazinon	–	**1**	.33
Dicamba	–	**4**	1.3
Dinoseb	**7**	7	2.3
Disulfoton	–	**.7**	.23
Fluometuron	–	**90**	30
Fonofos	–	**10**	3.3
Hexachlorocyclopentadiene	**50**	–	16
Lindane	**.2**	–	.07
Malathion	–	**100**	33
MCPA	–	**30**	9.9
Methomyl	–	**200**	66
Metolachlor	–	[1]**700**	231
Metribuzin	–	**70**	23
Oxamyl	**200**	–	66
Parathion methyl	–	**1**	.33
Picloram	**500**	–	165
Prometon	–	**100**	33
Propazine	–	**100**	33
Propham	–	**100**	33
Simazine	**4**	–	1.3
Tebuthiron	–	**500**	165
Terbacil	–	**90**	30
Terbufos	–	**.4**	.13
Trifluralin	–	**10**	3.3
Nitrate, in milligrams per liter	10	–	N/A
Nitrite, in milligrams per liter	1	–	N/A

[1] The newly proposed “ambient water-quality human-health criteria” for metolachlor is 69 µg/L (Pennsylvania Department of Environmental Protection, 2008, Triennial review of water quality standards: Pennsylvania Bulletin, v. 38, no. 2 (January 12, 2008), p. 241).

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