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Pesticides in Selected Water-Supply Reservoirs and Finished Drinking Water, 1999-2000: Summary of Results from a Pilot Monitoring Program

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Conversion Factors

Multiply	By	To obtain
mile (mi)	1.609	kilometer (km)
square mile (mi ²)	2.590	square kilometer (km ²)
acre	4,047	square kilometer (km ²)
Acre-foot (acre-ft)	1,233	cubic meter (m ³)
million gallons per day (Mgal/d)	3,785	cubic meters per day(m ³ /d)

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

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Abstract

In 1999, a pilot monitoring program was initiated by the U.S. Geological Survey and the U.S. Environmental Protection Agency to provide information on pesticide concentrations in drinking water and to assist in the implementation of the Food Quality Protection Act of 1996. Drinking-water utilities that withdrew from reservoirs were sampled because reservoirs are vulnerable to pesticide contamination, integrate pesticide loading from their watersheds, and show smaller temporal variations than streams. Sampling frequencies were designed to measure long-term mean and short-term peak concentrations of pesticides in drinking water. Samples were collected quarterly throughout the year and at weekly or bi-weekly intervals following the primary pesticide-application periods. Water samples were collected from the raw-water intake and from the finished drinking-water tap prior to entering the distribution system. At some sites, samples were also collected at the reservoir outflow.

Twelve water-supply reservoirs were sampled, ranging in size from 120 to 92,600 acre-feet normal capacity, with contributing watersheds ranging from 3.3 to 784 square miles. The sites are in California, Indiana, Ohio, Oklahoma, Louisiana, Missouri, South Carolina, South Dakota, New York, North Carolina, Pennsylvania, and Texas. In 1999, drought conditions affected parts of the Eastern United

States and California; therefore sampling was extended through 2000 at nine sites.

Analyses for pesticides in water samples were performed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado, using three analytical methods. Overall, these methods included 178 different pesticides and degradation products. Of these, 108 compounds were detected in at least one sample from a raw-water intake or finished-water tap. Many of these compounds, however, were detected in fewer than 5 percent of the samples and at concentrations very near the method reporting level. The observed detection frequencies for raw water are similar to those reported for 58 stream sites sampled from 1992-95 as part of the U. S. Geological Survey National Water-Quality Assessment Program. None of the pesticides were detected in finished water at a concentration greater than a National drinking-water criterion, such as a Maximum Contaminant Level or Health Advisory Level.

Widely used herbicides including atrazine, simazine, metolachlor, prometon, cyanazine, 2,4-D, tebuthiuron, and acetochlor were the most frequently detected pesticides in both intake and finished-water samples. Detection frequencies for these compounds ranged from 35.6 to 96.3 percent in raw-water samples and from 18.7 to 95.6 percent in finished-water samples. Four triazine-herbicide degradation products also were detected in more than 60 percent of all samples.

Diazinon and chlorpyrifos were the two most frequently detected insecticides in raw-water samples, with 35.3 percent and 5.3 percent detection frequencies, respectively. Neither of these insecticides were detected in finished water. Malaoxon, the principal oxidative transformation product of malathion, was detected in 11 finished-water samples and none of the raw-water samples. In three of the samples where malaoxon was detected in finished water, the corresponding intake sample showed measurable concentrations of malathion. Diazoxon, the principal oxidative transformation product of diazinon, was not included as an analyte on any of the three methods used in this study.

Introduction

In 1999, the U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency (USEPA) initiated a pilot monitoring program to provide data on pesticide concentrations in drinking water. USEPA's Office of Pesticide Programs (OPP) has responsibility under the Food Quality Protection Act (FQPA) of 1996 to assess aggregate risk from exposure to pesticides in drinking water based on available data. Prior to implementation of this pilot program, however, there were few available data sets that contained information on pesticide concentrations in finished drinking water on a national scale, as most available data sets generally cover only selected compounds or local areas. USEPA's Office of Ground Water and Drinking Water (OGWDW) is responsible for regulating contaminant levels in public drinking-water supplies under the Clean Water Act of 1999. With this responsibility, OGWDW gathers information on the occurrence of contaminants, including pesticides, in drinking-water supplies. The pilot program described in this report was implemented to begin to fill this important data gap, and to provide more information about appropriate methods for national monitoring of pesticides in drinking water.

Since 1986, the USGS National Water-Quality Assessment (NAWQA) Program has collected thousands of streamwater and ground-water samples for pesticide analysis. The USGS National Water Quality Laboratory (NWQL) has developed techniques for analysis of large groups of pesticide compounds with low reporting limits. The NAWQA data sets provide the only nationally consistent pesticide concentration data for a large suite of

compounds. OPP currently uses the NAWQA data in their drinking-water and aquatic-exposure assessments; however, these data are not collected from public water supplies and, therefore, may not reflect exposure to pesticides in drinking water.

The pilot monitoring program described in this report was designed to provide information on the occurrence of pesticides in drinking water in a variety of geographic settings using sampling and analytical techniques that have been tested and used by the USGS NAWQA Program. Sampling focused on drinking-water utilities that withdraw from reservoirs because reservoirs are considered to be highly vulnerable to pesticide contamination, integrate pesticide loading from their watersheds, and show smaller temporal variations than streams. Although collecting data on the occurrence of pesticides in drinking water is not specifically within the objectives and current design of the NAWQA program, the NAWQA program has the infrastructure for collecting samples from raw and treated drinking water to meet USEPA's data requirement. The sampling approach implemented in 1999 was designed by a team of scientists from USEPA and USGS. Because of drought conditions in the Eastern United States and California in 1999, the pilot program was extended through 2000 at nine of the twelve monitoring sites.

Purpose and Scope

The purpose of this report is to present and summarize the data collected during the pilot monitoring program conducted in 1999 and 2000. The report also describes the design of the monitoring program and the broad array of goals and objectives for this study. The pesticide concentration data from the program are summarized for the entire data set, and for individual monitoring sites.

The pilot monitoring program was conducted as a data-collection program to provide data for subsequent analysis by scientists within the USGS, the USEPA OPP and OGWDW, and other interested parties. This report summarizes only the raw data from this study; however, additional analysis is required to fully meet the overall goals of the study.

Acknowledgments

The United States Environmental Protection Agency (USEPA) Office of Pesticide Programs (OPP), the USGS National Water-Quality Assessment Program (NAWQA), and the USEPA Office of Ground Water and Drinking Water (OGWDW) provided financial support for this pilot monitoring program. Their support and collaboration during the planning and execution of this pilot program are greatly appreciated.

Special thanks are extended to the management and staff of each of the participating community water systems who granted access to USGS staff for sample collection, and provided assistance to the study team. Their willingness to participate in this voluntary effort in the interest of developing a better understanding of their water system is greatly appreciated.

The contribution of many dedicated USGS personnel throughout the country that assisted with site selection, program design, sample collection, data management, and analysis activities is also acknowledged. The authors also wish to thank the staff of the USGS NWQL for performing the laboratory analyses and for permitting analysis by two new laboratory methods concurrent with final method development and testing.

Pilot Monitoring Program Design

The pilot monitoring program was designed as a first step towards a long-term goal of characterizing human exposure to pesticide residues in drinking water derived from surface-water sources. A team of scientists from USGS and OPP, with input from other USEPA and USGS experts, developed the sampling approach to collect data on the occurrence of pesticides in drinking-water sources that are linked to pesticide concentrations observed in finished drinking water. The design enables the resultant data set to be used to support the following data-analysis objectives:

- 1) Ecological risk assessments for reservoir systems;
- 2) Analysis of the relation between sampling frequency and the precision of estimates of peak concentrations of pesticides in community water systems;
- 3) Analysis of the concentration of pesticides in finished drinking water in relation to source-water concentrations and overall water-treatment processes;
- 4) Analysis of the relation of pesticide concentrations in reservoirs to watershed and reservoir characteristics; and
- 5) Evaluation and development of watershed and reservoir models.

This study focused on small drinking-water supply reservoirs in areas with high pesticide use, and will provide information that can be linked to the NAWQA database on pesticide occurrence in surface water. The analytical approach used the unique capability of the NWQL to analyze water samples for a broad suite of pesticide compounds with low levels of detection. The results of this pilot program may be used to increase the technical level and cost-effectiveness of future pesticide-monitoring programs.

General Sampling Approach

A comprehensive sampling approach was required for the pilot program due to the number of intended uses for the monitoring data. The primary sampling approach specified water-sample collection of raw water from a Community Water System (CWS) intake and of the finished water at the entry point to the distribution system. These two samples, collected sequentially, provide the basis for comparing pesticide concentrations in pre- and post-treatment drinking water. CWSs supplied by reservoirs were chosen as the focus of this pilot effort because reservoirs integrate pesticide loadings over time. Pesticide concentrations in reservoirs show smaller variations over short periods of time than free-flowing streams. Although residence time within a water-treatment facility is variable and can extend for many hours, the small temporal variability of pesticide concentrations in reservoirs improves the link between raw- and finished-water samples collected at nearly the same time.

Samples were collected at the outflow of many of the reservoirs because conditions at an intake may differ substantially from average reservoir conditions. This was done so comparisons could be made between the pesticide concentrations observed at an intake with a more representative sample reflecting water leaving the reservoir. Although these data are not necessary for assessing pesticide exposure, they provide the primary basis for ecological risk assessments and for relating pesticide concentrations to watershed and reservoir characteristics.

A schematic diagram for the general sampling approach at a reservoir and a CWS is shown in figure 1. The finished-water sample was collected from a water tap, representative of the treated water entering the distribution system (labeled as sampling location "A"). In nearly all cases, this was the tap used by the utility for routine monitoring. In instances where a water supplier has multiple treatment facilities, it was determined that one facility and one tap would be selected at random and sampled throughout the duration of the program. In practice, each facility included in the pilot program had only one such tap. The finished-water sample provides the best practical measure of pesticide concentrations that the

supplied population is exposed to in drinking water. The lag time between final treatment and delivery to a drinking-water tap may be long and vary considerably among distribution systems. Because this can allow additional time for degradation and transformation of pesticides, the measured levels at the finished-water sampling location may be somewhat different than the actual concentrations to which consumers are exposed.

Raw-water samples were collected from a tap on the intake supply line (shown in figure 1 as sampling location "B"). When no intake tap existed, raw-water samples were collected from the reservoir at the intake in use at the time of sampling. Pesticide analyses of raw-water samples show the pesticide occurrence in source water prior to the effects of treatment. Raw-water samples were collected in conjunction with finished-water samples to determine the levels of influent concentrations at these CWSs, to permit a general evaluation of the efficiency of water-treatment processes in removing residues, and to identify transformations that may result from treatment. Due to variation in retention time during the treatment process, the raw and finished water samples are not precisely paired. The goal of pairing the raw and finished samples in this study is to provide a general understanding of the relative impact of treatment processes on pesticide removal and transformation, and to identify areas that may require additional study.

A sample from the reservoir outflow (shown as sampling site "C" in figure 1) was collected at selected sites during each routine sampling trip, and was intended to approximate average reservoir concentrations at the time of sampling. This measure was designed to provide a consistent link between observed concentrations and reservoir and watershed characteristics. Studies have shown that water-quality and pesticide concentrations can vary considerably within any reservoir system (Elkhart and others, 1999). Vertical stratification and seasonal mixing in deeper reservoirs have been shown to be sources of variability, and horizontal stratification in large dendritic reservoirs has been shown to be another source of variability. It is generally recognized that the intake location for many water supplies may not be an ideal indicator of average reservoir conditions. The reservoirs included in this study were generally small, however, and variations in concentrations within the reservoir are expected to be slight. Outflow samples were chosen as the primary measure of reservoir concentrations because they integrate pesticide concentrations within the reservoir system and provide data on pesticide flux through reservoirs and their watersheds. Several of the pilot

monitoring sites had drinking-water intakes located at or very near the reservoir outflow. In these cases, only the intake was sampled and the intake was assumed to be representative of outflow concentrations. In addition, several of the reservoirs experienced prolonged periods without releases. Outflow samples were not collected during these periods.

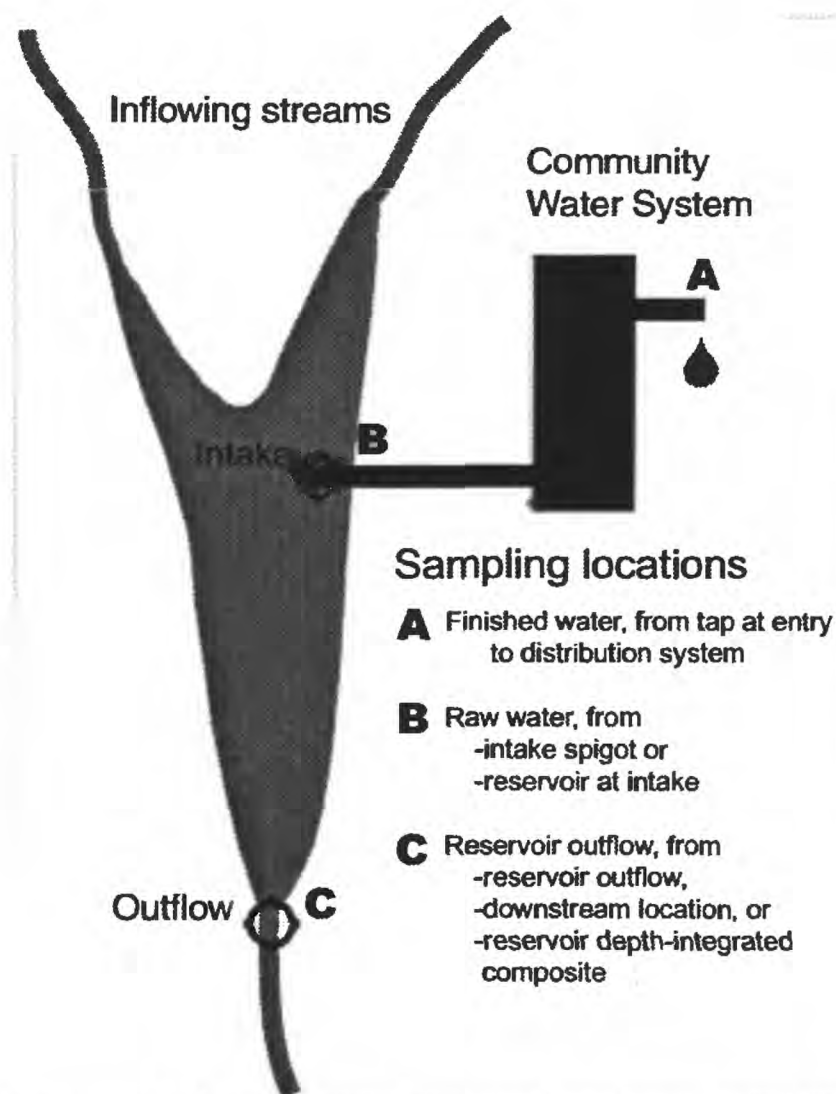


Figure 1. General on-site sampling locations for reservoirs and community water systems.

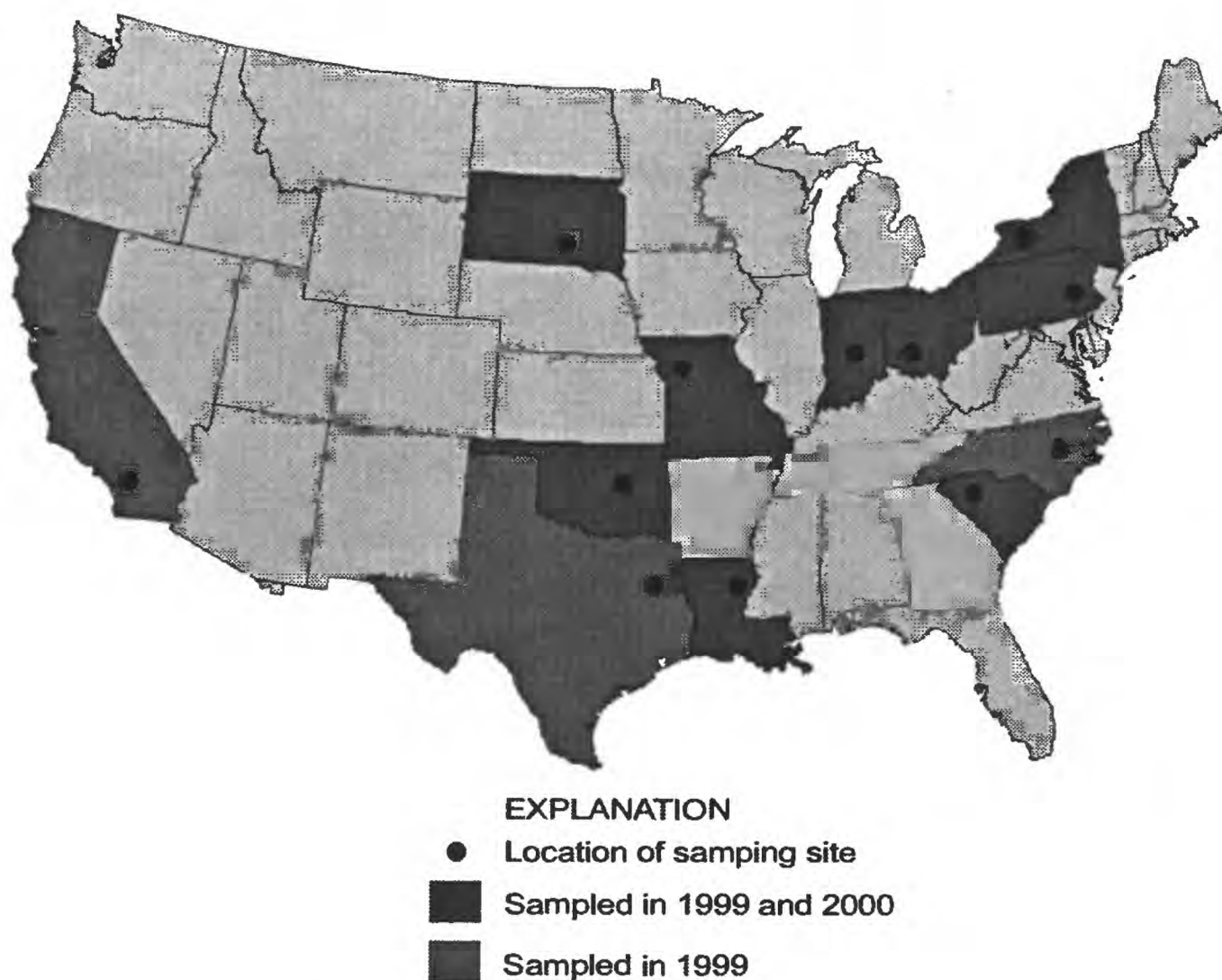


Figure 2. Locations of 12 reservoirs and community water systems included in the pilot monitoring program.

Description of Sampling Sites

Each sampling site included in this study consisted of a reservoir and Community Water System. This study focuses on small drinking-water supply reservoirs in areas with high pesticide use in order to test the sampling approach in areas where pesticides are probably present. Sampling sites were selected from a variety of geographic regions and included different cropping patterns in order to assess different pesticide-use patterns. Because this program was implemented within the NAWQA design structure, strong consideration was given to candidate sites that were within existing NAWQA Study Units.

A candidate list of sites was developed from an analysis of CWS sites from the Safe Drinking Water Information System /Federal Version (SDWIS/FED) (USEPA, 1998), and from recommendations from local NAWQA Study Units and USGS District offices. Twelve water-supply reservoirs, considered to be vulnerable to pesticide contamination, were selected from the list of candidates (fig. 2; table 1). The 12 sites are located in California (CA), Indiana (IN), Ohio (OH), Oklahoma

(OK), Louisiana (LA), Missouri (MO), South Carolina (SC), South Dakota (SD), New York (NY), North Carolina (NC), Pennsylvania (PA), and Texas (TX). The primary factors considered in assessing vulnerability were reservoir size, and estimates of pesticide use and runoff potential; however, no direct measure of the last two factors was readily available for contributing watersheds during the design process. Small reservoirs in high pesticide-use areas were anticipated to have high rates of pesticide occurrence. Thus, the ideal candidate reservoirs were mostly small reservoirs located in high pesticide-use areas, with a high runoff potential. Three sources of data were used together as surrogates for watershed pesticide-use rates, including: county row-crop production, county estimates of pesticide use, and mapped land-cover data. Site selection was conducted by reviewing maps and other data for each potential CWS and reservoir to determine: (1) whether the contributing land use was largely agricultural or developed, (2) the primary cropping patterns, and (3) relative pesticide use rates for a variety of compounds. Many candidate reservoirs were eliminated

Table 1. Characteristics of reservoirs and community water systems included in pilot monitoring program

[See page 16 for a description of sampling frequencies]

State	Reservoir name	Community water system	Location	Population served ¹ (thousands)	Reservoir capacity ² (acre-feet)	Watershed size (square miles)	Sampling frequency
CA	Canyon Reservoir	Elsinore Valley Municipal Water District	Lake Elsinore	81.1	11,867	758	Base
IN ³	Eagle Creek Reservoir	Indianapolis Water Company	Indianapolis	801	24,000	170	Enhanced
LA ³	Lake Bruin	Tensas Water Distribution Association, Inc.	St. Joseph	0.4	--	21.4	Base
MO ³	Higginsville Reservoir	City of Higginsville Municipal Utilities	Higginsville	4.7	1,661	4.9	High
NY ³	LeRoy Reservoir	Village of LeRoy Water Department	LeRoy	6.3	196	3.3	Base
NC	Tar River Reservoir	Tar River Water Treatment Plant	Rocky Mount	56 ⁴	11,200	784	Base
OH ³	East Fork Lake	Clermont Water Authority	Batavia	80 ⁵	92,600	218	Base
OK ³	Lake Arcadia	Edmonds Water Supply	Arcadia	53	120	98.1	High
PA ³	Blue Marsh Reservoir	Western Berks Water Authority	Reading	25	22,897	175	Base
SC ³	South Pacolet Reservoir	Spartanburg Waterworks	Chesnee	1.9	22,400	414	High
SD ³	Lake Mitchell	Mitchell Water Department	Mitchell	13.8	8,960	579	Base
TX	Lake Waxahachie	City of Waxahachie Water Treatment Plant	Waxahachie	23 ⁶	13,500	31.3	High

1 Data obtained from Marilee Horn, U.S. Geological Survey, written commun., 1999.

2 Data obtained from National Inventory of Dams, U.S. Army Corps of Engineers, 1996.

3 Sites sampled in 1999 and 2000.

4 Jay Van Hoose, Tar River Water Treatment Plant, oral commun., 2001.

5 Eric Heiser, Clermont Water Authority, written commun. 2001.

6 Leonard Leinfelder, City of Waxahachie, written commun., 2001.

from consideration because they are upstream from the principal agricultural lands. Other factors considered in the selection of sampling sites were spatial representation across the country, integration with ongoing monitoring efforts, and willing participation by the water-supply utility. Where possible, sites were selected on reservoirs located downstream from NAWQA fixed stream-monitoring sites so that additional data could be collected to represent the flux of pesticides into reservoirs. Several of the sites selected have ongoing monitoring programs within the watershed or reservoir studies. As a final check, each site was evaluated in relation to National maps of county pesticide-use estimates (Thelin and Gianessi, 2000) to determine the watershed's representation of regional pesticide-use patterns. The 12 sites selected were determined to be vulnerable to the pesticides used

regionally, however, they are not necessarily the most vulnerable sites in any given region.

During the site-selection process, the limitations of available National data sets for CWSs and watershed characteristics became evident. CWS latitude-longitude locations were frequently inaccurate or unavailable in SDWIS, and relatively little information was available that identified the type of water body used for water supply. Marilee Horn (U.S. Geological Survey, written commun., 1998) supplied additional information on water-supply intakes serving populations greater than 10,000 people.

The 12 sites selected for the pilot monitoring program include reservoirs ranging in size from 120 to 92,600 acre-ft normal capacity and watersheds ranging from 3.3 to 784 mi² (square miles). Watershed boundaries were delineated for each of the reservoirs sampled and land-use

characteristics were summarized by intersecting the watershed boundary with the 30-m (meter) resolution National Land Cover Dataset (NLCD) (Vogelmann, 2001). Ten of the 12 sites were selected to represent agricultural land use, with percent total agricultural land ranging from 24.4 to 94.9 percent (table 2). The CA and OK sites were selected because urban areas were deemed to be the predominant influence on water quality in their basins. The urban area in the CA watershed has grown considerably since the early 1990's when the satellite imagery, which provides the basis for the NLCD, was collected and most of this growth has occurred near the reservoir.

The major crops grown in each of the watersheds generally reflect national cropping patterns. Table 3 summarizes the major crop groups grown in each county intersecting the watersheds, and uses the classifications provided by Gilliom and Thelin (1997). These crop classifications are based on the 1992 Census of Agriculture (U.S. Department of Commerce, 1995) and may differ from crops actually grown during the study period. Many of the sites selected include areas with substantial amounts of corn, soybeans, wheat, and alfalfa—four of the most widely grown crops in the country. An effort was made to include sites that encompass regionally important crop groups including tobacco in NC and orchards in SC.

Table 2. Land-use characteristics in watersheds upstream from the pilot monitoring sites

State	Reservoir	Primary land-use groups ¹ in percent			NLCD agriculture sub-groups, in percent			
		Agriculture	Urban	Forest	Pasture	Row crop	Grass-lands	Small grains
CA	Canyon	28.7	8.1	60.6	2.1	13.2	10.9	2.6
IN	Eagle Creek	86.3	4.6	7.5	21.2	65.2		
LA	Bruin	64.9	0.1	9.8	2.5	58.0		4.5
MO	Higginsville	81.7	0.6	12.0	43.7	37.0	0.6	0.4
NC	Tar River	24.4	2.4	71.5	7.8	16.6		
NY	Leroy	81.8	0.1	13.7	51.8	30.0		
SC	South Pacolet	28.9	9.9	59.7	13.0	15.9		
SD	Mitchell	94.9	0.4	0.4	47.7	41.7	4.5	1.0
OH	East Fork	72.3	2.3	23.4	28.7	43.5		
OK	Arcadia	34.5	39.5	22.2	9.8	2.2	21.5	1.0
PA	Blue Marsh	67.0	2.5	28.8	49.2	17.8		
TX	Waxahachie	84.5	0.8	11.0	51.5	20.8	11.4	0.7

¹ Land-use data from National Land Cover Dataset (NLCD) (Vogelmann, 2001).

Table 3. Major row-crop groups grown in counties intersecting pilot monitoring program watersheds

[>, greater than]

State	Reservoir	Classification of row crops on a county basis ¹	
		County	Crop and total harvested acreage on a county basis, in percent
CA	Canyon	Riverside	Wheat and other grains > 20 Alfalfa > 20
IN	Eagle Creek	Hamilton, Boone, Marion, Hendricks	Corn > 20 Soybeans > 20
LA	Bruin	Tensas	Corn > 20 Soybeans > 20
MO	Higginsville	Lafayette	Corn > 20 Soybeans > 20
NY	Leroy	Wyoming	Corn > 50
		Genesee	Corn > 20 Wheat and other grains > 20 Vegetables > 10
NC	Tar River	Granville	Tobacco > 50
		Franklin, Polk, Vance	Wheat and other grains > 20 Soybeans > 20
		Nash	Wheat and other grains > 20 Soybeans > 20 Cotton > 10
OH	East Fork	Clinton, Brown, Clermont	Corn > 20 Soybeans > 20
SC	South Pacolet	Spartanburg, Greenville	Corn>20 Soybeans>20 Wheat and other grains>20
SD	Mitchell	Sanborn	Corn>20 Alfalfa>20 Soybeans >20
		Jerauld	Corn>20 Alfalfa>20 Wheat and other grains>20
		Aurora, Davison	Corn > 20 Soybeans > 20
OK	Arcadia	Oklahoma	Wheat and other grains > 50
PA	Blue Marsh	Berks, Lebanon	Corn > 50
TX	Waxahachie	Ellis	Corn > 20 Wheat and other grains > 20

¹ from Gilliom and Thelin, 1997

The type of water treatment used at each of the selected CWSs was not used as a selection criterion. Interviews were conducted with staff from each of the CWSs to assemble a consistent coding of the treatment processes used at each site and a record of the chemicals used during each step of the treatment processes. A summary of this information is listed in table 4.

CWSs generally use one or a combination of four basic treatment types. These include disinfection, mixing, flocculation, and filtration. There are several methods of disinfecting raw water. These include chlorination, pasteurization, ultraviolet radiation, distillation, and ozonation. There are also many types of filtration units for treating raw water. These include micro-filtration, activated carbon filters, oxidizing filters, sand, and neutralizing filters. Each treatment step can occur at any point during the treatment process. The point at which it occurs may influence how well unwanted elements such as pesticides are eliminated from the raw water. At eight of the sites (MO, TX, OH, CA, IN, SC, NY, and PA), chlorine is added during pre-disinfection. In OK, ozone is added instead. At nine of the sites (MO, TX, OH, OK, IN, SC, NC, NY, and PA), flocculation is followed by filtration. In all of the states listed above, post-disinfection

occurred before storage and included the addition of chlorine in some form. In seven of the states (OH, IN, SD, SC, NC, NY, and PA), fluoride was also added to bring the concentration to approximately 1 milligram per liter.

Two sites, CA and OH, underwent significant operational changes during the course of the pilot monitoring program. The CA site closed for major renovations just prior to the intended start of sampling. Sampling was delayed until July 1999, and continued until December 1999, when the facility closed. During the startup of a new facility, the treatment process may be somewhat unstable and results may differ from those collected while a facility is in normal operation. In March 2000, the OH site shifted from a more conventional treatment system using powdered activated carbon to an advanced treatment system using granular activated carbon (GAC).

Table 4. Order of water-treatment stages and chemicals used during treatment for 12 community water systems included in the pilot monitoring program

[GAC, granular activated carbon; PAC powdered activated carbon]

California Site	Indiana Site	Louisiana Site
Elsinore Valley Municipal Water District Lake Elsinore, CA	Indianapolis Water Company Indianapolis, IN	Tensas Water Distribution Association, Inc. St. Joseph, LA
Canyon Reservoir	Eagle Creek Reservoir	Lake Bruin
 screen/pump	 screen/pump	 surface intake
 Pre-Disinfection chlorine (optional) aluminum salts	 Pre-Disinfection chlorine, carbon (optional)	 Clarification chlorine, aluminum, and soda ash added
 Rapid Mix cationic polymer	 Splitter and Rapid Mix chlorine, aluminum sulfate, polymers, carbon (optional), lime potassium permanganate	 Filtration
 Accelerator chlorine (optional) non-ionic polymer	 Mixing and Settling Basin	 Reservoir
 Pre-Chlorination sodium hydroxide	 chlorine, polymer, and PAC added	 Distribution
 Dual-Media Filters	 Filter Plant	
 Post-Chlorination	 fluoride, ammonia	
 Clearwell Storage	 Finished Water Reservoir	
 Holding Pond	 chlorine	
 Distribution	 Distribution	

Table 4. Order of water-treatment stages and chemicals used during treatment for 12 community water systems included in the pilot monitoring program--continued

<u>Missouri Site</u> City of Higginsville Municipal Utilities Higginsville, MO	<u>New York Site</u> Village of LeRoy Water Department LeRoy, NY	<u>North Carolina Site</u> Tar River Water Treatment Plant Rocky Mount, NC
Higginsville Reservoir	Leroy Reservoir	Tar River Reservoir
 screen/pump	 screen/pump	 screen/pump
 Pre-Disinfection chlorine dioxide	 Pre-Disinfection chlorine, PAC, potassium permanganate	 Pre-Disinfection aluminum salts and pre-caustic
 Flash Mixer polymer coagulant	 Flocculation aluminum salts/polymers	 Flash Mixer polymer
 Flocculation/Sedimentation lime	 Filtration rapid sand and mixed media	 Flocculation
 Flash Mixer sodium silica fluoride	 Post-Disinfection chlorine, fluoride, ortho-phosphate	 Sediment Basin
 Flocculation/Sedimentation chlorine	 Clearwell Storage	 Dual Media Filtration chlorine
 Dual Media Filtration sand with GAC cap	 Storage	 Post-Disinfection post-caustic, fluoride, chlorine, and phosphate
 Post-Disinfection chlorine	 Distribution	 Clearwell Storage
 Clearwell Storage		 Distribution
 Distribution		

Table 4. Order of water-treatment stages and chemicals used during treatment for 12 community water systems included in the pilot monitoring program--continued

Ohio Site Clermont Water Authority	Oklahoma Site Edmonds Water Supply	Pennsylvania Site Western Berks Water Authority
Batavia, OH	Arcadia, OK	Reading, PA
East Fork (Harsha Lake)	Lake Arcadia	Blue Marsh Reservoir
screen/pump	screen/pump	reservoir release
Pre-Disinfection	Aeration	Tulpehocken Creek
potassium permanganate, chlorine dioxide		
	Pre-Disinfection	screen/pump
Rapid Mix	ozone	
aluminum		Pre-Disinfection
	Flocculation / Clarification	powdered activated carbon, potassium permanganate, chlorine dioxide, and lime
Flocculation	polymers/lime	
pH adjustment, polymers		Flocculation / Clarification
	Solids Contact / Clarification	aluminum sulfate
Settling	carbon dioxide	
		Filtration
Filtration	Post-Disinfection	sand and anthracite
rapid sand with GAC	ozone	hydrofluosilicic acid
Post-Disinfection	Polyphosphate Polymer	Ammonium Sulfate
phosphate, flouride, chlorine and caustic soda	chlorine	chloramines
Clearwell Storage	Mixed Media Filters	Corrosion control
	multimedia	phosphate
Distribution		
	Carbon Filter	Clearwell Storage
	granular activated carbon	
		Reservoir
	Post-Disinfection	
	chlorine	Distribution
	Clearwell Storage	
	Distribution	

Table 4. Order of water-treatment stages and chemicals used during treatment for 12 community water systems included in the pilot monitoring program--continued

<u>South Carolina Site</u> Spartanburg Waterworks	<u>South Dakota Site</u> Mitchell Water Department Mitchell, SD	<u>Texas Site</u> City of Waxahachie Water Treatment Plant Waxahachie, TX
Chesnee, SC		
South Pacolet Reservoir (Lake Bowen)	Lake Mitchell	Lake Bardwell
		(seasonal, used to recharge Lake Waxahachie)
Municipal Reservoir #1	screen/pump	
	GAC Polymers	screen/pump
screen/pump		
Pre-Disinfection	lime, aluminum sulfate	Lake Waxahachie
liquid alum, lime, carbon,	polymers added	
chlorine, and polymer		screen/pump
	chlorine dioxide, and fluoride added	
Hydraulic Flocculation		Pre-Disinfection
aluminum salts, polymers	ammonium poly phosphate added	potassium permanganate (seasonal, taste and odor)
		free chlorine
Dual Media High Rate Filters	Post-Disinfection	
	chlorine	Flocculation
Post-Disinfection		iron salts (ferric sulfate),
fluoride, lime, phosphate, and chlorine	Distribution	
		Disinfection
Clearwell Storage		chloramines
Distribution		Filtration
		dual media sand / anthracite
		Corrosion Control
		caustic soda (pH control)
		hydrofluorisisilic acid
		Clearwell Storage
		Distribution

Table 5. Process parameters of water from 12 community water systems participating in the pilot monitoring program

[Mgal/D, million gallons per day; mg/L, milligrams per liter; PAC, powdered activated carbon; TOC, total organic carbon; n.a., not available]

State	System name	Average flow-through time (hours)	Average flow-through rate (Mgal/d)	Water quality properties				Seasonal modifications to treatment process
				pH (standard units)	Alkalinity (mg/L)	Hardness (mg/L)	TOC (mg/L)	
CA	Elsinore Valley Municipal Water District	3.25	5	7.5	91	250	6 - 8	None
IN	Indianapolis Water Company	8.75	n.a.	8.2	128	200	4	PAC added as needed following spring runoff
LA	Tensas Water Distribution Association, Inc.	1	n.a.	7.5	25.8	78.3	n.a.	None
MO	City of Higginsville Municipal Utilities	26	1	7.9 - 9.2	63 - 120	90 - 145	4.7	treated with copper sulfate, May through September
NY	Village of LeRoy Water Department	0.29	0.75	7.8 - 9.0	40 - 100	~140	4.4	Increase potassium permanganate in summer/fall for taste and odor; PAC used as backup
NC	Tar River Water Treatment Plant	4-5	10	7	12	12	4-6	None
OH	Clermont Water Authority	23	5	7.7	95	126	5.2	0.25 mg/L potassium permanganate in winter - 3.0 or greater by late June
OK	Edmonds Water Supply	n.a.	n.a.	7.9 - 8.8	137	150	5.8	Adjust ozone treatment if taste and odor is present
SC	Spartanburg Waterworks	4	11	6.9	17	15	3.8	None
SD	Mitchell Water Department	12 - 13	1.1 - 4.3	9.2	32	222	n.a.	n.a.
PA	Western Berks Water Authority	7 - 9	4	7.2	138	172	2 - 3	None
TX	City of Waxahachie Water Treatment Plant	10	6	7.7	100	108	4 - 8	Potassium permanganate (as needed for taste and odor)

Process parameters including average flow-through time and average flow-through rate are reported for each of the 12 CWS plants in table 5. Water-quality parameters of raw water including normal ranges of pH, alkalinity, hardness, and total organic carbon are also included in table 5 as they were reported by the CWSs. Several CWSs reported seasonal modifications to the treatment process that are used to address an increase in flow, increased sedimentation, or other changes in physical and chemical characteristics of the source water.

The average flow-through time from collection of raw water to the completion of the finished water ranged from 0.29 (NY) to 26 (MO) hours. Flow-through time was dependent on the total amount of water treated and the amount of time that the treated water remained in the clearwells. Seasonal modifications are regularly made at many of the sites investigated, and are mainly intended to control the taste and odor of the water.

Sampling Frequency

One objective of this study was to provide estimates of annual-mean pesticide concentrations and high concentrations that occur for short periods of time, such as the annual 95th and 99th percentile concentration. An analysis of sampling-frequency requirements by the International Life Sciences Institute (ILSI, 1998) recommended a fixed-frequency sampling program of 100 times per year to develop measures of chronic (long-term) and acute (short-term) exposure to pesticides in water from streams. This level of effort was impractical for this pilot program and was not necessary to meet the primary goal of comparing raw- and finished-water concentrations. However, the sampling frequency implemented was designed to characterize the occurrence of commonly occurring pesticides and to identify compounds that may occur for only a short period of time at concentrations greater than the laboratory detection level.

The sampling frequency for this study was determined on the basis of data from Perry Lake, a large midwestern reservoir in Kansas. During 1993-94, Perry Lake was sampled on a daily basis and analyzed for triazine herbicides using Enzyme-Linked Immuno Assay kits—a low-cost method for performing large numbers of analyses—with supplemental samples sent to research labs for confirmation. The Perry Lake data were provided by Peter Van Meter (U.S. Geological Survey, written commun., 1998) and were analyzed using quarterly, monthly, bimonthly, 4-times monthly, and 10-times monthly sampling frequencies. In the analysis of Perry Lake data, 10,000 replicates of each sampling frequency were performed using a random starting date. Estimates of the mean and standard deviation showed that quarterly sampling was adequate to determine the annual-mean concentration of atrazine (table 6) (Charles Crawford, U.S. Geological Survey, written commun., 1998). Estimates of the maximum value and 95th percentile showed that, based on sufficiently small standard deviations, reasonable measures of the actual values could be determined using a monthly sampling frequency. Since this scenario is based on a large reservoir system and a comparatively long-lived analyte, a semi-weekly sampling frequency was selected as the base level for this program.

A similar test scenario was performed on data from a pesticide runoff / reservoir model. OPP modeled daily atrazine and bromoxynil concentrations using the Pesticide Root Zone Model-Exposure Analysis Model System (PRZM-EXAMS) with the Shipman Reservoir scenario (U.S. Environmental Protection Agency, 1998). The watershed characteristics are representative of cotton grown on a Loring silt loam in Mississippi using conventional and no-till management. Application rates and timing were standardized to allow comparison between pesticides with different environmental fate and

transport characteristics, since bromoxynil is significantly more reactive in the environment than atrazine. Table 7 presents a summary of these scenarios using 1976 precipitation data, showing the expected percentiles and mean value, in addition to the mean and standard deviation of 10,000 simulated sampling years for one-week and two-week sampling intervals. The standard deviation of the bromoxynil test is always a greater percentage of the expected value than for the atrazine test—indicating that more frequent sampling is necessary for reactive compounds in order to achieve the same level of precision. A 2-week sampling interval sufficiently characterized the 90th percentile bromoxynil concentration with a standard deviation of 20 percent of the peak model value. In contrast, weekly sampling significantly improved the estimate of the 90th percentile concentration with a standard deviation less than 5 percent of the peak model value.

Table 6. Summary of atrazine-concentration distributions based on 10,000 trials of selected fixed-frequency sampling strategies on daily concentration data from Perry Lake, Kansas, 1993-94

[Values, concentrations in micrograms per liter; n.d., not determined]						
	Percentile					Maximum
	50 th	75 th	90 th	95 th	99 th	
Reported values, based on daily samples	1.720	3.170	3.379	3.475	3.640	3.790
<u>Quarterly sampling</u>						
Value	1.684	3.040	n.d.	n.d.	n.d.	3.437
Standard deviation	0.209	0.172	n.d.	n.d.	n.d.	0.135
<u>Monthly sampling</u>						
Value	1.691	3.102	3.408	3.536	n.d.	3.566
Standard deviation	0.105	0.149	0.064	0.094	n.d.	0.109
<u>Bimonthly sampling</u>						
Value	1.703	3.138	3.390	3.501	n.d.	3.636
Standard deviation	0.052	0.102	0.039	0.054	n.d.	0.090
<u>4-times monthly sampling</u>						
Value	1.712	3.171	3.385	3.493	n.d.	3.715
Standard deviation	0.026	0.018	0.021	0.030	n.d.	0.066
<u>10-times monthly sampling</u>						
Value	1.715	3.170	3.382	3.480	3.665	3.775
Standard deviation	0.009	0.006	0.010	0.016	0.033	0.011

Table 7. Summary statistics of 1-week and 2-week sampling-interval test scenarios using PRZMS-EXAMS¹ model-predicted atrazine and bromoxynil concentration for a small midwestern reservoir based on 1976 precipitation records and equivalent application rates

[Values, concentrations in micrograms per liter]					
	Expected Value	1-Week sampling interval		2-Week sampling interval	
		Mean	Standard deviation	Mean	Standard deviation
<u>Atrazine</u>					
Maximum value	4.710	4.586	0.091	4.387	0.204
99 th percentile	4.590	4.586	0.091	4.387	0.204
95 th percentile	4.040	4.060	0.066	4.043	0.072
90 th percentile	3.700	3.699	0.070	3.749	0.070
Mean	1.483	1.483	0.022	1.515	0.037
<u>Bromoxynil</u>					
Maximum value	2.090	1.504	0.386	1.428	0.504
99 th percentile	1.460	1.504	0.386	1.428	0.504
95 th percentile	0.460	0.496	0.063	0.461	0.128
90 th percentile	0.134	0.122	0.031	0.125	0.027
Mean	0.066	0.066	0.015	0.083	0.026

¹ U.S. Environmental Protection Agency, 1998

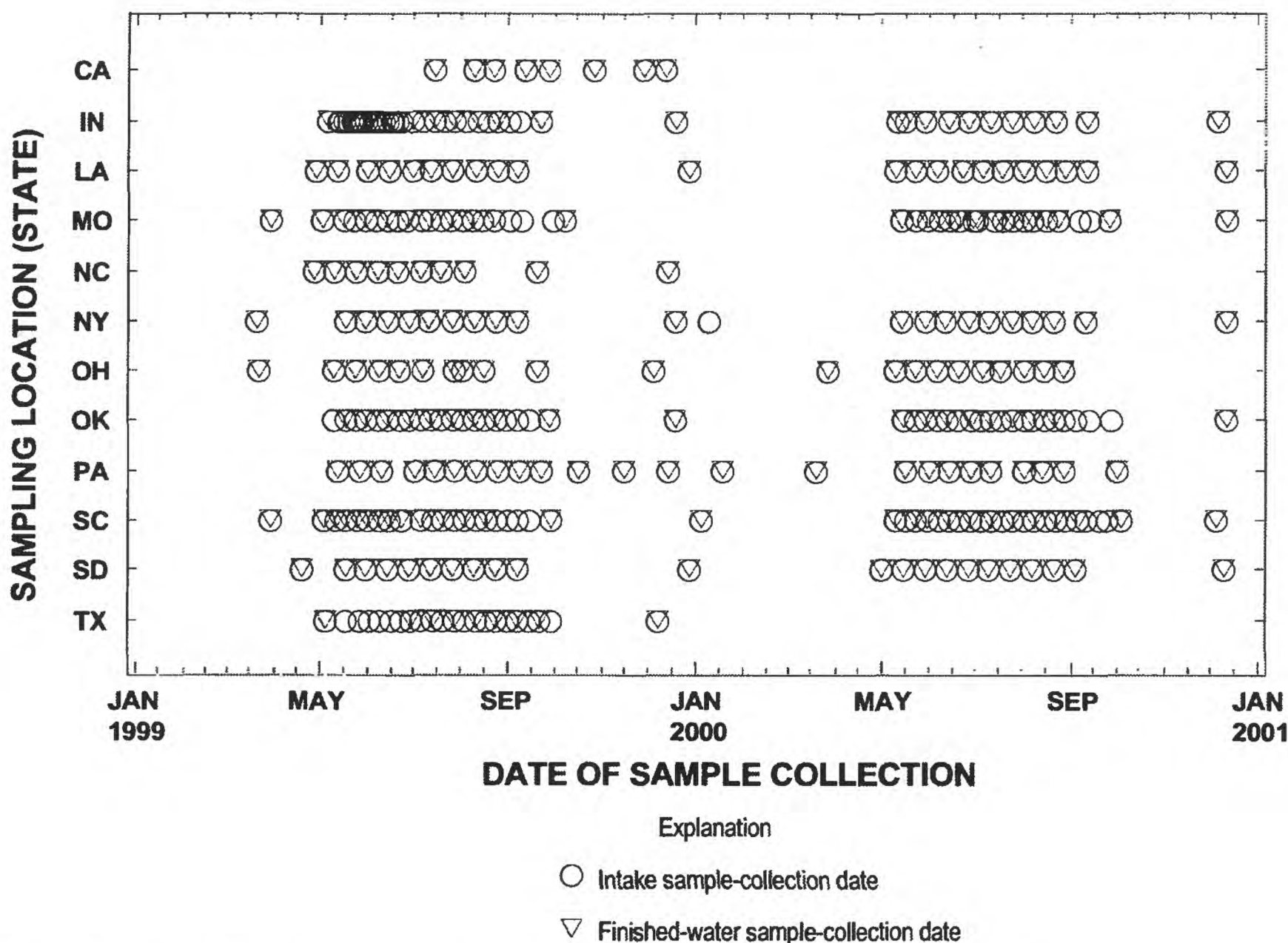


Figure 3. Sample-collection dates at the 12 pilot monitoring program sites in 1999 and 2000.

Based on both the Perry Lake concentration data and PRZMS-EXAMS model results, the design team chose to implement three sampling frequencies (see table 1):

- Base sampling frequency-- included quarterly sampling, plus semi-weekly sampling for a 4-month period following pesticide application, with samples collected from water intake, finished-water tap, and reservoir outflow (11 samples per year).
- High-frequency sampling-- supplemented the base sampling frequency with intake-water samples collected weekly over the 6-month period with highest pesticide applications (26 samples per year).
- Enhanced sampling--supplemented the high-frequency sampling by collecting samples from the intake site every 3 days for about 1 month after spring corn herbicide application (37 samples per year).

Because pesticide concentrations are often serially correlated and concentrations vary most during the principal growing season, the weekly, semi-weekly, and enhanced sampling intervals were scheduled around the principal application season, based on local knowledge and analysis of historical data for these areas. Thus, the measurements from the pilot program are representative of compounds that are used and mobilized during the period sampled and are less representative of concentrations during the remainder of the year. The dates that samples were collected from each monitoring site are shown in figure 3. The actual sampling frequency may differ somewhat from the designed frequency because of site-specific scheduling and associated logistical concerns. The enhanced sampling frequency was used at the IN site in 1999. These data are intended to support an analysis of precision in sample statistics to further quantify the results of the pilot monitoring program and other similar data sets. In 2000, all sites were sampled at the base sampling frequency and no samples were collected from reservoir outflows.

Methods of Sample Collection, Analysis, and Quality Assurance

The field and data-collection methods used in this study followed or were adapted from standard USGS protocols, and provided a high-quality data set that is consistent with the NAWQA Program and other USGS trace-organic water-chemistry data-collection efforts. The sample-collection, sample-handling, and data-management protocols were outlined for all project participants in an approved quality-assurance project plan, which documented the standard operating procedures to be followed. The laboratory methods used in this study encompass standard USGS methods, which have been reviewed and approved by the USGS, and developmental methods that are considered provisional for samples analyzed during the study period.

Field Methods

All water samples were collected by USGS personnel using sample-collection protocols documented by the USGS and the NAWQA Program (Wilde and others, 1998). Consistent site-visit and sample-documentation forms were completed at the time of sampling at each site. During each site visit, water samples were collected from the intake and finished-water spigot and where necessary, the spillway, for the analyses of dissolved pesticides. Finished-water samples were collected directly from a spigot and filtered. Raw-water samples were collected from the intake or outflow site using either the equal-width-increment or grab method. All samples were filtered into a 1-L glass amber bottle. Samples were processed using methods described in Shelton (1994), however it was not necessary to use a cone splitter to process samples. Samples were shipped using overnight carriers in sealed coolers to the USGS NWQL for analysis. No preservatives or quenching agents, such as sodium thiosulfate to remove residual chlorine, were added to the water samples. In order to minimize the risk of cross-contamination, all sampling equipment was cleaned according to standard protocols that include a thorough cleaning with soapy tap water, followed by a distilled-water rinse, and a final rinse with laboratory-grade methanol. Quality-assurance measures were conducted in a manner consistent with the NAWQA stream-sampling quality-assurance plan (Mueller and others, 1997). All analytical data were computerized and returned to the offices responsible for sample collection, then compiled into a single project data set.

Analytical Methods

Three different laboratory methods were selected for use during the pilot monitoring program—a USGS approved method and two developmental methods. The primary method, known as method 2001 (or schedule 2001) uses C-18 solid-phase extraction and gas chromatography / mass spectrometry (GC/MS) to determine concentrations of 47 pesticides and pesticide degradates in water samples (Zaugg and others, 1995). The two developmental methods were included in this program in order to greatly expand the available information on the occurrence of a wide number of pesticides and pesticide degradates in surface water across the Nation, and to test for the occurrence of these compounds in drinking-water supplies. These methods were included with the knowledge that the methods were developmental and that their performance may be more variable than would be expected of methods that have been thoroughly tested and approved. The two developmental methods were approved by the USGS in 2001—without any changes to the procedures.

Method 2001 was first developed in the early 1990s as a means of isolating and quantifying a broad range of target compounds while achieving low-level method reporting limits (ranging from .001 to .018 parts per billion). The pesticides selected for inclusion in this method were based on national use rates and their chemical properties, which would permit isolation using the C-18 cartridge and analysis by GC/MS. Thus, this method encompasses many of the more widely used pesticides, including many triazine and acetanilide herbicides; selected carbamate compounds; and selected organophosphate insecticides. Two pesticide metabolites, deethylatrazine and 2,6 diethylaniline, are also included in this method. Method 2001 is the principal pesticide analysis used throughout the Nation by the NAWQA Program.

Standard performance of method 2001 for untreated water samples has been documented based on quality-assurance samples collected by the NAWQA Program from 1992-96 (Jeffrey Martin, 1999). That report provides spiked-sample recovery data for each analyte included in method 2001, and indicates laboratory performance across a range of time and sample matrices. Therefore, these results are more indicative of the performance of the method from monitoring data than performance estimates provided in the method documentation. Each sample analyzed during the pilot program was spiked with a standard aliquot of a surrogate matrix prior to extraction, which may be used to track the performance of the analysis for individual samples. These results are reported as a percent of the expected value. Surrogate-spike recoveries are included in the accompanying pilot monitoring program data sets.

Some pesticide-concentration data from method 2001 are reported as qualified estimates. These samples have an "E" in the parameter's remark field. There are two cases where concentrations are reported as qualified estimates. The first case includes the permanently qualified compounds deethylatrazine, azinphos-methyl, carbaryl, carbofuran, and terbacil. During method development, deethylatrazine exhibited consistently low recoveries (9-19 percent) but was retained in the method due to its national relevance. The other four compounds exhibited variable recoveries and thus are reported as qualified estimates. The second case includes qualitative detections of concentrations less than the statistically determined Method Reporting Level (MRL).

The first developmental method is provisional method 9002 (also known as schedule 9002), which is an adaptation of the same C-18-solid-phase extraction and GC/MS technology used in method 2001. The method provides a quantitative analysis of 20 parent pesticides and 21 pesticide degradates. Qualitative estimates are provided for 14 parent pesticides and 20 degradates that through testing, showed greater bias, higher variability, or shorter holding times than the other compounds. The details of this adaptation are described in Sandstrom and others (2001) and should be used as a guide in the interpretation of the results from this method. Selection of candidate parent compounds for testing under this method was based on national rankings of pesticide use, the existence of current NWQL methods for these compounds, and the chemical characteristics that make analysis by this method favorable. Only compounds without an existing method were tested. Inclusion of pesticide degradates was based on whether the parent compound was included in a current NWQL method and the availability of analytical standards.

Method 9002 was implemented for conditional analysis by the NAWQA Program in March 1999, when the pilot monitoring program started. The method was approved for routine analysis in 2001 and is now referred to as method 2002. Although the method is now approved, the data collected during this program must be considered provisional, as the analyses were performed prior to method approval. Thus, these data will not be included as part of the USGS's publicly accessible National Water Information System (NWIS). These data are available to the public; however, they must be accompanied by the documentation of analytical methodology in accordance with USGS policy (U.S. Geological Survey Office of Water Quality Technical Memorandum No. 98.05, 1998). During the period of study, no changes were made to the method or instrument settings. Therefore, the data from method 9002 should be consistent throughout the study, with the possible exception of the first 2 months, when the instruments were brought on line (Mark Sandstrom, U.S. Geological Survey, oral commun., 1999).

The second developmental method, provisional method 9060, is a substantially new technique using solid-phase extraction and high-performance liquid chromatography/mass spectrometry (HPLC/MS) for the instrumental analysis of extracts. This method is designed to determine low-level concentrations of 64 polar pesticides and pesticide degradates. The use of HPLC/MS for this method provides improved sensitivity and selectivity over a previous method that included many of the same compounds, particularly in the presence of dissolved organic matter. Complete documentation of method 9060, now known as method 2060, can be found in Furlong and others (2001).

Samples analyzed using method 9060 pose the same set of qualifications as described for method 9002. The data are to be considered provisional, and interpreted with the knowledge that variability in concentration detections and quantifications may be greater than expected in a production method. An additional qualification should be given to samples analyzed during 1999, the first year of study. During this period, while the method was still in the testing phase, the NWQL received an unusually large number of requests for this method—an amount greater than their instrumental capacity. As a result, a significant backlog developed and many samples were stored in refrigerators before extraction well beyond recommended holding times, with some as long as 180 days. NWQL has additional holding-time studies underway that may identify the compounds most vulnerable to degradation. Sample-holding times are available for each of the samples collected during the pilot monitoring program. By December 1999, NWQL had resolved the backlog by adding additional instruments and analysts. The likely implications of extended holding times for the pilot monitoring program's provisional method 9060 are as follows—first, it is likely that in 1999, some compounds in some samples may have degraded to less than the MRL prior to extraction and analysis. Second, it is likely that reported concentrations are lower than would have been determined through extraction and analysis within prescribed holding times. And finally, it is possible that transformations may have occurred that produced a detectable degrade or elevated the concentration of a degradation compound relative to the concentration at the time of sampling. Ongoing NWQL holding-time studies may indicate which compounds are more susceptible to degradation and transformation.

Summary of Results from the Pilot Monitoring Program

may have been strongly affected by the drought, and was a primary consideration in the decision to extend sampling through 2000.

Summary tables are presented for each of the laboratory methods performed during the pilot monitoring program. These tables provide a systematic view of the analytical results for samples from raw-water-supply intake and finished-water sampling locations and are ordered by detection frequency to aid the reader in identifying the most commonly detected compounds. Summary tables were not prepared for the reservoir-outflow sites because much of the information was redundant between raw-water samples at the intake and reservoir-outflow samples. In addition, not all sampling sites included a reservoir-outflow sampling point. A summary of analytical results for individual sampling sites is presented as supplemental information at the end of this report.

Each summary table presents the MRL for all compounds analyzed, summarizes the detection frequency, and presents the upper bounds of detected concentrations as the maximum value and 95th percentile concentrations. Those compounds that were included in the analysis but were not detected in any sample are listed with their MRL following the table. The summary statistics presented in tables 8, 9, and 10 are an aggregation of all data collected in this study, so that although the percent detection frequencies, 95th percentile values and maximum concentrations reflect the data as a whole, they do not represent conditions at any one site. The summary statistics are also influenced more by samples from the frequently sampled sites than the other sites. No measure of central tendency, such as mean or median value, is presented for the entire data set because only 11 compounds had detection frequencies greater than 50 percent. Median concentrations are presented for individual sites where detection frequencies exceeded 50 percent in the supplemental tables. The supplemental tables also present the higher-level concentrations as 90th percentiles because many sites had an insufficient number of samples to calculate the 95th percentile.

In 1999, drought conditions extended across the Eastern United States and California, thus the conditions measured at six sites in 1999 (CA, OH, NC, NY, PA, and SC) were not representative of average runoff patterns. Drought conditions ended in the Eastern States in September 1999, when Hurricane Floyd produced flood conditions at most of the eastern sites. LeRoy Reservoir in NY had pesticide concentration data collected in 1998 from another program (Phillips and others, 1999). In 1998 the maximum observed concentration of metolachlor was greater than 2.0 µg/L (micrograms per liter); and in 1999, the maximum concentration was 0.17 µg/L. This indicates that concentrations and detection frequencies from 1999

Gas Chromatography / Mass Spectrometry (method 2001)

The results of analysis using method 2001 show that widely used herbicides are frequently detected in raw-water samples from water-supply intakes. Atrazine, metolachlor, and simazine were detected at every raw-water intake site; and deethylatrazine, a triazine degradate, was detected in raw-water samples from all sites except CA. Each of these compounds was detected in more than 90 percent of the 323 raw-water samples. Other commonly used herbicides including prometon, cyanazine, tebuthiuron, acetochlor, and alachlor were detected in greater than 26 percent of all intake samples. Insecticides were detected less frequently in intake samples than herbicides. Diazinon (35.3 percent) and chlorpyrifos (5.3 percent) were the two most frequently detected insecticides, with *p,p'*-DDE, azinphos-methyl, carbaryl, carbofuran, and dieldrin occurring in fewer than 5 percent of all raw-water samples. In all, 17 compounds were detected in less than 5 percent of the intake samples. In most cases, the occurrence of these compounds is limited to only a few sites. The observed detection frequencies for intake-water samples are similar to those reported for 58 stream sites sampled by the NAWQA program during 1992-95 (Larson and others, 1998).

Herbicides were frequently detected in finished-water samples and the high-use compounds were found in frequencies only slightly lower than those of raw water. Metribuzin, however, was detected in nearly 15 percent of the intake samples and was not detected in any finished-water sample. None of the herbicides were detected in finished water at a concentration greater than a national drinking-water criterion.

Six insecticides (*p,p'*-DDE, azinphos-methyl, carbaryl, carbofuran, fonofos, and phorate) were detected in finished-water samples, with each of these compounds detected in less than 3 percent of the samples. Fonofos was detected in three finished-water samples and phorate in one sample—neither of these compounds was detected in raw water. Three of the organophosphorus insecticides found in raw-water samples (diazinon, chlorpyrifos, and malathion) were not detected in any finished-water samples. Several studies have shown that organophosphorus compounds are readily oxidized in the presence of chlorine (Adnan and Yurdun, 1999; Aizawa and others, 1994). The oxidative products of these compounds include diazoxon, chlorpyrifos-oxygen analog, and malaoxon.

Table 8. Summary of analysis of pesticides in water samples from water-supply intakes and finished water-supply taps using gas chromatography / mass spectrometry—U.S. Geological Survey National Water Quality Laboratory method 2001

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; ()=qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance; H, herbicide; D, degradate; I, insecticide]

Compound (class)	Samples from raw-water intake (n = 323)					Samples from finished-water tap (n = 228)			
	Method reporting level	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value
Atrazine (H)	0.001	311(8)	96.3	0.516	11.600	218(13)	95.6	1.400	2.470
Simazine (H)	0.005	293(6)	90.7	0.028	1.520	192(7)	84.2	0.385	0.571
Deethylatrazine (D)	0.002	289(289)	89.5	0.080	0.771	203(203)	89.0	0.265	0.352
Metolachlor (H)	0.002	288(12)	89.2	0.033	3.320	198(4)	86.8	0.336	0.661
Prometon (H)	0.018	241(164)	74.6	0.017	0.138	145(109)	63.6	0.067	0.103
Cyanazine (H)	0.004	145(4)	44.9	0.007	0.332	96(3)	42.1	0.128	0.355
Tebuthiuron (H)	0.010	135(87)	41.8	0.010	0.030	64(46)	28.1	0.019	0.032
Acetochlor (H)	0.002	115	35.6	0.002	0.334	69(1)	30.3	0.061	0.395
Diazinon (I)	0.002	114(20)	35.3	0.002	0.101	0	0.0	---	---
Alachlor (H)	0.002	87(5)	26.9	0.002	0.655	51(4)	22.4	0.027	0.148
Metribuzin (H)	0.004	47	14.6	0.004	0.291	0	0.0	---	---
Pronamide (H)	0.003	34	10.5	0.003	0.048	9(1)	3.9	---	0.017
EPTC (H)	0.002	25(5)	7.7	0.002	0.037	12(1)	5.3	0.005	0.030
Chlorpyrifos (I)	0.004	17(9)	5.3	0.004	0.034	0	0.0	---	---
Dacthal (H)	0.002	16(15)	5.0	0.002	0.014	8(8)	3.5	---	0.004
<i>p,p'</i> -DDE (I)	0.006	14(14)	4.3	---	0.006	6(6)	2.6	---	0.006
Trifluralin (H)	0.002	9(9)	2.8	---	0.009	5(4)	2.2	---	0.009
Azinphos-methyl (I)	0.001	8(8)	2.5	---	0.144	5(5)	2.2	---	0.114
Terbacil (H)	0.007	7(7)	2.2	---	0.100	0	0.0	---	---
Carbaryl (I)	0.003	7(7)	2.2	---	0.047	2(2)	0.9	---	0.041
Malathion (H)	0.005	6	1.9	---	0.106	0	0.0	---	---
Pendimethalin (H)	0.004	6	1.9	---	0.125	3	1.3	---	0.010
Fonofos (I)	0.003	0	0.0	---	---	3	1.3	---	0.040
Carbofuran (I)	0.003	2(2)	0.6	---	0.050	3(3)	1.3	---	0.030
2,6 Diethylaniline (D)	0.003	2(2)	0.6	---	0.003	1(1)	0.4	---	0.003
Phorate (I)	0.002	0	0.0	---	---	1(1)	0.4	---	0.011
Benfluralin (H)	0.002	1(1)	0.3	---	0.010	0	0.0	---	---
Butylate (H)	0.002	1(1)	0.3	---	0.002	0	0.0	---	---
Dieldrin (I)	0.001	1(1)	0.3	---	0.010	0	0.0	---	---
Linuron (H)	0.002	1	0.3	---	0.035	0	0.0	---	---
Molinate (H)	0.004	1(1)	0.3	---	0.004	0	0.0	---	---
Napropamide (H)	0.003	1(1)	0.3	---	0.007	0	0.0	---	---
Parathion-methyl (I)	0.006	1	0.3	---	0.061	0	0.0	---	---
Triallate (H)	0.001	1(1)	0.3	---	0.002	0	0.0	---	---

The following compounds were not detected in any water sample. Method detection level in micrograms per liter shown in ()'s. **Herbicide:** Ethalfluralin (0.004), Pebulate (0.004), Propachlor (0.007), Propanil (0.004), Thiobencarb (0.002), **Insecticide:** alpha-HCH (0.002), Disulfoton (0.017), Ethoprop (0.003), Lindane (0.004), Parathion (0.004), Permethrin, *cis* (0.005), Propargite (0.013), Terbufos (0.013),

Gas Chromatography / Mass Spectrometry (provisional method 9002)

Compounds included in NWQL provisional method 9002 were generally detected much less frequently than compounds in method 2001. Two compounds were detected in more than 10 percent of the intake samples—3,4-dichloroaniline with 19.9 percent detections, and prometryn with 16.1 percent detections (table 9). 3,4-dichloroaniline was detected in only one finished-water sample and prometryn was not detected in any finished-water samples. 3,4-Dichloroaniline is a degradation product of three different compounds: linuron, propanil, and neburon. Sandstrom and others (2001) reported that diuron may be transformed to 3,4-dichloroaniline in the gas chromatograph injection port and that some percentage of the reported concentration of this compound may originate from diuron in the sample extract.

Twenty-one degradation products were found in water samples using this method—17 in raw water and 14 in finished-water samples. Malaoxon, the principal oxidative transformation product of malathion, was detected in 11 finished-water samples and none of the raw-water samples. In three of the samples where malaoxon was detected in finished water, the corresponding intake sample showed measurable concentrations of malathion. Other transformation products that were detected in more finished-water samples than intake samples include: azinphos-methyl-oxon, fenamiphos sulfone, terbufos-O-analogue sulfone, and 4-chloro-2-methyl phenol (a degradate of MCPA and MCPB). Chlorpyrifos oxygen analog was not detected in any finished-water samples, although chlorpyrifos was detected in 5.3 percent of the raw-water samples using method 2001.

Most compounds detected with this method were found in four or fewer of the intake or finished-water samples, with most concentrations observed at or near the method detection level. Of these, 23 were detected in raw-water samples and 16 were detected in finished-water samples. Forty-one of the 75 compounds reported were not detectable in any intake or finished-water sample.

Table 9. Summary of analysis of moderate-use pesticides and degradates in water samples from water-supply intakes and finished water-supply taps using gas chromatography / mass spectrometry—U.S. Geological Survey National Water Quality Laboratory provisional method 9002

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; ()=qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance; H, herbicide; D, degradate; I, insecticide; F, fungicide]

Compound (Class)	Samples from raw-water intake (n = 317)					Samples from finished-water tap (n = 221)			
	Method reporting level	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value
3,4-Dichloroaniline (D)	0.008	63(21)	19.9	0.019	0.061	1(1)	0.5	---	0.008
Prometryn (H)	0.005	51(23)	16.1	0.026	0.041	0	0.0	---	---
Malaoxon (D)	0.016	0	0.0	---	---	11(3)	5.0	0.016	0.556
3-Trifluoromethylaniline (D)	0.005	12(11)	3.8	---	0.008	0	0.0	---	---
2-[2-Ethyl-6-methylphenyl amino]-1-propanal (D)	0.016	11(9)	3.5	---	0.074	6(6)	2.7	---	0.016
2,5-Dichloroaniline (D)	0.005	10(2)	3.2	---	0.020	2(1)	0.9	---	0.009
Azinphos-methyl-oxon (D)	0.031	1	0.3	---	0.263	4(4)	1.8	---	0.063
4-Chloro-2-methyl phenol (D)	0.005	1(1)	0.3	---	0.005	4(4)	1.8	---	0.007
2-Chloro-2,6-diethylacet-anilide (D)	0.008	4	1.3	---	0.012	0	0.0	---	---
Dimethoate (I)	0.005	4(1)	1.3	---	0.022	0	0.0	---	---
Metalaxyl (F)	0.016	4(4)	1.3	---	0.016	2(2)	0.9	---	0.016
4-(Hydroxymethyl) pendimethalin (D)	0.031	3(3)	0.9	---	0.045	1(1)	0.5	---	0.126
1,4-Naphthoquinone (D)	0.008	3(3)	0.9	---	0.008	1(1)	0.5	---	0.008
1-Naphthol (D)	0.005	3(3)	0.9	---	0.228	0	0.0	---	---
Endosulfan sulfate (D)	0.008	3(2)	0.9	---	0.009	2(2)	0.9	---	0.008
Myclobutanil (F)	0.008	3(2)	0.9	---	0.015	0	0.0	---	---
Tebupirimphos (I)	0.008	3(3)	0.9	---	0.008	0	0.0	---	---
4,4'-Dichlorobenzo-phenone (D)	0.008	0	0.0	---	---	2(2)	0.9	---	0.008
Fenamiphos sulfone (D)	0.008	1(1)	0.3	---	0.008	2(1)	0.9	---	0.016
Terbufos-O-analogue sulfone (D)	0.016	0	0.0	---	---	2(2)	0.9	---	0.016
Fenamiphos sulfoxide (D)	0.031	2(1)	0.6	---	0.033	1(1)	0.5	---	0.031
Hexazinone (H)	0.008	2(2)	0.6	---	0.008	0	0.0	---	---
Tefluthrin metabolite [R 119364] (D)	0.005	2(2)	0.6	---	0.005	0	0.0	---	---
Tefluthrin metabolite [R 152912] (D)	0.008	2(1)	0.6	---	0.021	0	0.0	---	---
3,5-Dichloroaniline (D)	0.005	0	0.0	---	---	1	0.5	---	0.009
Bifenthrin (I)	0.005	0	0.0	---	---	1(1)	0.5	---	0.005
Iprodione (F)	0.031	0	0.0	---	---	1(1)	0.5	---	0.031
Isofenphos (I)	0.008	1(1)	0.3	---	0.008	1(1)	0.5	---	0.008
cis-Propiconazol (F)	0.005	1(1)	0.3	---	0.005	0	0.0	---	---
Disulfoton sulfone (D)	0.005	1	0.3	---	0.013	0	0.0	---	---
Disulfoton sulfoxide (D)	0.016	1(1)	0.3	---	0.016	0	0.0	---	---
Methidathion (I)	0.008	1	0.3	---	0.110	0	0.0	---	---
Tefluthrin (I)	0.008	1(1)	0.3	---	0.008	0	0.0	---	---
trans-Propiconazol (F)	0.005	1(1)	0.3	---	0.005	0	0.0	---	---

The following compounds were not detected in any water sample. Method detection level in micrograms per liter shown in ()'s.

Defoliant: Tribuphos (0.016); **Fungicide:** E-Dimethomorph (0.031), Z-Dimethomorph (0.031), Ethion monoxon (0.008); **Herbicide:** Cycloate (0.016), Oxyfluorfen (0.016), Terbutylazine (0.005); **Insecticide:** Cyhalothrin (0.008), Cyfluthrin (0.031), Cypermethrin (0.031), Dicrotophos (0.016), Ethion (0.005), Fenthion (0.005), Phosmet (0.008), Profenofos (0.008), Propetamphos (0.016), Sulfotepp (0.005), Sulprofos (0.005), Temephos (0.031); **Nematocide:** Fenamiphos (0.016); **Plant Growth Regulator:** Flumetralin (0.016); **Degradate:** 2-Amino-N-isopropylbenzamide (0.005), 2-Ethyl-6-methylaniline (0.005), 3-Phenoxybenzyl alcohol (0.031), 4-Chlorobenzylmethyl sulfone (0.008), Chlorpyrifos oxygen analog (0.016), c-Methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate (0.016), 2-(4-tert-butylphenoxy) cyclohexanol (0.016), Diclorvos (0.005), alpha-Endosulfan (0.016), beta-Endosulfan (0.016), Endosulfan-ether (0.016), Fenthion sulfoxide (0.008), Fonofos oxygen analog (0.016), O-ethyl-O-methyl-S-propylphosphorothioate (0.005), t-Methyl-3-(2,2-dichlorovinyl)-2,2-dimethyl-(1-cyclopropane)-carboxylate (0.016), Paraoxon-ethyl (0.031), Paraoxon-methyl (0.031), Phorate oxon (0.031), Phosmet oxon (0.016), Tebupirimphos oxygen analog (0.016)

High-Performance Liquid Chromatography / Mass Spectrometry (provisional method 9060)

Sample results for NWQL provisional method 9060 (table 10) also show that the widely used herbicides are often detected in samples of both raw and finished water. This method provides data on three additional triazine degradation products that are not included in method 2001, including: 2-hydroxyatrazine, deisopropylatrazine, and desethyl-desisopropylatrazine. Each of these compounds was detected in greater than 60 percent of the raw- and finished-water samples and the maximum observed concentrations were nearly equal between the two sample sources. Atrazine and deethylatrazine are included in method 9060 and method 2001, however, the MRL for these compounds, as well as other compounds, in method 9060 are generally much greater than for compounds included in method 2001, and range from 0.01 to 0.114 µg/L. Therefore, the detection frequencies based on this method are expected to be somewhat lower for compounds that are included in both methods.

Nine herbicides and one fungicide (metalaxyl) were detected in greater than 10 percent of the raw-water samples. Four of these compounds (diuron, bentazon, chlorimuron-ethyl, and sulfometuron-methyl) were detected in less than 10 percent of the finished-water samples. A total of 48 pesticide compounds were detected in intake or finished-water samples. An additional 16 compounds were included in the method but not detected in any water samples.

Caffeine is not a widely used pesticide or a degradation product, but it was included in this method because of its utility as an indicator of wastewater effluent and because its chemical characteristics make it well suited for this analytical technique. Caffeine was detected in about 36 percent of all intake samples.

Table 10. Summary of analysis of pesticides in water samples from water-supply intakes and finished water-supply taps using high performance liquid chromatography / mass spectrometry—U.S. Geological Survey National Water Quality Laboratory provisional method 9060

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; ()=qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance; H, herbicide; D, Degradate; I, insecticide; F, fungicide]

Compound	Samples from raw-water intake (n = 312)					Samples from finished-water tap (n = 225)			
	Method reporting Level	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value
Atrazine (H)	0.074	265(140)	84.9	1.888	6.176	185(86)	82.2	1.118	1.944
2-Hydroxyatrazine (D)	0.193	256(255)	82.3	1.263	2.058	182(182)	81.3	1.008	1.785
Deisopropylatrazine (D)	0.074	250(210)	80.1	0.195	0.386	146(136)	64.9	0.081	0.178
Deethylatrazine (D)	0.087	249(196)	79.8	0.340	0.546	167(147)	74.6	0.201	0.267
Desethyl desisopropyl atrazine (D)	0.060	216(184)	69.2	0.079	0.150	141(137)	62.7	0.060	0.150
2,4-D (H)	0.077	179(92)	57.4	0.158	0.414	98(60)	43.6	0.132	0.634
Metalaxyl (F)	0.057	133(123)	42.6	0.057	0.351	80(79)	35.6	0.057	0.072
Tebuthiuron (H)	0.077	118(118)	37.8	0.077	0.077	42(42)	18.7	0.077	0.077
Diuron (H)	0.079	117(70)	37.5	0.319	0.540	13(13)	5.8	0.079	0.079
Caffeine*	0.081	112(88)	35.9	0.108	88.000	24(24)	10.7	0.081	0.081
Bentazon (H)	0.019	80(80)	25.6	0.021	0.344	21(21)	9.3	0.019	0.019
2,4-D methyl ester (D)	0.087	77(77)	24.7	0.087	0.087	44(42)	19.6	0.087	0.136
Dicamba (H)	0.096	61(45)	19.6	0.100	0.192	35(31)	15.6	0.096	0.147
Chlorimuron-ethyl (H)	0.037	52(45)	16.7	0.037	0.058	4(4)	1.8	---	0.040
Bromacil (H)	0.081	49(47)	15.7	0.081	0.481	2(2)	0.9	---	0.481
Sulfometuron-methyl (H)	0.039	38(21)	12.2	0.095	0.160	6(6)	2.7	---	0.039
Fluometuron (H)	0.062	24(5)	7.7	0.145	0.264	19(17)	8.4	0.062	0.100
Clopyralid (H)	0.041	21(8)	6.7	0.042	0.170	4(3)	1.8	---	0.059
Benomyl (F)	0.022	20(19)	6.5	0.022	0.038	2(2)	0.9	---	0.215
Picloram (H)	0.071	11(1)	3.5	---	1.441	11(1)	4.9	0.094	0.389
Imazaquin (H)	0.103	14(14)	4.5	---	0.351	9(9)	4.0	---	0.111
Nicosulfuron (H)	0.065	9(9)	2.9	---	0.139	8(8)	3.6	---	0.093
Imazethapyr (H)	0.088	10(10)	3.4	---	0.133	3(3)	1.4	---	0.088
Flumetsulam (H)	0.087	9(9)	2.9	---	0.088	4(4)	1.8	---	0.087
MCPA (H)	0.059	9(7)	2.9	---	0.121	1	0.4	---	0.077
Diphenamid (H)	0.058	7(7)	2.2	---	0.058	3(3)	1.3	---	0.058
Norflurazon (H)	0.077	6(5)	1.9	---	0.414	0	0.0	---	---
Bromoxynil (H)	0.057	0	0.0	---	---	4(4)	1.8	---	0.057
Oryzalin (H)	0.071	3	1.0	---	0.127	4(2)	1.8	---	0.095
Triclopyr (H)	0.101	3(3)	1.0	---	0.101	4(4)	1.8	---	0.101
Acifluorfen (H)	0.062	5(5)	1.7	---	0.062	1(1)	0.5	---	0.062
3(4-chlorophenyl)-1-methyl urea (D)	0.092	5(5)	1.6	---	0.092	0	0.0	---	---
Metsulfuron-methyl (H)	0.114	4(3)	1.3	---	1.194	1(1)	0.4	---	0.200
Dichlorprop (H)	0.050	3(3)	1.0	---	0.050	1(1)	0.4	---	0.050
Oxamyl oxime (D)	0.064	0	0.0	---	---	2(2)	0.9	---	0.064
2,4-DB (H)	0.054	0	0.0	---	---	2(2)	0.9	---	0.054
Carbaryl (I)	0.063	2(2)	0.6	---	0.063	0	0.0	---	---
Carbofuran (I)	0.057	2(2)	0.6	---	0.057	1(1)	0.4	---	0.057
Dinoseb (H)	0.043	2(2)	0.6	---	0.043	1(1)	0.4	---	0.043
Siduron (H)	0.093	2(2)	0.6	---	0.093	0	0.0	---	---

* Caffeine is not a pesticide compound, however it is included in this method.

Table 10 Summary of analysis of pesticides in water samples from water-supply intakes and finished water-supply taps using high performance liquid chromatography / mass spectrometry—U.S. Geological Survey National Water Quality Laboratory provisional method 9060 –Continued.

Compound	Samples from raw-water intake (n = 312)					Samples from finished-water tap (n = 225)				
	Method reporting level	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value	Number of detections	Detection frequency in percent	95 th percentile value	Maximum value	
Propoxur (I)	0.059	1(1)	0.3	---	0.059	1	0.5	---	0.823	
3-Hydroxycarbofuran (D)	0.062	0	0.0	---	0.062	1(1)	0.4	---	0.062	
Bendiocarb (I)	0.061	0	0.0	---	0.061	1(1)	0.4	---	0.061	
Neburon (H)	0.075	1(1)	0.3	---	0.075	1(1)	0.4	---	0.075	
Propiconazole (F)	0.064	1(1)	0.3	---	0.064	1(1)	0.4	---	0.064	
Chloramben methyl ester (H)	0.114	1	0.3	---	0.126	0	0.0	---	---	
Aldicarb sulfone (D)	0.160	1(1)	0.3	---	0.160	0	0.0	---	---	
Imidacloprid (I)	0.106	1(1)	0.3	---	0.106	0	0.0	---	---	
Terbacil (H)	0.095	1(1)	0.3	---	0.100	0	0.0	---	---	

The following compounds were not detected in any water sample. Method detection level in micrograms per liter shown in ()'s:

Herbicide: Chlorothalonil (0.049), Cycloate (0.054), Fenuron (0.074), Linuron (0.070), MCPB (0.063), Protham (0.072), Tribenuron-methyl (0.068), **Insecticide:** Aldicarb (0.082), Methiocarb (0.080), Methomyl (0.077), Oxamyl (0.016), **Degrade:** 3-keto-carbofuran (0.072), Aldicarb sulfoxide (0.027), Bensulfuron-methyl (0.048), Dacthal monoacid (0.072), Methomyl oxime (0.010),

Summary

The pilot monitoring program described in this report was initiated by the U.S. Geological Survey National Water-Quality Assessment Program and the U.S. Environmental Protection Agency Office of Pesticide Programs to provide monitoring data on pesticide concentrations in drinking water because the Office of Pesticide Programs has responsibility under the Food Quality Protection Act of 1996 to assess aggregate risk from exposure to pesticides in drinking water based on available data. This program was designed to fill important data gaps and to provide more information about appropriate methods for National monitoring of pesticides in drinking water. This report presents and summarizes the data collected during the pilot monitoring program conducted in 1999 and 2000. The design of the monitoring program is described in order to facilitate effective analysis of the data collected to meet a broad array of goals and objectives.

The pilot monitoring program was designed as a first step towards a long-term goal of characterizing human exposure to pesticide residues in drinking water derived from surface-water sources. The principal goal of this program is to develop a data set on the occurrence of pesticides in drinking-water sources that is tied to pesticide concentrations observed in finished drinking water. Reservoirs and community water systems that withdraw from reservoirs were selected for this pilot monitoring program because reservoirs are considered to

be highly vulnerable to pesticide contamination, serve as integrators of pesticide loading from their watersheds, and are important sources of drinking water.

Twelve community water systems supplied by reservoirs were selected for study based on their vulnerability to pesticides from their contributing watersheds. The reservoirs sampled range in size from 120 to 92,600 acre-feet normal capacity, with contributing watersheds ranging from 3.3 to 784 square miles and are located in California, Indiana, Ohio, Oklahoma, Louisiana, Missouri, South Carolina, South Dakota, New York, North Carolina, Pennsylvania, and Texas. Ten of these sites were selected because they were representative of regional agricultural practices and two sites (Oklahoma and California) were selected because they were representative of urban pesticide runoff.

The primary sampling approach involved sample collection from the raw-water intake as well as from the finished-water tap located at the entry point to the distribution system. Samples were also collected at the outflow of many of the reservoirs because the water-quality conditions at an intake may substantially differ from average reservoir conditions. All samples were collected by trained U.S. Geological Survey personnel, following sample-collection protocols documented by the U.S. Geological Survey. The sampling frequency was designed to characterize the occurrence of commonly occurring pesticides and to identify compounds that may occur for only a short period of time at concentrations greater than the laboratory reporting level. Each site was sampled quarterly over a one-year period, with semi-

weekly samples collected during a 4-month period coincident with the most intensive application season. Four sites had additional raw-water samples collected every week for a 6-month period. In 1999, drought conditions extended across the Eastern United States and California, thus the conditions measured at six sites in 1999 were not representative of average runoff patterns. This was a primary consideration in the decision to extend sampling at nine sites through 2000.

Three laboratory methods were used during the pilot monitoring program—an approved method and two developmental methods. Together, these three methods measure 178 different pesticides and pesticide degradation products in filtered-water samples. The primary method, method 2001, uses C-18 solid-phase extraction and gas chromatography / mass spectrometry to determine concentrations of 47 pesticides and pesticide metabolites in water samples. The two developmental methods were included in this program in order to expand the available information on the occurrence of a wide number of pesticides and pesticide degradates in surface water across the Nation, and to test for the occurrence of these compounds in drinking-water supplies. These methods were included with the knowledge that the methods were developmental and that the performance of the methods may be more variable than would be expected of a thoroughly tested and approved method. Provisional method 9002 is an adaptation of the C-18 solid-phase extraction and gas chromatography / mass spectrometry technology used in method 2001. The method provides a quantitative analysis of 20 parent pesticides and 21 pesticide degradates, and provides qualitative estimates for 14 parent pesticides and 20 degradates. Provisional method 9060 is a substantially new technique using graphitized carbon solid-phase extraction and high-performance liquid chromatography/mass spectrometry for the instrumental analysis of extracts. This method is designed to determine low-level concentrations of 64 polar pesticides and pesticide degradates.

Overall, the three methods provided analyses for 178 different parent pesticide or degradation products. Of these, 108 compounds were detected in at least one sample of raw water at an intake or of finished water. Many of these compounds, however, were detected in fewer than 5 percent of the samples and at concentrations very near the method reporting level. The observed detection frequencies for intake water are similar to those reported for 58 stream sites sampled by the NAWQA program in 1992-95.

The results show that widely used herbicides and triazine degradation products are frequently detected in samples from water-supply intakes as well as in finished-water samples. Atrazine, simazine, and metolachlor were detected in at least one raw-water sample from each of the 12 monitoring sites; and deethylatrazine, a triazine degradate, was detected in raw-water samples from all

sites except the California site. Other commonly used herbicides including metolachlor, prometon, cyanazine, 2,4-D, tebuthiuron, acetochlor and alachlor were detected in more than 26 percent of all intake samples. Insecticides were detected less frequently in intake samples than herbicides. Four triazine-herbicide degradation products (2-hydroxyatrazine, deisopropylatrazine, deethylatrazine, and desethyl-deisopropylatrazine) were detected in more than 60 percent of both the raw and finished-water samples. None of the herbicides were detected in finished water at a concentration greater than a National drinking-water criterion.

Insecticides were detected less frequently in water samples than herbicides. Diazinon and chlorpyrifos were the two most frequently detected insecticides (detected in 35.3 percent and 5.3 percent of the raw-water samples, respectively). Neither diazinon, chlorpyrifos, nor malathion, three organophosphorus insecticides, were detected in any finished-water samples. Several studies have shown that organophosphorus compounds are readily oxidized in the presence of chlorine, with the oxidative products of these compounds being diazinon, chlorpyrifos oxygen analog, and malaoxon. Malaoxon, the principal oxidative transformation product of malathion, was detected in 11 finished-water samples and none of the raw-water samples. In three of the samples where malaoxon was detected in finished water, the corresponding intake sample showed measurable concentrations of malathion. Chlorpyrifos oxygen analog was not detected in any water sample, and diazoxon was not included as an analyte on any of the three methods.

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Supplemental Tables

Table 11. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Canyon Reservoir near Elsinore, California

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Prometon	8	8(1)	100	0.025	0.028	0.028
Simazine	8	8	100	0.078	0.091	0.091
Diazinon	8	7	87.5	0.015	0.045	0.045
Tebuthiuron	8	6(6)	75.0	0.007	0.012	0.012
Atrazine	8	4(2)	50.0	0.002	0.006	0.006
Dacthal	8	4(4)	50.0	0.001	0.003	0.003
Metolachlor	8	3(1)	37.5	---	0.005	0.005
Tri-allate	8	1(1)	12.5	---	0.002	0.002
Trifluralin	8	1(1)	12.5	---	0.002	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	8	8	100	0.044	0.061	0.061
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Sulfometuron-methyl	8	8(3)	100	0.098	0.131	0.131
Diuron	8	7	87.5	0.340	0.540	0.540
3(4-chlorophenyl)-1-methyl urea	8	5(5)	62.5	0.008	0.026	0.026
Desethyl desisopropylatrazine	8	5(5)	62.5	0.005	0.011	0.011
2-Hydroxyatrazine	8	3(3)	37.5	---	0.028	0.028
Deisopropylatrazine	8	3(3)	37.5	---	0.019	0.019
Tebuthiuron	8	3(3)	37.5	---	0.011	0.011
Bromacil	8	1(1)	12.5	---	0.005	0.005
Caffeine*	8	1(1)	12.5	---	0.026	0.026
Dicamba	8	1(1)	12.5	---	0.090	0.090
MCPA	8	1(1)	12.5	---	0.011	0.011
Norflurazon	8	1	12.5	---	0.414	0.414

* Caffeine is not a pesticide compound, however it is included in this method.

Table 12. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Elsinore Valley Municipal Water District, California

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Prometon	8	8(3)	100	0.022	0.030	0.030
Simazine	8	8	100	0.062	0.078	0.078
Atrazine	8	4(3)	50.0	0.002	0.005	0.005
Tebuthiuron	8	4(3)	50.0	0.003	0.018	0.018
Dacthal	8	2(2)	25.0	---	0.002	0.002
Metolachlor	8	1	12.5	---	0.003	0.003
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	8	2(2)	25.0	---	0.028	0.028
Desethyl desisopropylatrazine	8	2(2)	25.0	---	0.013	0.013
Tebuthiuron	8	2(2)	25.0	---	0.008	0.008

Table 13. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Eagle Creek Reservoir, Indiana

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	48	48	100	1.050	1.840	2.140
Deethylatrazine	48	48(48)	100	0.091	0.198	0.290
Metolachlor	48	48	100	0.308	0.765	0.950
Prometon	48	47(29)	97.9	0.016	0.030	0.034
Acetochlor	48	41	85.4	0.060	0.119	0.188
Simazine	48	38	79.2	0.018	0.025	0.028
Cyanazine	48	30	62.5	0.008	0.028	0.035
Tebuthiuron	48	23(16)	47.9	---	0.010	0.012
Diazinon	48	19(6)	39.6	---	0.008	0.010
Metribuzin	48	19	39.6	---	0.020	0.025
Alachlor	48	12(1)	25.0	---	0.010	0.014
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	48	9(8)	18.8	---	0.004	0.014
2-[2-Ethyl-6-methylphenyl) Amino]-1-propan	48	1(1)	2.1	---	---	0.007
cis-Propiconazol	48	1(1)	2.1	---	---	0.005
Fenamiphos sulfoxide	48	1	2.1	---	---	0.033
trans-Propiconazol	48	1(1)	2.1	---	---	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	48	48(25)	100	0.891	1.423	2.280
Deethylatrazine	48	48(34)	100	0.112	0.211	0.303
2-Hydroxyatrazine	48	47(47)	97.9	0.552	0.878	1.335
Deisopropylatrazine	48	45(44)	93.8	0.030	0.074	0.097
Metaxyl	48	44(44)	91.7	0.011	0.025	0.030
2,4-D	48	42(9)	87.5	0.120	0.192	0.356
Desethyl desisopropylatrazine	48	42(37)	87.5	0.028	0.068	0.106
Chlorimuron-ethyl	48	38(33)	79.2	0.018	0.037	0.058
Tebuthiuron	48	38(38)	79.2	0.003	0.007	0.010
Diuron	48	36(36)	75.0	0.030	0.055	0.065
2,4-D methyl ester	48	34(34)	70.8	0.017	0.044	0.067
Bentazon	48	31(31)	64.6	0.008	0.021	0.026
Dicamba	48	22(13)	45.8	---	0.117	0.161
Clopyralid	48	20(7)	41.7	---	0.079	0.170
Caffeine*	48	16(16)	33.3	---	0.023	0.034
Bromacil	48	12(12)	25.0	---	0.023	0.051
MCPA	48	5(4)	10.4	---	0.011	0.121
Diphenamid	48	3(3)	6.3	---	---	0.004
Flumetsulam	48	3(3)	6.3	---	---	0.059
Imazaquin	48	2(2)	4.2	---	---	0.060
Sulfometuron-methyl	48	2(2)	4.2	---	---	0.009
Metsulfuron-methyl	48	1(1)	2.1	---	---	0.002
Triclopyr	48	1(1)	2.1	---	---	0.037

* Caffeine is not a pesticide compound, however it is included in this method.

Table 14. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at Eagle Creek Reservoir, Indiana

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	11	11	100	1.080	1.530	1.560
Cyanazine	11	11	100	0.015	0.017	0.021
Deethylatrazine	11	11(11)	100	0.120	0.200	0.208
Metolachlor	11	11	100	0.334	0.409	0.433
Prometon	11	10(9)	90.9	0.012	0.018	0.020
Acetochlor	11	9	81.8	0.059	0.108	0.132
Simazine	11	9	81.8	0.013	0.017	0.017
Metribuzin	11	6	54.5	0.009	0.014	0.025
Tebuthiuron	11	3(1)	27.3	---	0.011	0.011
Alachlor	11	2(1)	18.2	---	0.003	0.004
Diazinon	11	2(2)	18.2	---	0.003	0.004
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	11	1(1)	9.1	---	---	0.007
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2,4-D	11	11(4)	100	0.166	0.221	0.319
2-Hydroxyatrazine	11	11(11)	100	0.692	1.017	1.619
Atrazine	11	11(7)	100	0.848	1.198	1.392
Deethylatrazine	11	11(7)	100	0.110	0.198	0.200
Deisopropylatrazine	11	11(11)	100	0.026	0.046	0.054
Desethyl desisopropylatrazine	11	10(10)	90.9	0.027	0.058	0.066
Metalaxyl	11	10(10)	90.9	0.012	0.024	0.028
2,4-D methyl ester	11	7(6)	63.6	0.022	0.078	0.165
Chlorimuron-ethyl	11	7(6)	63.6	0.024	0.033	0.041
Tebuthiuron	11	7(7)	63.6	0.003	0.007	0.010
Bentazon	11	5(5)	45.5	---	0.011	0.011
Diuron	11	5(5)	45.5	---	0.030	0.052
Dicamba	11	4(4)	36.4	---	0.060	0.062
Caffeine*	11	2(2)	18.2	---	0.016	0.030
Clopyralid	11	2(1)	18.2	---	0.040	0.053
Bromacil	11	1(1)	9.1	---	---	0.028

* Caffeine is not a pesticide compound, however it is included in this method.

Table 15. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Indianapolis Water Company, Indiana

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	22	22	100	0.830	1.490	1.700
Deethylatrazine	22	22(22)	100	0.097	0.220	0.253
Metolachlor	22	22	100	0.145	0.360	0.661
Prometon	22	22(10)	100	0.019	0.028	0.032
Simazine	22	19	86.4	0.017	0.022	0.025
Acetochlor	22	13	59.1	0.018	0.105	0.121
Cyanazine	22	11	50.0	0.003	0.023	0.030
Tebuthiuron	22	6(5)	27.3	---	0.009	0.011
Alachlor	22	3	13.6	---	0.005	0.012
Fonofos	22	2	9.1	---	---	0.023
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	22	1(1)	4.5	---	---	0.003
Fenamiphos sulfoxide	22	1(1)	4.5	---	---	0.022
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	22	22(22)	100	0.386	0.918	1.525
Deethylatrazine	22	22(14)	100	0.148	0.229	0.242
Atrazine	22	21(9)	95.5	0.575	1.123	1.519
2,4-D	22	20(3)	90.9	0.109	0.185	0.317
Deisopropylatrazine	22	20(19)	90.9	0.035	0.084	0.087
Desethyl desisopropylatrazine	22	18(15)	81.8	0.031	0.079	0.083
Metalaxyl	22	17(17)	77.3	0.012	0.022	0.026
2,4-D methyl ester	22	16(15)	72.7	0.018	0.042	0.087
Dicamba	22	12(9)	54.5	0.016	0.110	0.119
Diuron	22	10(10)	45.5	---	0.024	0.026
Tebuthiuron	22	9(9)	40.9	---	0.006	0.011
Bentazon	22	7(7)	31.8	---	0.010	0.016
Caffeine*	22	4(4)	18.2	---	0.010	0.026
Clopyralid	22	3(2)	13.6	---	0.030	0.059
Diphenamid	22	3(3)	13.6	---	0.003	0.006
Bromoxynil	22	1(1)	4.5	---	---	0.011
Chlorimuron-ethyl	22	1(1)	4.5	---	---	0.040
Flumetsulam	22	1(1)	4.5	---	---	0.030
MCPA	22	1	4.5	---	---	0.077
Oryzalin	22	1	4.5	---	---	0.071
Propoxur	22	1	4.5	---	---	0.823

* Caffeine is not a pesticide compound, however it is included in this method

Table 16. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Lake Bruin, Louisiana

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	22	22	100	0.848	0.991	1.020
Cyanazine	22	22	100	0.173	0.238	0.332
Deethylatrazine	22	22(22)	100	0.156	0.188	0.195
Simazine	22	22	100	0.121	0.164	0.184
Metolachlor	22	21	95.5	0.013	0.026	0.033
Tebuthiuron	22	7(7)	31.8	---	0.006	0.009
Prometon	22	6(6)	27.3	---	0.005	0.008
Malathion	22	5	22.7	---	0.023	0.106
Chlorpyrifos	22	3	13.6	---	0.005	0.008
Trifluralin	22	3(3)	13.6	---	0.002	0.002
Terbacil	22	2(2)	9.1	---	---	0.054
Dacthal	22	1	4.5	---	---	0.014
Diazinon	22	1	4.5	---	---	0.010
EPTC	22	1(1)	4.5	---	---	0.011
Parathion-methyl	22	1	4.5	---	---	0.061
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Prometryn	20	20	100	0.031	0.039	0.041
3-Trifluoromethylaniline	20	12(11)	60.0	0.003	0.007	0.008
3,4-Dichloroaniline	20	8(7)	40.0	---	0.007	0.011
2,5-Dichloroaniline	20	1	5.0	---	---	0.011
2-[2-Ethyl-6-methylphenyl) amino]-1-propanal	20	1(1)	5.0	---	---	0.074
Dimethoate	20	1	5.0	---	---	0.007
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	21	21(20)	100	0.483	0.970	1.044
Atrazine	21	21(4)	100	0.549	1.104	1.698
Deethylatrazine	21	21(15)	100	0.099	0.121	0.172
Deisopropylatrazine	21	21(20)	100	0.043	0.061	0.131
Fluometuron	21	21(2)	100	0.157	0.238	0.264
2,4-D	21	20(5)	95.2	0.085	0.140	0.180
Diuron	21	19(15)	90.5	0.045	0.101	0.139
Desethyl desisopropylatrazine	21	12(12)	57.1	0.006	0.019	0.027
2,4-D methyl ester	21	10(10)	47.6	---	0.027	0.051
Metalaxyl	21	6(6)	28.6	---	0.005	0.040
Norflurazon	21	5(5)	23.8	---	0.005	0.011
Tebuthiuron	21	4(4)	19.0	---	0.003	0.004
Dicamba	21	2(2)	9.5	---	---	0.039
Imazethapyr	19	1(1)	5.3	---	---	0.004
Bromacil	21	1(1)	4.8	---	---	0.481
Caffeine*	21	1	4.8	---	---	0.143
Siduron	21	1(1)	4.8	---	---	0.003

* Caffeine is not a pesticide compound, however it is included in this method.

Table 17. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at Lake Bruin, Louisiana

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	4	4	100	0.972	1.000	1.000
Cyanazine	4	4	100	0.126	0.139	0.139
Deethylatrazine	4	4(4)	100	0.110	0.154	0.154
Metolachlor	4	4	100	0.028	0.032	0.032
Simazine	4	4	100	0.158	0.162	0.162
Chlorpyrifos	4	3	75.0	0.005	0.006	0.006
Trifluralin	4	2(2)	50.0	0.001	0.002	0.002
Prometon	4	1(1)	25.0	---	0.003	0.003
Tebuthiuron	4	1(1)	25.0	---	0.009	0.009
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	3	3(2)	100	0.006	0.008	0.008
Prometryn	3	3	100	0.024	0.024	0.024
3-Trifluoromethylaniline	3	1(1)	33.3	---	0.007	0.007
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2,4-D	4	4	100	0.099	0.142	0.142
2-Hydroxyatrazine	4	4(4)	100	0.727	0.865	0.865
Atrazine	4	4(3)	100	0.934	1.243	1.243
Deethylatrazine	4	4(4)	100	0.096	0.147	0.147
Deisopropylatrazine	4	4(4)	100	0.060	0.070	0.070
Desethyl desisopropylatrazine	4	4(4)	100	0.008	0.015	0.015
Diuron	4	4(4)	100	0.041	0.060	0.060
Fluometuron	4	4	100	0.231	0.247	0.247
2,4-D methyl ester	4	3(3)	75.0	0.008	0.013	0.013
Metalaxyl	4	2(2)	50.0	0.001	0.004	0.004
Norflurazon	4	1(1)	25.0	---	0.009	0.009

Table 18. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Tensas Water Distribution Association, Inc., Louisiana

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	21	21	100	0.733	0.832	0.851
Cyanazine	21	21	100	0.117	0.170	0.355
Deethylatrazine	21	21(21)	100	0.134	0.170	0.194
Simazine	21	21	100	0.102	0.138	0.173
Metolachlor	21	19(1)	90.5	0.011	0.023	0.027
Prometon	21	7(7)	33.3	---	0.005	0.007
Tebuthiuron	21	5(5)	23.8	---	0.004	0.008
Dacthal	21	1(1)	4.8	---	---	0.004
Trifluralin	21	1(1)	4.8	---	---	0.002
<i>p,p'</i> -DDE	21	1(1)	4.8	---	---	0.001
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Malaoxon	21	11(3)	52.4	0.008	0.128	0.556
4-Chloro-2-methylphenol	21	4(4)	19.0	---	0.006	0.007
4,4'-Dichlorobenzophenone	21	2(2)	9.5	---	---	0.003
Isofenphos	21	1(1)	4.8	---	---	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	22	22(22)	100	0.449	1.045	1.172
Atrazine	22	22(5)	100	0.389	0.699	0.840
2,4-D	22	21(10)	95.5	0.077	0.114	0.124
Deethylatrazine	22	20(20)	90.9	0.049	0.078	0.091
Deisopropylatrazine	22	18(17)	81.8	0.022	0.065	0.085
Fluometuron	22	18(16)	81.8	0.031	0.077	0.100
2,4-D methyl ester	22	14(14)	63.6	0.009	0.021	0.045
Desethyl desisopropylatrazine	22	11(11)	50.0	---	0.018	0.028
Bromoxynil	22	3(3)	13.6	---	0.012	0.021
Dicamba	22	2(2)	9.1	---	---	0.042
Metalaxyl	22	2(2)	9.1	---	---	0.005
Tebuthiuron	22	1(1)	4.5	---	---	0.002

Table 19. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Higginsville Reservoir, Missouri

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	40	40	100	2.600	5.880	11.600
Deethylatrazine	40	40(40)	100	0.410	0.624	0.771
Simazine	40	40(2)	100	0.199	0.634	0.769
Metolachlor	40	39	97.5	0.334	2.250	3.320
Prometon	40	37(26)	92.5	0.013	0.024	0.026
Alachlor	40	31(2)	77.5	0.012	0.394	0.655
Cyanazine	40	26(1)	65.0	0.008	0.021	0.024
Acetochlor	40	22	55.0	0.008	0.027	0.031
Diazinon	40	14	35.0	---	0.011	0.022
Metribuzin	39	9	23.1	---	0.083	0.291
2,6-Diethylaniline	40	1(1)	2.5	---	---	0.001
Azinphos-methyl	40	1(1)	2.5	---	---	0.034
Carbaryl	40	1(1)	2.5	---	---	0.008
Chlorpyrifos	40	1	2.5	---	---	0.034
Dacthal	40	1(1)	2.5	---	---	0.002
Malathion	40	1	2.5	---	---	0.007
Tebuthiuron	40	1(1)	2.5	---	---	0.003
Terbacil	40	1(1)	2.5	---	---	0.007
<i>p,p'</i> -DDE	40	1(1)	2.5	---	---	0.003
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Prometryn	38	12(12)	31.6	---	0.004	0.005
2,5-Dichloroaniline	38	9(2)	23.7	---	0.011	0.017
2-Chloro-2,6-diethylacetanilide	38	4	10.5	---	0.010	0.012
Myclobutanil	38	2(1)	5.3	---	---	0.015
4-(Hydroxymethyl) pendimethalin	38	2(2)	5.3	---	---	0.016
Tebupirimphos	38	2(2)	5.3	---	---	0.007
1-Naphthol	38	1(1)	2.6	---	---	0.228
2-[2-Ethyl-6-methylphenyl) amino]-1-propanal	38	1(1)	2.6	---	---	0.010
3,4-Dichloroaniline	38	1	2.6	---	---	0.011
Fenamiphos sulfoxide	38	1(1)	2.6	---	---	0.008
Methidathion (Supracide)	38	1	2.6	---	---	0.010
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	36	36(36)	100	1.010	1.612	2.058
Atrazine	36	36(34)	100	1.492	3.223	6.176
Deethylatrazine	36	35(14)	97.2	0.292	0.399	0.546
Deisopropylatrazine	36	35(17)	97.2	0.120	0.201	0.260
Metalaxyl	36	35(27)	97.2	0.033	0.077	0.104
Desethyl desisopropylatrazine	36	28(20)	77.8	0.039	0.088	0.092
2,4-D	36	23(18)	63.9	0.037	0.078	0.133
Caffeine*	36	16(6)	44.4	---	0.179	0.435

* Caffeine is not a pesticide compound, however it is included in this method.

Table 19. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Higginsville Reservoir, Missouri—continued

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)--Continued						
2,4-D methyl ester	36	7(7)	19.4	---	0.018	0.041
Bentazon	36	4(4)	11.1	---	0.003	0.008
Chlorimuron-ethyl	36	4(4)	11.1	---	0.006	0.018
Dicamba	36	4(3)	11.1	---	0.047	0.126
Flumetsulam	36	4(4)	11.1	---	0.006	0.027
Acifluorfen	35	3(3)	8.6	---	---	0.022
Imazaquin	36	1(1)	2.8	---	---	0.012
MCPA	36	1	2.8	---	---	0.061
Nicosulfuron	36	1(1)	2.8	---	---	0.017
Propoxur	36	1(1)	2.8	---	---	0.005
Tebuthiuron	36	1(1)	2.8	---	---	0.027

Table 20. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at Higginsville Reservoir, Missouri

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Alachlor	11	11(1)	100	0.182	0.482	0.643
Atrazine	11	11	100	3.140	5.690	6.200
Deethylatrazine	11	11(11)	100	0.429	0.728	0.754
Metolachlor	11	11	100	1.380	2.870	3.580
Prometon	11	10(4)	90.9	0.019	0.025	0.028
Simazine	11	10	90.9	0.397	0.603	0.805
Acetochlor	11	8	72.7	0.013	0.023	0.029
Cyanazine	11	8(1)	72.7	0.013	0.021	0.021
Diazinon	11	7	63.6	0.006	0.015	0.018
Metribuzin	10	4	40.0	---	0.202	0.265
Tebuthiuron	11	1(1)	9.1	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
2-Chloro-2,6-diethylacetanilide	9	3	33.3	---	0.012	0.012
Terbutylazine	8	1(1)	12.5	---	1.500	1.500
3,4-Dichloroaniline	9	1	11.1	---	0.070	0.070
Myclobutanil	9	1(1)	11.1	---	0.006	0.006
Tebupirimphos	9	1(1)	11.1	---	0.005	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	10	10(10)	100	2.408	3.904	4.068
Deethylatrazine	10	10(6)	100	0.235	0.460	0.577
Deisopropylatrazine	10	10(9)	100	0.114	0.201	0.258
2-Hydroxyatrazine	10	9(9)	90.0	1.276	1.951	2.175
Desethyl desisopropylatrazine	10	9(7)	90.0	0.040	0.301	0.514
Metalaxyl	10	9(7)	90.0	0.037	0.074	0.077
Caffeine*	10	7(5)	70.0	0.056	0.130	0.150
2,4-D	10	4(3)	40.0	---	0.089	0.115
2,4-D methyl ester	10	2(2)	20.0	---	0.011	0.013
Flumetsulam	10	2(2)	20.0	---	0.021	0.029
Acifluorfen	9	1(1)	11.1	---	0.029	0.029
Chlorimuron-ethyl	10	1(1)	10.0	---	0.013	0.026

* Caffeine is not a pesticide compound, however it is included in this method.

Table 21. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at City of Higginsville Municipal Utilities, Missouri

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	25	25	100	0.722	1.190	1.300
Deethylatrazine	25	25(25)	100	0.100	0.249	0.296
Metolachlor	25	25	100	0.063	0.453	0.514
Simazine	25	24	96.0	0.020	0.087	0.092
Prometon	25	19(19)	76.0	0.004	0.010	0.012
Alachlor	25	14(2)	56.0	0.004	0.051	0.056
Cyanazine	25	12(1)	48.0	---	0.019	0.020
Acetochlor	25	10	40.0	---	0.011	0.022
Carbaryl	25	1(1)	4.0	---	---	0.004
Phorate	25	1(1)	4.0	---	---	0.001
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Azinphos-methyl-oxon	20	2(2)	10.0	---	0.004	0.010
2-[2-Ethyl-6-methylphenyl) amino]-1-propanal	20	1(1)	5.0	---	---	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	25	25(5)	100	0.269	0.772	1.013
2-Hydroxyatrazine	25	24(24)	96.0	0.260	0.574	1.210
Deethylatrazine	25	24(23)	96.0	0.042	0.153	0.201
Deisopropylatrazine	25	21(21)	84.0	0.013	0.048	0.071
Metalaxyl	25	21(20)	84.0	0.012	0.042	0.072
Desethyl desisopropylatrazine	25	17(17)	68.0	0.014	0.029	0.036
2,4-D	25	9(8)	36.0	---	0.035	0.131
Caffeine*	25	6(6)	24.0	---	0.024	0.035
Dicamba	25	2(2)	8.0	---	---	0.054
Imazethapyr	23	1(1)	4.3	---	---	0.004
Benomyl	25	1(1)	4.0	---	---	0.215
Bentazon	25	1(1)	4.0	---	---	0.004
Chlorimuron-ethyl	25	1(1)	4.0	---	---	0.009
Imazaquin	25	1(1)	4.0	---	---	0.008
Oryalin	25	1(1)	4.0	---	---	0.012

* Caffeine is not a pesticide compound, however it is included in this method.

Table 22. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Tar River Reservoir, North Carolina

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Deethylatrazine	10	10(10)	100	0.006	0.009	0.010
Prometon	10	10(10)	100	0.010	0.014	0.015
Atrazine	10	9	90.0	0.020	0.042	0.043
Metolachlor	10	9	90.0	0.020	0.045	0.046
Simazine	10	8	80.0	0.012	0.019	0.022
Diazinon	10	5(2)	50.0	0.001	0.011	0.012
Carbaryl	10	1(1)	10.0	---	0.002	0.004
Tebuthiuron	10	1	10.0	---	0.006	0.011
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Fenamiphos sulfone	10	1(1)	10.0	---	0.002	0.005
Metalaxyl	10	1(1)	10.0	---	0.003	0.005
Prometryn	10	1(1)	10.0	---	0.002	0.004
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	10	7(7)	70.0	0.043	0.102	0.110
Atrazine	10	6(6)	60.0	0.003	0.025	0.027
Bentazon	10	4(4)	40.0	---	0.083	0.107
Caffeine*	10	4(4)	40.0	---	0.046	0.057
Desethyl desisopropylatrazine	10	3(3)	30.0	---	0.003	0.003
Fluometuron	10	3(3)	30.0	---	0.012	0.017
Diuron	10	2(2)	20.0	---	0.042	0.069
2,4-D	10	1(1)	10.0	---	0.009	0.018
Chloramben methyl ester	10	1	10.0	---	0.063	0.126
Picloram	10	1	10.0	---	0.037	0.075

* Caffeine is not a pesticide compound, however it is included in this method.

Table 23. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at Tar River Reservoir, North Carolina

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	1	1	100	0.011	0.011	0.011
Deethylatrazine	1	1(1)	100	0.003	0.003	0.003
Metolachlor	1	1	100	0.009	0.009	0.009
Prometon	1	1(1)	100	0.011	0.011	0.011
Simazine	1	1	100	0.008	0.008	0.008
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	1	1(1)	100	0.015	0.015	0.015
Atrazine	1	1(1)	100	0.008	0.008	0.008
Caffeine*	1	1(1)	100	0.014	0.014	0.014

* Caffeine is not a pesticide compound, however it is included in this method.

Table 24. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Tar River Water Treatment Plant, North Carolina

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Prometon	10	10(10)	100	0.008	0.013	0.014
Atrazine	10	9	90.0	0.014	0.030	0.034
Deethylatrazine	10	9(9)	90.0	0.007	0.009	0.009
Metolachlor	10	9	90.0	0.012	0.016	0.016
Simazine	10	8(1)	80.0	0.008	0.016	0.018
Dacthal	10	1(1)	10.0	---	0.001	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Fenamiphos sulfone	10	2(1)	20.0	---	0.011	0.016
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	10	7(7)	70.0	0.048	0.091	0.101
Atrazine	10	6(6)	60.0	0.005	0.018	0.023
Desethyl desisopropylatrazine	10	5(5)	50.0	0.001	0.005	0.007
Metalaxyl	10	2(2)	20.0	---	0.002	0.003
2,4-D	10	1(1)	10.0	---	0.017	0.034
3-Hydroxycarbofuran	10	1(1)	10.0	---	0.005	0.009
Caffeine*	10	1(1)	10.0	---	0.015	0.031
Deethylatrazine	10	1(1)	10.0	---	0.004	0.007
Deisopropylatrazine	10	1(1)	10.0	---	0.002	0.005
Dicamba	10	1(1)	10.0	---	0.005	0.011
Fluometuron	10	1(1)	10.0	---	0.002	0.003
Neburon	10	1(1)	10.0	---	0.001	0.002
Triclopyr	10	1(1)	10.0	---	0.009	0.017

* Caffeine is not a pesticide compound, however it is included in this method.

Table 25. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at LeRoy Reservoir, New York

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	22	22	100	0.178	0.229	0.490
Deethylatrazine	22	22(22)	100	0.070	0.099	0.127
Metolachlor	22	22	100	0.093	0.243	0.442
Cyanazine	22	16(1)	72.7	0.014	0.049	0.079
Simazine	22	15(2)	68.2	0.005	0.008	0.008
EPTC	22	13(3)	59.1	0.003	0.014	0.037
Alachlor	22	9	40.9	---	0.065	0.176
Prometon	22	7(7)	31.8	---	0.007	0.008
Acetochlor	22	2	9.1	---	---	0.009
2,6-Diethylaniline	22	1(1)	4.5	---	---	0.002
Butylate	22	1(1)	4.5	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Disulfoton sulfone	20	1	5.0	---	---	0.013
Disulfotone sulfoxide	20	1(1)	5.0	---	---	0.006
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	20	20(20)	100	0.299	0.767	1.083
Atrazine	20	20(10)	100	0.103	0.175	0.219
Deethylatrazine	20	20(20)	100	0.047	0.074	0.091
Metalaxyl	20	17(16)	85.0	0.026	0.050	0.072
Deisopropylatrazine	20	14(14)	70.0	0.013	0.031	0.041
Desethyl desisopropylatrazine	20	13(13)	65.0	0.018	0.043	0.052
Bentazon	20	9(9)	45.0	---	0.120	0.344
2,4-D	20	3(3)	15.0	---	0.026	0.031
Caffeine*	20	3(3)	15.0	---	0.014	0.024
Imazaquin	20	3(3)	15.0	---	0.008	0.022
Flumetsulam	20	2(2)	10.0	---	0.012	0.088
2,4-D methyl ester	20	1(1)	5.0	---	---	0.006
Aldicarb sulfone	20	1(1)	5.0	---	---	0.007
Dicamba	20	1(1)	5.0	---	---	0.031
MCPA	20	1(1)	5.0	---	---	0.018
Metsulfuron-methyl	20	1	5.0	---	---	0.148
Neburon	20	1(1)	5.0	---	---	0.009
Oryzalin	20	1	5.0	---	---	0.071
Picloram	20	1(1)	5.0	---	---	1.441

* Caffeine is not a pesticide compound, however it is included in this method.

Table 26. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Village of LeRoy Water Department, New York

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography -- mass spectrometry; HPLC-MS, high performance liquid chromatography -- mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	21	21	100	0.162	0.225	0.459
Deethylatrazine	21	21(21)	100	0.072	0.110	0.151
Metolachlor	21	21	100	0.093	0.222	0.410
Cyanazine	21	13	61.9	0.015	0.051	0.072
Alachlor	21	8	38.1	---	0.055	0.148
Simazine	21	7(2)	33.3	---	0.008	0.008
Prometon	21	2(2)	9.5	---	---	0.008
Fonofos	20	1	5.0	---	---	0.009
2,6-Diethylaniline	21	1(1)	4.8	---	---	0.002
Acetochlor	21	1	4.8	---	---	0.014
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Azinphos-methyl-oxon	20	2(2)	10.0	---	0.013	0.026
2,5-Dichloroaniline	20	1(1)	5.0	---	---	0.004
3,5-Dichloroaniline	20	1	5.0	---	---	0.009
Iprodione	20	1(1)	5.0	---	---	0.023
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	20	20(20)	100	0.303	0.913	1.175
Atrazine	20	20(10)	100	0.115	0.159	0.199
Deethylatrazine	20	20(20)	100	0.039	0.067	0.258
Metalaxyl	20	18(18)	90.0	0.022	0.047	0.055
Desethyl desisopropylatrazine	20	12(12)	60.0	0.013	0.037	0.043
Deisopropylatrazine	20	11(11)	55.0	0.011	0.037	0.059
Flumetsulam	20	3(3)	15.0	---	0.028	0.037
Imazaquin	20	3(3)	15.0	---	0.011	0.111
2,4-D	20	2(2)	10.0	---	0.011	0.024
2,4-DB	20	2(2)	10.0	---	0.003	0.011
Bentazon	20	2(2)	10.0	---	0.004	0.011
Dichlorprop	20	1(1)	5.0	---	---	0.018
Benomyl	20	1(1)	5.0	---	---	0.005
Dicamba	20	1(1)	5.0	---	---	0.018
Triclopyr	20	1(1)	5.0	---	---	0.041

Table 27. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at East Fork Lake, Ohio

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Acetochlor	21	21	100	0.031	0.136	0.284
Alachlor	21	21	100	0.014	0.053	0.105
Atrazine	21	21	100	0.230	3.240	3.860
Cyanazine	21	21	100	0.149	0.210	0.233
Deethylatrazine	21	21(21)	100	0.074	0.448	0.668
Metolachlor	21	21	100	0.294	0.682	1.010
Simazine	21	21	100	0.032	0.437	0.625
Metribuzin	21	19	90.5	0.012	0.042	0.095
Tebuthiuron	21	17(6)	81.0	0.011	0.015	0.015
Prometon	21	14(14)	66.7	0.007	0.013	0.013
Diazinon	21	10(1)	47.6	---	0.013	0.015
Chlorpyrifos	21	2(2)	9.5	---	---	0.004
Carbaryl	21	1(1)	4.8	---	---	0.012
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	21	5(5)	23.8	---	0.004	0.005
2-[2-Ethyl-6-methylphenyl)amino]-1-propan		21	1(1)	4.8	---	---
Metalaxyl	21	1(1)	4.8	---	---	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	19	19(12)	100	0.154	1.888	2.718
Deethylatrazine	19	19(18)	100	0.038	0.381	0.458
Deisopropylatrazine	19	19(18)	100	0.024	0.225	0.269
2-Hydroxyatrazine	18	17(17)	94.4	0.334	0.543	1.636
Desethyl desisopropylatrazine	19	17(15)	89.5	0.030	0.071	0.134
Metalaxyl	19	14(13)	73.7	0.016	0.045	0.086
2,4-D	19	13(6)	68.4	0.076	0.120	0.139
Tebuthiuron	19	13(13)	68.4	0.006	0.010	0.011
Caffeine*	19	10(10)	52.6	0.020	0.035	0.047
Chlorimuron-ethyl	19	9(7)	47.4	---	0.042	0.050
2,4-D methyl ester	19	8(8)	42.1	---	0.016	0.030
Bentazon	19	7(7)	36.8	---	0.042	0.079
Imazaquin	19	6(6)	31.6	---	0.065	0.084
Imazethapyr	18	4(4)	22.2	---	0.084	0.111
Diphenamid	19	3(3)	15.8	---	0.026	0.038
Acifluorfen	18	2(2)	11.1	---	0.013	0.015
Diuron	19	2(2)	10.5	---	0.013	0.020
Picloram	19	1	5.3	---	---	0.430
Terbacil	19	1(1)	5.3	---	---	0.013

* Caffeine is not a pesticide compound, however it is included in this method.

Table 28. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at East Fork Lake, Ohio

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; ().qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Acetochlor	11	11	100	0.020	0.037	0.041
Alachlor	11	11(1)	100	0.011	0.033	0.129
Atrazine	11	11	100	0.389	0.465	2.390
Cyanazine	11	11	100	0.163	0.178	0.250
Deethylatrazine	11	11(11)	100	0.082	0.121	0.182
Metolachlor	11	11	100	0.238	0.449	0.689
Simazine	11	11	100	0.026	0.034	0.035
Tebuthiuron	11	9(3)	81.8	0.011	0.012	0.012
Prometon	11	6(6)	54.5	0.003	0.005	0.007
Metribuzin	11	3	27.3	---	0.010	0.013
<i>p,p'</i> -DDE	11	2(2)	18.2	---	0.001	0.002
Chlorpyrifos	11	1	9.1	---	---	0.006
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	10	1(1)	10.0	---	0.002	0.003
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	11	11(6)	100	0.221	0.331	0.358
Deethylatrazine	11	11(11)	100	0.048	0.057	0.065
Desethyl desisopropylatrazine	11	10(10)	90.9	0.022	0.043	0.045
Metalaxyl	11	10(10)	90.9	0.012	0.023	0.027
2-Hydroxyatrazine	10	9(9)	90.0	0.428	0.584	0.598
2,4-D	11	9(9)	81.8	0.042	0.058	0.135
Deisopropylatrazine	11	9(9)	81.8	0.023	0.030	0.033
Tebuthiuron	11	7(7)	63.6	0.002	0.009	0.009
Caffeine*	11	6(6)	54.5	0.027	0.047	0.081
2,4-D methyl ester	11	5(5)	45.5	---	0.023	0.033
Chlorimuron-ethyl	11	4(4)	36.4	---	0.020	0.021
Bentazon	11	3(3)	27.3	---	0.007	0.010
Acifluorfen	10	2(2)	20.0	---	0.003	0.003
Dinoseb	11	1(1)	9.1	---	---	0.001
Imazaquin	11	1(1)	9.1	---	---	0.010

* Caffeine is not a pesticide compound, however it is included in this method.

Table 29. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Clermont Water Authority, Ohio

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	21	20(2)	95.2	0.095	0.166	0.208
Metolachlor	21	20	95.2	0.041	0.238	0.384
Deethylatrazine	21	18(18)	85.7	0.017	0.061	0.078
Acetochlor	21	15	71.4	0.016	0.032	0.045
Alachlor	21	14(1)	66.7	0.006	0.013	0.027
Simazine	21	14(1)	66.7	0.010	0.020	0.024
Cyanazine	21	10	47.6	---	0.135	0.211
Prometon	21	5(5)	23.8	---	0.003	0.007
Tebuthiuron	21	5(5)	23.8	---	0.009	0.009
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	19	16(16)	84.2	0.059	0.404	0.463
Atrazine	20	16(13)	80.0	0.045	0.123	0.160
Desethyl desisopropylatrazine	20	16(16)	80.0	0.014	0.022	0.030
Deethylatrazine	19	13(13)	68.4	0.008	0.044	0.053
Metalaxyl	20	13(13)	65.0	0.009	0.024	0.025
Deisopropylatrazine	20	8(8)	40.0	---	0.021	0.032
2,4-D	20	5(4)	25.0	---	0.056	0.089
Imazaquin	20	5(5)	25.0	---	0.012	0.014
Caffeine*	20	4(4)	20.0	---	0.021	0.041
Tebuthiuron	20	3(3)	15.0	---	0.004	0.006
Imazethapyr	19	2(2)	10.5	---	0.036	0.038
Acifluorfen	19	1(1)	5.3	---	---	0.016
2,4-D methyl ester	20	1(1)	5.0	---	---	0.009
Bentazon	20	1(1)	5.0	---	---	0.009
Dicamba	20	1(1)	5.0	---	---	0.025

* Caffeine is not a pesticide compound, however it is included in this method.

Table 30. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Lake Arcadia, Oklahoma

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	41	41	100	0.286	0.595	0.745
Deethylatrazine	41	41(41)	100	0.046	0.067	0.095
Prometon	41	41	100	0.086	0.113	0.138
Simazine	41	41	100	0.971	1.300	1.520
Diazinon	41	40	97.6	0.051	0.080	0.101
Metolachlor	41	40(2)	97.6	0.012	0.029	0.039
Pronamide	41	34	82.9	0.023	0.038	0.048
Tebuthiuron	41	33(5)	80.5	0.017	0.023	0.024
Dacthal	41	7(7)	17.1	---	0.002	0.004
Terbacil	41	4(4)	9.8	---	---	0.024
Chlorpyrifos	41	2(1)	4.9	---	---	0.004
Benfluralin	41	1(1)	2.4	---	---	0.001
<i>p,p'</i> -DDE	41	1(1)	2.4	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	41	31	75.6	0.013	0.022	0.034
2-[2-Ethyl-6-methylphenyl) amino]-1-propanal	41	6(4)	14.6	---	0.011	0.037
1,4-Naphthoquinone	41	1(1)	2.4	---	---	0.005
4-Chloro-2-methylphenol	41	1(1)	2.4	---	---	0.003
Azinphos-methyl-oxon	41	1	2.4	---	---	0.263
Isofenphos	41	1(1)	2.4	---	---	0.007
Metalaxyl	41	1(1)	2.4	---	---	0.005
Myclobutanil	41	1(1)	2.4	---	---	0.006
Prometryn	41	1(1)	2.4	---	---	0.003
Tefluthrin metabolite [R 119364]	41	1(1)	2.4	---	---	0.004
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	39	39(39)	100	0.099	0.321	0.357
Atrazine	39	39(8)	100	0.199	0.519	0.618
Deisopropylatrazine	39	39(27)	100	0.133	0.223	0.386
Deethylatrazine	39	38(38)	97.4	0.029	0.038	0.051
Diuron	39	38(2)	97.4	0.278	0.379	0.435
Caffeine*	39	35(24)	89.7	0.073	0.102	0.133
2,4-D	39	34(19)	87.2	0.073	0.098	0.154
Tebuthiuron	39	34(34)	87.2	0.008	0.013	0.015
Bromacil	39	28(26)	71.8	0.043	0.084	0.136
Sulfometuron-methyl	39	28(16)	71.8	0.033	0.126	0.160
Desethyl desisopropylatrazine	39	27(22)	69.2	0.034	0.077	0.114
Dicamba	39	22(17)	56.4	0.037	0.105	0.192
Benomyl	39	14(13)	35.9	---	0.031	0.038
2,4-D methyl ester	39	8(8)	20.5	---	0.016	0.041
Metalaxyl	39	6(6)	15.4	---	0.003	0.351

* Caffeine is not a pesticide compound, however it is included in this method.

Table 30. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Lake Arcadia, Oklahoma—continued.

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)--continued						
Dichlorprop	39	2(2)	5.1	---	---	0.036
Bentazon	39	2(2)	5.1	---	---	0.011
Imazethapyr	38	1(1)	2.6	---	---	0.103
Clopyralid	39	1(1)	2.6	---	---	0.024
MCPA	39	1(1)	2.6	---	---	0.004
Metsulfuron-methyl	39	1(1)	2.6	---	---	1.194
Triclopyr	39	1(1)	2.6	---	---	0.017

Table 31. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at Lake Arcadia, Oklahoma

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	10	10	100	0.299	0.659	0.687
Deethylatrazine	10	10(10)	100	0.032	0.056	0.059
Prometon	10	10(3)	100	0.060	0.104	0.107
Simazine	10	10	100	0.629	1.500	1.580
Metolachlor	10	8	80.0	0.014	0.034	0.038
Tebuthiuron	10	8(3)	80.0	0.012	0.022	0.024
Diazinon	10	7(2)	70.0	0.027	0.096	0.111
Pronamide	10	6	60.0	0.016	0.040	0.045
<i>p,p'</i> -DDE	10	2(2)	20.0	---	0.002	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
3,4-Dichloroaniline	10	5(1)	50.0	0.003	0.029	0.031
Azinphos-methyl-oxon	10	1	10.0	---	0.150	0.300
Metalaxyl	10	1(1)	10.0	---	0.003	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	10	10(6)	100	0.174	0.600	0.659
Deisopropylatrazine	10	10(8)	100	0.048	0.155	0.156
2-Hydroxyatrazine	10	9(9)	90.0	0.164	0.315	0.346
Desethyl desisopropylatrazine	10	9(9)	90.0	0.013	0.037	0.038
Deethylatrazine	10	8(8)	80.0	0.013	0.036	0.037
Diuron	10	8(3)	80.0	0.141	0.425	0.448
Tebuthiuron	10	6(6)	60.0	0.004	0.013	0.015
Bromacil	10	5(5)	50.0	0.016	0.069	0.072
Caffeine*	10	5(2)	50.0	0.025	0.220	0.329
Sulfometuron-methyl	10	5(1)	50.0	0.045	0.162	0.194
Dicamba	10	3(3)	30.0	---	0.065	0.067
Terbacil	10	2(2)	20.0	---	0.046	0.051
2,4-D	10	1(1)	10.0	---	0.033	0.065
2,4-DB	10	1	10.0	---	0.027	0.054
Benomyl	10	1(1)	10.0	---	0.014	0.027
Metalaxyl	10	1(1)	10.0	---	0.001	0.002

* Caffeine is not a pesticide compound, however it is included in this method.

Table 32. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Edmonds Water Supply, Oklahoma

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	19	19	100	0.269	0.346	0.385
Deethylatrazine	19	19(19)	100	0.040	0.062	0.062
Prometon	19	19	100	0.072	0.084	0.103
Simazine	19	19	100	0.395	0.463	0.571
Metolachlor	19	18	94.7	0.007	0.010	0.012
Tebuthiuron	19	18(2)	94.7	0.022	0.031	0.032
Pronamide	19	8	42.1	---	0.012	0.017
Dacthal	19	4(4)	21.1	---	0.002	0.003
Trifluralin	19	1	5.3	---	---	0.005
<i>p,p'</i> -DDE	19	1(1)	5.3	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
2-[2-Ethyl-6-methylphenyl]amino]-1-propanol	19	4(4)	21.1	---	0.005	0.014
Metalaxyl	19	1(1)	5.3	---	---	0.004
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	19	19(7)	100	0.163	0.337	0.416
2-Hydroxyatrazine	19	17(17)	89.5	0.060	0.308	0.345
Tebuthiuron	19	17(17)	89.5	0.010	0.017	0.018
Deisopropylatrazine	19	15(9)	78.9	0.053	0.137	0.178
Deethylatrazine	19	14(14)	73.7	0.012	0.023	0.037
2,4-D	19	12(12)	63.2	0.026	0.044	0.054
Desethyl desisopropylatrazine	19	11(11)	57.9	0.004	0.035	0.039
Dicamba	19	8(8)	42.1	---	0.049	0.063
Sulfometuron-methyl	19	6(6)	31.6	---	0.008	0.024
Oxamyl oxime	19	2(2)	10.5	---	0.013	0.014
Triclopyr	19	2(2)	10.5	---	0.012	0.013
Bendiocarb	19	1(1)	5.3	---	---	0.004
Caffeine*	19	1(1)	5.3	---	---	0.009
Clpyralid	19	1(1)	5.3	---	---	0.027

* Caffeine is not a pesticide compound, however it is included in this method.

Table 33. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Blue Marsh Reservoir, Tulpehocken Creek, Pennsylvania

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	23	23	100	0.094	0.761	1.600
Deethylatrazine	23	23(23)	100	0.104	0.197	0.255
Metolachlor	23	23	100	0.025	0.268	0.520
Simazine	23	22	95.7	0.036	0.092	0.123
Prometon	23	21(21)	91.3	0.009	0.015	0.017
Tebuthiuron	23	11(11)	47.8	---	0.007	0.009
Acetochlor	23	10	43.5	---	0.036	0.048
Alachlor	23	10(1)	43.5	---	0.011	0.021
Cyanazine	23	9(1)	39.1	---	0.026	0.037
Diazinon	23	7(1)	30.4	---	0.007	0.015
Pendimethalin	23	6	26.1	---	0.022	0.125
Chlorpyrifos	23	5(2)	21.7	---	0.004	0.012
Carbaryl	23	4(4)	17.4	---	0.008	0.047
Trifluralin	23	3(3)	13.0	---	0.001	0.002
<i>p,p'</i> -DDE	23	3(3)	13.0	---	0.002	0.002
Carbofuran	23	2(2)	8.7	---	---	0.019
Dacthal	23	1(1)	4.3	---	---	0.003
EPTC	23	1(1)	4.3	---	---	0.002
Linuron	23	1	4.3	---	---	0.010
Napropamide	23	1(1)	4.3	---	---	0.003
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Dimethoate	24	3(1)	12.5	---	0.006	0.022
Endosulfan sulfate	24	3(2)	12.5	---	0.005	0.009
Tefluthrin metabolite [R 152912]	24	2(1)	8.3	---	---	0.021
1,4-Naphthoquinone	24	1(1)	4.2	---	---	0.004
1-Naphthol	24	1(1)	4.2	---	---	0.006
2-[2-Ethyl-6-methylphenyl) amino]-1-propanal	24	1(1)	4.2	---	---	0.006
3,4-Dichloroaniline	24	1(1)	4.2	---	---	0.004
Hexazinone	24	1(1)	4.2	---	---	0.005
Tefluthrin	24	1(1)	4.2	---	---	0.003
Tefluthrin metabolite [R 119364]	24	1(1)	4.2	---	---	0.005
Tebupirimphos	24	1(1)	4.2	---	---	0.006
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Deethylatrazine	24	24(24)	100	0.063	0.120	0.228
Atrazine	24	23(14)	95.8	0.063	0.553	1.253
2-Hydroxyatrazine	24	22(22)	91.7	0.073	0.206	0.295
Desethyl desisopropylatrazine	24	22(13)	91.7	0.047	0.079	0.102
Caffeine*	24	15(14)	62.5	0.035	0.074	0.085
Deisopropylatrazine	24	14(14)	58.3	0.011	0.033	0.118
Bentazon	24	8(8)	33.3	---	0.008	0.013
Bromacil	24	7(7)	29.2	---	0.012	0.014

* Caffeine is not a pesticide compound, however it is included in this method.

Table 33. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Blue Marsh Reservoir, Tulpehocken Creek, Pennsylvania—continued

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)--continued						
2,4-D	24	5(5)	20.8	---	0.026	0.056
Benomyl	24	5(5)	20.8	---	0.016	0.030
Dicamba	24	4(4)	16.7	---	0.045	0.094
Metalaxyl	24	4(4)	16.7	---	0.007	0.014
Diuron	24	3(3)	12.5	---	0.003	0.041
Imazethapyr	21	2(2)	9.5	---	---	0.041
Imazaquin	23	2(2)	8.7	---	---	0.351
Carbofuran	24	2(2)	8.3	---	---	0.010
Tebuthiuron	24	2(2)	8.3	---	---	0.005
Carbaryl	24	1(1)	4.2	---	---	0.005
Dinoseb	24	1(1)	4.2	---	---	0.003
Nicosulfuron	24	1(1)	4.2	---	---	0.022
Oryzalin	24	1	4.2	---	---	0.071

Table 34. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Western Berks Water Authority, Pennsylvania

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	23	23	100	0.056	0.470	0.740
Deethylatrazine	23	23(23)	100	0.069	0.119	0.200
Metolachlor	23	23	100	0.015	0.155	0.245
Simazine	23	22(1)	95.7	0.016	0.039	0.056
Prometon	23	21(21)	91.3	0.008	0.012	0.012
Acetochlor	23	9(1)	39.1	---	0.016	0.025
Alachlor	23	8(1)	34.8	---	0.008	0.010
Cyanazine	23	7(1)	30.4	---	0.014	0.019
Tebuthiuron	23	7(7)	30.4	---	0.005	0.005
Carbofuran	23	3(3)	13.0	---	0.008	0.010
Pendimethalin	23	3	13.0	---	0.006	0.009
<i>p,p'</i> -DDE	23	2(2)	8.7	---	---	0.002
Carbaryl	23	1(1)	4.3	---	---	0.003
EPTC	23	1(1)	4.3	---	---	0.001
Trifluralin	23	1(1)	4.3	---	---	0.001
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Endosulfan sulfate	24	2(2)	8.3	---	---	0.005
Terbufos-O-analogue sulfone	24	2(2)	8.3	---	---	0.015
1,4-Naphthoquinone	24	1(1)	4.2	---	---	0.003
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	23	23(16)	100	0.034	0.271	0.588
Deethylatrazine	23	23(23)	100	0.035	0.079	0.138
Desethyl desisopropylatrazine	23	22(22)	95.7	0.031	0.046	0.055
2-Hydroxyatrazine	23	20(20)	87.0	0.044	0.099	0.200
Deisopropylatrazine	23	13(13)	56.5	0.003	0.020	0.042
Caffeine*	23	8(8)	34.8	---	0.023	0.071
Bentazon	23	5(5)	21.7	---	0.005	0.011
Metalaxyl	23	4(4)	17.4	---	0.005	0.007
2,4-D	23	3(3)	13.0	---	0.019	0.035
Dicamba	23	3(3)	13.0	---	0.019	0.055
Bromacil	23	1(1)	4.3	---	---	0.481
Carbofuran	23	1(1)	4.3	---	---	0.004
Dinoseb	23	1(1)	4.3	---	---	0.002
Metsulfuron-methyl	23	1(1)	4.3	---	---	0.030
Propiconazole	23	1(1)	4.3	---	---	0.001
Tebuthiuron	23	1(1)	4.3	---	---	0.003

* Caffeine is not a pesticide compound, however it is included in this method.

Table 35. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at South Pacolet Reservoir, South Carolina

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Simazine	45	45	100	0.030	0.051	0.059
Atrazine	45	38(6)	84.4	0.005	0.008	0.010
Tebuthiuron	45	24(23)	53.3	0.003	0.008	0.008
Prometon	45	23(23)	51.1	0.002	0.005	0.013
Deethylatrazine	45	19(19)	42.2	---	0.004	0.005
Metolachlor	45	19(9)	42.2	---	0.005	0.006
Azinphos-methyl	43	7(7)	16.3	---	0.054	0.144
Diazinon	45	5(5)	11.1	---	0.001	0.003
Chlorpyrifos	45	4(4)	8.9	---	---	0.002
<i>p,p'</i> -DDE	45	3(3)	6.7	---	---	0.002
Dacthal	45	2(2)	4.4	---	---	0.001
Dieldrin	45	1(1)	2.2	---	---	0.002
Molinate	45	1(1)	2.2	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
1,4-Naphthoquinone	44	1(1)	2.3	---	---	0.002
1-Naphthol	44	1(1)	2.3	---	---	0.008
Hexazinone	44	1(1)	2.3	---	---	0.007
Metalaxyl	44	1(1)	2.3	---	---	0.011
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Deisopropylatrazine	44	20(20)	45.5	---	0.011	0.016
Tebuthiuron	44	19(19)	43.2	---	0.005	0.007
Desethyl desisopropylatrazine	44	16(16)	36.4	---	0.007	0.047
Bentazon	44	12(12)	27.3	---	0.007	0.013
2,4-D	44	10(10)	22.7	---	0.029	0.078
Atrazine	44	10(10)	22.7	---	0.003	0.021
Diuron	44	7(7)	15.9	---	0.007	0.068
Caffeine*	44	5(4)	11.4	---	0.005	88.000
2-Hydroxyatrazine	44	4(4)	9.1	---	---	0.041
Metalaxyl	44	2(2)	4.5	---	---	0.015
Benomyl	43	1(1)	2.3	---	---	0.006
Dichlorprop	44	1(1)	2.3	---	---	0.021
2,4-D methyl ester	44	1(1)	2.3	---	---	0.016
Carbaryl	44	1(1)	2.3	---	---	0.006
Deethylatrazine	44	1(1)	2.3	---	---	0.008
Dicamba	44	1(1)	2.3	---	---	0.049
Dinoseb	44	1(1)	2.3	---	---	0.003
Imidacloprid	44	1(1)	2.3	---	---	0.030
Metsulfuron-methyl	44	1(1)	2.3	---	---	0.168
Propiconazole	44	1(1)	2.3	---	---	0.004
Siduron	44	1(1)	2.3	---	---	0.007
Triclopyr	44	1(1)	2.3	---	---	0.087

* Caffeine is not a pesticide compound, however it is included in this method.

Table 36. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at South Pacolet Reservoir, South Carolina

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Simazine	16	16	100	0.041	0.047	0.047
Atrazine	16	13(3)	81.3	0.005	0.006	0.007
Tebuthiuron	16	9(9)	56.3	0.006	0.009	0.010
Deethylatrazine	16	8(8)	50.0	---	0.003	0.004
Metolachlor	16	5(2)	31.3	---	0.005	0.005
Prometon	16	3(3)	18.8	---	0.004	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Desethyl desisopropylatrazine	15	9(9)	60.0	0.002	0.005	0.006
Tebuthiuron	15	6(6)	40.0	---	0.005	0.006
Caffeine*	15	3(3)	20.0	---	0.015	0.016
Deisopropylatrazine	15	3(3)	20.0	---	0.009	0.010
Bentazon	15	2(2)	13.3	---	0.002	0.005
2-Hydroxyatrazine	15	1(1)	6.7	---	---	0.009
Atrazine	15	1(1)	6.7	---	---	0.002
Bendiocarb	15	1(1)	6.7	---	---	0.001
Diuron	15	1(1)	6.7	---	---	0.011
Metsulfuron-methyl	15	1(1)	6.7	---	---	0.003
Terbacil	15	1(1)	6.7	---	---	0.021

* Caffeine is not a pesticide compound, however it is included in this method.

Table 37. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Spartanburg Waterworks, South Carolina

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Simazine	27	27	100	0.027	0.039	0.051
Atrazine	27	23(8)	85.2	0.004	0.007	0.008
Deethylatrazine	27	14(14)	51.9	0.001	0.003	0.004
Tebuthiuron	27	11(11)	40.7	---	0.006	0.008
Metolachlor	27	9(3)	33.3	---	0.005	0.005
Prometon	27	7(7)	25.9	---	0.003	0.004
Azinphos-methyl	25	5(5)	20.0	---	0.038	0.114
<i>p,p'</i> -DDE	27	2(2)	7.4	---	---	0.002
Pronamide	27	1(1)	3.7	---	---	0.003
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
2-[2-Ethyl-6-methylphenyl)amino]-1-propanol	26	1(1)	3.8	---	---	0.007
Bifenthrin	26	1(1)	3.8	---	---	0.002
Metalaxyl	26	1(1)	3.8	---	---	0.009
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Deisopropylatrazine	26	9(9)	34.6	---	0.010	0.013
Desethyl desisopropylatrazine	26	8(8)	30.8	---	0.018	0.036
Tebuthiuron	26	8(8)	30.8	---	0.004	0.005
Bentazon	26	4(4)	15.4	---	0.005	0.010
Atrazine	26	3(3)	11.5	---	0.002	0.003
2,4-D	26	2(2)	7.7	---	---	0.021
2-Hydroxyatrazine	26	2(2)	7.7	---	---	0.007
Bromacil	26	1(1)	3.8	---	---	0.013
Dicamba	26	1(1)	3.8	---	---	0.016
Diuron	26	1(1)	3.8	---	---	0.008
Metalaxyl	26	1(1)	3.8	---	---	0.004
Oryzalin	26	1(1)	3.8	---	---	0.037

Table 38. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Lake Mitchell, South Dakota

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	21	21	100	1.320	2.310	2.530
Cyanazine	21	21(1)	100	0.025	0.035	0.038
Deethylatrazine	21	21(21)	100	0.273	0.363	0.444
Metolachlor	21	21	100	0.025	0.061	0.079
Prometon	21	21(21)	100	0.010	0.012	0.015
Acetochlor	21	19	90.5	0.030	0.249	0.334
Simazine	21	15(2)	71.4	0.007	0.014	0.016
EPTC	21	10	47.6	---	0.030	0.036
Alachlor	21	3	14.3	---	0.011	0.013
Tebuthiuron	21	2(2)	9.5	---	---	0.004
Trifluralin	21	2(2)	9.5	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
4-(Hydroxymethyl)pendimethalin	21	1(1)	4.8	---	---	0.045
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	21	21(21)	100	0.725	1.350	1.664
Atrazine	21	21(12)	100	1.098	1.745	2.508
Deethylatrazine	21	21(10)	100	0.199	0.259	0.302
Deisopropylatrazine	21	21(14)	100	0.073	0.108	0.160
2,4-D	21	17(6)	81.0	0.082	0.102	0.414
Desethyl desisopropylatrazine	21	14(11)	66.7	0.027	0.062	0.074
Picloram	21	8	38.1	---	0.259	0.360
Nicosulfuron	21	7(7)	33.3	---	0.086	0.139
2,4-D methyl ester	21	6(6)	28.6	---	0.011	0.054
Dicamba	21	4(3)	19.0	---	0.030	0.104
Metalaxyl	21	4(4)	19.0	---	0.007	0.008
Imazethapyr	19	2(2)	10.5	---	0.071	0.133
Bentazon	21	1(1)	4.8	---	---	0.015
Caffeine*	21	1(1)	4.8	---	---	0.019
Chlorimuron-ethyl	21	1(1)	4.8	---	---	0.021
Diuron	21	1(1)	4.8	---	---	0.010
Oryzalin	21	1	4.8	---	---	0.127
Tebuthiuron	21	1(1)	4.8	---	---	0.008

* Caffeine is not a pesticide compound, however it is included in this method.

Table 39. Statistical summary of pesticides and degradates detected in water samples from the reservoir-outflow monitoring site at Lake Mitchell, South Dakota

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Acetochlor	9	9	100	0.102	0.395	0.395
Atrazine	9	9	100	1.720	2.660	2.660
Cyanazine	9	9	100	0.032	0.065	0.065
Deethylatrazine	9	9(9)	100	0.151	0.395	0.395
Metolachlor	9	9	100	0.039	0.083	0.083
Prometon	9	9(9)	100	0.010	0.018	0.018
Simazine	9	9	100	0.013	0.016	0.016
Alachlor	9	4	44.4	---	0.017	0.017
EPTC	9	4	44.4	---	0.038	0.038
Trifluralin	9	2(2)	22.2	---	0.003	0.003
Carbaryl	9	1(1)	11.1	---	0.001	0.001
Tebuthiuron	9	1(1)	11.1	---	0.006	0.006
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
2,5-Dichloroaniline	9	1(1)	11.1	---	0.005	0.005
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	9	9(9)	100	0.999	1.913	1.913
Atrazine	9	9(8)	100	1.466	1.821	1.821
Deethylatrazine	9	9(3)	100	0.129	0.237	0.237
Deisopropylatrazine	9	9(6)	100	0.058	0.089	0.089
2,4-D	9	8(3)	88.9	0.095	0.702	0.702
Desethyl desisopropylatrazine	9	7(7)	77.8	0.024	0.058	0.058
2,4-D methyl ester	9	4(4)	44.4	---	0.077	0.077
Nicosulfuron	9	3(3)	33.3	---	0.128	0.128
Imazethapyr	8	1(1)	12.5	---	0.027	0.027
Chlorimuron-ethyl	9	1(1)	11.1	---	0.023	0.023
Diuron	9	1(1)	11.1	---	0.011	0.011
Metalaxyl	9	1(1)	11.1	---	0.007	0.007

Table 40. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at Mitchell Water Department, South Dakota

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	22	22	100	1.165	2.110	2.470
Cyanazine	22	22(1)	100	0.024	0.038	0.051
Deethylatrazine	22	22(22)	100	0.244	0.328	0.352
Metolachlor	22	22	100	0.024	0.058	0.072
Prometon	22	22(22)	100	0.010	0.013	0.017
Acetochlor	22	21	95.5	0.027	0.289	0.395
Simazine	22	15(2)	68.2	0.006	0.012	0.014
EPTC	22	11	50.0	0.002	0.019	0.029
Alachlor	22	4	18.2	---	0.009	0.011
Tebuthiuron	22	3(3)	13.6	---	0.002	0.004
Trifluralin	22	2(2)	9.1	---	---	0.002
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
2,5-Dichloroaniline	21	1	4.8	---	---	0.009
4-(Hydroxymethyl)pendimethalin	21	1(1)	4.8	---	---	0.029
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	22	22(22)	100	0.765	1.344	1.785
Atrazine	22	22(11)	100	1.032	1.728	1.944
Deethylatrazine	22	22(11)	100	0.172	0.206	0.267
Deisopropylatrazine	22	22(20)	100	0.055	0.071	0.141
2,4-D	22	19(11)	86.4	0.070	0.337	0.634
2,4-D methyl ester	22	13(12)	59.1	0.008	0.055	0.136
Desethyl desisopropylatrazine	22	13(12)	59.1	0.018	0.054	0.069
Picloram	22	11(1)	50.0	0.047	0.276	0.389
Nicosulfuron	22	8(8)	36.4	---	0.074	0.093
Dicamba	22	4(3)	18.2	---	0.046	0.147
Chlorimuron-ethyl	22	2(2)	9.1	---	---	0.026
Diuron	22	2(2)	9.1	---	---	0.029
Metalaxyl	22	2(2)	9.1	---	---	0.010
Bentazon	22	1(1)	4.5	---	---	0.015
Oryzalin	22	1	4.5	---	---	0.095

Table 41. Statistical summary of pesticides and degradates detected in water samples from the water-supply intake monitoring site at Lake Waxahachie, Texas

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	22	22	100	0.531	0.577	0.612
Deethylatrazine	22	22(22)	100	0.104	0.128	0.137
Metolachlor	22	22	100	0.045	0.066	0.078
Simazine	22	18	81.8	0.016	0.018	0.021
Tebuthiuron	22	10(10)	45.5	---	0.006	0.008
Diazinon	22	6(5)	27.3	---	0.004	0.004
Prometon	22	6(6)	27.3	---	0.006	0.008
<i>p,p'</i> -DDE	22	6(6)	27.3	---	0.002	0.003
Alachlor	22	1(1)	4.5	---	---	0.004
Analysis of Moderate-Use Pesticides and Degradates by GC-MS (NWQL provisional method 9002)						
Prometryn	22	17(9)	77.3	0.006	0.010	0.013
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
Atrazine	22	22(5)	100	0.359	0.533	0.741
Deethylatrazine	22	22(22)	100	0.052	0.073	0.098
2-Hydroxyatrazine	22	19(19)	86.4	0.425	0.549	0.714
Deisopropylatrazine	22	19(19)	86.4	0.010	0.024	0.038
Desethyl desisopropylatrazine	22	17(17)	77.3	0.007	0.014	0.016
2,4-D	22	11(10)	50.0	0.009	0.074	0.079
Caffeine*	22	5(5)	22.7	---	0.027	0.038
Tebuthiuron	22	3(3)	13.6	---	0.002	0.005
2,4-D methyl ester	22	2(2)	9.1	---	---	0.030
Bentazon	22	2(2)	9.1	---	---	0.006
Diuron	22	2(2)	9.1	---	---	0.008
Diphenamid	22	1(1)	4.5	---	---	0.002
Metalaxyl	22	1(1)	4.5	---	---	0.003

* Caffeine is not a pesticide compound, however it is included in this method.

Table 42. Statistical summary of pesticides and degradates detected in water samples from the finished-water monitoring site at City of Waxahachie Water Treatment Plant, Texas

[Concentrations shown in micrograms per liter; --- indicates value reported as less than the method reporting level; GC-MS, gas chromatography – mass spectrometry; HPLC-MS, high performance liquid chromatography – mass spectrometry; (), qualified estimates of pesticide concentrations-- for concentrations quantified less than the method reporting level and for compounds with low and variable recoveries based on method performance]

Compound	Number of analyses	Detections (qualified estimates)	Detection frequency, in percent	Median value	90 th percentile value	Maximum value
Analysis of Pesticides by GC-MS (NWQL method 2001)						
Atrazine	9	9	100	0.515	0.589	0.589
Deethylatrazine	9	9(9)	100	0.111	0.134	0.134
Metolachlor	9	9	100	0.039	0.050	0.050
Simazine	9	8	88.9	0.017	0.020	0.020
Tebuthiuron	9	5(5)	55.6	0.005	0.008	0.008
Prometon	9	3(3)	33.3	---	0.008	0.008
Analysis of Pesticides and Degradates by HPLC-MS (NWQL provisional method 9060)						
2-Hydroxyatrazine	8	8(8)	100	0.480	0.728	0.728
Atrazine	8	8(1)	100	0.389	0.717	0.717
Deethylatrazine	8	8(8)	100	0.066	0.089	0.089
Deisopropylatrazine	8	8(8)	100	0.014	0.020	0.020
Desethyl desisopropylatrazine	8	6(6)	75.0	0.010	0.013	0.013
2,4-D	8	4(4)	50.0	0.014	0.060	0.060
Tebuthiuron	8	1(1)	12.5	---	0.003	0.003