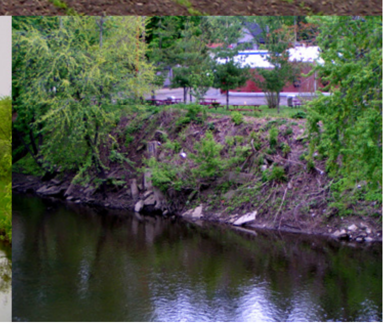
In cooperation with Michigan Department of Environmental Quality

Screening for the Pesticides Atrazine, Chlorpyrifos, Diazinon, Metolachlor, and Simazine in Selected Michigan Streams, March–November 2005



Scientific Investigations Report 2007–5077

U.S. Department of the Interior
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Cover.

Top: Emerging crops on a farm field in the Lake St. Clair Watershed, Michigan (Photograph by Cyndi Rachol, U.S. Geological Survey)

Bottom Left: Black River, Michigan (Photograph by Lisa Fogarty, U.S. Geological Survey)

Bottom Middle: Pine River, Michigan (Photograph by Lisa Fogarty, U.S. Geological Survey)

Bottom Right: Grand River at Lansing, Michigan (Photograph by Lisa Fogarty, U.S. Geological Survey)

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U.S. Geological Survey
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Conversion Factors, Vertical Datum, and Abbreviations

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=(1.8×°C)+32

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

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

Abbreviations

µg/L	Microgram(s) per liter
EWI	Equal Width Increment
GIS	Geographic Information Systems
L-HA	Lifetime Health Advisory
MCL	Maximum Contaminant Level
MDEQ	Michigan Department of Environmental Quality
MDL	Method Detection Limit
mL	Milliliter
NAWQA	National Water Quality Assessment
RFD	Reference Dose
USGS	U.S. Geological Survey
WCMP	Water Chemistry Monitoring Program

Screening for the Pesticides Atrazine, Chlorpyrifos, Diazinon, Metolachlor, and Simazine in Selected Michigan Streams, March–November 2005

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Abstract

From March through November 2005, the U.S. Geological Survey, in cooperation with the Michigan Department of Environmental Quality (MDEQ), did a statewide screening to aid in understanding the occurrence and distribution of selected pesticides in Michigan streams. Stream-water samples were collected from 23 sites throughout Michigan. In all, 320 water samples were analyzed by use of rapid immunoassay methods for the herbicides atrazine, metolachlor, and simazine and the insecticides chlorpyrifos and diazinon. On one occasion (June, 2005), atrazine concentrations exceeded the Michigan water-quality value (7.3 micrograms per liter) at the Black River in St. Clair County. Neither chlorpyrifos nor diazinon was detected during April through September. MDEQ detected chlorpyrifos in streams throughout the state in November. Herbicide concentrations were highest in samples influenced by intensive agriculture; however, median herbicide concentrations were similar among agricultural and urban sites. Concentrations of herbicides were very low to undetected in undeveloped areas. Seasonal patterns were also evident during the sampling period. Increased concentrations generally occurred in late spring to early summer. At 11 sites, daily sampling was done every day for 5 days following a rainfall after herbicide application in the area. Substantial changes in concentrations of herbicides—greater than tenfold from the previous day—were observed during the daily sampling. No consistent relation was found between concentration and streamflow. Results of this study may be used to aid in the development of a more comprehensive pesticide monitoring study for the State of Michigan.

Introduction

The U.S. Geological Survey (USGS) has documented the occurrence of several groups of pesticides in surface waters across the United States, including streams in Michigan (Frey, 2000; Gilliom and others, 2006; Scribner and others, 2005). Streams in agricultural areas have been reported to be most affected by pesticides primarily because of the amounts of pesticides applied for agricultural use. Michigan has approximately 10.1 million acres of agricultural land, primarily located in the southern part of the Lower Peninsula. Pesticides are commonly used to control insects (insecticides) and weeds (herbicides) for field and fruit crops. Herbicides are also used for nonagricultural weed control along roadsides and rights-of-way, on golf courses, and on lawns and gardens; nonagricultural uses of insecticides include forest management, and insect control around homes, other buildings, and gardens. Because many pesticides have been documented to be carcinogens or endocrine disruptors (Extension Toxicology Network, 2006), pesticide contamination of surface waters may pose a risk to human health if the water is used as a drinking-water supply or if considerable bodily contact with the water occurs. In addition, contamination of surface water also may have negative effects on wildlife and aquatic ecosystems. Because of the concerns over the effects of pesticides on human, wildlife, and aquatic-ecosystem health, the USGS, in cooperation with Michigan Department of Environmental Quality (MDEQ), conducted a pesticide-screening study from March to November 2005 to determine the occurrence patterns of pesticides in selected Michigan streams. Thirteen of these streams were already being sampled as part of the Michigan

Water Chemistry Monitoring Program (WCMP) (Michigan Department of Environmental Quality, 2002). Eleven additional streams were selected to specifically investigate the seasonality of pesticide occurrence and of pesticide-occurrence in relation to land use. Selected streams throughout Michigan were tested for the herbicides atrazine, metolachlor, and simazine and the insecticides chlorpyrifos and diazinon by means of enzyme-linked immunoassays.

Purpose and Scope

This report presents the results of a statewide screening study of selected pesticides in Michigan streams and relates them to seasonal and land-use patterns. This study was designed to provide preliminary data to the state to help develop a more comprehensive pesticide-monitoring effort in Michigan. This report includes concentrations of atrazine, chlorpyrifos, diazinon, metolachlor, and simazine, which were measured by means of enzyme-linked immunoassays, for stream-water samples collected from March through November 2005 at 23 sites. In addition, this report contains data collected by MDEQ as part of year-long monitoring of 50 streams in the state that were analyzed by means of the same immunoassay techniques. The expected uncertainty in the results due to method limitations is also described.

Background

Pesticides are a general group of chemicals used to control nuisance pests such as weeds (herbicides), insects (insecticides), and fungi (fungicides). The U.S. Environmental Protection Agency (USEPA) classifies compounds into several categories so that health and environmental scientists can more accurately assess the impact of the concentration of a pesticide in water with various uses (recreation, fishing, and consumption). The maximum contaminant level (MCL, an annual average concentration) is the highest level of contaminant that is allowed in drinking water and represents enforceable standards. The lifetime health advisory (L-HA) is a concentration of a chemical in drinking water that should not cause any adverse noncarcinogenic effects from a lifetime of human consumption by a 70-kg adult who consumes 2L of water a day. The reference dose (RfD) is an estimate of a daily oral exposure that does not represent appreciable risk of negative effects over a lifetime (U.S. Environmental Protection Agency, 2004b). These benchmarks are provided in table 1 for atrazine, metolachlor, simazine, diazinon, and chlorpyrifos, along with other benchmarks used to protect wildlife and aquatic life. Surface waters are affected by pesticides through a variety of pathways including spray drift from nearby application, surface runoff, and ground-water discharge. The amount of pesticide detected is often related to the use of pesticide in the watershed, geological and hydrological characteristics, and the fate and transport mechanisms of that particular compound (Gilliom and others, 2006). The pesticides chosen for this study were based on the availability of immunoassay methods and pesticide-use statistics in Michigan.

Pesticide degradation compounds, or degradates, have been shown to be important components of overall pesticide occurrence in water and have been reported in surface waters (Battaglin and others, 2003; Boxall and others, 2004; Scribner and others, 2005). However, the present study focuses on parent compounds and does not address pesticide degradation compounds, although some may cross-react with parent-compound immunoassays.

Herbicides

Herbicides used to control weeds for field crops are applied prior to plant growth (preemergence) and again after plants have emerged (postemergence). Because herbicides are applied in the spring, when rainfall can be heavy and there is little vegetation to take up water or prevent runoff, increased herbicide concentrations during this time are common for stream water in agricultural areas (Thurman and others, 1991; Gilliom and others, 2006). Three immunoassay methods were selected to measure atrazine, simazine, and metolachlor in stream waters. Given the limitation of the available analytical methods, these herbicides were selected because they are either currently applied or have historically been applied to three major crops in the state: corn (atrazine and metolachlor), soybeans (atrazine), and fruit crops (simazine). A national USGS study of stream waters detected atrazine, metolachlor, and simazine in approximately 85 percent, 80 percent, and 60 percent, respectively, of samples from agricultural-areas (Gilliom and others, 2006).

One of the most widely used herbicides is atrazine, a triazine herbicide used for the control of broadleaf weeds. In Michigan, atrazine is primarily used in agriculture for weed control in corn fields. In 2004, approximately 1,814,000 lb of atrazine was applied to 68 percent of the cornfields in the State (National Agricultural Statistics Service, 2006). The solubility of atrazine in water is 33 mg/L, which indicates that atrazine is readily soluble in water and is likely to wash off soil during precipitation and be transported through surface runoff. The half-life of atrazine in soil is approximately 60 days (Scribner and others, 2005). Atrazine is considered a possible carcinogen and may cause cardiovascular or reproductive difficulties (U.S. Environmental Protection Agency, 2002). The State of Michigan Rule

57 water-quality criteria for atrazine in surface waters is 7.3 µg/L based on the final chronic value (FCV) (Michigan Administrative Code, 2006). Other criteria used for atrazine include the USEPA drinking-water standard of 3 µg/L and the Canadian aquatic-life value of 1.8 µg/L (table 1). These latter two criteria do not apply to the samples collected as part of this study; however, they may be useful for putting concentrations detected from this study into a management perspective.

Simazine, a triazine compound similar to atrazine, is most commonly used on fruit crops. In 2003, approximately 22,000 lb of simazine was applied to fruit crops in Michigan (Michigan Agricultural Statistics, 2003–04). Simazine is less soluble in water than is atrazine, with a solubility of 6.2 mg/L; this indicates that less simazine would be transported in surface runoff from soil than atrazine (Scribner and others, 2005). The half-life of simazine in soil is approximately 75 days, which makes it more persistent in soil than atrazine (Scribner and others, 2005). The USEPA classifies simazine as toxicity class IV (practically nontoxic), and only high doses are reported to have health effects (Extension Toxicology Network, 2006). The Michigan Rule 57 water-quality criterion established for simazine is 17 µg/L (Michigan Administrative Code, 2006; table 1).

Metolachlor, a chloroacetanilide herbicide, is typically a preemergence herbicide used in agriculture for control of broadleaf and annual grassy weeds for several crops, primarily corn and soybeans. In 2003, approximately 22,600 lb of metolachlor was applied to field crops (corn and fall potatoes) in Michigan (National Agricultural Statistics Service, 2006). In the 1990s, metolachlor was used much more frequently on a variety of field crops. The amount used in 2003 is significantly down from the 2,274,700 lb used in 1998 (National Agricultural Statistics Service, 2006), owing to an increased use of glyphosate on glyphosate-tolerant crops and improved metolachlor formulation that allows for reduced application rates. Metolachlor is listed as a slightly toxic compound (USEPA toxicity class III). It is only slightly toxic through ingestion and is not readily absorbed through the skin. Metolachlor is somewhat persistent and can be quite mobile, depending on soil type. The half-life of metolachlor in the 6- to 12-inch soil-depth range is between 7 to 292 days (U.S. Environmental Protection Agency, 1995).

Insecticides

Insecticides are not typically applied in agricultural areas until late summer, when insects threaten crop production, and they are not as widely used as herbicides; rather, they are used in areas where insects are a problem. Insecticides also are commonly used for nonagricultural pest control. Very few immunoassays have been developed for insecticides. Diazinon has been identified as an urban-use pesticide (Gilliom and others, 2006), whereas chlorpyrifos is typically used for agricultural purposes. For these reasons—the availability of immunoassay methods of detection and the historical and present use in the state—diazinon and chlorpyrifos were analyzed in this study. Gilliom and others (2006) report diazinon and chlorpyrifos in about 12 percent of samples collected in a nationwide study of stream waters.

Diazinon, an organophosphate insecticide, has historically been used to control insects in residential buildings, homes, and gardens (70 percent of the chemical use). Diazinon is an enzyme inhibitor in humans and can affect the nervous system; symptoms of exposure range from mild to severe, including death. In 1998, USEPA canceled registration for diazinon use on golf courses and sod farms because of toxic effects on birds that often congregate in those areas; in 2004, USEPA stopped the sale of all outdoor diazinon home, lawn, and garden products (U.S. Environmental Protection Agency, 2004a). The USEPA classifies diazinon as a restricted-use pesticide and has set a lifetime health advisory of 0.6 µg/L (U.S. Environmental Protection Agency, 2004a). As a result, diazinon use has declined significantly in the last 8 years. Diazinon is not persistent, having a half life of only 14–28 days (Extension Toxicology Network, 2006). The Michigan Rule 57 water-quality value for diazinon is 0.004 µg/L (Michigan Administrative Code, 2006).

Chlorpyrifos is a broad-spectrum organophosphate insecticide that is used on grains, vegetables, and fruit, as well as on lawns, and it is registered for direct use on sheep and turkeys. In 2003, approximately 183,700 lb of chlorpyrifos were reported to have been applied to crops in Michigan (National Agricultural Statistics Service, 2006), primarily to fruit and corn. Chlorpyrifos has a moderate toxicity in humans and can affect the lungs, heart, and central nervous system. Chlorpyrifos absorption through the skin is limited, but contact may cause skin or eye irritation (Extension Toxicology Network, 2006). Michigan's Rule 57 water-quality criterion for chlorpyrifos in surface waters is 0.002 µg/L (Michigan Administrative Code, 2006), whereas the USEPA has set a lifetime health-advisory level of 20 µg/L (table 1).

Previous Studies

Previous studies have detected several different pesticides in surface waters and ground waters in Michigan (Duris and others, 2004; Duris and Haack, 2005, Gilliom and others, 2006). In a 2004 study in Huron County, Mich. (Duris and Haack, 2005), atrazine was

Table 1. Benchmark standards for pesticides selected for this study.

[USEPA, U.S. Environmental Protection Agency; µg/L, micrograms per liter; µg/kg/d, micrograms per kilogram per day; na, not available]

Compound	Michigan surface-water standard[1] (µg/L)	USEPA Maximum Contaminant Level[2] (MCL) (µg/L)	USEPA Lifetime Health Advisory[2] (µg/L)	Canadian aquatic-life criteria[3] (µg/L)	USEPA Reference Dose[2] (µg/kg/d)
Atrazine	7.30	3.00	na	1.80	35.00
Chlorpyrifos	.002	na	20	.0035	3.00
Diazinon	.004	na	.6	na	.009
Metolachlor	15	na	100.0	7.80	150.00
Simazine	17	4.00	4.00	10.00	5.00

[1] Michigan Administrative Code (2006).
[2] U.S. Environmental Protection Agency (2004b).
[3] Canadian Council of Ministries of the Environment (2003).

detected at eight surface water sites in both May and August, 2004 and metolachlor was detected at 3 different surface water sites in both May and August, 2004. Simazine was detected in two August samples and diazinon was detected in two May samples. In addition, several other pesticides were detected in these samples, including degradation products from triazine herbicides. In another watershed-based study, immunoassays were used to detect triazine herbicides (including atrazine) in the St. Joseph River watershed (Duris and others, 2004). In that study, triazine herbicides were detected in 69 percent of the samples. Diazinon, metolachlor, and simazine also were detected in this study; capillary-column gas chromatography/mass spectrometry was used to analyze selected samples. Both studies were limited in the number of samples collected (a maximum of four samples collected at each site during the year). The USGS National Water-Quality Assessment Program (NAWQA) collected samples during 1996–98 for pesticide analysis at three stream locations in Michigan as part of the Lake Erie–Lake St. Clair Basin Study (Frey, 2001). In that study, atrazine was present in all samples with concentrations as high as 7.3 µg/L, and metolachlor was present in 97 percent of the samples at concentrations as high as 37.3 µg/L. Chlorpyrifos concentrations were greater than the Michigan Rule 57 water-quality criterion of 0.002 µg/L in 11 samples (17 percent). Diazinon also was detected at all three locations, with concentrations in 35 percent of the samples greater than Michigan Rule 57 water-quality value of 0.004 µg/L. Like the other studies, the USGS NAWQA study also reported several other pesticides at these sites.

Methods and Approach

Two sampling components were involved in this study. The first was sampling of the 13 statewide sites in conjunction with the MDEQ WCMP; each site was sampled 12 times between April and November 2005 (fig. 1). The second was sampling of the 11 intensive-study sites for specific land-use comparisons; each site in the intensive-study group was sampled approximately biweekly, April through September 2005, with an additional 5-day intensive-sampling period after preemergence pesticide application, as determined by monitoring Michigan State University Crop Advisory Team alerts (fig. 2).

Description of Study Sites

Sampling locations are shown in figure 2 and listed in table 2. Thirteen sites were sampled 12 times from March through November 2005, as part of a statewide Water Chemistry Monitoring Program conducted by USGS and MDEQ (referred to as WCMP sites; fig. 2). Most of these sites are near the mouths of major rivers and represent large drainage areas. Intensive-study sites were chosen in the Grand, the Shiawassee, and the larger Lake St. Clair watersheds and sampled from April through September 2005. Selection of these sites was based on the availability of a real-time USGS streamgage at the site, use of the site for other studies, and a need to include small stream systems and sites in areas of known heavy agricultural or local urban land use. Land-use and drainage basin calculations are described

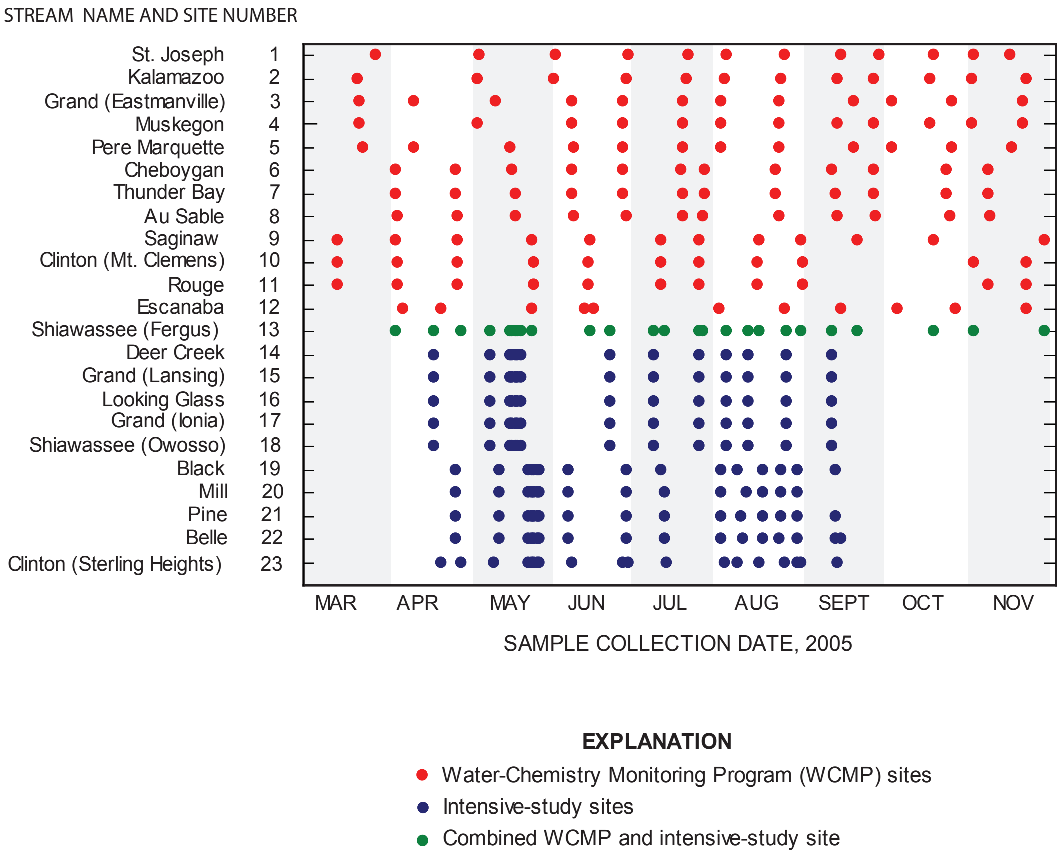

Figure 1. Sample-collection dates for sites sampled in selected Michigan streams, March–November 2005. (Site locations are shown on figure 2 and site information is listed in table 2.)

in more detail in the "Methods and Approach" section of the report and are listed in table 3.

Three sites are listed as agricultural sites because of heavy agricultural land use upstream, but the sample-collection site was actually in an urban setting: the sites at Grand River at Lansing, Saginaw River at Essexville, and St. Joseph River at St. Joseph are all surrounded by homes, urban buildings, or industry.

Sample Collection

Stream-water samples were collected in the main stream channel about 1m below the surface or at mid-depth if the stream was less than 1m deep. Samples were collected by means of dip sampling methods, as described by Wilde and others (1999). Samples were collected in a 250 mL baked, amber glass bottle that was approved for pesticide analysis. After being filled, sample bottles were stored at 4°C out of ultraviolet (UV) light until they were processed. Samples were processed in batches on a monthly basis; therefore, holding times ranged from a few days to several weeks.

In addition to the USGS streamgages at all intensive-study sites, some sites had a continuous water-quality monitor. For sites without a water-quality monitor, field personnel measured water temperature, specific conductance, dissolved oxygen, and pH with a multiparameter probe during site visits. Streamflow and other water-quality constituents were also measured at the WCMP study sites in conjunction with the USGS and MDEQ statewide monitoring program.

Immunoassays

Immunoassays were used to quantify triazine herbicides (specifically, atrazine and simazine), metolachlor, diazinon, and chlorpyrifos. The immunoassay method allows for a rapid, relatively inexpensive screening for pesticides in surface waters. It is important to note these assays, although selective for one particular compound,

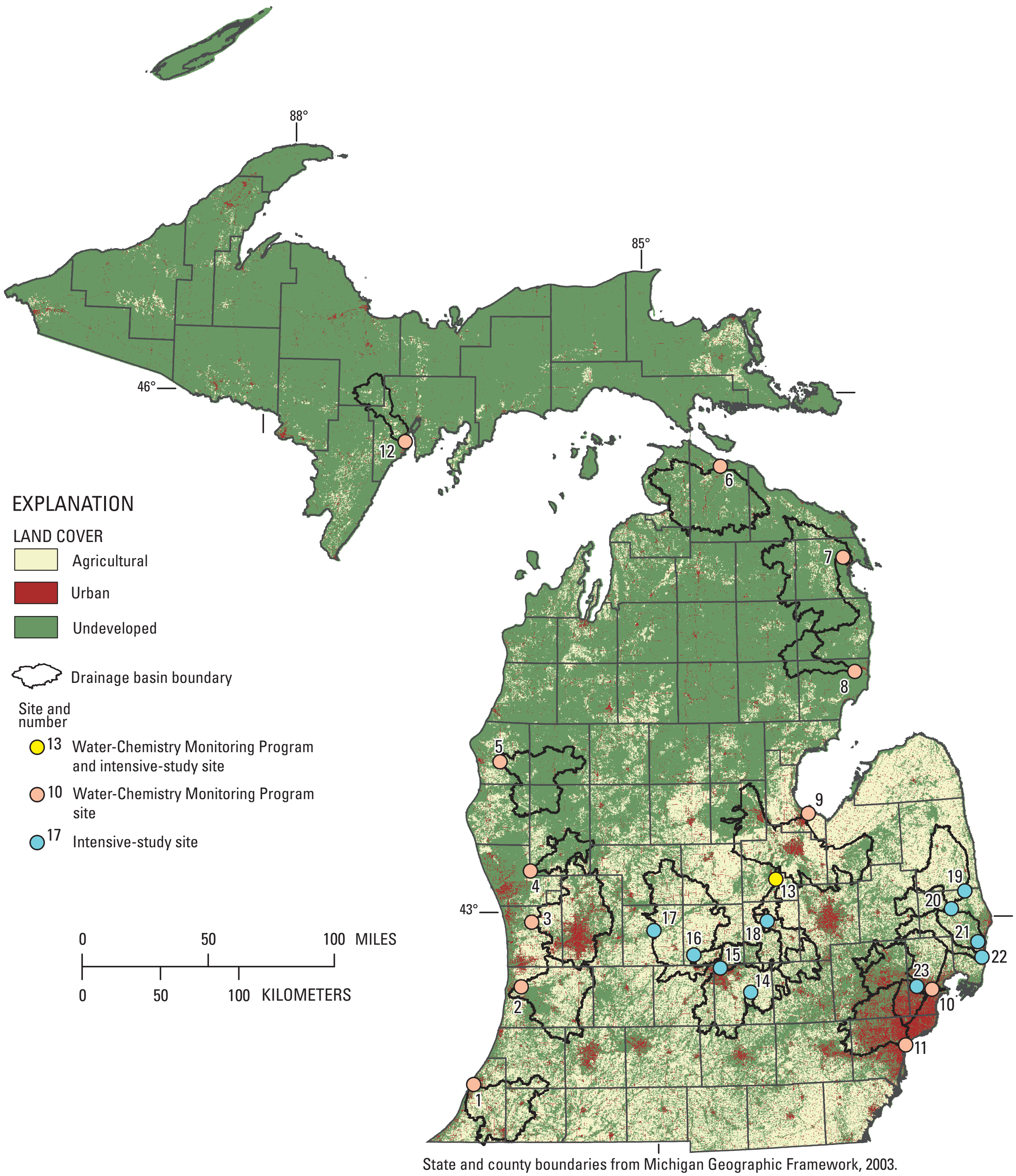

Figure 2. Surface-water sampling sites and effective contributing drainage basin (25 mile upstream buffer area) for the Water-Chemistry Monitoring Program sites (WCMP) and intensive-study sites, Michigan. Land-cover data from Michigan Department of Natural Resources, 2001.

Table 2. Sample-collection site number, name, location, and watershed (as shown in figures 1 and 2.).

[USGS, U.S. Geological Survey; WCMP, water-chemistry monitoring project]

Map number	USGS station number	USGS station name	Latitude	Longitude	Watershed
		WCMP sites			
1	04102080	St. Joseph River at Napier Ave at St. Joseph, Mich.	42.0892 N	86.4747 W	St. Joseph
2	04108660	Kalamazoo River at New Richmond, Mich.	42.6517 N	86.1078 W	Kalamazoo
3	04119400	Grand River near Eastmanville, Mich.	43.0242 N	86.0264 W	Lower Grand
4	04122030	Muskegon River near Bridgeton, Mich.	43.3181 N	86.0364 W	Muskegon
5	04122500	Pere Marquette River at Scottville, Mich.	43.9450 N	86.2787 W	Pere Marquette-White
6	04132052	Cheboygan River (pond) at Lincoln Ave at Cheboygan, Mich.	45.6339 N	84.4811 W	Cheboygan
7	04135020	Thunder Bay River near Alpena, Mich.	45.0939 N	83.4998 W	Thunder Bay
8	04137500	Au Sable River near Au Sable, Mich.	44.4364 N	83.4339 W	Au Sable
9	04157065	Saginaw River at Weadock Road at Essexville, Mich.	43.6281 N	83.8366 W	Saginaw
10	04165553	Clinton River at Moravian Dr. at Mt. Clemens, Mich.	42.5959 N	82.9088 W	Clinton
11	04168550	River Rouge at River Rouge, Mich.	42.2806 N	83.1288 W	Detroit
12	040590345	Escanaba River at Wells, Mich.	45.7811 N	87.0675 W	Escanaba
		Combined WCMP and intensive-study site			
13	04145000	Shiawassee River near Fergus, Mich.	43.2547 N	84.1055 W	Shiawassee
		Intensive-study sites			
14	04111500	Deer Creek near Dansville, Mich.	42.6084 N	84.3208 W	Upper Grand
15	04113000	Grand River at Lansing, Mich.	42.7506 N	84.5553 W	Upper Grand
16	04114498	Looking Glass River near Eagle, Mich.	42.8281 N	84.7594 W	Upper Grand
17	04116000	Grand River at Ionia, Mich.	42.9720 N	85.0692 W	Lower Grand
18	04144500	Shiawassee River at Owosso, Mich.	43.0150 N	84.1811 W	Shiawassee
19	04159492	Black River near Jeddo, Mich.	43.1525 N	82.6241 W	St. Clair
20	04159900	Mill Creek near Avoca, Mich.	43.0545 N	82.7346 W	St. Clair
21	04160398	Pine River near Marysville, Mich.	42.8586 N	82.5380 W	St. Clair
22	04160625	Belle River near Marine City, Mich.	42.7684 N	82.5121 W	St. Clair
23	04161820	Clinton River at Sterling Heights, Mich.	42.6145 N	83.0266 W	Clinton

do not necessarily distinguish that compound from other closely related compounds. For example, the atrazine assay used in this study is designed to detect atrazine to concentrations as low as 0.046 µg/L, but other triazine compounds such as simazine, cyanazine, and triazine degradates may cross-react with the atrazine assay with less specificity than the target compound. Similar types of cross-reactions have been noted for each of the immunoassays used in this study. These cross-reactions are described in the manufacturer's insert and listed in table 4, along with detection limits for each assay. Typically, immunoassay methods have higher detection limits than other analytical methods and often are not as precise; however, they are quick and economical screening tools.

Samples were analyzed by use of RaPID immunoassay kits and spectrophotometer RPA-1 (Strategic Diagnostics Inc., Newark, Del.) according to manufacturer instructions for the detection of atrazine, metolachlor, simazine, chlorpyrifos, and diazinon.

Table 3. Land-use percentages and classification for study sites.

[USGS, U.S. Geological Survey; mi², square miles]

USGS station number	Stream name (location)	Site drainage area[1,2] (mi²)	Land-use percentage in watershed			Dominant land-use classification
			Agriculture	Urban	Undeveloped	
04160625	Belle River	179	73	2	25	Agricultural
04160398	Pine River	195	60	2	38	Agricultural
04159900	Mill Creek	169	78	1	21	Agricultural
04159492	Black River	406	86	1	13	Agricultural
04157065	Saginaw River	1025	61	9	30	Agricultural
04145000	Shiawassee River (Fergus)	215	81	6	13	Agricultural
04144500	Shiawassee River (Owosso)	317	73	4	23	Agricultural
04119400	Grand River (Eastmanville)	756	55	14	31	Agricultural
04116000	Grand River (Ionia)	980	77	2	21	Agricultural
04114498	Looking Glass River	198	63	6	31	Agricultural
04113000	Grand River (Lansing)	649	70	8	22	Agricultural
04111500	Deer Creek	16	82	0	18	Agricultural
04108660	Kalamazoo River	613	60	1	39	Agricultural
04102080	St. Joseph River	533	65	6	29	Agricultural
04168550	River Rouge	456	16	62	22	Urban
04165553	Clinton River (Mt. Clemens)	705	34	34	32	Urban
04161820	Clinton River (Sterling Heights)	318	27	26	47	Urban
040590345	Escanaba River	216	15	1	84	Undeveloped
04137500	Au Sable River	235	2	0	98	Undeveloped
04135020	Thunder Bay River	915	15	1	84	Undeveloped
04132052	Cheboygan River	863	13	1	86	Undeveloped
04122500	Pere Marquette River	519	11	1	88	Undeveloped
04122030	Muskegon River	184	32	1	67	Undeveloped

[1]Drainage area is the drainage area calculated for each site by applying a 25-mile upstream buffer for each site and combining all subwatersheds that fall within the buffered area,

[2]Michigan Department of Environmental Quality, 1998.

Land-Use Characterization

Land-use characteristics surrounding each sampling point were determined as land-coverage percentages by use of ArcView software, version 3.3, and the following GIS data: 2001 Michigan land cover (Michigan Department of Natural Resources, 2001); 1:24,000-scale Michigan watershed boundaries (Michigan Department of Environmental Quality, 1998); and point data depicting locations of Michigan water-quality-sampling points. A 25-mi upstream buffer was generated around each of the 23 water-quality sites. All 1:24,000-scale watersheds that were upstream from the water-quality sites that fell within this 25-mi upstream buffer were selected from the watershed-boundary data set and aggregated to create new watersheds, or water-quality site drainage basins, by eliminating the subwatershed boundaries. This resulted in 23 distinct watersheds in which land-cover area values were then computed for each land-cover type. The resulting land-cover areas were converted into percentages of agriculture (pastures, row crops, orchards, and small grains), urban land (urban, commercial, and residential), and undeveloped land (forest, grasslands, wetlands, water, and all other) compared with the overall area of the respective drainage basins. A site was classified as agricultural if it had greater than 50 percent agricultural land use associated with it. A site was classified as urban if it had less than 50 percent agricultural and greater than 25 percent urban land use associated with it. Sites with less than 50 percent agriculture and less than 25 percent urban land use were classified as undeveloped.

Table 4. Immunoassay detection limits and cross-reactive compounds.

[MDL, method detection limit; µg/L, micrograms per liter]

Immunoassay analyte	MDL (µg/L)	Number of relevant cross-reactive compounds	Relevant cross-reactive compounds
Atrazine	0.046	11	Ametryn, cyanazine, desethylatrazine[1], desisopropyl atrazine[1], 2-hydroxy atrazine[1], prometon, prometryn, propazine, simazine, terbutryn, terbutylazine
Simazine	.033	10	Ametryn, atrazine, cyanazine, desethylatrazine[1], desisopropyl atrazine[1], propazine, prometon, prometryn, terbutryn, terbuthylazine
Metolachlor	.05	5	Acetochlor, alachlor, butachlor, metalaxyl, propachlor
Chlorpyrifos	.10	4	Chlorpyrifox-methyl, diazinon, pirimiphos-ethyl, terbufos
Diazinon	.022	3	Diazoxon, pirimiphos-ethyl, pirimiphos-methyl

[1] Triazine herbicide degradation product.

Statistics and Data Handling

Immunoassay data results were recorded as determined by the spectrophotometer, based on a standard curve for each run. In some cases, the resulting value was below the method detection limit (MDL) (table 4) set by the manufacturer for that analysis, and is reported as "estimated values". If the instrument returned a value of nondetection, then the value is reported as less than the MDL. Median detected values were computed for each site and for each pesticide as appropriate. Estimated values were used in these calculations, but nondetections were not.

Statistical differences were determined in the data with respect to land use and seasonality. Patterns in land use with respect to pesticide concentrations were determined by grouping data into the categories of agricultural, urban, or undeveloped. Notched box plots and Kruskal-Wallis tests were used to determine statistical differences in median pesticide concentrations for the different land-use groups. Seasonal patterns in pesticide concentrations were determined by plotting the individual sample concentration for each pesticide and grouping the samples by land use. Locally weighted scatter plot smoothing (LOWESS), with a span of 0.4, was applied to determine patterns in data over time (Cleveland, 1979).

Uncertainties and Analytical Limitations

Only a single analysis was typically done for each sample. However, six samples were chosen that ranged from the highest detectable concentrations to nondetections to be analyzed in triplicate for each assay. Means and standard deviations were computed for each triplicate set. Linear regression was used to estimate the expected error for samples not analyzed in triplicate (intra-assay variation). The same sample was also analyzed on multiple dates to determine variations in data results due to changes in assay kit lots, personnel, or other day-to-day variations (inter-assay variation). Results indicate increasing variation with increasing pesticide concentrations (fig. 3). Greater variation was seen for the metolachlor assay than for the atrazine or simazine assays. Because multiple analyses involved different assay lots and different personnel, inter-assay variation was determined by analyzing several samples on multiple occasions. Samples were chosen to repre-

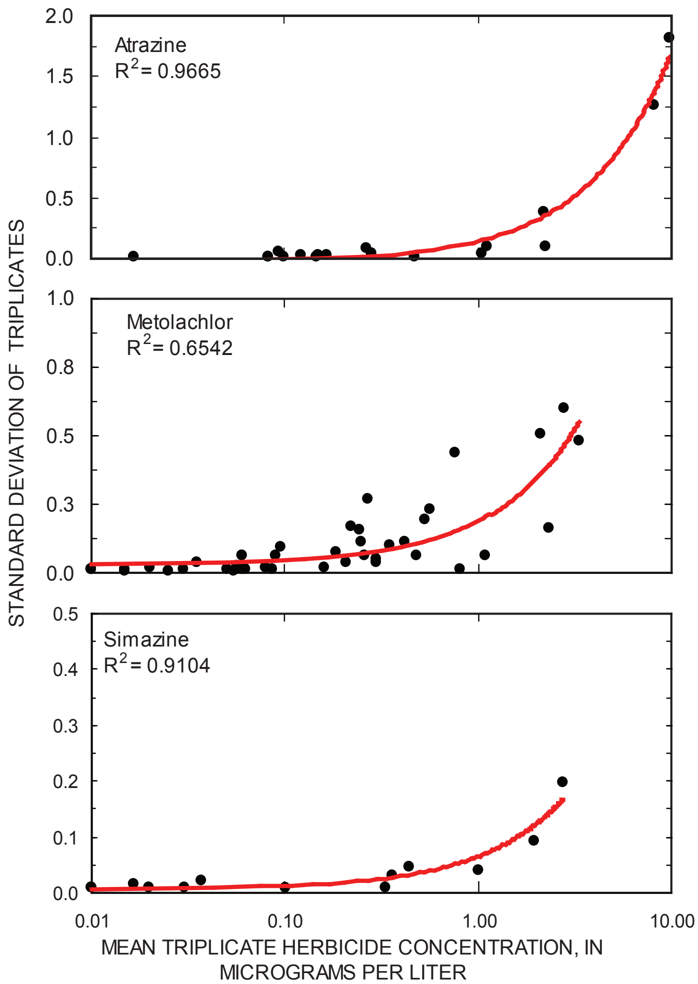

Figure 3. Standard deviation of triplicates for herbicide concentrations.

sent a range in pesticide concentrations. Results again showed greater variation in samples with higher pesticide concentrations (fig. 4).

Several internal controls were used to define the variation in assay results in this study. Field personnel collected 10 field-blank samples by pouring organic-free water into a sample bottle while at a site, and these blanks were analyzed as though they were regular samples. In addition, a laboratory blank (a sample of the organic-free water not handled in the field) was analyzed. Positive controls of known concentrations included with immunoassay kits were run alongside the samples for every analysis. Average field-blank concentrations of the constituents of interest were less than their respective MDLs; however, concentrations of some constituents in individual field blanks exceeded MDLs. Atrazine in field blanks (n=10) ranged from 0.01 to 0.09 µg/L, with a mean concentration of 0.04 µg/L. Metolachlor field-blank concentrations (n=10) ranged from below detection limit to 0.09 µg/L, with a mean concentration of 0.04 µg/L. Simazine was detected in 4 of the 10 field blanks, with a maximum concentration of 0.02 µg/L and a mean of 0.01 µg/L. The organic-free blank water used for the field blanks was also analyzed, resulting in concentrations of 0.04, 0.07, and 0.02 µg/L for atrazine, metolachlor, and simazine, respectively. The field and lab blanks resulted in detectable concentrations of each herbicide tested. Most were below the method quantification limit, but there were three blanks (one atrazine, and two metolachlor) just above the quantification limit.

To determine the effect of holding time, several samples were analyzed over a 250-day period; all samples had been stored at 4°C in the dark. The selected samples spanned a range of concentrations, and each sample was analyzed in triplicate three to four times during a 6-month period (about every 6 weeks). The results of these analyses over time for atrazine are shown in figure 5. No change in concentration was observed during the first 4 months of the study. After 4 months, changes in concentrations exceeded the expected error determined for both the inter- and intra-assay variations tests. Results were similar for metolachlor and simazine. Because no insecticides were detected in this study, a holding-time analysis could not be done. No samples were analyzed beyond a 4-month holding time except for the samples used in the holding-time study.

To compare results from different sampling techniques and analytical methods, surface-water samples were collected at the USGS site 04161820 (Clinton River at Sterling Heights, Mich.) on three sampling dates (April 21, June 29, and August 30) in conjunction with USGS National Water-Quality Assessment Program (NAWQA). Laboratory results were compared to immunoassay results by collecting an equal-width-increment (EWI) sample (Webb and others, 1999), sending a sample to the USGS National Water Quality Laboratory for detection of a suite of selected filtered pesticides and degradates by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry (Zaugg and others, 1995), and analyzing the sample by the immunoassay methods already described. A single-dip sample was also collected at the same time as the EWI sample and was analyzed by immunoassay to compare sampling techniques. Because this sampling was done in conjunction with NAWQA, sampling was limited to the Clinton River at Sterling Heights, the only location where site networks for NAWQA and this study overlapped. Concentrations were very low for all tested pesticides but were consistent among the two sampling techniques and analytical methods.

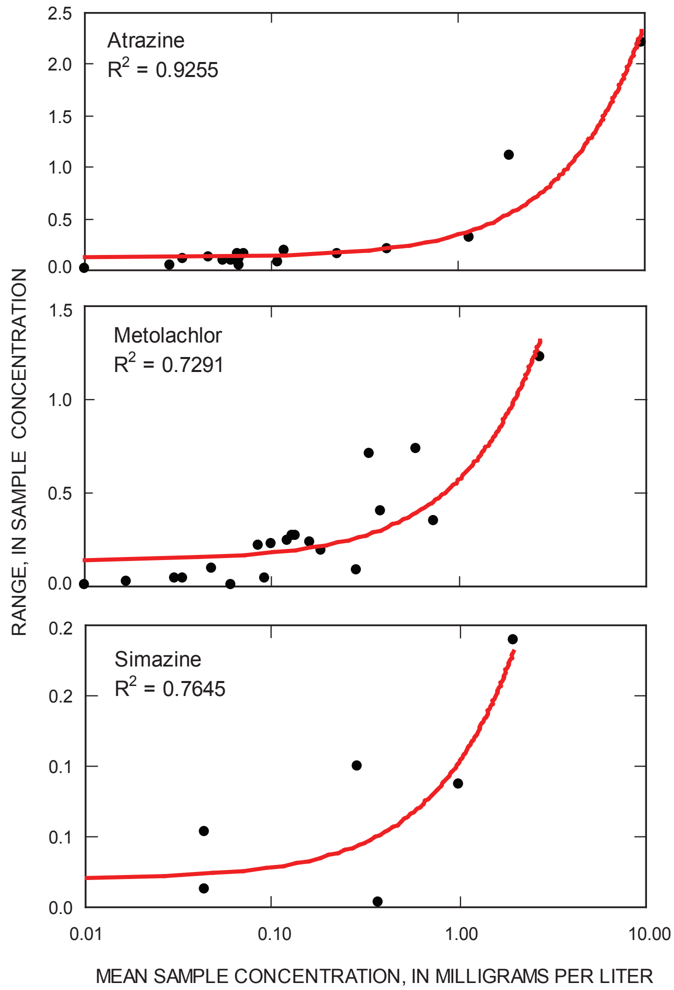

Figure 4. Range of variation in concentration measurement in relation to pesticide concentration.

Pesticide Detections, Effects of Land Use, and Seasonal Patterns of Concentrations

Herbicides were frequently detected during this study, and at least one pesticide was detected in 90 percent of the samples. Similar to results from previous studies (Battaglin and others, 2003; Gilliom and other 2006) mixtures of pesticides were commonly detected (fig. 6). The effects of pesticide or other chemical mixtures are not fully understood but several studies on aquatic organisms have suggested that some chemical mixtures have an additive or synergistic toxic effect (Pape-Lindstrom and Lydy, 1997; Belden and Lydy, 2000; Anderson and Lydy, 2002; Jin-Clark and others, 2002). Because this study screened for only a few pesticides, further analysis would be needed to understand the full extent of other pesticides and degradates at Michigan stream sites. Studies have found that, in many cases, degradates are detected more frequently than their parent compounds (Kolpin and others, 2004; Battaglin and others, 2003), adding to the complexity of pesticide contamination at affected sites. A mixture of chemicals is likely at many stream locations in Michigan.

Herbicide Detection

Atrazine, metolachlor, and simazine were detected at all study sites (appendix 2). Atrazine was detected in 73 percent of the samples. Summary statistics for each site are listed in table 5. Atrazine concentrations ranged from less than MDL (0.046 µg/L) to 10.55 µg/L. The median detected concentration for all samples was 0.15 µg/L; in 86 samples, concentrations were below the MDL. The only site where atrazine concentration was greater than the MDL for every sample was the Grand River at Lansing (n=14), with a minimum concentration of 0.08 µg/L and a maximum of 0.88 µg/L (table 5). The highest median concentration was 0.45 µg/L, at the Pine River site. Out of 320 samples, the concentration in only 1 sample was greater than the Michigan Water Quality Rule 57 criterion for atrazine of 7.3 µg/L. This sample was collected at the Black River on June 7 and had an atrazine concentration of 10.55 µg/L.

Metolachlor was detected in 54 percent of the samples. Summary statistics for each site are listed in table 6. Concentrations ranged from less than the MDL (0.05 µg/L) to 3.02 µg/L, far less than any health or aquatic criteria that have been established for metolachlor (table 1). The median detected metolachlor concentration was 0.09 µg/L, and concentrations in 146 samples were below the MDL. The highest median value was 0.14 µg/L at the Pine River site.

Simazine was detected in 55 percent of the samples. Summary statistics for each site are listed in table 7. The median detected simazine concentration was 0.09 µg/L, and concentrations in 144 samples were below the MDL (0.033 µg/L). Median simazine concentrations at individual sites were highest at the Pine, Saginaw, and Belle Rivers (0.19, 0.18, 0.17 µg/L, respectively). As with atrazine and metolachlor, the highest detected simazine concentration was at the Black River site on June 7 (7.8 µg/L).

Insecticide Detection

The insecticides chlorpyrifos and diazinon were not detected in any sample collected in this study. The immunoassay methods used had high MDLs and did not include a measure of chlorpyrifos and diazinon degra-

Table 5. Summary statistics for atrazine concentrations.

[USGS, U.S. Geological Survey; MDL, method detection limit; µg/L, micrograms per liter]

USGS station number	Stream name (location)	Total number samples	Number detections above the MDL	Detected concentration (µg/L)		
				Maximum	Mean	Median
04102080	St. Joseph River	12	9	0.90	0.21	0.15
04108660	Kalamazoo River	12	9	.16	.09	.09
04111500	Deer Creek	14	10	.48	.16	.08
04113000	Grand River (Lansing)	14	14	.88	.26	.17
04114498	Looking Glass River	14	11	.30	.12	.11
04116000	Grand River (Ionia)	14	13	1.41	.24	.14
04119400	Grand River (Eastmanville)	12	7	.86	.17	.09
04122030	Muskegon River	12	6	.25	.06	.05
04122500	Pere Marquette River	12	3	.10	.04	.04
04132052	Cheboygan River	12	6	.12	.05	.05
04135020	Thunder Bay River	12	4	.15	.06	.05
04137500	Au Sable River	12	5	.14	.05	.04
04144500	Shiawassee River (Owosso)	14	12	.40	.15	.12
04145000	Shiawassee River (Fergus)	26	20	.97	.20	.13
04157065	Saginaw River	12	10	.71	.28	.27
04159492	Black River	16	15	10.55	1.04	.31
04159900	Mill Creek	15	12	.90	.25	.14
04160398	Pine River	16	14	1.75	.61	.45
04160625	Belle River	17	16	1.18	.36	.32
04161820	Clinton River (Sterling Heights)	19	14	.24	.09	.08
04165553	Clinton River (Mt. Clemens)	11	9	.34	.16	.15
04168550	River Rouge	11	9	.23	.11	.11
040590345	Escanaba River	11	6	.15	.06	.06

dates. In addition, application practices and sample-collection timing may influence detections in surface waters.

Diazinon was a widely used urban insecticide in the 1990s; since it was restricted in 1998, its use has significantly declined (National Agricultural Statistics Service, 2006). From 1996 to 1998, diazinon was detected at concentrations as high as 0.197 µg/L at the Clinton River at Sterling Heights and 0.028 µg/L at the Black River near Jeddo (Frey, 2001). The lack of detection in any sample collected in this study is indicative of this change in diazinon use.

Chlorpyrifos is an insecticide used in agriculture. Unlike herbicides that are used in widespread application for weed prevention, insecticides such as chlorpyrifos are applied only in insect-infected areas. The immunoassay detection limit for chlorpyrifos is 0.1 µg/L, an order of magnitude higher than herbicide detection limits and two orders of magnitude higher than the State of Michigan Rule 57 water-quality criterion for chlorpyrifos (0.002 µg/L). Therefore, a lack of detections is not necessarily an indication of attainment of the state water-quality criterion.

Insecticides are typically applied in late summer, when insects are most problematic. In 2005, there was a significant dry period from August to October. The lack of rain during the typical application period might have prevented transport of the insecticides to surface waters.

Table 6. Summary statistics for metolachlor concentrations.

[USGS, U.S. Geological Survey; MDL, method detection limit; µg/L, micrograms per liter]

USGS station number	Stream name (location)	Total number samples	Number detections above the MDL	Detected concentration (µg/L)		
				Maximum	Mean	Median
04102080	St. Joseph River	12	6	1.00	0.13	0.06
04108660	Kalamazoo River	12	6	.19	.06	.06
04111500	Deer Creek	14	8	.39	.11	.08
04113000	Grand River (Lansing)	14	7	.43	.09	.06
04114498	Looking Glass River	14	8	.13	.06	.06
04116000	Grand River (Ionia)	14	8	.40	.10	.07
04119400	Grand River (Eastmanville)	12	6	.51	.09	.05
04122030	Muskegon River	12	5	.11	.05	.05
04122500	Pere Marquette River	12	3	.07	.03	.04
04132052	Cheboygan River	12	3	.12	.04	.03
04135020	Thunder Bay River	12	2	.12	.03	.03
04137500	Au Sable River	12	5	.15	.05	.03
04144500	Shiawassee River (Owosso)	14	10	.15	.07	.07
04145000	Shiawassee River (Fergus)	26	16	.27	.08	.07
04157065	Saginaw River	12	11	.44	.12	.08
04159492	Black River	16	13	3.02	.36	.08
04159900	Mill Creek	15	6	.23	.06	.04
04160398	Pine River	16	15	.76	.21	.14
04160625	Belle River	17	10	.71	.13	.06
04161820	Clinton River (Sterling Heights)	19	9	.17	.05	.04
04165553	Clinton River (Mt. Clemens)	11	10	.25	.11	.06
04168550	River Rouge	11	6	.17	.07	.05
040590345	Escanaba River	11	1	.11	.04	.04

During this study, the MDEQ was conducting a concurrent pesticide-monitoring project in which chlorpyrifos was sampled for in May, July, September, and November at 50 randomly chosen sites throughout the state. With the exception of one site, chlorpyrifos was not detected in May, July, or September (Christine Aiello, Michigan Department of Environmental Quality, written communication, 2006). After fall rains in October and November, chlorpyrifos was detected at 18 of the 50 sites (fig. 7).

Effects of Land Use

Land use plays a major role in the presence of pesticides in surface waters. In areas where pesticides are heavily used, the surface waters are more affected. As mentioned previously, sites were characterized as agricultural, urban, or undeveloped on the basis of land-use percentages from GIS coverage (table 3).

The range in concentrations and median value are shown for each herbicide and land-use group in figure 8. The highest detected herbicide concentrations were in samples collected at agricultural sites. Atrazine, metolachlor, and simazine median concentrations were less than their respective MDL for the undeveloped

Table 7. Summary statistics for simazine concentrations.

[USGS, U.S. Geological Survey; MDL, method detection limit; µg/L, micrograms per liter]

USGS station number	Stream name (location)	Total number samples	Number detections above the MDL	Detected concentration (µg/L)		
				Maximum	Mean	Median
04102080	St. Joseph River	12	9	0.87	0.31	0.07
04108660	Kalamazoo River	12	4	.18	.04	.01
04111500	Deer Creek	14	7	.36	.08	.04
04113000	Grand River (Lansing)	14	10	.43	.17	.13
04114498	Looking Glass River	14	8	.33	.06	.05
04116000	Grand River (Ionia)	14	13	1.67	.24	.12
04119400	Grand River (Eastmanville)	12	8	.83	.12	.04
04122030	Muskegon River	12	2	.05	.02	.01
04122500	Pere Marquette River	12	2	.07	.01	.00
04132052	Cheboygan River	12	2	.04	.01	.01
04135020	Thunder Bay River	12	1	.04	.01	.01
04137500	Au Sable River	12	0	.02	.01	.01
04144500	Shiawassee River (Owosso)	14	8	.39	.08	.05
04145000	Shiawassee River (Fergus)	26	16	1.32	.15	.05
04157065	Saginaw River	12	9	1.24	.23	.18
04159492	Black River	16	16	7.80	.83	.15
04159900	Mill Creek	15	11	.86	.20	.06
04160398	Pine River	16	15	2.62	.62	.19
04160625	Belle River	17	15	1.74	.37	.17
04161820	Clinton River (Sterling Heights)	19	7	.08	.03	.02
04165553	Clinton River (Mt. Clemens)	11	6	.23	.06	.03
04168550	River Rouge	11	3	.26	.04	.02
040590345	Escanaba River	11	4	.06	.02	.02

sites, and the median simazine concentration for the urban group was less than the MDL. Results from a Kruskal-Wallis test showed a statistically significant difference in atrazine ($p = 1.85e\text{-}14$), metolachlor ($p = 8.87e\text{-}7$), and simazine ($p = 0$) concentrations from the three different land-use types. The median concentrations of atrazine and metolachlor for the undeveloped group were significantly lower than those for the agricultural and urban groups, but the difference in the median concentrations between the agricultural and urban groups was not significant. In addition, the median simazine concentration for the agricultural group was significantly higher than those of the urban and undeveloped groups, but the difference between the urban and undeveloped groups was not significant.

Individual pesticide concentrations and land use are shown for each site in figures 9–11. The highest concentrations are in samples from agricultural sites; however, high percentage of agriculture was not consistently correlated with high pesticide concentrations. For example, the drainage area of Deer Creek, a small stream in the Grand River watershed, is 82 percent agriculture (corn and soybeans); however, herbicide concentrations at this site were similar to those at urban sites. This was the case for several agricultural sites (figs. 9–11). More detailed sampling—including sampling of storm runoff—and more information on site characteristics—such as amount of tile drainage—would be needed to fully understand the effects of land use and pesticide application on water quality in streams.

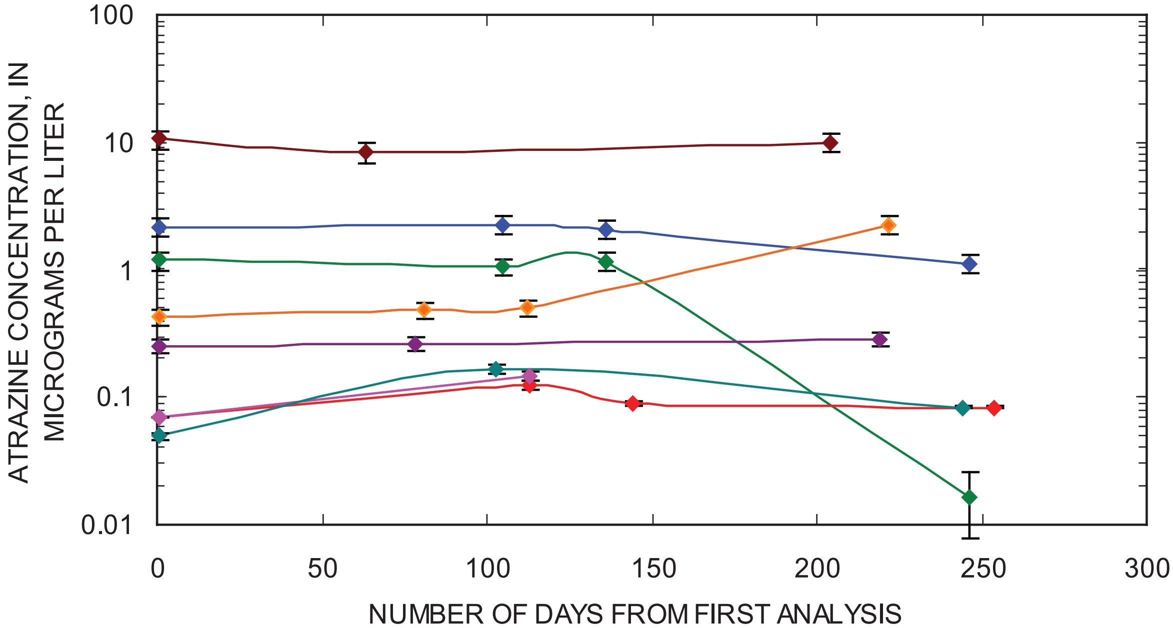

Figure 5. Effects of holding time on atrazine concentrations.

Because of the many nonagricultural weed-control uses for herbicides (road rights-of-way, turfgrass, gardens), it is not surprising that detectable amounts of herbicides were found in streams at urban/residential land-use sites. Median concentrations of atrazine and metolachlor were very similar for agricultural and urban areas. This similarity could be the result of upstream agricultural influences at many of the urban sites. In areas such as the northern part of the Lower Peninsula and the Upper Peninsula of Michigan where there is little agricultural or urban/residential land, few herbicides were detected in stream-water samples.

Seasonal Patterns

Seasonal patterns in atrazine, metolachlor, and simazine concentrations were evident for each land-use type (fig. 12). LOWESS smoothing was applied to determine the seasonal pattern in data for each land-use type. For the triazine herbicides, atrazine and simazine, both agricultural and urban samples tended to peak late May into June. A broader peak extended into August for atrazine, and a much narrower peak shows a rapid decrease in simazine concentrations beginning in late June. Thurman and others (1991) reported similar seasonal results, with increased pesticide concentrations during "spring flush." Metolachlor concentrations peaked in May for agricultural samples. Metolachlor concentrations remained low throughout the study for urban samples, but slight decreases in

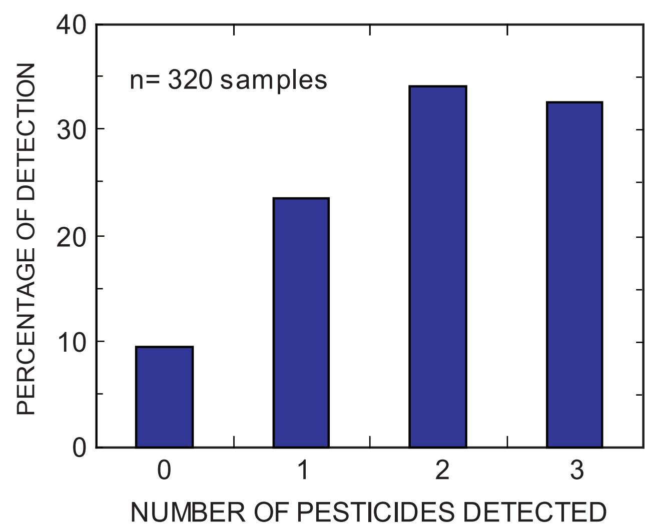

Figure 6. Percentage of samples with multiple pesticide detections in Michigan selected streams, March–November, 2005.

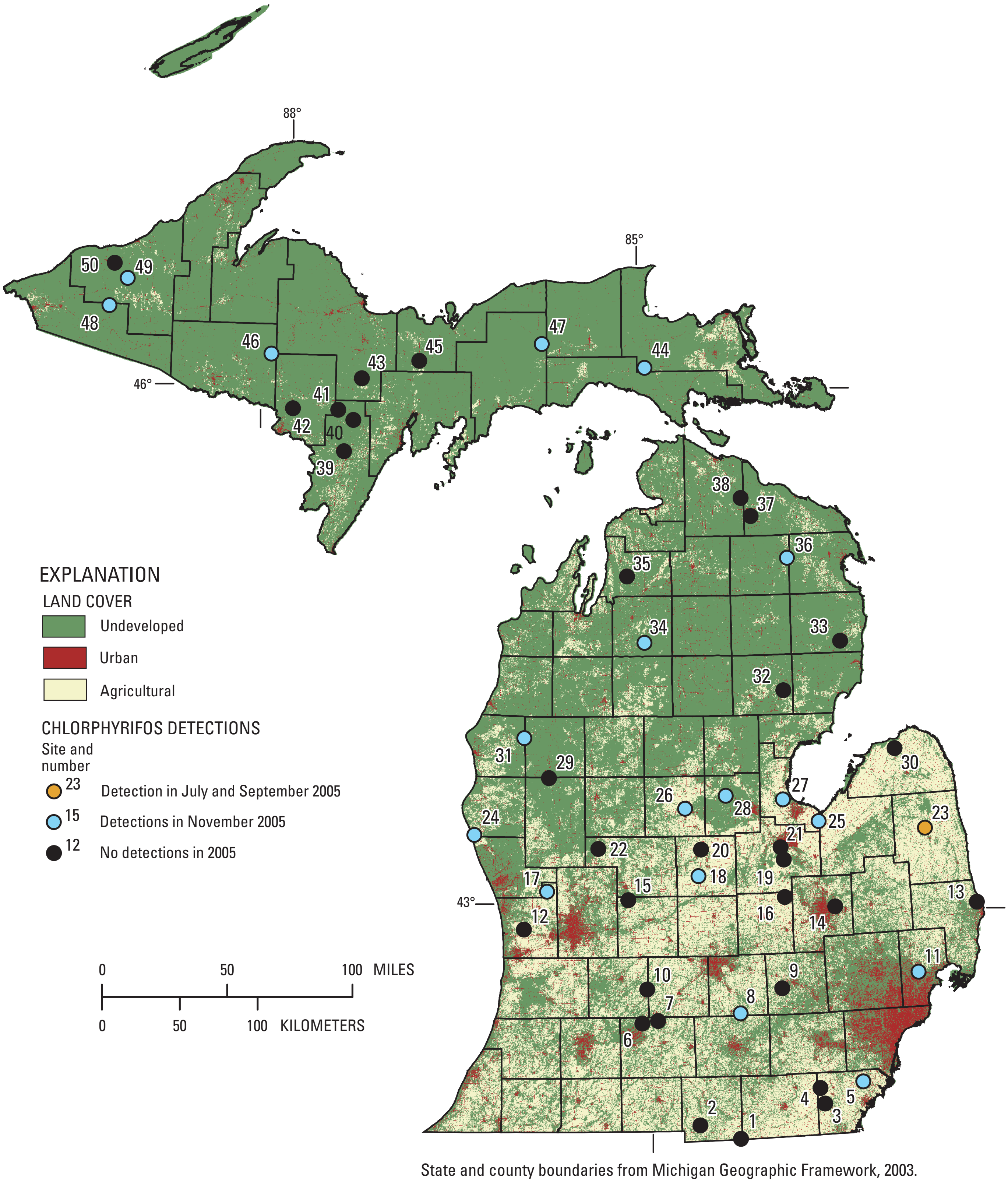

Figure 7. Sites sampled by Michigan Department of Environmental Quality where chlorpyrifos was detected in July, September, or November 2005. Land-cover data from Michigan Department of Natural Resources, 2001.

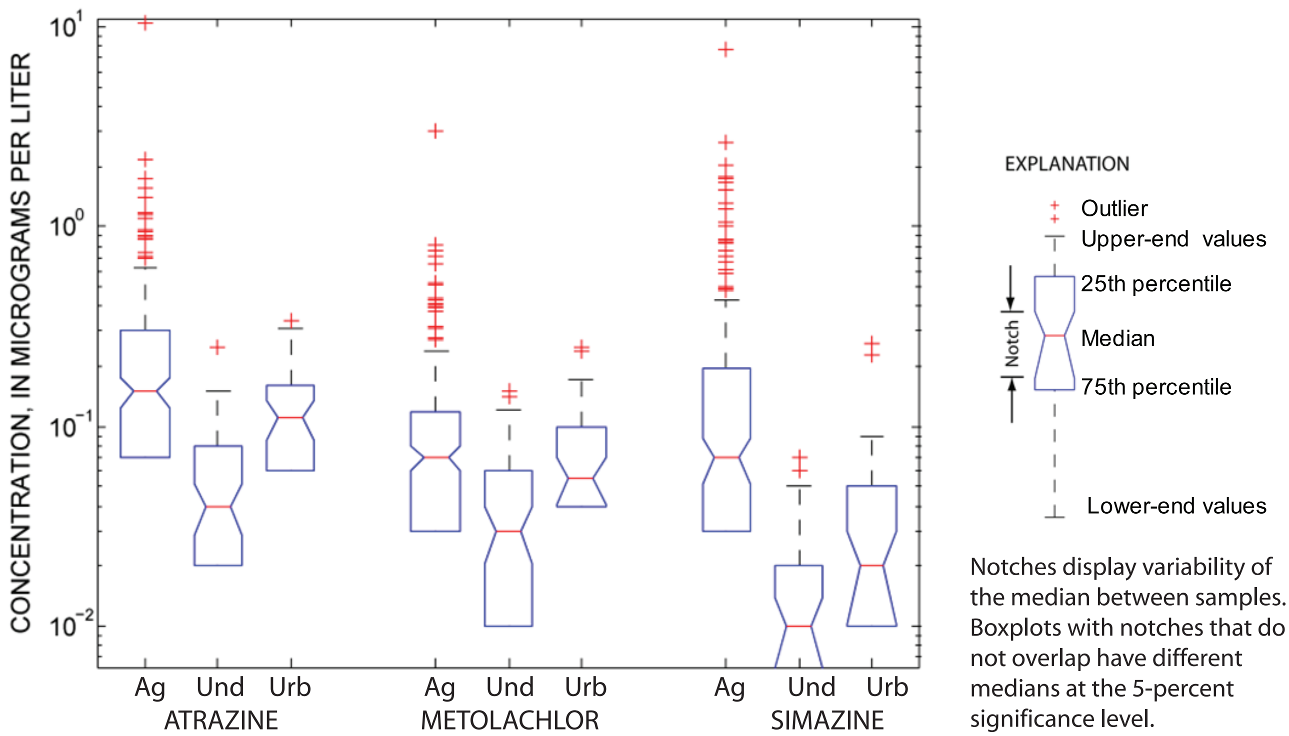

Figure 8. Herbicide concentrations for samples collected in three different land-use types: agricultural (Ag; n=208 samples), undeveloped (Und; n=70 samples), and urban (Urb; n=42 samples) from selected Michigan streams, March–November, 2005.

concentrations were detected in May, followed by a small, steady increase in concentration from June through September. Undeveloped land-use samples behaved much differently from the agricultural or urban samples. Pesticide concentrations were much lower (near or below the MDL) for most samples from the undeveloped sites, but there was an upward trend in atrazine concentration in late July through August, followed by a gradual decrease through the fall. Simazine concentrations for the undeveloped sites remained below the MDL until mid-September then increased slightly through the fall. Metolachlor concentrations followed a nearly identical pattern as simazine for the undeveloped-site samples.

This study examined seasonal effects on pesticide concentration from March through November of a single year. Because weather is a major influence on agriculture practices, as well as chemical transport and degradation, seasonal trends in pesticide concentrations may vary from year to year. Long-term monitoring of pesticides concentrations in streams would be necessary to understand long-term-seasonal trends.

The seasonal patterns show periods within the growing season during which pesticides are most likely to affect water bodies; therefore, these patterns could be used to help direct concentrated sampling and management efforts (Battaglin and Hay, 1996). The results of the current study indicate that herbicides are most likely to be present in stream water at higher concentrations in early summer than late summer or fall. Further studies would be needed during this timeframe to understand the effects that rainfall, runoff, ground water, and other

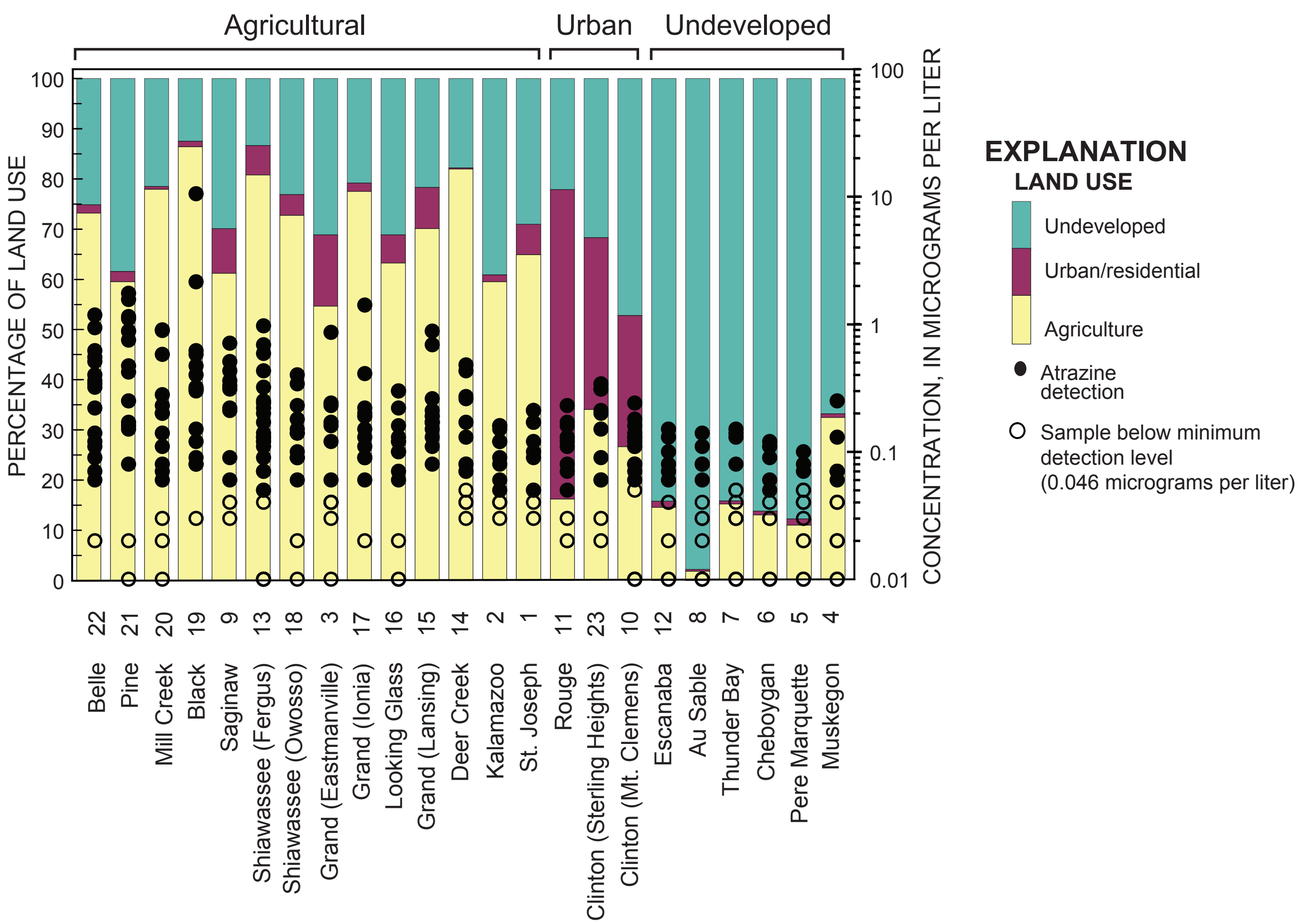

Figure 9. Atrazine concentration in samples collected at each study site, with corresponding land-use percentages from selected Michigan streams, March–November, 2005. (Site locations are shown on figure 2 and site information is listed in table 2. Land-cover data from Michigan Department of Natural Resources, 2001.)

components of the hydrological cycle might have on herbicide concentrations at each stream location.

Results of Intensive Sampling

Herbicides are typically applied in the spring (May–June), which in Michigan usually coincides with wetter conditions than in the summer and early fall. The highest pesticide concentrations generally occurred during these spring months. To determine daily fluctuation in concentrations, samples were collected for 5 consecutive days following a runoff-producing rain event after herbicide application at the intensive-study sites. Michigan State University Field Crop Advisory Team Alerts (*http://www.ipm.msu.edu/field-cat.htm#*) indicated that, in most areas, herbicides had been applied just prior to the mid-May intensive sampling. Results of the intensive daily sampling are shown in figures 13–15. Most pesticide concentrations appeared to be related to streamflow, with increased concentrations during periods of increased streamflow.

There also were indications of a more complex relation at some sampling locations. For instance, the highest detected concentration at the Grand River at Lansing site (fig. 13) occurred late in the week, whereas the peak in the streamflow hydrograph occurred early in the week. This site is in a highly urban area affected by agriculture upstream, and streamflow is influenced by upstream dams; both conditions could explain the delayed reaction. A similar pattern was found at the Shiawassee River near Fergus site (fig. 14). Atrazine concentrations were

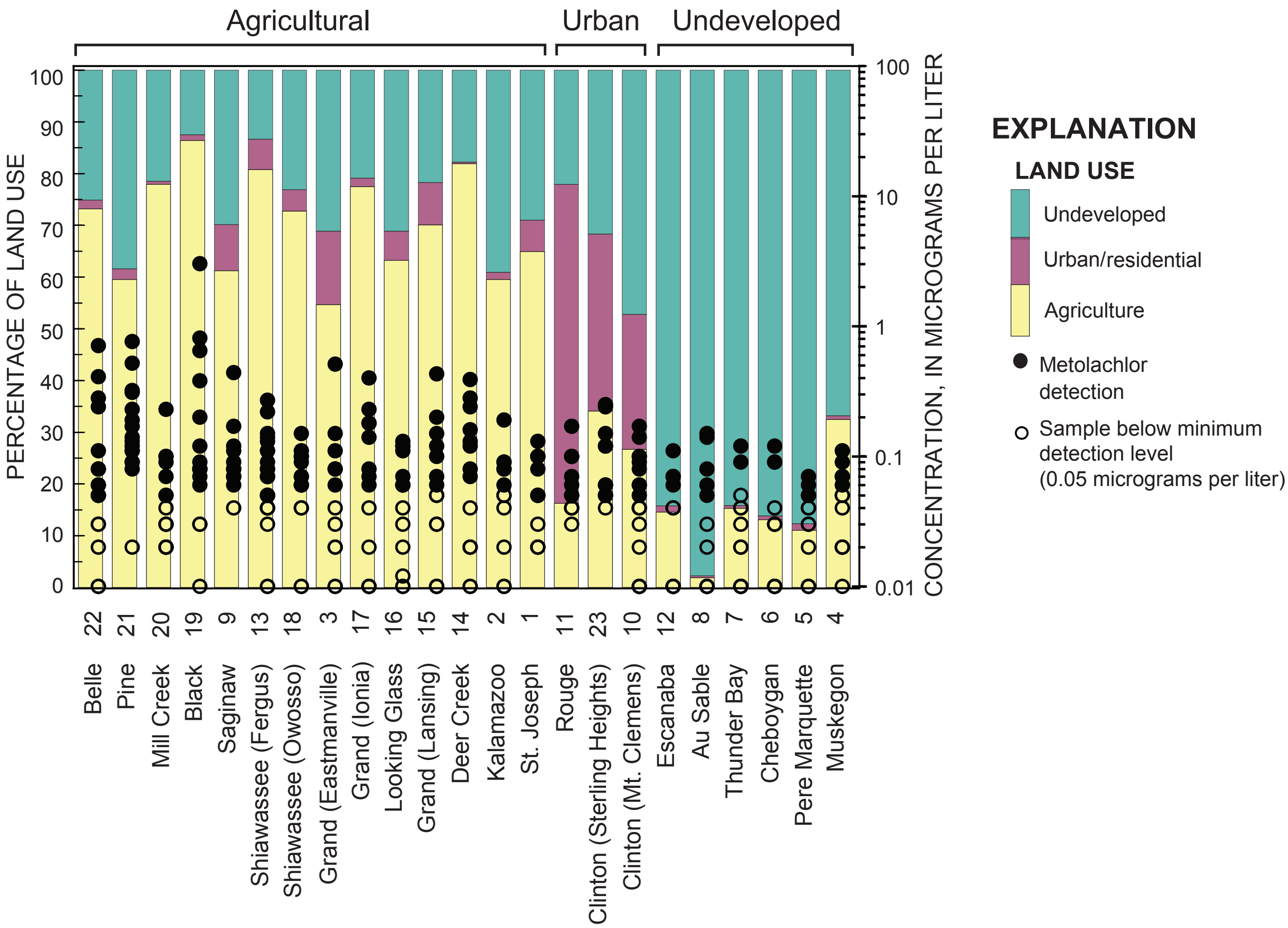

Figure 10. Metolachlor concentration in samples collected at each study site, with corresponding land-use percentages from selected Michigan streams, March–November, 2005. (Site locations are shown on figure 2 and site information is listed in table 2. Land-cover data from Michigan Department of Natural Resources, 2001.)

less than the MDL on the first two days of sampling during a peak in streamflow but increased later in the week.

The timing of the intensive sampling was intended to pick up some of the high concentrations expected after herbicide application. Because rainfall occurred overnight, none of these samples was collected during the rain events that may have caused pesticides to enter the system with runoff. In addition, timing and amounts of applications may have varied among the sampling locations, and such differences also would influence expected concentrations. The highest pesticide concentration detected at each site did not always occur during this intensive sampling period. These results indicate that concentrations of pesticides in streams can vary quickly with time over the hydrograph, and each stream may differ in its relation of herbicide concentration to streamflow. A more comprehensive sampling that includes shorter time intervals between samples over a longer length of time may improve the ability to relate the effects of pesticide application and rainfall to increased concentrations of pesticides in surface waters.

Comparison with Previous NAWQA Data

The NAWQA program collected pesticide data from 1996 to 1998 (Frey, 2001) for two sites included in this study: the Black River near Jeddo (USGS Station 04159492) and the Clinton River at Sterling Heights (USGS station 04161820). Figures 16 and 17 show the results of the NAWQA study and compare them to the current study (2005). It should be noted that the analyti-

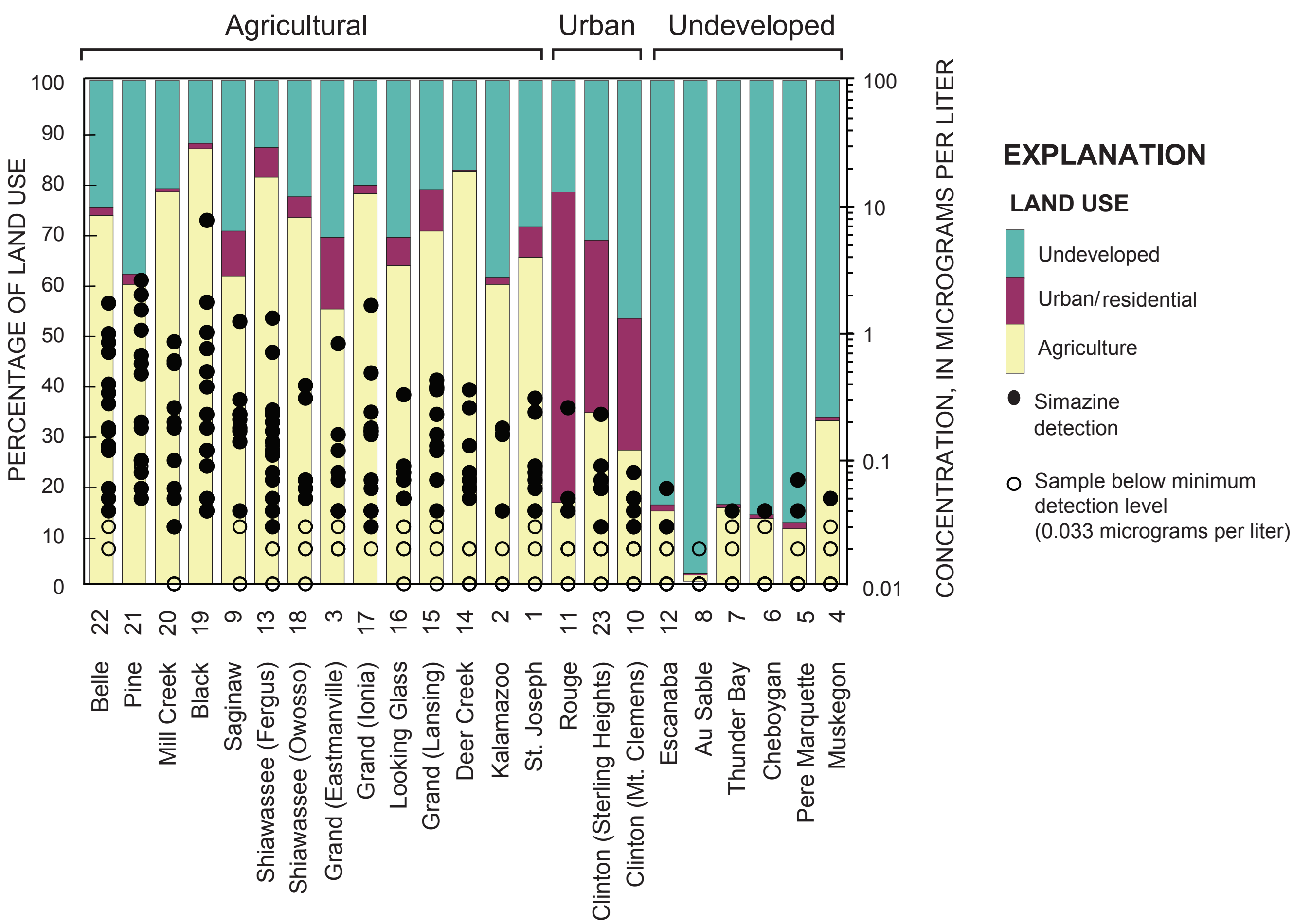

Figure 11. Simazine concentration in samples collected at each study site, with corresponding land-use percentages from selected Michigan streams, March–November, 2005. (Site locations are shown on figure 2 and site information is listed in table 2. Land-cover data from Michigan Department of Natural Resources, 2001.)

cal methods used in the NAWQA study were much more sensitive than the immunoassay used in this study. It should also be noted that there are no data available on pesticide concentrations at these sites from 1998 through 2004 so the following discussion is limited only to the results of the NAWQA study and the present study. There may have been major changes in the concentrations of pesticides during the years for which there are no data.

In general, the results for atrazine are similar between the two studies (fig. 16). Atrazine concentrations in the Black River for this study reached a high of 10.55 µg/L in June. The NAWQA sampling at the Black River also showed peak atrazine concentrations in June, with concentrations as high as 7.3 µg/L. The drainage area for this site is predominately agricultural, and heavy rainfall typically occurs in May and early June. Therefore, it might be expected that the highest concentrations would occur during this time. Data from these two studies suggest that, since the late 1990s, there has not been much change in atrazine concentrations. Although concentrations at this site tend to approach or be greater than water-quality criteria, the concentration of atrazine at this site does not remain high throughout the year based on three years of data.

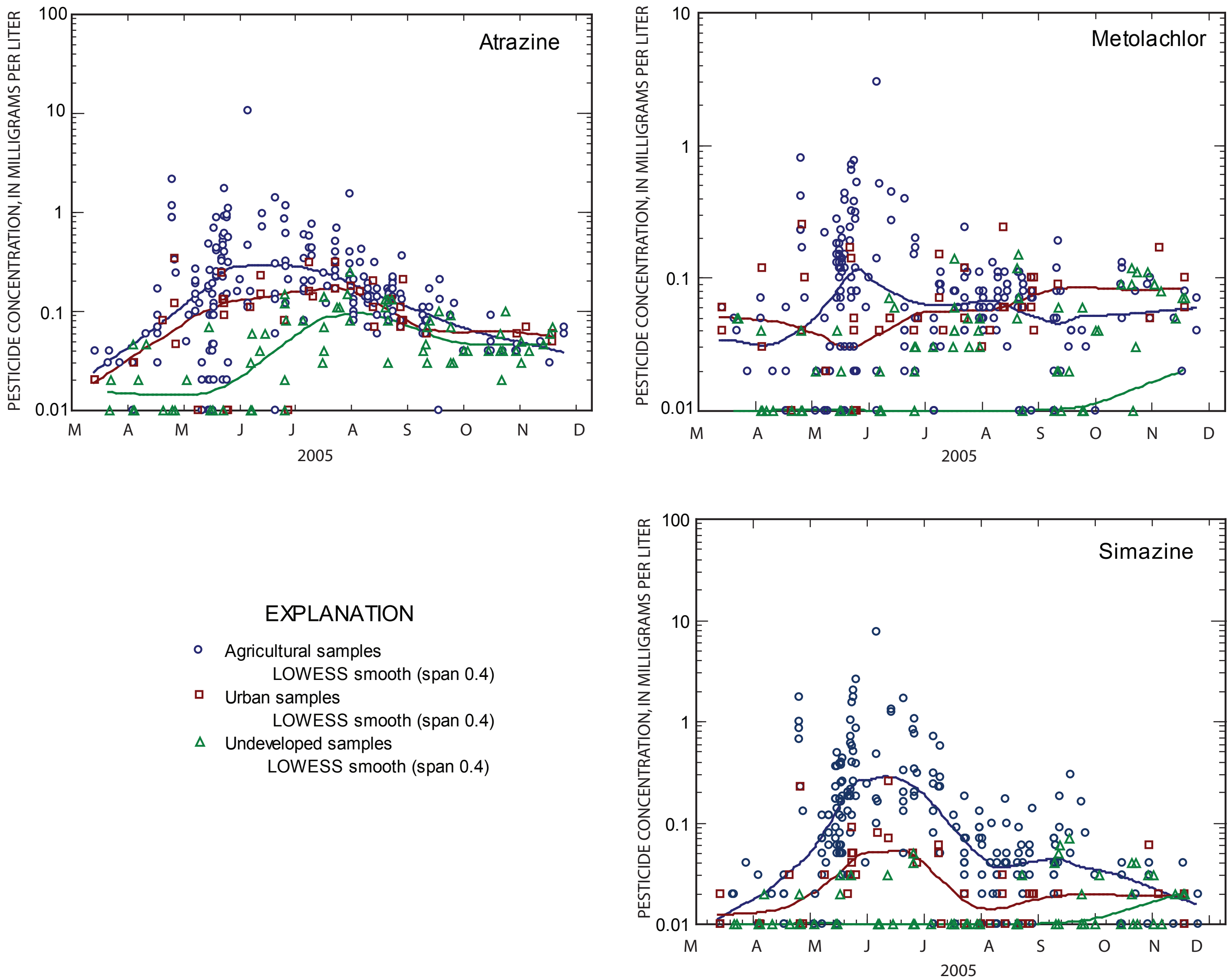

Figure 12. Seasonal patterns in atrazine, metolachlor, and simazine concentrations by land use from selected Michigan streams, March–November, 2005.

In contrast to the apparent lack of change in atrazine concentrations, metolachlor and simazine concentrations do appear to have changed since the late 1990s. In this study, the highest detected metolachlor concentration was found at the Black River site (3.02 µg/L); the NAWQA results showed 37 µg/L at this site in 1997. The difference in maximum concentration may be indicative of decreased metolachlor use (National Agricultural Statistics Service, 2006), owing to the introduction of glyphosate-tolerant crops and improved metolachlor formulations allowing for lower application rates. In contrast, simazine concentrations at the Black River site were higher in 2005 compared to 1996–97 NAWQA concentrations despite a reported decrease in simazine use (National Agricultural Statistics Service, 2006). One possible explanation for this could be the difference in analytical methods. The simazine immunoassay results in this study were likely influenced by cross-reactivity with atrazine or degradates in the assay, which would result in artificially high simazine concentrations. At the Clinton River at Sterling Heights site, atrazine, metolachlor, and simazine concentrations were low for both the

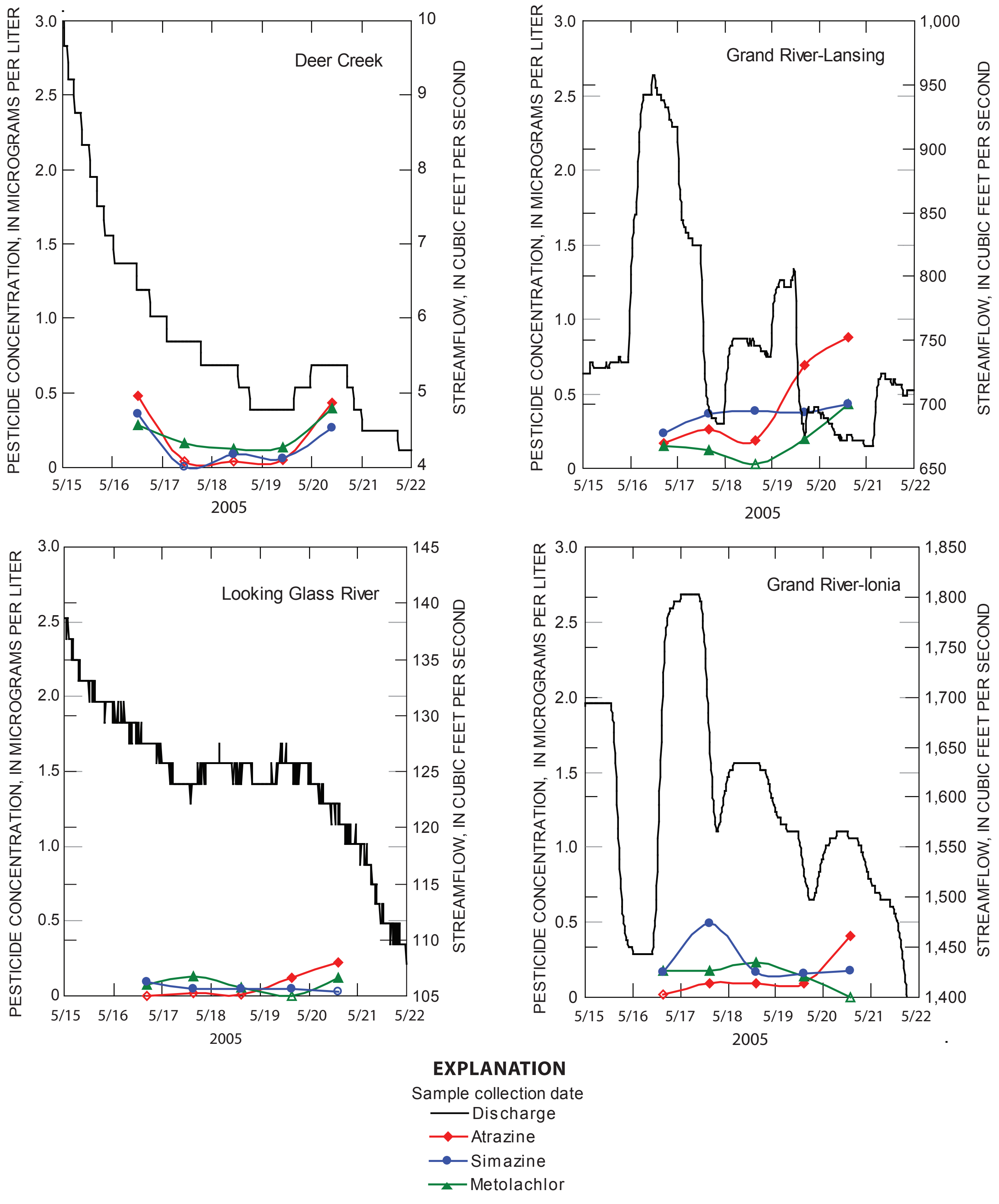

Figure 13. Herbicide concentrations and streamflow in May 2005 for Deer Creek, Grand River at Lansing and at Ionia, and Looking Glass River intensive-study sites, Michigan.

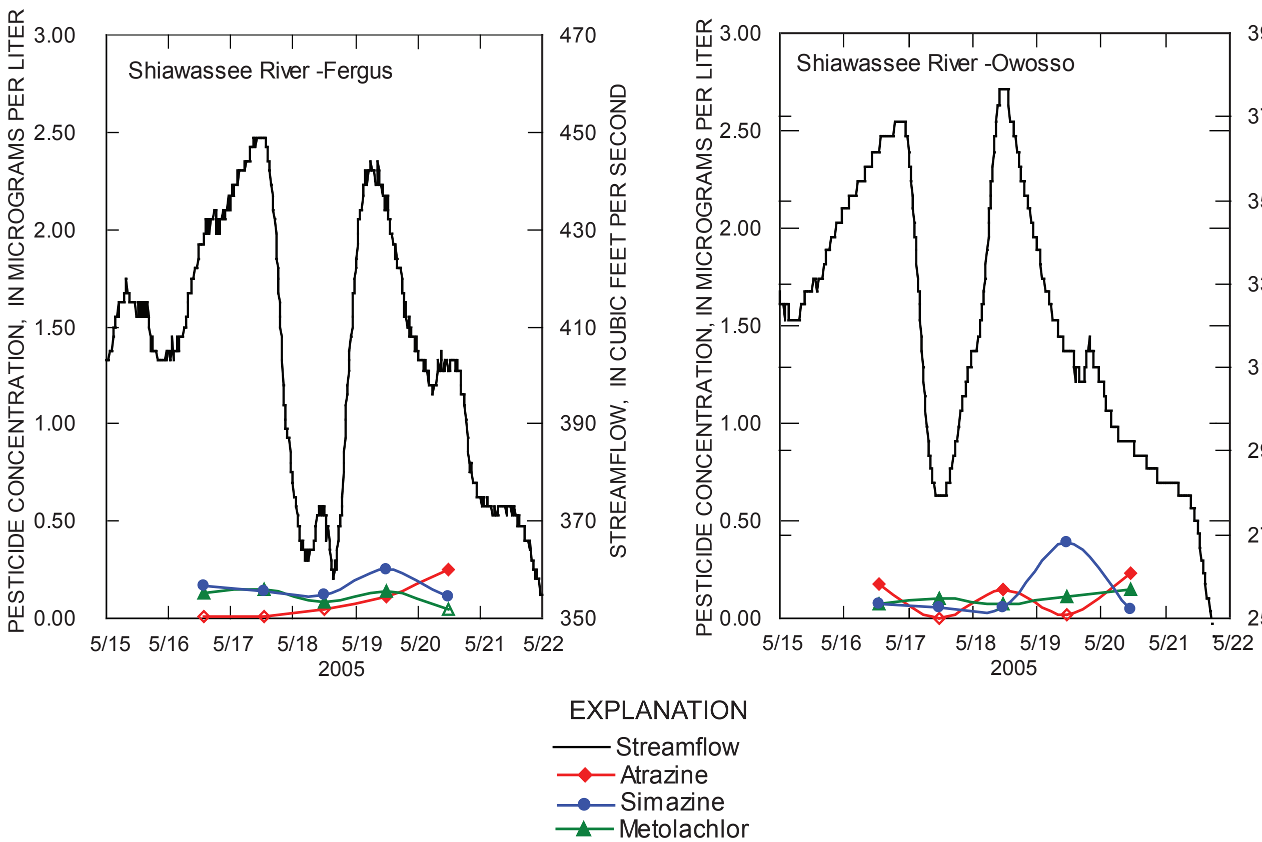

Figure 14. Herbicide concentrations and streamflow in May 2005 for the Shiawassee River intensive-study sites, Fergus and Owosso, Michigan.

1996–97 NAWQA study and the 2005 study (fig. 17). Concentrations of these pesticides in both studies were less than 1 µg/L. These low concentrations make it difficult to determine patterns in concentration over the year; however, the highest detected concentrations were in May or June. Diazinon and chlorpyrifos were not detected at the Black River site in 1996–97 nor in 2005. Both diazinon and chlorpyrifos were used in the past in urban environments, and both were detected at the urban Clinton River site in 1996–97. However, diazinon was not detected in 2005, and chlorpyrifos was detected only in November as part of the current MDEQ pesticide monitoring study previously described.

The NAWQA study, along with this current study, has allowed an historical comparison of pesticide concentrations at specific locations. Analytical methods and climate variability may influence results year to year. Long-term monitoring would be needed to detect detailed trends in the pesticide concentrations for these sites. Despite differences in methods, there are some similarities in results from the studies that may be useful to help determine the hydrochemical effects of pesticide management, such as decreased use or restrictions.

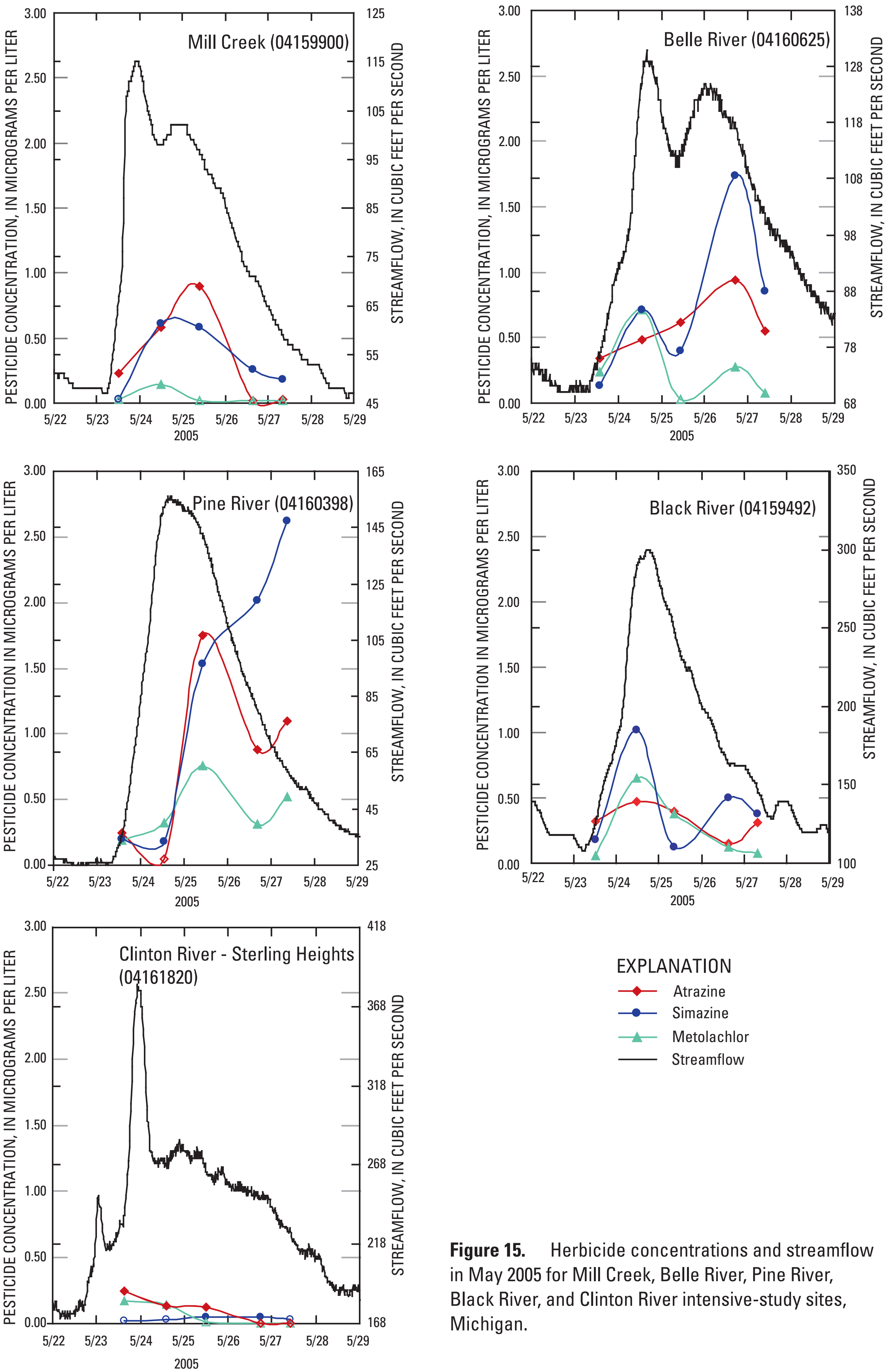

Figure 15. Herbicide concentrations and streamflow in May 2005 for Mill Creek, Belle River, Pine River, Black River, and Clinton River intensive-study sites, Michigan.

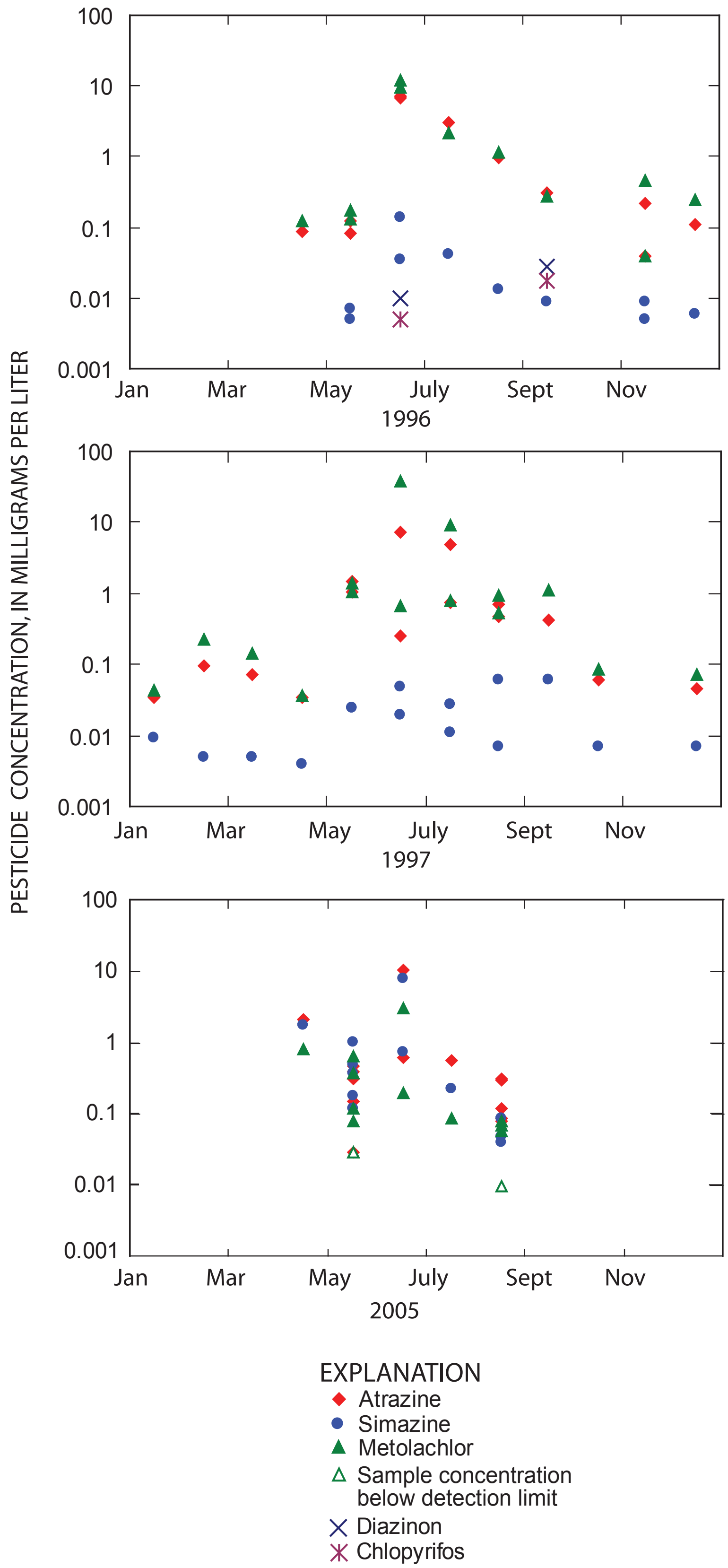

Figure 16. Pesticide concentrations at the Black River study site (USGS station 04159492), Michigan.

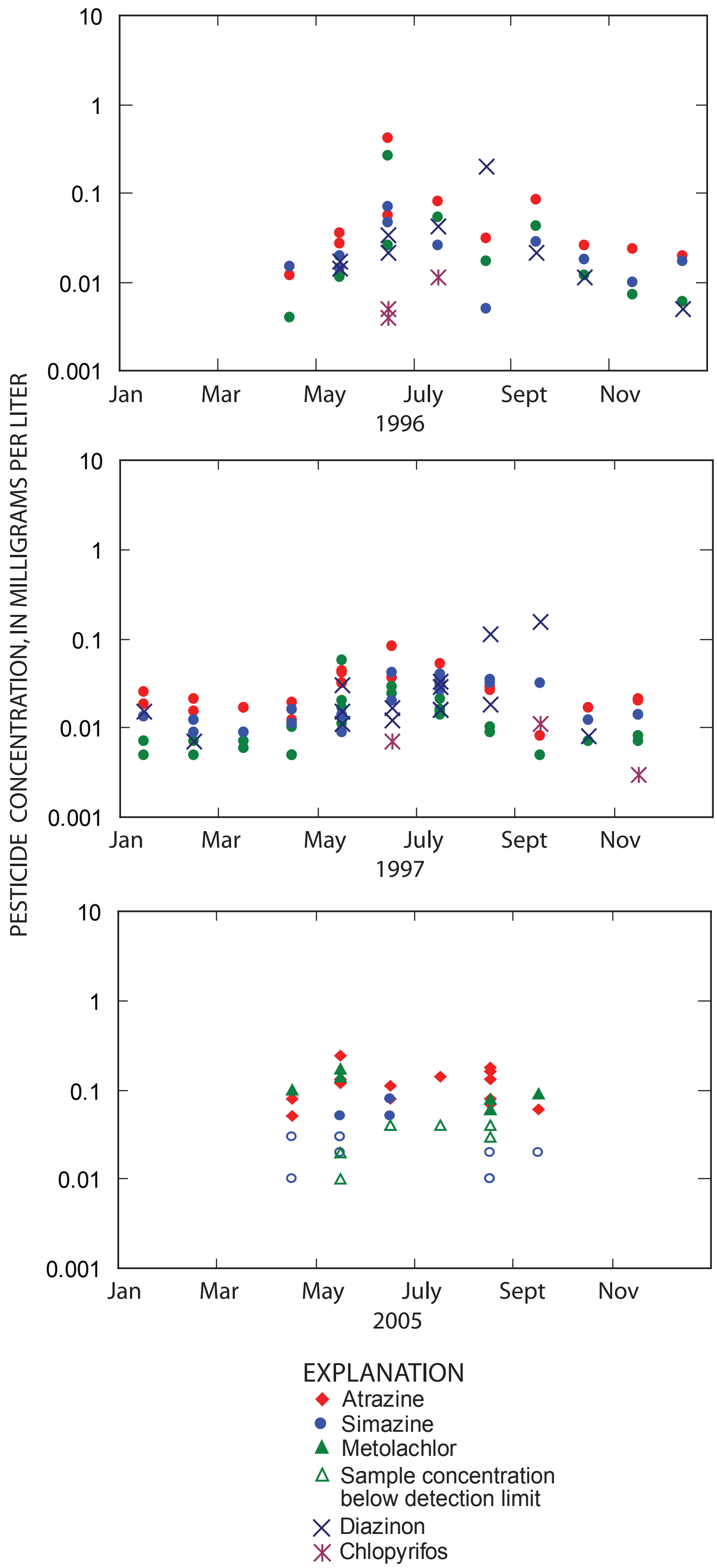

Figure 17. Pesticide concentrations at the Clinton River at Sterling Heights study site (USGS station 04161820), Michigan.

Summary and Conclusions

From March through November 2005, the U.S. Geological Survey, in cooperation with the Michigan Department of Environmental Quality, did a statewide screening of Michigan streams to aid in understanding the occurrence and distribution of selected pesticides. The purpose of this study was to use immunoassays as a screening tool for pesticides in 23 streams to attempt to relate pesticide concentrations to seasonal and land-use patterns. Five pesticides (atrazine, metolachlor, simazine, chlorpyrifos, and diazinon) were chosen for this study on the basis of assay availability and historical or current use in the state. The study showed that the occurrence of pesticides was widespread throughout the state with 90 percent of all samples containing at least one pesticide and 67 percent of all samples containing two or more pesticides. Seasonal and land-use patterns in pesticide concentrations were evident, indicating areas and time of year that pesticide concentrations are most likely to have negative effects on stream-water quality.

Atrazine, metolachlor, and simazine were commonly detected throughout this study (94, 91, and 86 percent of all samples, respectively). Chlorpyrifos and diazinon were not detected. Only one sample, from the Black River in St. Clair County in June, exceeded the Michigan Rule 57 water-quality criterion for any pesticide analyzed for. This sample was collected following herbicide application and recent rainfall and exceeded the Michigan Rule 57 water-quality criterion for atrazine. Although metolachlor and simazine were detected at all sites included in this study, Michigan Rule 57 water-quality criteria were not exceeded for these constituents. Patterns in pesticide concentrations by land use and season were identified. The highest concentrations of atrazine, metolachlor, and simazine occurred at stream sites dominated by agricultural land use. However, stream samples from areas of agricultural and urban land use had similar median concentrations for atrazine and metolachlor. Samples from streams in undeveloped areas had consistently lower concentrations of atrazine, metolachlor, and simazine, and median concentrations were less than the MDLs for the pesticides. Seasonal patterns indicate that higher concentrations or herbicides can be expected in early summer.

By relating seasonal and land-use patterns to pesticide concentrations, pesticide monitoring programs may be able to focus their efforts at targeted locations during specific times of the growing season. The results of this study indicate agricultural areas and urban areas may be affected by pesticides—particularly atrazine—and typically the greatest effects are seen from May to June. However, this study represents only a single sampling season and does not address yearly weather variability that may also influence pesticide concentrations in streams. Only long-term monitoring of pesticide concentrations in streams would show the effects of weather variability and changes in land-management practices. Sampling results in this study showed that changes in herbicide concentrations in the studied streams were rapid, occurring at least daily. Further studies addressing more detailed land characteristics such as more specific land uses, range of soil permeability, amount of tile drainage, and runoff potential on small time scales could help to better describe the transport of pesticides from application areas to streams and could aid in focusing monitoring efforts to areas of most concern.

This study screened for only five selected pesticides using immunoassay techniques. Other methods are available that are more costly but have more sensitive detection levels and can identify a larger number of compounds, including degradate products. From this study, it is evident that pesticides in Michigan streams commonly occur in combinations. Further studies comparing immunoassay analysis with more sensitive methods would be needed to determine the sensitivity of immunoassay methods used and to indicate whether other pesticides and degradates are present in these streams. In particular, a better understanding of the complex mixture of not only parent compounds but also degradate products would be needed to more fully characterize the effects pesticides have on water quality in Michigan streams.

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Appendixes 1 and 2

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study.

[USGS, U.S. Geological Survey; ft³/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft³/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04102080	St. Joseph River at Napier Ave. at St. Joseph, Mich.	03/28/05	1330	E 6,470	12.2	8.2	527	6.4
		05/05/05	1000	E 3,540	10.6	8.2	597	11.1
		06/02/05	1000	E 2,910	9.4	8.0	590	20.6
		06/29/05	1000	E 1,970	7.0	7.9	566	26.8
		07/21/05	1030	E 2,710	7.3	8.2	551	26.4
		08/04/05	1000	E 2,180	12.2	8.2	550	27.0
		08/25/05	1000	E 1,660	8.1	8.9	548	23.0
		09/15/05	1000	E 1,070	7.1	7.9	572	21.5
		09/29/05	1000	E 2,090	7.9	8.1	574	17.6
		10/19/05	1000	E 1,460	9.3	8.3	596	14.5
		11/03/05	1000	E 1,840	10.3	8.0	627	10.8
		11/16/05	1230	E 1,640	10.8	7.9	623	7.9
04108660	Kalamazoo River at New Richmond, Mich.	03/21/05	1200	3,000	2.4	8.0	565	2.5
		05/04/05	1300	1,790	13.7	8.8	586	9.4
		06/01/05	1130	1,510	10.6	8.0	587	19.0
		06/28/05	1130	1,210	6.8	7.5	533	25.8
		07/20/05	1300	1,620	8.9	7.9	573	25.9
		08/03/05	1100	1,240	8.1	7.9	545	25.5
		08/24/05	1115	1,090	8.3	8.0	597	21.1
		09/14/05	1300	894	7.1	8.0	570	23.3
		09/27/05	1300	1,050	9.4	8.1	623	18.0
		10/18/05	1300	1,020	10.6	8.4	632	13.6
		11/02/05	1145	1,140	11.5	8.2	698	9.2
		11/22/05	1100	1,350	11.7	8.5	652	3.9
04111500	Deer Creek near Dansville, Mich.	04/18/05	1115	5.9	12.0	7.9	669	12.7
		05/09/05	1000	5.0	10.5	7.8	663	13.2
		05/16/05	1200	6.5	10.7	7.9	653	10.2
		05/17/05	1040	5.7	13.0	7.8	650	9.7
		05/18/05	1015	5.2	9.6	7.7	664	11.4
		05/19/05	1010	4.9	8.8	7.7	673	12.0
		05/20/05	0950	5.2	9.1	7.7	654	11.3
		06/22/05	1015	2.0	7.6	7.7	669	17.8
		07/08/05	1020	1.2	8.4	7.8	658	19.6
		07/25/05	0905	3.7	6.9	7.8	511	23.2
		08/04/05	1240	.73	6.2	8.1	651	22.8
		08/12/05	0825	.58	6.6	8.4	622	20.7
		08/26/05	1430	.28	8.7	8.3	603	22.0
		09/12/05	1230	.07	5.0	7.8	616	20.3

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft³/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04113000	Grand River at Lansing, Mich.	04/18/05	1645	856	9.9	8.1	700	18.6
		05/09/05	1500	781	9.7	8.2	726	18.2
		05/16/05	1640	901	9.6	8.0	746	14.6
		05/17/05	1550	772	12.4	7.9	739	15.2
		05/18/05	1540	744	10.2	7.9	742	16.1
		05/19/05	1610	746	9.7	7.9	735	16.3
		05/20/05	1500	678	9.5	7.9	710	17.0
		06/22/05	1555	356	8.0	7.8	786	24.7
		07/08/05	1535	449	7.6	7.7	695	26.3
		07/25/05	1500	704	7.9	8.0	570	28.2
		08/04/05	1155	438	6.0	8.1	692	28.6
		08/12/05	1345	259	6.4	7.9	780	27.1
		08/26/05	1040	201	6.9	8.0	814	23.9
		09/12/05	1145	165	7.9	8.0	868	24.5
04114498	Looking Glass River near Eagle, Mich.	04/18/05	1600	179	11.0	8.0	726	17.6
		05/09/05	1420	139	13.7	8.2	764	17.4
		05/16/05	1610	130	10.1	8.0	816	12.9
		05/17/05	1520	126	12.8	7.8	780	12.9
		05/18/05	1500	127	10.4	7.9	779	15.5
		05/19/05	1515	127	9.2	7.8	783	14.1
		05/20/05	1425	123	10.1	7.9	764	16.3
		06/22/05	1520	85	11.0	7.9	780	22.2
		07/08/05	1510	92	9.8	8.0	736	22.9
		07/25/05	1420	115	8.6	7.9	563	25.3
		08/04/05	1135	47	7.3	8.1	783	24.1
		08/12/05	1415	41	11.1	8.3	785	23.4
		08/26/05	1000	31	7.3	8.2	829	18.5
		09/12/05	1000	17	8.5	7.9	841	19.5
04116000	Grand River at Ionia, Mich.	04/18/05	1440	2,010	11.7	8.3	695	16.3
		05/09/05	1330	1,500	11.2	8.2	733	17.5
		05/16/05	1520	1,590	10.2	8.0	742	14.1
		05/17/05	1420	1,710	13.0	7.9	320	14.3
		05/18/05	1355	1,630	10.9	8.0	739	15.6
		05/19/05	1410	1,540	9.8	8.0	759	15.0
		05/20/05	1345	1,550	10.3	8.0	732	15.7
		06/22/05	1430	1,320	6.7	8.0	685	23.2
		07/08/05	1425	732	18.0	8.7	666	26.0
		07/25/05	1400	1,680	7.8	8.1	711	27.9
		08/04/05	1050	759	6.9	8.3	590	27.2
		08/12/05	1230	528	9.1	8.4	644	25.1
		08/26/05	0915	472	5.04	7.9	692	20.9
		09/12/05	1050	344	5.9	7.8	740	21.7

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04119400	Grand River near Eastmanville, Mich.	03/22/05	1030	E 6,340	12.1	8.0	666	2.3
		04/11/05	1100	E 5,220	12.6	8.2	552	13.7
		05/11/05	0930	E 3,240	10.3	8.3	646	18.2
		06/08/05	1100	E 2,480	10.0	8.1	649	24.1
		06/27/05	1500	E 2,060	14.3	8.5	633	27.4
		07/19/05	1600	E 1,620	14.8	8.9	590	27.6
		08/02/05	1645	E 1,910	13.4	8.6	565	27.5
		08/23/05	1530	E 1,160	16.9	8.7	651	22.5
		09/20/05	1115	E 1,170	8.4	8.1	705	20.4
		10/04/05	1445	E 1,620	12.2	8.5	675	20.3
		10/26/05	1100	E 1,290	10.2	8.1	716	9.9
		11/21/05	1130	E 2,270	12.0	7.9	671	4.4
04122030	Muskegon River near Bridgeton, Mich.	03/22/05	1300	E 2,050	13.4	8.0	350	2.0
		05/04/05	0930	E 1,860	11.1	8.0	294	7.8
		06/08/05	1230	E 1,190	8.2	8.0	350	22.1
		06/27/05	1230	E 1,120	10.4	8.0	357	23.6
		07/19/05	1300	E 961	8.9	8.2	363	24.0
		08/02/05	1345	E 1,080	9.1	8.1	373	25.1
		08/23/05	1230	E 1,140	10.8	8.1	380	20.0
		09/14/05	1000	E 1,020	7.7	8.0	354	21.7
		09/27/05	1000	E 4,010	8.0	7.7	360	18.0
		10/18/05	1145	E 1,410	9.5	8.1	367	13.4
		11/02/05	1430	E 1,380	12.2	8.2	401	11.5
		11/21/05	1400	E 1,960	11.0	8.0	378	6.8
04122500	Pere Marquette River at Scottville, Mich.	03/23/05	0900	814	12.1	8.1	301	3.1
		04/11/05	1300	972	12.6	8.0	294	11.2
		05/16/05	1030	761	9.9	7.9	297	9.6
		06/09/05	0830	510	7.2	7.6	367	21.0
		06/27/05	1100	448	9.6	7.7	374	20.3
		07/19/05	1100	438	9.4	8.0	364	21.2
		08/02/05	1200	447	8.3	7.9	380	20.8
		08/23/05	1045	458	10.8	7.8	360	15.6
		09/20/05	1400	380	9.5	7.9	387	15.4
		10/04/05	1045	504	7.9	7.9	355	16.2
		10/26/05	1410	447	11.8	8.1	345	7.2
		11/17/05	0930	709	12.1	7.8	327	2.8

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft³/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft³/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04132052	Cheboygan River (pond) at Lincoln Ave at Cheboygan, Mich.	04/04/05	1300	E 1,340	11.9	7.9	288	3.6
		04/26/05	1120	E 1,410	11.8	8.2	329	6.3
		05/17/05	1345	E 1,580	11.2	8.3	284	10.3
		06/08/05	1215	E 852	8.8	8.2	328	21.2
		06/27/05	1145	E 1,360	8.4	8.3	314	24.3
		07/18/05	1330	E 545	8.2	8.4	309	28.1
		07/27/05	1030	E 624	7.2	8.2	321	24.1
		08/22/05	1200	E 844	7.8	8.2	300	20.7
		09/12/05	1230	E 662	NA	NA	NA	22.0
		09/27/05	1200	E 604	7.9	8.1	316	18.5
		10/24/05	1215	E 1,120	9.2	NA	320	11.2
		11/08/05	1130	E 1,140	10.2	8.1	323	8.4
04135020	Thunder Bay River at Alpena, Mich.	04/04/05	1630	E 3,320	13.2	7.8	240	2.0
		04/26/05	1530	E 1,980	11.2	8.1	364	6.8
		05/18/05	0740	E 741	9.3	8.2	383	11.8
		06/08/05	1530	E 422	8.1	8.2	381	22.4
		06/27/05	1500	E 413	7.9	8.3	355	24.4
		07/19/05	0800	E 262	6.2	8.0	344	26.3
		07/27/05	0800	E 428	6.4	8.1	319	24.2
		08/22/05	1430	E 924	7.1	8.0	330	20.7
		09/13/05	1500	E 281	7.5	8.4	340	23.1
		09/27/05	1530	E 531	7.5	7.9	341	18.7
		10/24/05	1715	E 545	10.1	NA	363	9.8
		11/08/05	1530	E 918	9.8	8.0	365	7.9
04137500	Au Sable River near Au Sable, Mich.	04/05/05	1000	2,380	12.9	8.2	304	2.7
		04/27/05	1000	1,710	10.6	8.1	272	8.7
		05/18/05	1135	996	9.4	8.1	292	12.4
		06/09/05	0900	1,160	8.7	8.1	312	19.8
		06/28/05	0950	1,080	7.4	8.1	310	23.1
		07/19/05	1100	1,180	7.1	8.2	316	25.6
		07/26/05	1530	1,810	7.1	8.2	309	25.9
		08/23/05	0930	1,370	7.5	8.0	301	22.7
		09/14/05	0900	1,270	7.4	8.0	294	22.8
		09/28/05	1000	1,850	7.9	8.0	239	19.8
		10/25/05	0900	1,030	8.9	NA	304	12.9
		11/09/05	0930	1,730	9.8	8.0	311	9.9

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04144500	Shiawassee River at Owosso, Mich.	04/18/05	1215	227	12.3	8.3	874	15.7
		05/09/05	1110	258	10.1	8.2	828	15.6
		05/16/05	1250	360	10.8	8.1	810	13.4
		05/17/05	1150	303	13.1	7.9	807	13.2
		05/18/05	1130	351	10.1	7.3	825	14.4
		05/19/05	1115	317	9.3	7.8	853	15.1
		05/20/05	1100	292	9.9	7.9	787	14.0
		06/22/05	1120	188	8.3	7.7	907	19.9
		07/08/05	1245	135	8.4	7.7	1,034	20.9
		07/25/05	1130	188	5.5	7.8	780	25.7
		08/04/05	1520	100	5.5	7.8	1,124	23.9
		08/12/05	1100	87	.5	8.3	1,182	22.1
		08/26/05	1320	58	8.5	8.2	1,130	21.9
		09/12/05	1415	43	7.0	7.5	1,122	22.7
04145000	Shiawassee River near Fergus, Mich.	04/04/05	0900	1,070	11.5	8.3	561	7.3
		04/18/05	1310	294	9.4	8.2	749	16.8
		04/28/05	0900	854	10.5	8.3	658	8.7
		05/09/05	1150	307	8.7	8.1	714	16.6
		05/16/05	1340	422	10.0	8.2	703	13.7
		05/17/05	1230	431	12.7	8.2	684	13.8
		05/18/05	1215	374	10.0	8.2	698	15.4
		05/19/05	1210	428	9.4	8.2	711	16.1
		05/20/05	1140	396	9.7	8.0	703	14.3
		05/24/05	0900	305	8.6	8.2	692	15.0
		06/15/05	1215	374	7.9	8.1	618	23.9
		06/22/05	1210	276	8.7	8.0	722	22.3
		07/08/05	1210	164	7.9	8.1	611	22.8
		07/12/05	0900	110	6.1	8.1	665	26.1
		07/25/05	1055	217	7.1	8.2	632	26.7
		07/26/05	1145	208	6.7	8.2	642	26.9
		08/04/05	1450	107	7.7	8.4	634	26.9
		08/12/05	1015	89	3.4	8.2	733	23.9
		08/16/05	0930	80	8.1	8.1	647	23.5
		08/26/05	1245	68	9.9	8.5	946	22.3
		08/31/05	0940	64	6.6	8.2	680	21.2
		09/12/05	1345	57	9.0	8.3	717	23.6
		09/21/05	1230	61	8.1	8.0	810	19.7
		10/19/05	1445	117	9.9	8.3	670	12.4
		11/03/05	1545	116	8.5	8.2	810	10.5
		11/29/05	1205	315	12.3	8.3	808	3.9

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft³/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04157065	Saginaw River at Weadock Road at Essexville, Mich.	03/14/05	1430	E 6,270	12.5	7.5	536	0.8
		04/04/05	1300	E 1,2500	11.4	8.1	444	6.4
		04/27/05	1430	E 8,490	10.0	7.8	660	8.9
		06/15/05	1100	E 8,510	5.1	7.4	545	23.5
		07/11/05	1400	E 1,330	10.4	8.5	707	26.5
		07/25/05	1445	E 1,920	8.1	8.1	709	28.1
		08/16/05	0800	E 1,240	6.3	7.8	660	25.5
		08/31/05	1110	E 1,090	6.1	8.1	735	23.2
		09/21/05	1030	E 887	6.5	7.8	853	21.4
		10/19/05	0950	E 3,320	7.3	8.0	730	13.6
		11/29/05	1030	E 1,150	12.6	8.0	756	1.7
04159492	Black River near Jeddo, Mich.	04/26/05	0945	1,970	11.7	8.1	524	5.3
		05/12/05	1100	129	11.5	8.5	745	14.3
		05/23/05	1145	136	8.7	8.0	761	15.2
		05/24/05	1150	257	9.6	8.0	757	15.2
		05/25/05	0840	233	9.2	8.0	545	12.7
		05/26/05	1520	175	10.1	8.1	712	17.0
		05/27/05	0752	144	8.2	8.0	727	16.3
		06/07/05	0900	300	6.9	8.0	758	22.4
		06/28/05	1100	58	8.9	8.3	811	27.2
		07/11/05	0900	35	7.4	7.8	790	23.4
		08/02/05	1030	37	9.6	8.5	702	26.4
		08/08/05	1100	25	9.4	8.5	775	25.2
		08/17/05	1200	25	8.4	8.2	792	22.2
		08/24/05	1000	24	9.0	8.2	800	19.4
		08/30/05	1030	31	8.0	8.2	784	22.9
		09/13/05	1030	14	9.9	8.3	800	22.2
04159900	Mill Creek near Avoca, Mich.	04/26/05	1135	526	NA	NA	NA	NA
		05/12/05	1245	51	NA	NA	NA	NA
		05/23/05	1230	76	NA	NA	NA	NA
		05/24/05	1222	102	NA	NA	NA	NA
		05/25/05	0912	94	NA	NA	NA	NA
		05/26/05	1545	74	NA	NA	NA	NA
		05/27/05	0817	57	NA	NA	NA	NA
		06/07/05	1025	52	7.8	8.0	841	23.8
		06/28/05	1211	19	13.2	8.3	813	27.7
		07/12/05	1000	10	NA	NA	NA	NA
		08/02/05	1145	8.6	8.0	8.1	761	26.3
		08/11/05	1145	6.4	NA	NA	NA	NA
		08/17/05	1415	7.0	9.4	8.2	850	23.8
		08/24/05	1130	6.8	9.7	8.3	829	19.0
		08/30/05	1115	8.6	8.1	8.1	618	22.9
		09/13/05	1130	4.3	8.6	8.2	820	22.0

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04160398	Pine River near Marysville, Mich.	04/26/05	1332	1,290	10.7	7.8	406	7.4
		05/12/05	1445	26	11.1	8.2	565	15.5
		05/23/05	1327	41	8.6	8.0	623	13.8
		05/24/05	1315	136	9.0	8.0	568	13.7
		05/25/05	1007	136	9.2	8.0	545	12.8
		05/26/05	1630	88	9.7	8.1	556	16.3
		05/27/05	0858	57	8.7	8.0	577	14.8
		06/07/05	1200	15	7.3	7.9	622	22.6
		06/28/05	1400	12	8.5	8.1	695	25.3
		07/12/05	1145	3.3	8.1	8.1	552	23.5
		08/02/05	1415	3.6	8.7	8.0	580	24.9
		08/08/05	1125	1.4	9.2	8.1	556	24.0
		08/17/05	1400	1.5	9.0	8.2	569	23.3
		08/24/05	1315	1.0	9.8	8.3	548	20.1
		08/30/05	1215	2.8	7.7	8.1	584	21.4
		09/13/05	1345	.44	9.4	8.2	586	21.8
04160625	Belle River near Marine City, Mich.	04/26/05	1532	592	10.3	8.1	622	8.4
		05/12/05	1515	74	10.8	8.2	901	15.6
		05/23/05	1400	80	8.4	8.1	864	14.5
		05/24/05	1337	115	9.4	8.1	884	14.3
		05/25/05	1038	117	9.4	8.1	857	13.8
		05/26/05	1655	119	10.1	8.2	892	16.4
		05/27/05	0921	102	8.7	8.3	898	16.1
		06/07/05	1340	49	6.8	8.0	1,040	23.7
		06/28/05	1530	33	8.3	8.1	991	25.6
		07/12/05	1315	21	7.5	8.2	882	23.6
		08/02/05	1615	29	8.9	8.2	960	24.7
		08/08/05	1200	19	7.6	8.2	1,200	23.4
		08/17/05	1430	16	10.1	8.3	1,511	22.8
		08/23/05	1330	13	8.8	8.2	1,705	19.4
		08/30/05	1245	20	7.1	8.1	1,599	21.7
		09/13/05	1515	7.5	8.4	8.2	1,159	20.8
		09/15/05	1130	7.6	6.5	8.1	1,370	20.0

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft³/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft³/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
04161820	Clinton River at Sterling Heights, Mich.	04/21/05	1100	105	9.5	8.1	1,238	12.1
		04/28/05	1130	407	11.6	8.2	1,062	9.1
		05/10/05	1000	166	8.5	8.0	955	15.9
		05/23/05	1500	266	8.3	8.0	1,000	14.5
		05/24/05	1440	292	9.0	8.1	997	14.4
		05/25/05	1135	273	9.2	8.1	947	14.3
		05/26/05	1747	256	8.6	8.1	926	17.5
		05/27/05	1017	226	8.5	8.1	921	16.2
		06/08/05	1455	82	8.0	8.0	1,114	24.1
		06/27/05	1445	84	9.0	8.1	1,011	24.7
		06/29/05	1130	90	7.2	7.6	1,060	23.4
		07/13/05	1445	65	9.1	8.2	1,060	25.4
		08/03/05	1130	95	7.6	8.1	910	24.6
		08/08/05	1430	65	10.1	8.3	1,010	24.3
		08/16/05	1515	64	8.6	8.2	995	22.5
		08/25/05	1100	53	9.3	8.2	1,094	19.2
		08/30/05	1101	67	7.5	7.9	1,020	21.4
		08/30/05	1100	67	7.7	8.1	1,003	20.8
		08/31/05	1100	66	8.1	7.5	996	20.7
		09/14/05	1600	35	8.6	8.2	1,072	21.7
04165553	Clinton River at Moravian Dr. at Mt. Clemens, Mich.	03/14/05	1200	619	13.3	7.8	1,068	2.4
		04/05/05	0900	687	10.8	8.3	952	7.8
		04/27/05	1205	1,710	9.4	7.8	900	8.8
		05/25/05	0900	413	7.8	7.8	1,040	13.7
		06/14/05	1130	301	4.1	7.5	1,030	22.6
		07/11/05	1200	121	5.3	7.7	1,020	24.0
		07/25/05	1200	1,100	6.6	7.6	527	24.3
		08/15/05	1230	191	5.4	7.6	830	22.3
		09/01/05	0945	129	5.2	7.5	915	21.2
		11/03/05	1330	E 268	7.4	7.8	923	10.2
		11/22/05	1350	E 442	10.1	7.8	964	5.4
04168550	River Rouge at River Rouge, Mich.	03/14/05	1000	E 369	13.9	7.8	238	.2
		04/05/05	1100	E 309	12.1	8.1	337	5.4
		04/27/05	1030	E 994	7.4	8.3	1,170	11.6
		05/25/05	1130	E 245	6.4	7.6	942	16.0
		06/14/05	1000	E 406	4.7	7.4	495	25.5
		07/11/05	1000	E 152	6.1	7.7	545	22.4
		07/25/05	1000	E 532	3.9	7.6	530	29.0
		08/15/05	1030	E 168	4.5	7.6	456	28.8
		09/01/05	1145	E 124	4.3	7.6	374	28.1
		11/08/05	1000	E 99	7.4	7.5	500	14.9
		11/22/05	1152	E 202	8.6	7.4	590	8.9

Appendix 1. Station name, sample-collection date and time, streamflow, and onsite measurements for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; ft^3/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter,°C, degrees Celsius; NA, data not available; E, estimated value]

USGS station number	USGS station name	Sample date	Sample time	Daily mean discharge (ft^3/s)	Dissolved oxygen (mg/L)	pH	Specific conductance (µS/cm)	Water temperature (°C)
040590345	Escanaba River at Wells, Mich.	04/07/05	1340	E 4,580	13.7	7.3	161	3.1
		04/21/05	1100	E 1,870	11.7	7.1	248	10.7
		05/24/05	1145	E 1,070	9.9	8.1	303	15.3
		06/13/05	1315	E 461	7.3	8.0	349	25.8
		06/16/05	1230	E 957	8.6	8.0	281	18.8
		08/01/05	1315	E 202	6.4	8.0	609	25.0
		08/25/05	1200	E 173	6.3	8.0	642	21.2
		09/15/05	1115	E 231	6.2	7.8	628	21.1
		10/06/05	1300	E 1,410	8.1	8.0	334	18.3
		10/27/05	1300	E 610	10.8	7.8	420	8.2
		11/22/05	0845	E 559	12.9	6.8	422	1.1

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study.

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04102080	St. Joseph River at Napier Ave. at St. Joseph, Mich.	03/28/05	E 0.03	ND	ND	E 0.02	0.04
		05/05/05	.09	ND	ND	E .02	E .02
		06/02/05	.21	ND	ND	.1	.24
		06/29/05	.21	ND	ND	.05	.31
		07/21/05	.18	ND	ND	.06	.09
		08/04/05	.21	ND	ND	.08	.07
		08/25/05	.17	ND	ND	.1	.06
		09/15/05	.17	ND	ND	E .02	.09
		09/29/05	.12	ND	ND	E .03	.08
		10/19/05	E .04	ND	ND	.13	E .03
		11/03/05	.05	ND	ND	.1	.04
		11/16/05	.05	ND	ND	.05	E .01
04108660	Kalamazoo River at New Richmond, Mich.	03/21/05	E .03	ND	ND	.05	E .02
		05/04/05	.05	ND	ND	E .01	ND
		06/01/05	.16	ND	ND	.06	.04
		06/28/05	.12	ND	ND	E .02	.18
		07/20/05	.12	ND	ND	.08	E .01
		08/03/05	.16	ND	ND	.05	ND
		08/24/05	.15	ND	ND	E .01	E .01
		09/14/05	.08	ND	ND	.19	.04
		09/27/05	.09	ND	ND	E .04	.16
		10/18/05	E .04	ND	ND	.09	ND
		11/02/05	E .04	ND	ND	.09	E .01
		11/22/05	.06	ND	ND	.08	E .01
04111500	Deer Creek near Dansville, Mich.	04/18/05	E .03	ND	ND	E .01	E .02
		05/09/05	.27	ND	ND	E .02	.07
		05/16/05	.48	ND	ND	.28	.36
		05/17/05	E .04	ND	ND	.16	ND
		05/18/05	E .04	ND	ND	.12	.08
		05/19/05	.05	ND	ND	.13	.06
		05/20/05	.43	ND	ND	.39	.26
		06/22/05	.13	ND	ND	E .02	.13
		07/08/05	.08	ND	ND	ND	ND
		07/25/05	.26	ND	ND	.24	.05
		08/04/05	.08	ND	ND	E .04	ND
		08/12/05	.07	ND	ND	.07	E .01
		08/26/05	.17	ND	ND	.08	E .01
		09/12/05	.07	ND	ND	E .02	E .02

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04113000	Grand River at Lansing, Mich.	04/18/05	0.17	ND	ND	ND	E 0.02
		05/09/05	.19	ND	ND	.05	.12
		05/16/05	.17	ND	ND	.15	.23
		05/17/05	.26	ND	ND	.12	.36
		05/18/05	.19	ND	ND	E .03	.38
		05/19/05	.69	ND	ND	.2	.37
		05/20/05	.88	ND	ND	.43	.43
		06/22/05	.15	ND	ND	E .03	.16
		07/08/05	.17	ND	ND	ND	.13
		07/25/05	.17	ND	ND	.06	.04
		08/04/05	.08	ND	ND	.07	E .01
		08/12/05	.13	ND	ND	.1	E .03
		08/26/05	.21	ND	ND	ND	E .03
		09/12/05	.11	ND	ND	.05	.07
04114498	Looking Glass River near Eagle, Mich.	04/18/05	.07	ND	ND	ND	ND
		05/09/05	.13	ND	ND	E .02	.05
		05/16/05	ND	ND	ND	.07	.09
		05/17/05	E .02	ND	ND	.13	.05
		05/18/05	E .01	ND	ND	.06	.05
		05/19/05	.12	ND	ND	ND	.05
		05/20/05	.22	ND	ND	.12	E .03
		06/22/05	.3	ND	ND	.06	.33
		07/08/05	.16	ND	ND	E .03	.08
		07/25/05	.3	ND	ND	.12	.07
		08/04/05	.1	ND	ND	E .04	E .01
		08/12/05	.12	ND	ND	.11	E .02
		08/26/05	.1	ND	ND	.06	E .02
		09/12/05	.06	ND	ND	ND	E .03
04116000	Grand River at Ionia, Mich.	04/18/05	.06	ND	ND	E .02	E .02
		05/09/05	.15	ND	ND	ND	.07
		05/16/05	E .02	ND	ND	.18	.17
		05/17/05	.09	ND	ND	.18	.49
		05/18/05	.09	ND	ND	.23	.17
		05/19/05	.09	ND	ND	.14	.16
		05/20/05	.41	ND	ND	ND	.18
		06/22/05	1.41	ND	ND	.4	1.67
		07/08/05	.2	ND	ND	ND	.24
		07/25/05	.22	ND	ND	E .04	.04
		08/04/05	.13	ND	ND	.07	.06
		08/12/05	.19	ND	ND	.08	.04
		08/26/05	.19	ND	ND	.06	.04
		09/12/05	.11	ND	ND	E .01	E .03

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04119400	Grand River near Eastmanville, Mich.	03/22/05	E 0.04	ND	ND	E 0.04	E 0.02
		04/11/05	.06	ND	ND	E .02	E .02
		05/11/05	.12	ND	ND	ND	.04
		06/08/05	.16	ND	ND	.51	.16
		06/27/05	.86	ND	ND	.15	.83
		07/19/05	.24	ND	ND	.08	.12
		08/02/05	.23	ND	ND	.06	.07
		08/23/05	.17	ND	ND	.11	.04
		09/20/05	ND	ND	ND	E .03	.08
		10/04/05	E .04	ND	ND	ND	E .03
		10/26/05	E .04	ND	ND	.08	E .02
		11/21/05	E .03	ND	ND	E .02	.04
04122030	Muskegon River near Bridgeton, Mich.	03/22/05	ND	ND	ND	.05	E .01
		05/04/05	E .02	ND	ND	E .02	ND
		06/08/05	ND	ND	ND	E .02	ND
		06/27/05	E .02	ND	ND	E .01	.05
		07/19/05	.07	ND	ND	E .04	ND
		08/02/05	.25	ND	ND	.05	ND
		08/23/05	.13	ND	ND	.07	ND
		09/14/05	.07	ND	ND	E .02	.05
		09/27/05	.07	ND	ND	.06	E .02
		10/18/05	E .04	ND	ND	.09	E .01
		11/02/05	E .04	ND	ND	.11	E .03
		11/21/05	.06	ND	ND	.07	E .02
04122500	Pere Marquette River at Scottville, Mich.	03/23/05	E .02	ND	ND	.05	E .01
		04/11/05	.05	ND	ND	ND	ND
		05/16/05	.07	ND	ND	E .04	ND
		06/09/05	E .01	ND	ND	E .01	ND
		06/27/05	ND	ND	ND	E .01	ND
		07/19/05	E .04	ND	ND	.06	ND
		08/02/05	.08	ND	ND	E .03	ND
		08/23/05	E .03	ND	ND	.07	ND
		09/20/05	.1	ND	ND	E .02	.07
		10/04/05	E .04	ND	ND	E .04	ND
		10/26/05	E .04	ND	ND	E .03	.04
		11/17/05	.05	ND	ND	.05	E .02
04132052	Cheboygan River (pond) at Lincoln Ave at Cheboygan, Mich.	04/04/05	E .01	ND	ND	ND	E .01
		04/26/05	ND	ND	ND	E .04	ND
		05/17/05	ND	ND	ND	E .01	E .01
		06/08/05	E .03	ND	ND	ND	ND
		06/27/05	.12	ND	ND	E .03	ND
		07/18/05	E .03	ND	ND	E .03	ND
		07/27/05	.11	ND	ND	E .03	ND
		08/22/05	.11	ND	ND	.12	E .01
		09/12/05	E .04	ND	ND	E .01	.04
		09/27/05	.09	ND	ND	E .01	E .01
		10/24/05	.06	ND	ND	.09	.04
		11/08/05	.05	ND	ND	.09	E .03

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04135020	Thunder Bay River at Alpena, Mich.	04/04/05	0.05	ND	ND	E 0.04	ND
		04/26/05	ND	ND	ND	ND	ND
		05/18/05	ND	ND	ND	ND	ND
		06/08/05	E .01	ND	ND	ND	E 0.01
		06/27/05	.08	ND	ND	E .02	.04
		07/19/05	.14	ND	ND	E .04	ND
		07/27/05	.08	ND	ND	E .03	ND
		08/22/05	.13	ND	ND	.05	E .01
		09/13/05	.05	ND	ND	E .02	ND
		09/27/05	E .03	ND	ND	ND	E .02
		10/24/05	E .04	ND	ND	.12	E .02
		11/08/05	E .03	ND	ND	.09	E .01
04137500	Au Sable River near Au Sable, Mich.	04/05/05	ND	ND	ND	ND	ND
		04/27/05	ND	ND	ND	E .01	ND
		05/18/05	ND	ND	ND	E .02	E .02
		06/09/05	.06	ND	ND	E .01	E .01
		06/28/05	.08	ND	ND	E .03	ND
		07/19/05	.14	ND	ND	.14	ND
		07/26/05	.11	ND	ND	.05	ND
		08/23/05	.08	ND	ND	.15	E .01
		09/14/05	E .03	ND	ND	.06	E .01
		09/28/05	E .03	ND	ND	ND	ND
		10/25/05	E .02	ND	ND	ND	E .01
		11/09/05	E .04	ND	ND	.08	E .01
04144500	Shiawassee River at Owosso, Mich.	04/18/05	.09	ND	ND	.06	ND
		05/09/05	.1	ND	ND	E .01	ND
		05/16/05	.18	ND	ND	.07	.07
		05/17/05	ND	ND	ND	.1	.06
		05/18/05	.15	ND	ND	.07	.06
		05/19/05	E .02	ND	ND	.11	.39
		05/20/05	.23	ND	ND	.15	.05
		06/22/05	.06	ND	ND	E .04	.05
		07/08/05	.34	ND	ND	E .04	.31
		07/25/05	.4	ND	ND	.1	E .02
		08/04/05	.09	ND	ND	.06	E .03
		08/12/05	.14	ND	ND	.06	E .03
		08/26/05	.14	ND	ND	.09	E .02
		09/12/05	.09	ND	ND	ND	.07

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04145000	Shiawassee River near Fergus, Mich.	04/04/05	E 0.01	ND	ND	0.05	ND
		04/18/05	.07	ND	ND	E .01	E 0.03
		04/28/05	.24	ND	ND	.07	.13
		05/09/05	.2	ND	ND	.22	E .03
		05/16/05	E .01	ND	ND	.13	.17
		05/17/05	E .01	ND	ND	.15	.14
		05/18/05	.05	ND	ND	.08	.12
		05/19/05	.11	ND	ND	.14	.25
		05/20/05	.25	ND	ND	E .03	.11
		05/24/05	.14	ND	ND	.07	.08
		06/15/05	.97	ND	ND	.27	1.32
		06/22/05	ND	ND	ND	E .04	.2
		07/08/05	.59	ND	ND	.05	.71
		07/12/05	.43	ND	ND	.08	.23
		07/25/05	.32	ND	ND	E .04	E .03
		07/26/05	.69	ND	ND	.11	.07
		08/04/05	.12	ND	ND	.05	E .02
		08/12/05	.17	ND	ND	.11	.05
		08/16/05	.12	ND	ND	.07	.04
		08/26/05	.22	ND	ND	.09	E .03
		08/31/05	.13	ND	ND	.07	E .01
		09/12/05	.09	ND	ND	E .01	.04
		09/21/05	.13	ND	ND	E .04	.05
		10/19/05	.05	ND	ND	.05	E .01
		11/03/05	E .04	ND	ND	.05	E .03
		11/29/05	.07	ND	ND	E .04	E .02
04157065	Saginaw River at Weadock Road at Essexville, Mich.	03/14/05	E .04	ND	ND	.06	E .01
		04/04/05	E .03	ND	ND	.07	E .03
		04/27/05	.33	ND	ND	.17	.23
		06/15/05	.71	ND	ND	.44	1.24
		07/11/05	.43	ND	ND	.09	.23
		07/25/05	.51	ND	ND	.07	.18
		08/16/05	.31	ND	ND	.11	.17
		08/31/05	.36	ND	ND	.08	.14
		09/21/05	.21	ND	ND	E .04	.3
		10/19/05	.09	ND	ND	.12	.04
		11/29/05	.06	ND	ND	.07	ND

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04159492	Black River near Jeddo, Mich.	04/26/05	2.15	ND	ND	0.81	1.77
		05/12/05	E .03	ND	ND	E .03	.12
		05/23/05	.32	ND	ND	E .03	.18
		05/24/05	.47	ND	ND	.65	1.02
		05/25/05	.4	ND	ND	.38	.12
		05/26/05	.15	ND	ND	.12	.5
		05/27/05	.31	ND	ND	.08	.38
		06/07/05	10.55	ND	ND	3.02	7.8
		06/28/05	.62	ND	ND	.2	.76
		07/11/05	.58	ND	ND	.09	.23
		08/02/05	.3	ND	ND	.08	.09
		08/08/05	.31	ND	ND	.06	.04
		08/17/05	.09	ND	ND	.08	.05
		08/24/05	.12	ND	ND	E .01	.09
		08/30/05	.08	ND	ND	.07	.05
		09/13/05	.08	ND	ND	.08	.04
04159900	Mill Creek near Avoca, Mich.	04/26/05	.89	ND	ND	.23	.86
		05/12/05	ND	ND	ND	E .03	.06
		05/23/05	.23	ND	ND	E .03	E .03
		05/24/05	.58	ND	ND	.1	.61
		05/25/05	.9	ND	ND	E .02	.58
		05/26/05	E .02	ND	ND	E .02	.26
		05/27/05	E .03	ND	ND	E .02	.18
		06/07/05	.11	ND	ND	E .02	.1
		06/28/05	.28	ND	ND	.05	.2
		07/12/05	.2	ND	ND	E .03	.05
		08/02/05	.2	ND	ND	.05	E .01
		08/11/05	.14	ND	ND	E .04	ND
		08/17/05	.06	ND	ND	.09	E .01
		08/24/05	.08	ND	ND	.07	E .01
		08/30/05	.07	ND	ND	.1	E .03
		09/13/05	NA	ND	ND	NA	NA
04160398	Pine River near Marysville, Mich.	04/26/05	.88	ND	ND	.23	.67
		05/12/05	E .01	ND	ND	E .02	.08
		05/23/05	.25	ND	ND	.19	.2
		05/24/05	E .02	ND	ND	.32	.18
		05/25/05	1.75	ND	ND	.76	1.53
		05/26/05	.88	ND	ND	.31	2.02
		05/27/05	1.1	ND	ND	.52	2.62
		06/07/05	.47	ND	ND	.14	.48
		06/28/05	1.15	ND	ND	.17	1.06
		07/12/05	.75	ND	ND	.09	.58
		08/02/05	1.56	ND	ND	.11	.09
		08/08/05	.42	ND	ND	.13	.1
		08/17/05	.17	ND	ND	.09	.1
		08/24/05	.16	ND	ND	.11	.05
		08/30/05	.15	ND	ND	.08	.06
		09/13/05	.08	ND	ND	.12	.06

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04160625	Belle River near Marine City, Mich.	04/26/05	1.18	ND	ND	0.41	1
		05/12/05	E .02	ND	ND	E .02	.12
		05/23/05	.34	ND	ND	.24	.13
		05/24/05	.51	ND	ND	.71	.71
		05/25/05	.62	ND	ND	E .03	.4
		05/26/05	.94	ND	ND	.28	1.74
		05/27/05	.55	ND	ND	.08	.85
		06/07/05	.12	ND	ND	E .01	.17
		06/28/05	.32	ND	ND	.05	.34
		07/12/05	.36	ND	ND	.11	.28
		08/02/05	.4	ND	ND	.06	.13
		08/08/05	.22	ND	ND	.05	E .02
		08/17/05	.14	ND	ND	E .03	.04
		08/23/05	.09	ND	ND	.06	E .03
		08/30/05	.07	ND	ND	ND	.05
		09/13/05	.06	ND	ND	.05	.06
		09/15/05	.11	ND	ND	.08	.18
04161820	Clinton River at Sterling Heights, Mich.	04/21/05	.08	ND	ND	ND	E .03
		04/28/05	.05	ND	ND	.1	E .01
		05/10/05		ND	ND	E .02	E .03
		05/23/05	.24	ND	ND	.17	E .02
		05/24/05	.13	ND	ND	.14	E .03
		05/25/05	.12	ND	ND	E .01	.05
		05/26/05	ND	ND	ND	ND	.05
		05/27/05	ND	ND	ND	ND	E .03
		06/08/05	.11	ND	ND	E .04	.08
		06/27/05	.08	ND	ND	E .04	.05
		06/29/05	ND	ND	ND	.05	.04
		07/13/05	.14	ND	ND	E .04	ND
		08/03/05	.18	ND	ND	E .03	ND
		08/08/05	.16	ND	ND	E .04	ND
		08/16/05	.07	ND	ND	.06	E .01
		08/25/05	.13	ND	ND	.06	E .01
		08/30/05	.07	ND	ND	.06	E .01
		08/30/05	.11	ND	ND	.1	E .02
		08/31/05	.08	ND	ND	.08	E .02
		09/14/05	.06	ND	ND	.09	E .02
04165553	Clinton River at Moravian Dr. at Mt. Clemens, Mich.	03/14/05	E .02	ND	ND	.06	E .01
		04/05/05	E .03	ND	ND	.12	E .01
		04/27/05	.34	ND	ND	.25	.23
		05/25/05	.09	ND	ND	.05	.09
		06/14/05	.15	ND	ND	.05	.07
		07/11/05	.31	ND	ND	.15	.06
		07/25/05	.31	ND	ND	.12	E .02
		08/15/05	.2	ND	ND	.24	E .03
		09/01/05	.21	ND	ND	E .04	E .02
		11/03/05	.06	ND	ND	.05	.06
		11/22/05	.06	ND	ND	.06	E .02

Appendix 2. Station name, sample-collection date, and atrazine, chlorpyrifos, diazinon, metolachlor, and simazine results for samples collected in this study. —Continued

[USGS, U.S. Geological Survey; µg/L, micrograms per liter; NA, not available; ND, concentration was nondetected and reported as less than method detection limit; E, estimated value if detected value was less than method detection limit]

USGS station number	USGS station name	Sample collection date	Atrazine (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
04168550	River Rouge at River Rouge, Mich.	03/14/05	E 0.02	ND	ND	E 0.04	E 0.02
		04/05/05	E .03	ND	ND	E .03	E .01
		04/27/05	.12	ND	ND	E .04	E .01
		05/25/05	.13	ND	ND	E .04	.04
		06/14/05	.23	ND	ND	.05	.26
		07/11/05	.16	ND	ND	.07	.05
		07/25/05	.17	ND	ND	.05	E .01
		08/15/05	.11	ND	ND	.06	E .02
		09/01/05	.08	ND	ND	.1	E .02
		11/08/05	.07	ND	ND	.17	E .02
		11/22/05	.05	ND	ND	.1	E .01
040590345	Escanaba River at Wells, Mich.	04/07/05	E .02	ND	ND	ND	E .02
		04/21/05	ND	ND	ND	E .01	ND
		05/24/05	ND	ND	ND	E .01	E .03
		06/13/05	E .04	ND	ND	.07	E .03
		06/16/05	.06	ND	ND	.06	E .01
		08/01/05	.15	ND	ND	E .04	E .01
		08/25/05	.13	ND	ND	ND	E .03
		09/15/05	.08	ND	ND	E .01	.06
		10/06/05	E .04	ND	ND	E .04	.04
		10/27/05	.1	ND	ND	.11	E .01
		11/22/05	.07	ND	ND	.07	E .02

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