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Water-Resources Investigations Report 02-4304

Occurrence and Distribution of Pesticides in the St. Lucie River Watershed, South-Central Florida, 2000-01, Based on Enzyme-Linked Immunosorbent Assay (ELISA) Screening

U.S. GEOLOGICAL SURVEY

Prepared in cooperation with the
FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

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by A.C. Lietz

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Tallahassee, Florida
2003

DEPARTMENT OF THE INTERIOR
GAIL A NORTON, Secretary

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U.S. Geological Survey
Suite 3015
227 N. Bronough Street
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CONVERSION FACTORS, ABBREVIATIONS AND ACRONYMS, AND DATUM

Multiply	By	To Obtain
inch (in.)	25.40	millimeter
foot (ft)	0.3048	meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
acre	0.4047	hectare
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
pound (lb)	0.4536	kilogram
pound per acre (lb/acre)	0.4536	kilogram per acre
pound per square mile (lb/mi^2)	0.4536	kilogram per square mile

ABBREVIATIONS

eV	electronvolt
kPa	kilopascal
L	liter
µg/L	microgram per liter
µL	microliter
mg/L	milligram per liter
mL	milliliter
mL/g	milliliter per gram
mL/min	milliliter per minute
mm	millimeter
ng	nanogram
ng/µL	nanogram per microliter
V	volt

ACRONYMS

CCC	Criteria continuous concentrations
CMS	Criteria maximum concentrations
DAR	Deethylatrazine/atrazine ratio
D^2R	Deisopropylatrazine/deethylatrazine ratio
EC_{50}	A concentration necessary for 50 percent of aquatic species tested to exhibit a toxic effect short of mortality
ELISA	Enzyme-Linked Immunosorbent Assay
FDEP	Florida Department of Environmental Protection
GC/MS	Gas chromatography/mass spectrometry
HLB	Hydrophobically and lipophilically balanced
IC_{50}	Inhibitory concentration
K_{oc}	Soil organic carbon sorption coefficient
LDD	Least detectable dose
MDL	Method detection limit
QAPP	Quality Assurance Project Plan
SFWMD	South Florida Water Management District
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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

$$°C = (°F - 32)/1.8$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD of 1929); horizontal coordinate information is referenced to the North American Datum of 1983 (NAD83).

Occurrence and Distribution of Pesticides in the St. Lucie River Watershed, South-Central Florida, 2000-01, Based on Enzyme-Linked Immunosorbent Assay (ELISA) Screening

By **A.C. Lietz**

Abstract

The St. Lucie River watershed is a valuable estuarine ecosystem and resource in south-central Florida. The watershed has undergone extensive changes over the last century because of anthropogenic activities. These activities have resulted in a complex urban and agricultural drainage network that facilitates the transport of contaminants, including pesticides, to the primary canals and then to the estuary. Historical data indicate that aquatic life criteria for selected pesticides have been exceeded. To address this concern, a reconnaissance was conducted to assess the occurrence and distribution of selected pesticides within the St. Lucie River watershed.

Numerous water samples were collected from 37 sites among various land-use categories (urban/built-up, citrus, cropland/pastureland, and integrated). Samples were collected at inflow points to primary canals (C-23, C-24, and C-44) and at control structures along these canals from October 2000 to September 2001. Samples were screened for four pesticide classes (triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates) by using Enzyme-Linked Immunosorbent Assay (ELISA) screening.

A temporal distribution of pesticides within the watershed was made based on samples collected at the integrated sites during different rainfall events between October 2000 and September 2001. Triazines were detected in 32 percent of the samples collected at the integrated sites. Chloroacetanilides were detected in 60 percent of the samples collected at the integrated sites, with most detections occurring at one site. Chlorophenoxy compounds were detected in 17 percent of the samples collected at the integrated sites. Organophosphates were detected in only one sample.

A spatial distribution and range of concentration of pesticides at the 37 sampling sites in the watershed were determined among land-use categories. Triazine concentrations ranged from highest to lowest in the citrus, urban/built-up, and integrated areas, respectively. The highest median triazine concentration was found in the cropland/pastureland area. Chloroacetanilide concentrations ranged from highest to lowest in the citrus, integrated, urban/built-up, and cropland/pastureland areas, respectively. Chlorophenoxy compound concentrations ranged from highest to lowest in the urban/built-up, integrated, citrus, and cropland/pastureland areas, respectively. The maximum concentrations of triazines, chloroacetanilides, and chlorophenoxy compounds were

0.63, 1.0, and 14 micrograms per liter, respectively. Organophosphate was detected once at an integrated site at a concentration of 0.20 microgram per liter.

Currently, the U.S. Environmental Protection Agency has no aquatic life guidelines for atrazine and metolachlor. However, assuming that all triazine and metolachlor concentrations from ELISA and gas chromatography/mass spectrometry (GC/MS) analyses were the result of atrazine and metolachlor detections, no concentrations exceeded the Canadian aquatic life guidelines for atrazine and metolachlor. One organophosphate detection (0.2 microgram per liter) did exceed the U.S. Environmental Protection Agency aquatic life guideline for chlorpyrifos.

The deethylatrazine/atrazine ratio (DAR) is an important indicator of atrazine transport in the environment. The DAR ranged from 0.25 to 0.33, indicating that postapplication runoff was the most likely source of atrazine to the environment at the time of sampling. Deisopropylatrazine is a metabolite of atrazine and structurally similar compounds, such as simazine and cyanazine. The deisopropylatrazine/deethylatrazine ratio (D^2R) is an indicator of nonpoint sources of deisopropylatrazine to the environment. The ratio ranged from 1 to 3 in this study, indicating simazine was an important source of deisopropylatrazine to the environment at the time of sampling, as opposed to atrazine alone. Confirmation analyses by GC/MS for triazines detected by ELISA indicated the presence of atrazine, simazine, deethylatrazine, and deisopropylatrazine. Metolachlor, however, or any of the pesticides for which the ELISA test is cross reactive (acetochlor, butachlor, propachlor, or alachlor) were not detected by GC/MS analysis. The chloroacetanilide detections may be the result of antibody cross reactivity with two metolachlor metabolites; namely, metolachlor ethane sulfonic acid (ESA) and metolachlor oxanilic acid (OA). Metalaxyl, a fungicide also used in the watershed, cross reacts with metolachlor antibodies at low concentrations.

Quality assurance efforts included the collection of duplicate samples and equipment blanks for every 10 and 20 environmental samples collected, respectively. All equipment blank test results showed concentrations below the method detection limit (MDL) for triazines, chlorophenoxy compounds, and organophosphates. Chloroacetanilide concentrations ranged from the method detection limit of 0.05 to 0.07 microgram per liter. Further results indicated statistically significant differences between triazines by ELISA and atrazine by GC/MS when ELISA results are converted to the MDL. There was, however, no statistically significant difference between triazines determined by ELISA and atrazine determined by GC/MS when ELISA results were converted to one-half the MDL.

INTRODUCTION

The ecological health of bays and estuaries has been a major concern across the Nation in recent decades. Estuaries represent one of the most productive natural ecosystems and are commonly referred to as "cradles of the ocean." Abundant aquatic organisms live in estuaries. In fact, estuaries in Florida are home to thousands of plant and animal species, including manatees, dolphins, sea turtles, and seahorses, as well as commercially and recreationally important fishes, crustaceans, and shellfish. Over the last half century, findings indicate that rapid urban and agricultural expansion has had an adverse effect on the ecological health of the estuaries in Florida.

The St. Lucie River and estuary is a valuable resource to the environmental and economic well-being of Martin and St. Lucie Counties in south-central Florida. Historical records indicate that the estuary once supported abundant and diverse flora and fauna, and water clarity was substantially greater in the past than it is today because of anthropogenic influences (St. Lucie River Issue Team Report, 1998). The man-made St. Lucie (C-44) Canal provides a hydraulic connection between Lake Okeechobee and the St. Lucie River and estuary. A problem associated with the C-44 Canal and other tributaries is the transport of excessive freshwater releases and contaminants to the estuary.

The St. Lucie River watershed contains an extensive agricultural and urban drainage network consisting of numerous farm ditches, culverts, and lateral canals that discharge water to the major canals for transport to the estuary.

Of particular concern is the potential effect that this network could have on the estuary as a result of transporting contaminants, especially pesticides, to the major tributaries and then to the estuary. To examine this problem, the U.S. Geological Survey (USGS), in cooperation with the Florida Department of Environmental Protection (FDEP), developed a reconnaissance study to document the occurrence, concentration, and distribution of selected pesticides during stormwater runoff within the St. Lucie River watershed using Enzyme-Linked Immunosorbent Assay (ELISA) screening.

Purpose and Scope

The purpose of this report is to present and summarize results of a water-quality reconnaissance for selected pesticides in the St. Lucie River watershed in south-central Florida using ELISA screening. Factors affecting pesticide occurrence and concentration in the environment are presented, and the temporal, spatial, and land-use variability of pesticides in the watershed are analyzed. Herbicide/metabolite ratios are presented and geochemical transport in the environment is discussed. Pesticide concentrations also are compared to U.S. Environmental Protection Agency (UESPA) and Canadian aquatic life water-quality standards. A quality assurance evaluation is presented, and results of pesticide residues assayed using ELISA are compared with those provided by gas chromatography/mass spectroscopy (GC/MS) analysis.

Previous Studies

Several studies have been conducted in Martin and St. Lucie Counties by the USGS and the South Florida Water Management District (SFWMD). Bearden (1972) described the water available in canals and shallow sediments in St. Lucie County. Miller (1978) documented the hydrologic setting of Martin County by describing major land features, climate, and surface- and ground-water resources. Federico (1983) summarized water-quality studies along the Upper East Coast, and Haunert and Startzmann (1985) described the short-term effects of freshwater discharge on the biota of the St. Lucie River and estuary.

Some investigations throughout the United States have used ELISA to document the occurrence of pesticide residues. Goolsby and others (1997) described the spatial variability of triazine herbicides in the Mississippi River and documented the origin, transport, and deposition patterns of herbicides and their metabolites across the midwestern and northeastern United States. Walker and others (2000) used ELISA and GC/MS analysis to determine pesticide residues in North Carolina, and Holman and others (2000) used ELISA to evaluate selected pesticides in surface-water supplies of North Carolina.

Acknowledgments

The author gratefully acknowledges the assistance of several individuals who provided information for this study. Dan Haunert of the SFWMD supplied a voluminous amount of material concerning the hydrology and natural resources of the St. Lucie River watershed. Dr. Chris Wilson, assistant professor at the University of Florida Institute of Food and Agricultural Sciences, supplied valuable information concerning agricultural practices and pesticide usage in the watershed. The author would also like to thank Richard Pfeuffer of the SFWMD for providing data from the SFWMD pesticide monitoring network. Appreciation is extended to other SFWMD staff for providing access to the levees and control structures in St. Lucie and Martin Counties.

DESCRIPTION OF STUDY AREA

The St. Lucie River watershed is located in Martin and St. Lucie Counties in south-central Florida. The watershed is divided by the North and South Forks of the St. Lucie River and consists of eight primary drainage basins (fig.1). These basins are the North Fork St. Lucie Basin, Tidal St. Lucie Basin, C-23 Basin, C-24 Basin, C-44 Basin and basins 4, 5, and 6 of the Bessey Creek Drainage Area. The St. Lucie River estuary, which is located along the Martin/St. Lucie County line, consists of inner and middle components. The inner component consists of the North and South Forks of the St. Lucie River; the middle component is formed by the convergence of these two forks (fig. 1). The inner and middle components of the estuary occupy surface areas of about 6.4 and 4.7 mi^2 (square miles), respectively. The middle estuary extends east for about 5 mi (miles) until reaching the Indian River Lagoon. Five tributaries discharge into the estuary and provide drainage for an area of about 827 mi^2 (St. Lucie River Issue Team Report, 1998).

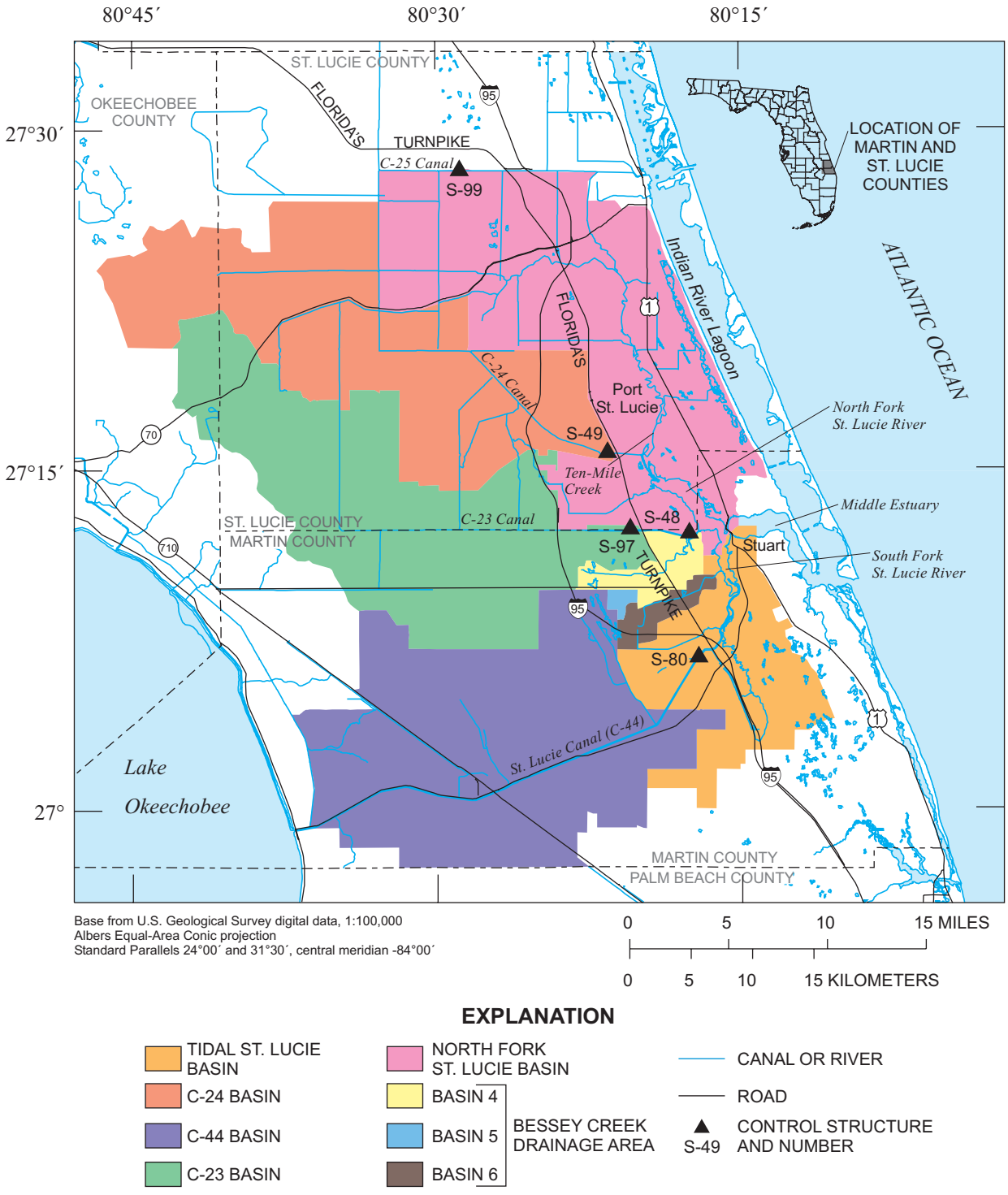

Figure 1. St. Lucie River watershed and primary drainage basins.

Environmental Setting

The St. Lucie River watershed is located within the Atlantic Coastal Ridge, Eastern Valley, and Osceola Plain physiographic subdivisions (Janicki and others, 1999). Most of the watershed lies within the Eastern Valley, which characteristically has land elevations ranging from 0 to 35 ft above National Geodetic Vertical Datum of 1929 (NGVD of 1929). The eastern and western parts of the watershed are located in the Atlantic Coastal Ridge and the Osceola Plain physiographic subdivisions, respectively. Land elevations in the Osceola Plain range from 40 to 60 ft above NGVD of 1929.

The St. Lucie River and estuary ecosystem, which is part of the Indian River Lagoon (fig. 1), has been modified by drainage activities that provide for urban expansion and agricultural operations in southeastern Florida. Most of the urbanization has occurred along the coastal areas, while agricultural activities have developed farther west. About 20 and 45 percent of the land in the area is used for urban and agricultural activity, respectively. The cattle and citrus industries are the dominant agricultural industries in Martin and St. Lucie Counties with limited acreage devoted to vegetables, nurseries, and aquaculture (St. Lucie River Issue Team, 1998, p. 25). Martin County has about 143,400 acres in rangeland, 45,700 acres in citrus, and 1,670 acres in other types of agriculture. St. Lucie County has about 72,300 acres in rangeland, 120,000 acres in citrus, and 1,790 acres in other types of agriculture (St. Lucie River Issue Team, 1998).

The population of Martin and St. Lucie Counties grew rapidly between 1970 and 1994 (fig. 2).

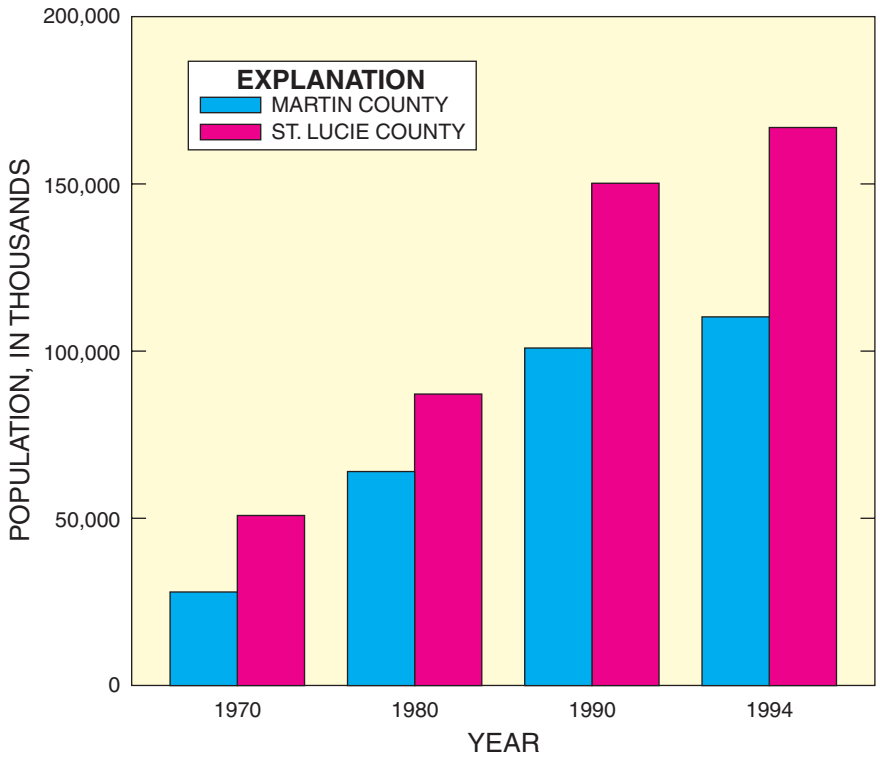

Figure 2. Population growth in Martin and St. Lucie Counties, 1970-94.

St. Lucie and Martin Counties have increased fourfold and threefold in population, respectively, since 1970. Martin County increased in population from 28,035 in 1970 to 110,227 in 1994, and St. Lucie County increased in population from 50,836 to 166,803 during the same period. In Martin County, 85.5 percent of the population resides in the city of Stuart; in St. Lucie County, 37.9 percent of the population resides in the city of Port St. Lucie (Treasure Coast Regional Planning Council, 2001).

The Martin/St. Lucie County area is dominated by a subtropical climate characterized by long, warm, humid summers and mild, dry winters. The average temperature is 23 °C, and the average annual rainfall is 55 in. (inches). About 75 percent of the rainfall occurs during the wet season from June to October and the remainder during the dry season from November to May. Rainfall during the summer usually results from brief, locally intense thunderstorm activity, whereas rainfall during the winter season results from frontal systems that are typically less intense but more widespread. Subtropical hurricanes are most likely to affect the area during the months of September and October.

Hydrologic Setting

The St. Lucie River watershed area has been altered substantially by drainage activities, begun in the early 20th century, to meet demands for agricultural, industrial, and residential uses. The St. Lucie River receives increasing amounts of freshwater runoff through

discharges from the St. Lucie (C-44) Canal, C-23 Canal, and C-24 Canal. These canals have gated control structures (S-80 along C-44, S-97 along C-23, and S-49 along C-24) that operate to discharge water during flood conditions and retard saltwater encroachment during dry periods.

The C-44 Canal, located entirely within the boundaries of Martin County and connected by the South Fork of the St. Lucie River (fig. 1), is operationally controlled by the U.S. Army Corps of Engineers (USACE). This man-made canal, completed in 1924, was originally designed to divert floodwaters from Lake Okeechobee. Construction of the C-44 Canal has affected the St. Lucie River and estuary by delivering excess freshwater to the estuary in order to lower water levels in Lake Okeechobee (Florida Department of Environmental Protection, 2000c). The periodic freshwater releases result in oligohaline conditions affecting the estuary. Summary statistics for structure S-80 located at the eastern end of the C-44 Canal indicate an average annual mean discharge of 761 ft^3/s (cubic feet per second), a maximum annual mean discharge of 4,152 ft^3/s, and a minimum annual mean discharge of 10 ft^3/s (Price and others, 1999, p. 47).

The C-23 and C-24 Canals drain into the North Fork of the St. Lucie River and are operated by the SFWMD to maintain flood control and supply water to urban and agricultural areas. The C-24 Canal was constructed in 1918 and improved during the 1950's as part of the Central and Southern Florida Flood Control Project. Originating in southwestern St. Lucie County, the C-23 Canal (also created during the 1950's as part of the Central and Southern Florida Flood Control Project) flows southward before turning east to run along the Martin/St. Lucie County boundary (Florida Department of Environmental Protection, 2000a). Structure S-97 along the C-23 Canal controls flow to structure S-48 in the east and regulates water levels in the western part of the C-23 Basin (fig. 1). The C-24 Canal discharges into the southern end of the North Fork of the St. Lucie River. The operating criteria for structure S-49 along the C-24 Canal varies seasonally and maintains optimum water-control stages and prevents saltwater intrusion in the canal (Florida Department of Environmental Protection, 2000b). Many lateral canals and ditches in the agricultural areas convey water to the primary canals, adversely affecting the drainage and stormwater characteristics of the St. Lucie River watershed. The canal system is recharged by rainfall and ground-water seepage. The system also supplies water for irrigation use in the agricultural areas.

The St. Lucie River watershed is underlain by the shallow surficial aquifer system and the deeper artesian Floridan aquifer system; both systems are separated by the intermediate confining unit. The surficial aquifer system is the principal source of water for municipal and domestic uses, whereas the Floridan aquifer system is a supplemental source for irrigation. The primary source of recharge to the surficial aquifer system is rainfall; however, much of the rainfall evaporates, transpires, or is lost as surface-water runoff. Water in the Floridan aquifer system is moderately to highly mineralized (Bearden, 1972, p. 8).

METHODS OF INVESTIGATION

Over the years, pesticide data for the St. Lucie River watershed have been collected as part of the SFWMD pesticide monitoring program begun in 1984. Data have been collected at structure S-80 along the St. Lucie (C-44) Canal in the St. Lucie River watershed (fig. 1) since 1988. Water is sampled and analyzed quarterly, whereas sediment is sampled and analyzed annually. The current SFWMD monitoring program covers southern Florida canal sites and includes analysis of 66 pesticides at 37 sites. These compounds include chemicals currently used in agricultural areas, chemicals regulated by the Florida Department of Environmental Protection (1996), and restricted-use pesticides. The SFWMD monitoring program provides data for assessing the status of water delivered to Lake Okeechobee, water-conservation areas, Everglades National Park, and Florida Bay (fig. 3). Data also are collected at major control structures throughout these areas.

Specific methods of data collection and analysis employed for this study were designed to collect the most representative sample possible under existing conditions and to provide the most accurate analytical results possible. The sampling and analytical procedures prescribed for this study are outlined in the Quality Assurance Project Plan (QAPP), which requires approval by the FDEP prior to sampling. The QAPP requires that an equipment blank be submitted for analysis for every 20 environmental samples collected and a duplicate sample for every 10 samples collected. Equipment blanks and duplicate samples

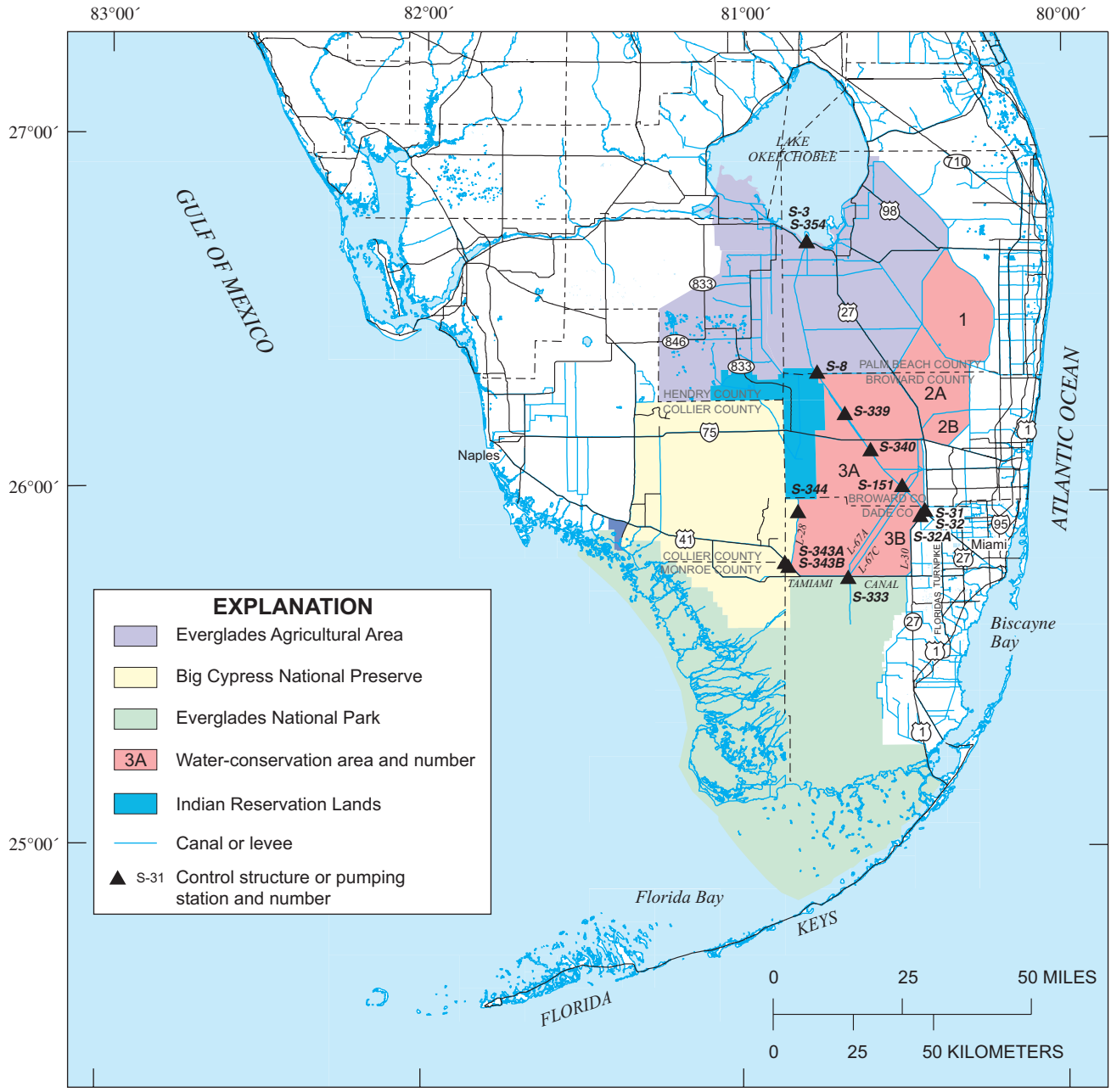

Figure 3. Location of major canals, control structures, pumping stations, and land-use areas in southern Florida (modified from Lietz, 2000).

were collected and processed in the same manner as the environmental samples. The QAPP also requires the confirmation of at least 10 percent of the ELISA analysis by using GC/MS analytical techniques. Semiquantitative screening for three herbicide classes (triazines, chloroacetanilides, and chlorophenoxy compounds) and one insecticide class (organophosphates) was determined by ELISA. Analysis by GC/MS was done for triazines and chloroacetanilides to confirm ELISA results.

The subsequent sections describe immunoassay screening (ELISA) and the sampling, laboratory, and analytical methods that were employed during this study. The period of data collection and analysis occurred from October 2000 to September 2001. Historical pesticide data are presented for the April 1992 to March 1998 period.

Immunoassay Screening

Immunoassay is a physical assay based on chemical and physical reactions that follow mathematically based laws. Immunoassay is based on the theory of the antibody/antigen reaction and was originally introduced in 1960 for clinical chemistry applications. The immunoassay has the following essential components: (1) an antigen, which is the analyte; (2) an antibody, which binds specifically to the antigen (analyte) in question; (3) a method to separate the free or unbound analyte from the bound analyte; (4) a label or tag on the analyte so it can be detected; and (5) standards or controls containing known concentrations of the analyte for interpreting the test results. The technique has been used to detect hormones, drugs and viruses and also has been used increasingly (over the past decade) to detect environmental contaminants, especially pesticides. The advantage of immunoassay screening in environmental applications is that analyses may be determined rapidly and are sensitive and cost effective.

Most environmental immunoassays are referred to as ELISA, which involve an enzyme conjugate that serves as a tracer. In the conjugate, an enzyme is bound to the target analyte and is used as the label or tag because it causes a color change that can be easily detected.

Sampling and Laboratory Methods

Stormwater samples were collected on a seasonal basis for this study. Individual sites were selected at inflow points to the St. Lucie (C-44), C-23, and C-24 Canals and at control structures S-48, S-49, S-80, and S-97 on the major tributaries located in urban/built-up, citrus, and cropland/pastureland land-use areas. A photograph of structure S-49 along the C-24 Canal is shown in figure 4. Photographs of an inflow point to the C-24 Canal in an urban area and in a citrus area are shown in figures 5 and 6, respectively.

Specific sampling protocols were used in the collection of water samples for ELISA and GC/MS analyses. Where possible, grab samples were collected near the middle of the canal or water body by using the weighted-bottle method. For samples analyzed by ELISA, a stainless steel basket sampler was used with a 125-mL (milliliter) amber-baked glass bottle inserted in the basket sampler. To reduce the risk of contamination, unpowdered latex gloves were used during sampling and sample handling. The samples were immediately chilled to 4 °C after collection and shipped within 48 hours to the USGS Water-Quality and Research Laboratory in Ocala, Florida. Samples for analysis by GC/MS were collected in the same manner as samples for analysis by ELISA. A stainless steel basket sampler was used with a 1-L (liter) amber-baked glass bottle inserted into the sampler. The samples were immediately chilled to 4 °C after collection. Before shipping to the Ocala Laboratory, the samples were filtered using glass fiber filters and an aluminum filter-support unit. Filtering was accomplished by way of a ceramic valveless metering pump using Teflon tubing.

Analytical Methods

Samples were analyzed using ELISA according to the magnetic particle assay method (Strategic Diagnostics, 2002), in which colloidal magnetic particles coated with antibodies bind to the specific pesticides for which analysis is desired. A small sample volume of the analyte was added to a test tube

Figure 4. Structure S-49 along the C-24 Canal.

Figure 5. An inflow point to the C-24 Canal in an urban area.

Figure 6. An inflow point to the C-24 Canal in a citrus area.

containing a suspension of the magnetic-coated antibody particles. Within minutes, a known amount of enzyme conjugate was added to the sample, and the pesticide of interest and the enzyme conjugate competed for a limited number of binding sites on the antibodies. This sample mixture was incubated for a period of time, and a magnetic method was used to remove the water sample and the unreacted enzyme conjugate from the test tube while the antibody-bound sample and conjugate remained in the tube. An enzyme substrate and chromogen were added to the test tube, causing a reaction with an enzyme on the conjugate that produced a blue color with an intensity inversely proportional to the amount of pesticide in the sample. A small amount of dilute sulfuric acid was added to the test tube to stop the reaction, producing a yellow color. Results were quantified by measuring the optical density of the yellow color using a colorimeter. Calibration curves were developed for each specific pesticide by using three standards of a known concentration and a zero concentration solution. Optical density measurements were obtained using a RPA-1 RaPID photometric analyzer.

Antibodies used in the magnetic particle method are slightly cross reactive with other pesticides, and this cross reactivity for the individual pesticide residues based on the least detectable dose (LDD) and inhibitory concentration (IC_{50}) is presented in table 1. (The IC_{50} is the concentration which causes a 50-percent reduction in optical density relative to a blank.) Laboratory quality control checks required by the QAPP included duplicate samples, continuing calibration standards, and quality control check samples and standards. All samples were refrigerated until analyses by ELISA and GC/MS. Analyses were made following the methods of Thurman and others (1990) and Meyer and others (1993).

Table 1. Cross reactivity of atrazine, chlorpyrifos, metolachlor, and 2,4-D antibodies with other structurally similar compounds based on least detectable dose and inhibitory concentration (IC_{50})

[Source: Strategic Diagnostics (2002); units shown in parts per billion; LDD is least detectable dose; IC_{50} is inhibitory concentration; > is greater than the value]

Structurally similar compound	LDD	IC_{50}	Structurally similar compound	LDD	IC_{50}	Structurally similar compound	LDD	IC_{50}	Structurally similar compound	LDD	IC_{50}
Atrazine[1]			**Chlorpyrifos[2]**			**Metolachlor[3]**			**2,4-D[4]**		
Ametryn	0.053	0.39	Chlorpyrifos-methyl	0.14	3.58	Acetochlor	0.06	6.55	Dichlorophenol	217	3,570
Propazine	.033	.74	Cyanazine	1.0	>10,000	Alachlor	1.3	84.0	Dichloroprop	117	7,500
Prometryn	.054	.64	Diazinon	.12	7.56	Butachlor	.26	52.0	MCPA	7.80	159
Prometon	.056	2.22	Disulfoton	26.2	688	Metalaxyl	.06	5.60	MCPD	57	1,470
Simazine	.340	4.90	Fenitrothion	159	4,590	Propachlor	1.0	2,500	Silvex (2,4,5-TP)	167	2,060
Terbuthylazine	.310	15.5	Lindane	10.6	218				Triclopyr	830	>10,000
Terbutryn	.090	5.50	Pirimiphos-ethyl	.32	57.1				2,4-D Butoxyethyl ester	.13	3.10
Desethyl atrazine	.062	3.21	Pirimiphos-methyl	19.8	688				2,4-D Butoxy-propylene ester	1.21	31.1
Desisopropyl atrazine	.8	217	Terbufos	10.3	2,180				2,4-D Butyl ester	.19	2.40
			2-Hydroxy atrazine	1.1	148				2,4-D Ethyl ester	.05	.82
			3,5,6-Trichloro-2-pyridinol	>10,000	>10,000				2,4-D Isooctyl ester	2.08	30.0
									2,4-D Isopropyl ester	.07	1.44
									2,4-D Methyl ester	.12	1.64
									2,4-D Propylene glycol ester	.05	.79
									2,4-D Sec-butyl ester	.13	2.20
									2,4-DB	3.95	139
									2,4,5-T	2.98	190
									4-Chlorophenoxy-acetic acid	61	1,220

[1]The least detectable dose is 0.05 parts per billion, and the inhibitory concentration is 0.72 parts per billion.

[2]The least detectable dose is 0.10 parts per billion, and the inhibitory concentration is 0.94 parts per billion.

[3]The least detectable dose is 0.05 parts per billion, and the inhibitory concentration is 0.85 parts per billion.

[4]The least detectable dose is 0.70 parts per billion, and the inhibitory concentration is 15.9 parts per billion.

Herbicides and selected herbicide degradates were isolated from water samples and analyzed for propanil, 5 chloroacetanilide and 10 triazine herbicides, and 2 triazine herbicide degradates by solid-phase extraction and GC/MS similar to the methods of Thurman and others (1990) and Meyer and others (1993). Water samples were spiked with 100 µL (microliters) of a 1.23-ng/µL (nanogram per microliter) solution of terbuthylazine and atrazine-d_5 as a surrogate standard. Samples containing 125 mL of water were evacuated through solid-phase extraction cartridges (Waters Chromatography, Milford, MA). These cartridges were rinsed with 2 mL of ultrapure water and eluted with 8 mL of ethylacetate into 15-mL glass conical-bottom test tubes containing 0.25 mL of ultrapure water. The sample eluate was spiked with 100 ng (nanograms) of an internal standard, phenanthrene-d_{10}, vortexed, and the ethylacetate layer pipetted into a clean conical-bottom test tube. The sample eluate was evaporated to a volume of 75 µL using a TurboVap workstation (Zymark), and the sample eluate was transferred to a chromatography vial with a 300-µL glass insert and refrigerated at -10 °C until analyzed by GC/MS.

GC/MS analyses were done on a Shimadzu 17A GC (Palo Alto, CA) and a QP 5050A mass selective detector using selected ion monitoring after the method of Thurman and others (1990). Operating conditions were ionization voltage at 70 eV (electron volts), ion source temperature at 280 °C, and electron multiplier 0 V (volts) above autotune. Direct capillary interface was at 210 °C, initial gas chromatography oven temperature at 60 °C, and a ramp rate at 7 °C per minute daily tuned with perflurotributylamine. The compounds were separated using 0.25-µ (microhm) 5 percent diphenyl – 95 percent dimethylsiloxane film (Bellefonte, PA), with a helium carrier gas at a flow rate of 1 mL per minute and initial head pressure of 57 kPa (kilopascals) ramped at 2.7 kPa per minute to 129 kPa. Quantification of the base peak of each compound was based on the response of the 188 ion of the internal standard, phenanthrene-d_{10}. Confirmation of the compound was based on the presence of the molecular ion (if present) or the base peak and one to two confirming ions with a retention-time match of ±0.2 percent relative to phenanthrene-d_{10}. The quantitation limit for all of the compounds analyzed by this method was 0.05 µg/L (microgram per liter).

OCCURRENCE AND DISTRIBUTION OF PESTICIDES IN THE WATERSHED

Pesticides are applied throughout the Nation to combat various problems. Many pesticides are herbicides used to control unwanted weed growth, whereas others are insecticides or fungicides used to kill harmful pests or fungi. Although pesticides are used to combat specific organisms or vegetative growth, they may be widely disseminated throughout the environment and result in unwanted effects on humans and aquatic life. As opposed to pesticides used in the past such as organochlorines, current pesticides generally are more soluble, do not adsorb as readily to sediment particles, and have shorter soil half lives. Thus, pesticides are more likely to exist in the environment in the dissolved phase, resulting mainly from surface runoff and not from transport based on adsorption to sediment particles.

A list of the pesticides detected at structure S-80 along the St. Lucie (C-44) Canal within the SFWMD monitoring network, in terms of percentage of detections and the range of concentrations and means, is presented in table 2. These data were based on water samples collected from April 1992 to March 1998. Three detections of ethion at structure S-80 exceeded the 48-hour

Table 2. Percentage of detections, mean concentrations, and concentration ranges for pesticides from water samples at structure S-80 along the St. Lucie (C-44) Canal, April 1992 to March 1998

[Concentrations are in micrograms per liter. Detections of 29 samples were made at S-80 from the South Florida Water Management District monitoring network]

Pesticide	Percentage of detections	Mean concentration	Concentration range
Norflurazon	93	0.40	0.01-0.80
Atrazine	59	.25	.034-1.0
Bromacil	55	.46	.067-1.7
Simazine	52	.20	.02-1.2
Diuron	28	.73	.4-1.3
Ethion	14	.27	.025-.83
Ametryn	10	.014	.012-.017
Alpha endosulfan	10	.0036	.00-.0065
Endosulfan sulfate	7	.035	.022-.048
Beta endosulfan	3	.0052	.0052-.0052

EC_{50} reported for *Daphnia magna,* an indicator species for aquatic macroinvertebrates. A fourth detection exceeded the acute toxicity level of 0.02 µg/L for *Daphnia magna*. In 1994, a major fish kill on Ten Mile Creek was attributed to toxic concentrations of pesticides.

For this study, the four classes of pesticides analyzed by ELISA include triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates. These classes were represented by the ELISA test for atrazine, chlorpyrifos, metolachlor, and 2,4-D (table 1). Atrazine, a selective triazine herbicide used to control broadleaf and grassy weeds, is classified as a restricted-use pesticide because of its potential to contaminate ground water. Chlorpyrifos is a broad-spectrum organophosphate insecticide used to control various pests on crops, lawns, and ornamental plants. Metolachlor, part of the chloroacetanilide chemical group, is a preemergent herbicide used to control broadleaf and annual grassy weeds. The 2,4-D chlorophenoxy compound is used to control broadleaf weeds in agriculture, rangeland, and cropland/pastureland applications. Specific information relating to crop applications in Florida and toxicity for each of these pesticides is presented in table 3.

There is a positive correlation between the amount of pesticide used and its occurrence in the environment (Crawford, 2001). The crops for which atrazine, chlorpyrifos, metolachlor, and 2,4-D are applied and the annual application (in pounds per year) of these four pesticides in Florida are presented in table 4. Total amounts applied per year in decreasing order are 1,264,241 lbs (pounds) for atrazine; 834,495 lbs for 2,4-D; 288,925 lbs for chlorpyrifos; and 109,361 lbs for metolachlor.

Factors Affecting Occurrence of Pesticides

Numerous factors may affect the occurrence and concentration of pesticides in the environment. These factors include chemical and physical properties of the pesticides, amounts and methods of application, hydrogeomorphic characteristics, soil properties, agricultural practices, land-use and seasonal crop planting patterns, and rainfall-runoff patterns following pesticide applications.

Table 3. Selected crop applications and toxicity of selected pesticides

Application				Toxicity	Persistence/solubility	Breakdown agent
Crop	Amount (pounds per acre)	Average number of applications per year	Percentage of Florida acreage			
Atrazine						
Sweet corn	1.19	1	20	Moderate in humans. Slight in fish and other aquatic life	Highly persistent in soil. Moderately soluble in water	Hydrolysis, microorganism biodegradation
Chlorpyrifos						
Orange	0.57-1.07	1.6-2.2	5-7	Moderate for humans. High for freshwater fish, aquatic invertebrates, and estuarine and marine organisms	Moderately persistent in soils; half life in soil is usually from 60 to 120 days. Persistence in water varies depending on formulation	In soil, ultraviolet light, chemical hydrolysis, soil microbes. In water, volatilization
Grapefruit	1.61-1.88	1.2-1.5	5-18			
Tomato	0.64-0.97	2.2-4.5	36-46			
Metalochlor						
Sweet corn	1.19	1	20	Moderate for cold and warm water fish	Moderately persistent in soil. Highly persistent in water. (Half life may exceed 200 days)	Photodegradation in the top few inches. Breakdown is mainly dependent on microbial activity
Cabbage	1.58	0.2	None			
2,4-D						
Grazing pasture	[1]45	1.32	13	Some formulations are highly toxic to fish; others are less toxic	Low soil persistence. Half life is usually less than 7 days	Soil and aquatic microorganisms

[1]Fluid ounces per acre.

Table 4. Crops and total amount of atrazine, chlorpyrifos, metolachlor, and 2,4-D applied annually in Florida

Atrazine		Chlorpyrifos		Metolachlor		2,4-D	
Crop	Annual amount (pounds)	Crop	Annual amount (pounds)	Crop	Annual amount (pounds)	Crop	Annual amount (pounds)
Corn	95,491	Alfalfa	148	Cabbage	2,636	Corn	24,485
Sod	29,985	Cabbage	8,816	Celery	823	Oats	134
Sorghum	5,082	Citrus	74,830	Corn	29,382	Other hay	11,400
Sugarcane	1,090,838	Collards	71	Green beans	14,891	Pasture	75,104
Sweet corn	42,845	Corn	1,469	Peanuts	30,673	Seed crops	1,000
		Cotton	33,512	Potatoes	6,188	Sod	45,955
		Peanuts	75,148	Sorghum	847	Sorghum	282
		Pecans	1,192	Soybeans	6,153	Sugarcane	674,106
		Sod	6,519	Sweet corn	10,376	Wheat	2,029
		Sorghum	565	Sweet peppers	7,392		
		Soybeans	2,051				
		Sweet corn	28,293				
		Sweet peppers	7,338				
		Tobacco	4,804				
		Tomatoes	44,169				
Total	1,264,241	Total	288,925	Total	109,361	Total	834,495

High herbicide concentrations are often associated with high streamflow events that occur during the first several weeks following herbicide application (Crawford, 2001). For most pesticides, the bulk of runoff from a field is associated with a critical rainfall event that generally occurs within 2 weeks of pesticide application (Wauchope, 1978). Pesticide concentrations in runoff may vary based on the differences in natural factors such as geology, geomorphology, and soil type (Crawford, 2001). Methods of application can affect the probability of pesticide transport through the hydrologic system. Pesticides incorporated into the soil reduce the probability of transport by runoff as opposed to pesticides applied directly on the surface of foliage or the soil.

The physical and chemical properties of the four pesticides (atrazine, chlorpyrifos, metolachlor, and 2,4-D) analyzed by the ELISA test (table 5) are critical for determining which pesticide is most likely to occur and be transported in the environment. The greater the solubility the more likely the pesticide is to be transported in streams. A pesticide is considered to be water soluble with a solubility greater than

Table 5. Physical and chemical properties of specific pesticides analyzed by Enzyme-Linked Immunosorbent Assay (ELISA) screening

[mg/L, milligrams per liter; mL/g, milliliters per gram; <, less than the value]

Pesticide	Class	Water solubility (mg/L at 25 degrees Celsius)	Soil organic carbon sorption coefficient (mL/g)	Soil half life (days)
Atrazine	Triazine herbicide	33	100	60-l00
Chlorpyrifos	Organophosphate insecticide	2	6,070	60-120
Metolachlor	Chloroacetanilide herbicide	530	200	15-70
2,4-D	Chlorophenoxy herbicide	900	20	<7

30 mg/L (milligrams per liter) at 25 °C (Goolsby and others, 1993). Based on a water solubility of 900 mg/L, 2,4-D is the most soluble of the four pesticides followed by metolachlor at 530 mg/L and atrazine at 33 mg/L (table 5); atrazine is considered to be moderately soluble in water. Removal of atrazine in the aquatic environment is the result of chemical hydrolysis and biodegradation (Extension Toxicology Network, 2002). Chlorpyrifos at 2 mg/L is not considered soluble in water based on these criteria.

Other chemical and physical properties that likely affect pesticide occurrence in the environment are the soil organic carbon sorption coefficient (K_{oc}) and soil half life. A critical measure of the capacity of a pesticide to adsorb to soil particles and to be transported is the K_{oc}. A coefficient less than 500 mL/g (milliliter per gram) indicates transport primarily in the dissolved phase; a coefficient greater than 1,000 mL/g indicates transport primarily as a result of adsorption to soil particles. Based on K_{oc}, atrazine, metolachlor, and 2,4-D are most likely to be transported in the dissolved phase, and chlorpyrifos is most likely to be transported as a result of adsorption to soil particles (table 5). As for soil half life, the higher the half life the more likely the pesticide persists and is available for transport in the environment. Atrazine and chlorpyrifos have relatively high soil half lives from 60 to 100 days and 60 to 120 days, respectively; metolachlor and 2,4-D have soil half lives of between 15 and 70 days and less than 7 days, respectively (table 5).

Soil properties also influence pesticide transport in the environment. The St. Lucie River watershed is dominated by two soil types: soils of the flatwoods and soils of the sloughs and freshwater marshes. These soils may be further classified into one or two hydrologic soil groups based on increasing soil runoff potential. Most of the watershed is classified into groups B/D and D, with B classified as low to moderate runoff potential and D classified as high runoff potential – low infiltration rate (Janicki and others, 1999). A high soil runoff potential increases the likelihood that a pesticide will be transported in the environment.

Variability of Pesticides

Concentrations of pesticides in water vary by season and are related to land use. For this study, water samples were collected during or following several rainfall events between October 2000 and September 2001. Rainfall amounts measured from rain gages at structures S-49, S-80, and S-97 during the various rainfall events are presented in table 6. No rain gage is present at structure S-48.

Pesticide sampling was conduced at 37 sites that fall under four land-use categories: urban/built-up, citrus, cropland/pastureland, and integrated (fig. 7 and table 7). In this report, the urban/built-up, citrus, and cropland/pastureland land-use categories are represented by area, and the integrated land-use category is represented by specific sites. The integrated sites are gated control structures S-48 DNS and UPS (fig. 7, site nos. 32 and 33), S-49 UPS (fig. 7, site no. 34), S-80 UPS (fig. 7, site no. 35), and S-97 DNS and UPS (fig. 7, site nos. 36 and 37) located in urban/built-up areas. When the gates are open, these structures represent flow from various land-use categories, and hence are referred to as integrated sites.

Table 6. Rainfall data from structures S-49, S-80, and S-97 from October 2000 to September 2001 and number of pesticide samples collected during these rainfall events

Date	Rainfall (inches)[1]			Number of samples collected
	S-49	S-80	S-97	
10/04/00	3.10	2.43	3.25	31
01/23/01	.33	.62	.75	6
03/20/01	.55	1.17	.65	8
03/30/01	1.99	2.00	2.96	8
05/24/01	.83	.23	1.62	10
06/27/01	.79	.10	1.31	11
07/11/01	4.60	2.15	3.34	11
08/02/01	5.39	1.18	6.75	4

[1]The 24-hour rainfall total ending at 0700 on the indicated date.

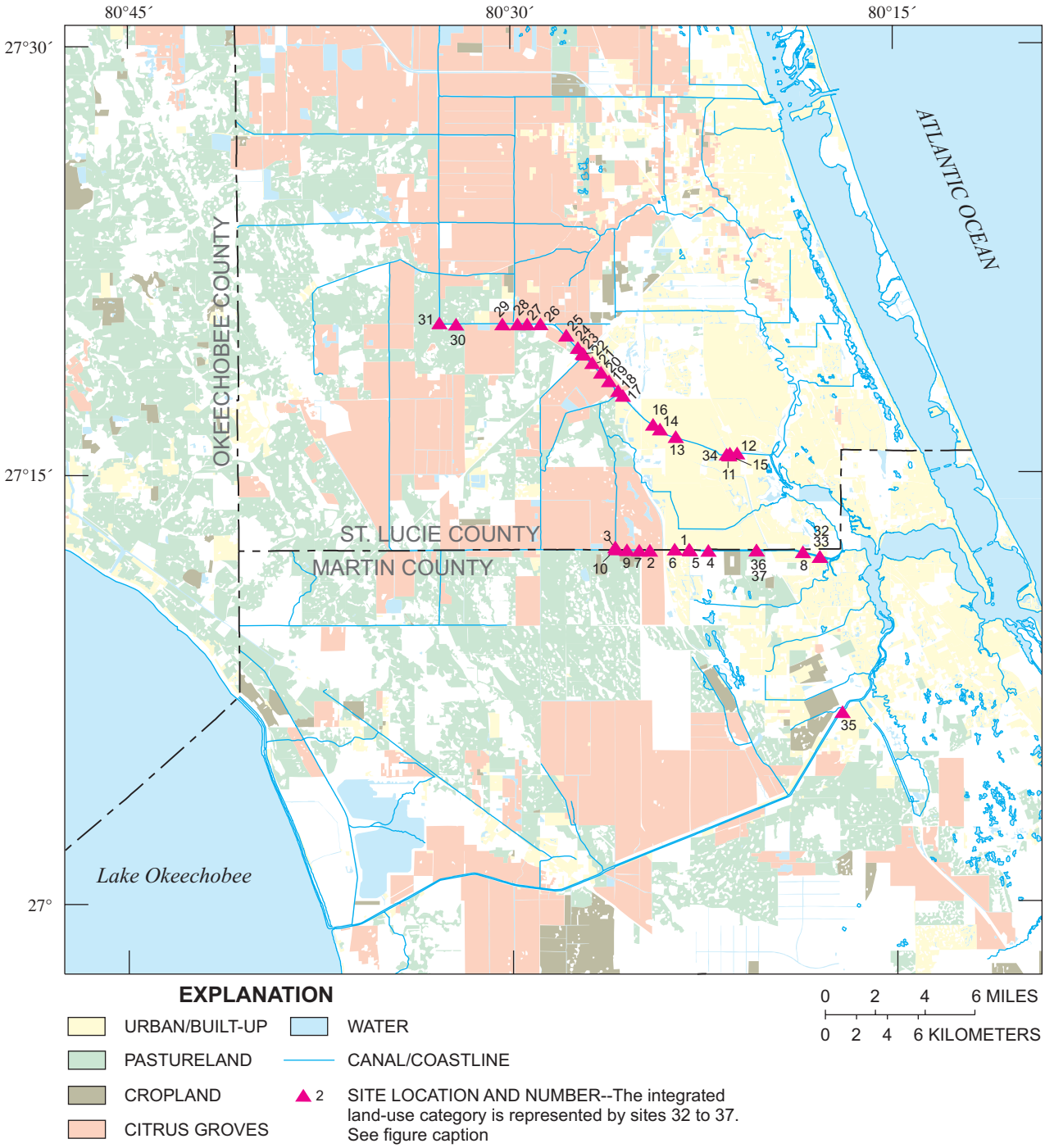

Figure 7. Location of pesticide sampling sites and major land uses in the St. Lucie River watershed. Site identifications are given in table 7. Integrated sites 32 to 37 are gated control structures located in urban/built-up areas; when the gates are open, structures represent flow from various land-use categories.

Table 7. Pesticide sampling site numbers and major land-use categories in the St. Lucie River watershed

[Site locations are shown in figure 7. USGS, U.S. Geological Survey]

Map number (this report only)	Site number	USGS site identification number	Latitude	Longitude	Land-use category[1]
1	C-23-1W	271222080230400	271222	802304	Urban/built-up
2	C-23-2W	271222080233800	271222	802338	Urban/built-up
3	C-23-4W	271223080255700	271227	802557	Citrus
4	C-23-5W	271219080221900	271219	802219	Urban/built-up
5	C-23-6W	271220080230200	271220	802302	Urban/built-up
6	C-23-7W	271220080243600	271220	802436	Citrus
7	C-23-8W	271220080250100	271220	802501	Cropland/pastureland
8	C-23-9E	271215080183700	271215	801837	Urban/built-up
9	C-23-9W	271221080253000	271221	802530	Cropland/pastureland
10	C-23-10W	271222080255600	271223	802556	Cropland/pastureland
11	C-24-1E	271539080212900	271539	802129	Urban/built-up
12	C-24-2E	271543080211000	271543	802110	Urban/built-up
13	C-24-2W	271618080233400	271618	802334	Urban/built-up
14	C-24-3W	271634080241100	271634	802411	Urban/built-up
15	C-24-4E	271543080212700	271543	802127	Urban/built-up
16	C-24-4W	271644080242700	271644	802427	Urban/built-up
17	C-24-6W	271745080253800	271745	802538	Citrus
18	C-24-7W	271755080254900	271755	802549	Citrus
19	C-24-8W	271816080261000	271816	802610	Citrus
20	C-24-9W	271834080262900	271834	802629	Citrus
21	C-24-10W	271854080264900	271854	802649	Citrus
22	C-24-11W	271912080270900	271912	802709	Citrus
23	C-24-12W	271914080271200	271914	802712	Citrus
24	C-24-13W	271926080272300	271926	802723	Citrus
25	C-24-14W	271952080275000	271952	802750	Citrus
26	C-24-15W	271016080285100	272016	802851	Cropland/pastureland
27	C-24-16W	272016080292200	272016	802922	Cropland/pastureland
28	C-24-17W	272016080294500	271016	802945	Cropland/pastureland
29	C-24-18W	272016080302000	272016	803020	Citrus
30	C-24-21W	272016080320900	272016	803209	Cropland/pastureland
31	G-79 UPS	272019080324800	272019	803248	Cropland/pastureland
32	S-48 DNS	271205080175701	271205	801757	Integrated
33	S-48 UPS	271205080175700	271205	801757	Integrated
34	S-49 UPS	271541080213500	271541	802135	Integrated
35	S-80 UPS	02277000	270639	801706	Integrated
36	S-97 DNS	271219080202601	271219	802026	Integrated
37	S-97 UPS	271219080202600	271219	802026	Integrated

[1]Integrated sites are gated control structures located in urban/built-up areas; when the gates are open, these structures represent flow from various land-use categories.

Because of the cross reactivity of the antibodies of the specific pesticide (atrazine, chlorpyrifos, metolachlor, or 2,4-D) with structurally similar compounds, the results are reported here in terms of pesticide classes (triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates) rather than individual pesticides. The frequency of detections for pesticides varied based upon the number of samples collected and the total sites sampled among the land-use categories in the St. Lucie River watershed. Detections referred to in this report represent concentrations above the method detection limit (MDL). The percentage of pesticides detected based on the number of sites sampled and the number of samples collected for triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates is shown in figure 8.

For the number of samples collected from all of the sites, chloroacetanilides were detected at 57 percent of the sites, followed by triazines (39 percent), chlorophenoxy compounds (14 percent), and organophosphates (1 percent). For the total sites sampled, chloroacetanilides were detected at 89 percent of the sites followed by triazines (68 percent), chlorophenoxy compounds (27 percent), and organophosphates (3 percent). In both cases, the highest percentages of detections were for chloroacetanilides followed by triazines, chlorophenoxy compounds, and organophosphates. The percentage of sites for which one or more classes of pesticides were detected is shown in figure 9. The percentage of sites having detections represents 19 percent for one class, 73 percent for two classes, 16 percent for three classes, and 3 percent for four classes.

The percentage of detections above the MDL also was determined for the four pesticide classes based on land-use categories (fig. 10). For triazines, the detections were 64 percent for cropland/pastureland, 43 percent for citrus, 36 percent for integrated, and 29 percent for urban/built-up land uses. For chloroacetanilides, the detections were 79 percent for cropland/pastureland, 71 percent for urban/built-up, 61 percent for integrated, and 43 percent for citrus land uses. For chlorophenoxy compounds, the detections were 36 percent for cropland/pastureland, 15 percent for integrated, 8 percent

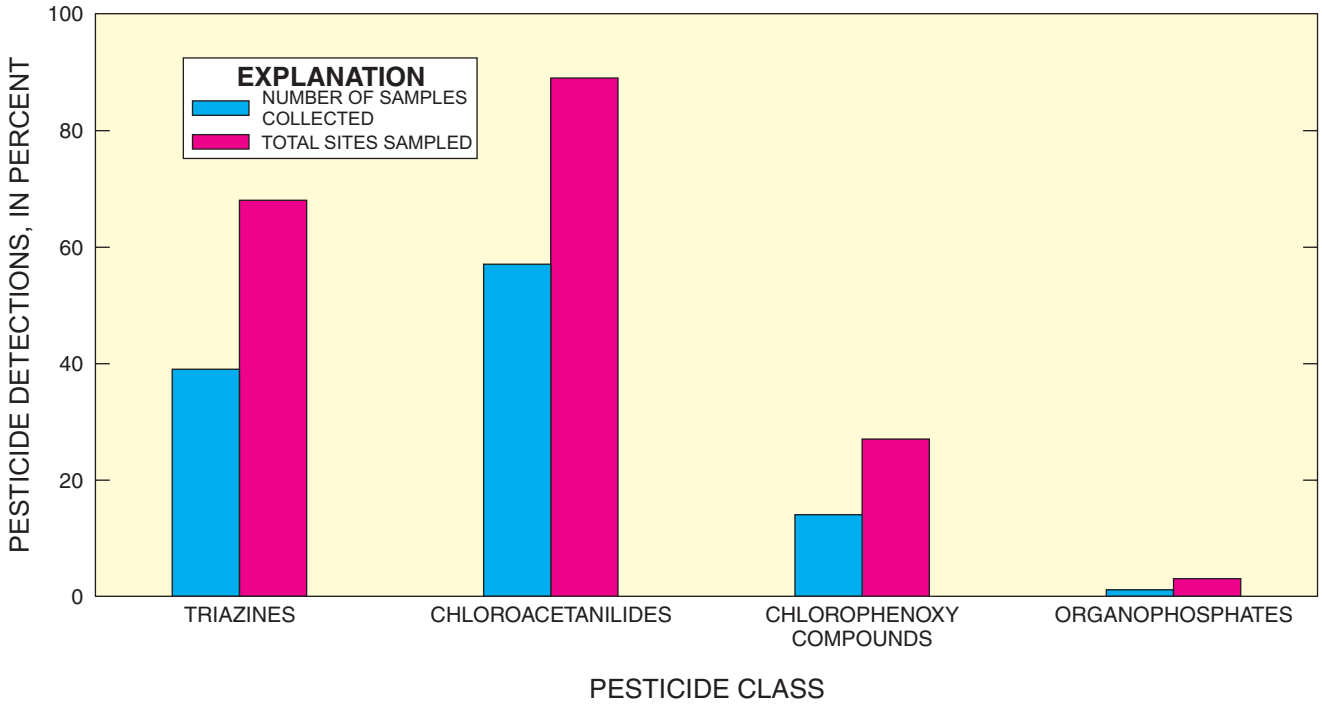

Figure 8. Percentage of pesticide detections based on number of samples collected and total sites sampled among the four classes of pesticides analyzed by Enzyme-Linked Immunosorbent Assay (ELISA) screening.

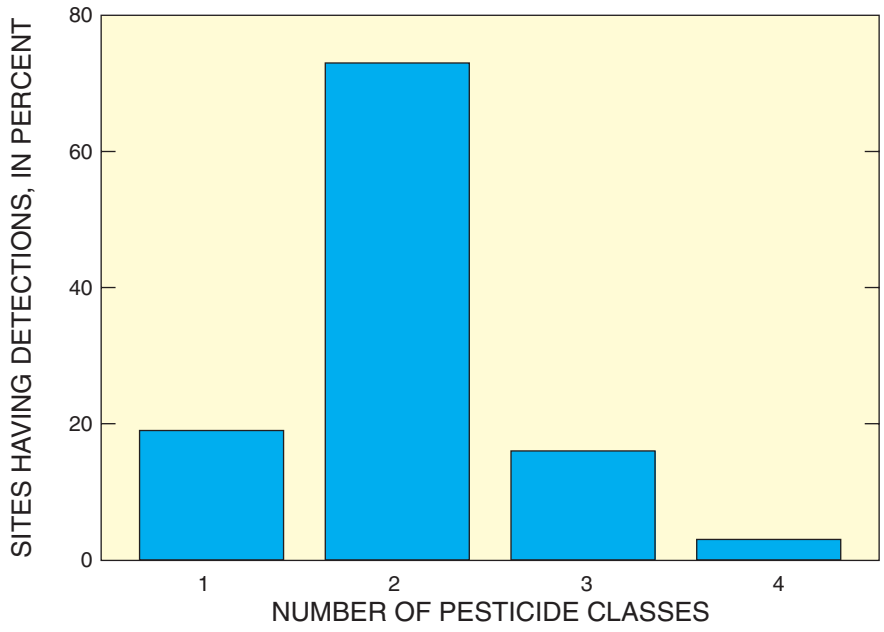

Figure 9. Percentage of sites having detection for one or more classes of pesticides.

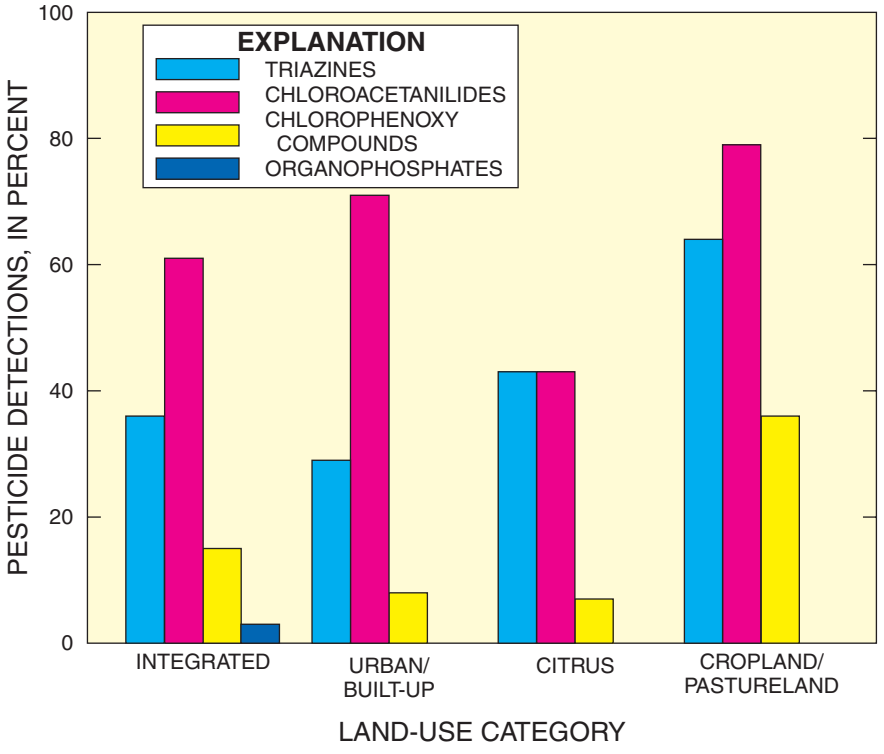

Figure 10. Pesticide detections from Enzyme-Linked Immunosorbent Assay (ELISA) analyses based on land-use categories.

for urban/built-up, and 7 percent for citrus land uses. The lower percentage of detections for chlorophenoxy compounds may be related to the MDL of 0.7 µg/L as compared to the lower MDL of 0.05 µg/L for triazines and chloroacetanilides. Organophosphates were detected only once at integrated site S-49 (fig. 10). The highest percentages of detections for triazines, chloroacetanilides, and chlorophenoxy compounds were all from the cropland/pastureland category.

Temporal Variability

A temporal distribution of pesticides in the St. Lucie River watershed was assessed by collecting water samples at the integrated sites during different rainfall events. For sampling at the integrated sites (S-48 UPS, S-49 UPS, S-80 UPS, and S-97 UPS), pesticides were detected throughout the October 2000 to September 2001 period. The same number of samples were not collected at all of the sites, which may affect analytical results. Triazine concentrations ranged from the MDL (0.05 µg/L) at all of the sites to 0.34 µg/L at site S-48 UPS (fig. 11). Compared to the other sites, triazine concentrations were detected most often above the MDL at site S-80 UPS. Maximum triazine concentrations were detected during the rainfall events of October 3-4, 2000, and July 11, 2001. These maximum triazine concentrations were detected in samples collected at sites S-48 UPS and S-97 UPS in October 2000 and at sites S-49 UPS and S-80 UPS in July 2001. Triazines were detected in 32 percent of all samples collected at the integrated sites.

Chloroacetanilide concentrations ranged from the MDL (0.05 µg/L) at all of the integrated

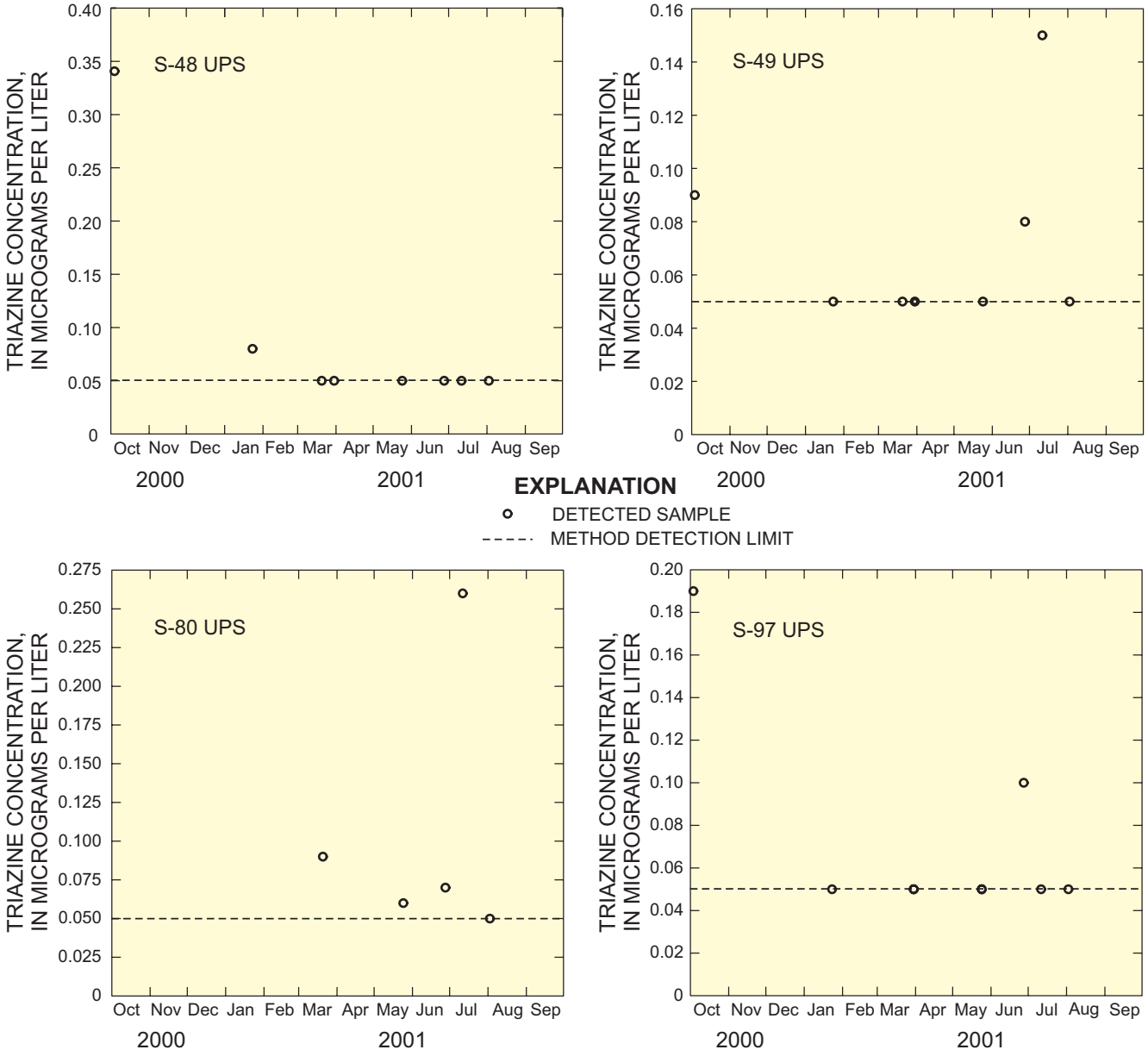

Figure 11. Triazine concentrations at the integrated sites from October 2000 to September 2001.

sites to 0.30 µg/L at sites S-48 UPS and S-97 UPS (fig. 12). Compared to the other sites, chloroacetanilide concentrations were detected most often above the MDL at site S-48 UPS. Maximum chloroacetanilide concentrations were detected during the rainfall events of October 3-4, 2000, January 23, 2001, July 11, 2001, and August 2, 2001. These maximum chloroacetanilide concentrations were detected in samples collected at sites S-48 UPS and S-97 UPS in October 2000, site S-80 UPS in July 2001, and site S-49 UPS in January, July, and August 2001. Chloroacetanilide concentrations were detected in 60 percent of all samples collected at the integrated sites.

Chlorophenoxy compound concentrations ranged from the MDL (0.07 µg/L) at all of the integrated sites to 1.6 µg/L at site S-49 UPS (fig. 13). Concentrations of chlorophenoxy compounds were detected most often above the MDL at site S-48 UPS. The remaining three integrated sites (S-49 UPS, S-80 UPS, and S-97 UPS) had only one concentration above the MDL, which occurred during the rainfall event of August 2, 2001. Chlorophenoxy compounds were detected in 17 percent of the samples collected at the integrated sites.

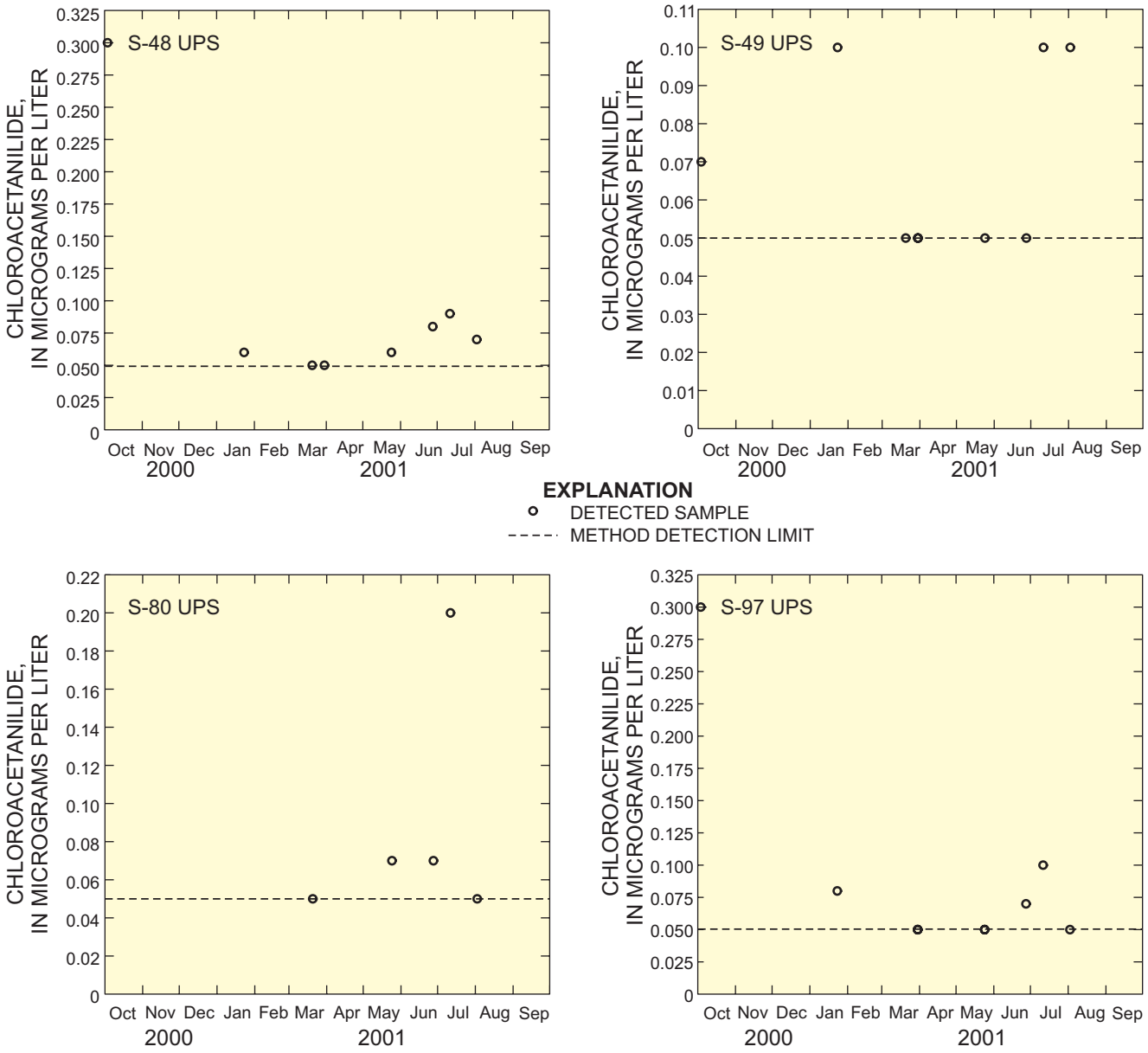

Figure 12. Chloroacetanilide concentrations at the integrated sites from October 2000 to September 2001.

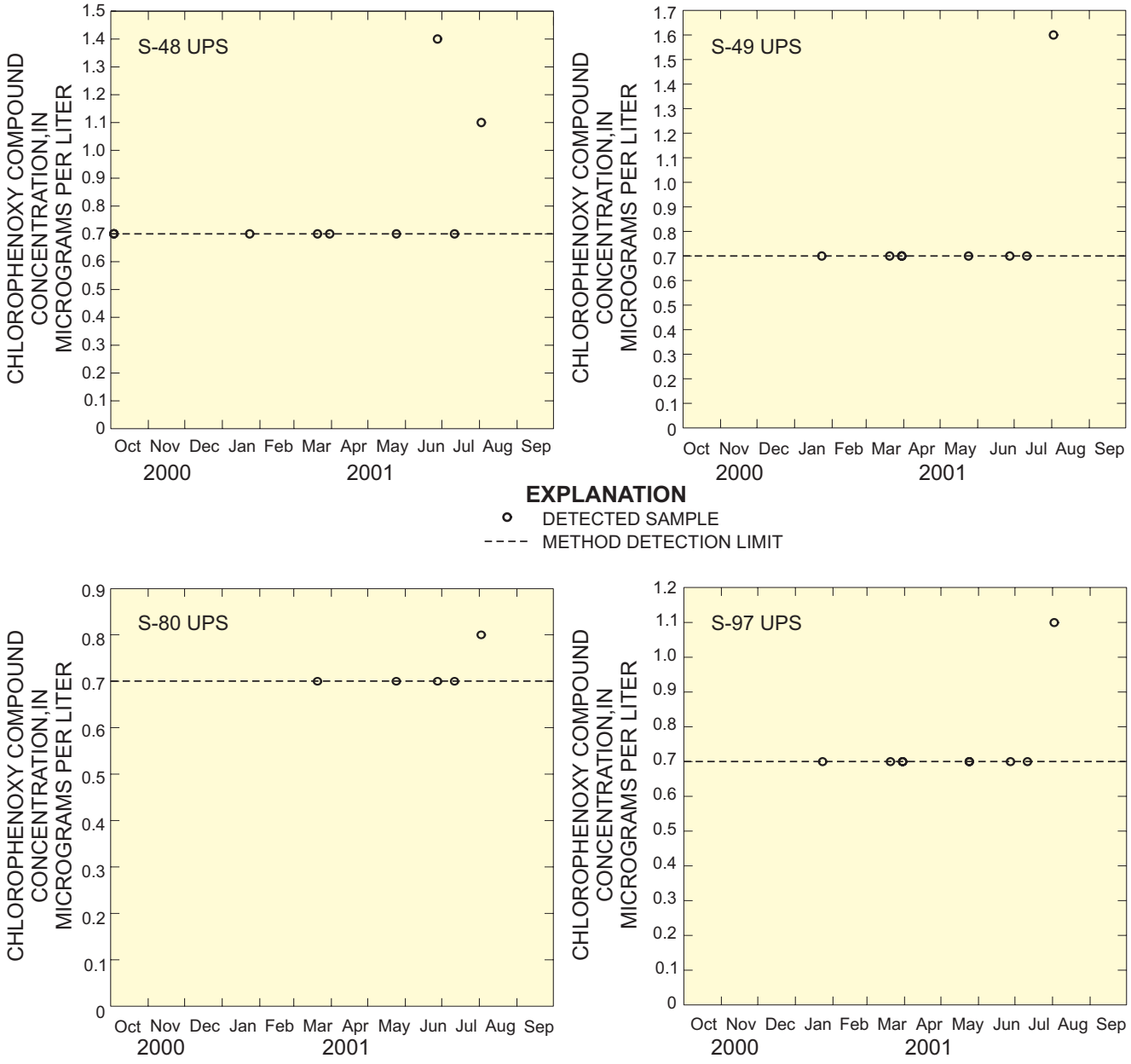

Figure 13. Chlorophenoxy compound concentrations at the integrated sites from October 2000 to September 2001.

One organophosphate concentration was detected above the MDL (0.10 µg/L) at site S-49 UPS (0.20 µg/L) during the rainfall event of March 30, 2001 (fig. 14). No organophosphate concentrations were above the MDL at the remaining three integrated sites. Organophosphates were detected in only 3 percent of the samples collected at the integrated sites.

Spatial Distribution

Pesticide detections varied among the different land uses in the St. Lucie River watershed. Water samples could not be collected throughout the entire reach of the primary canals because of physical impediments. Additionally, water samples could not be collected at inflow points on the St. Lucie (C-44) Canal because of the absence of right-of-ways. Detections for triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates and the spatial variability of these pesticide classes among land uses within the St. Lucie River watershed are shown in figures 15 to 18, respectively.

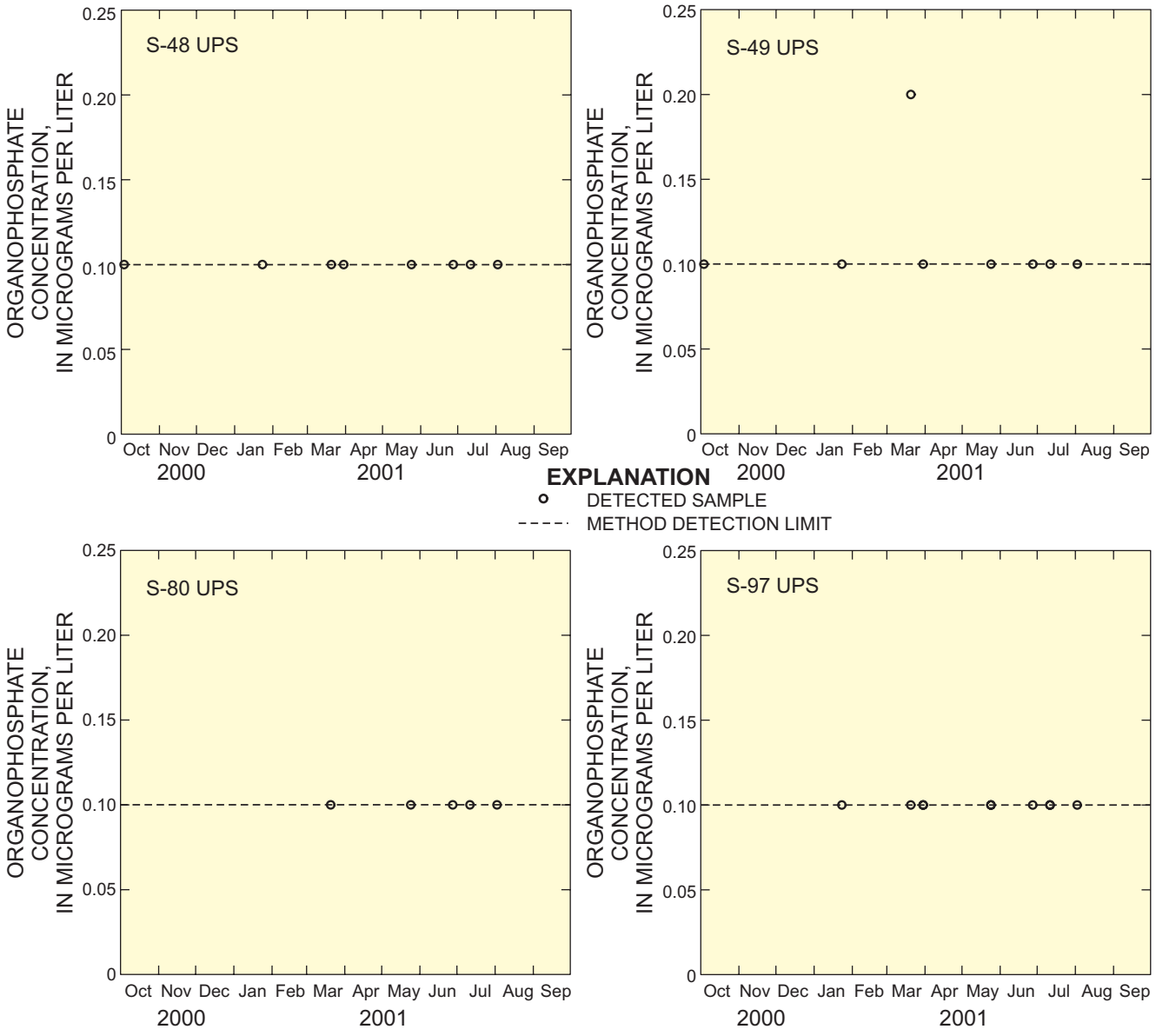

Figure 14. Organophosphate concentrations at the integrated sites from October 2000 to September 2001.

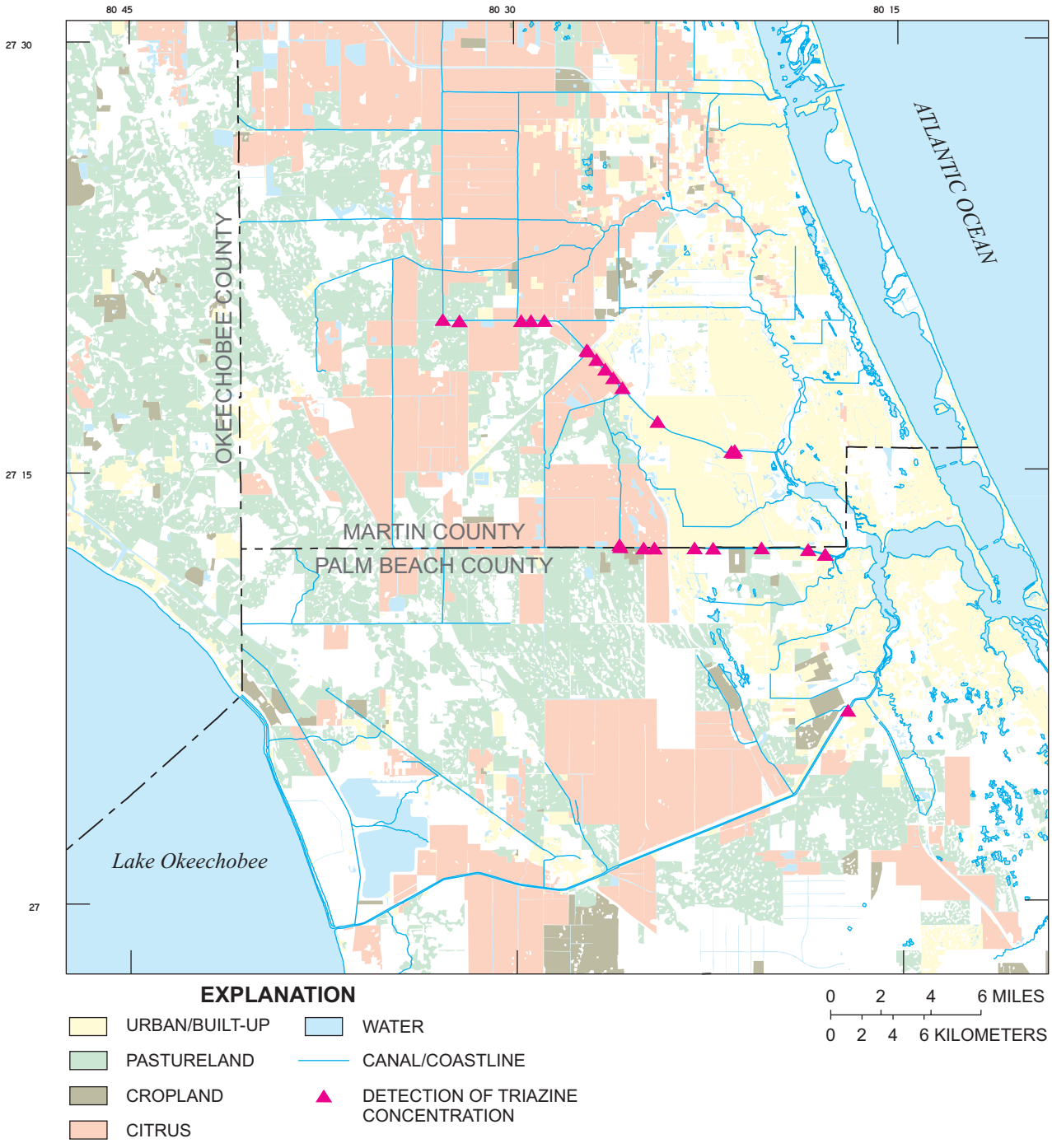

Figure 15. Spatial distribution of triazines among various land uses in the St. Lucie River watershed.

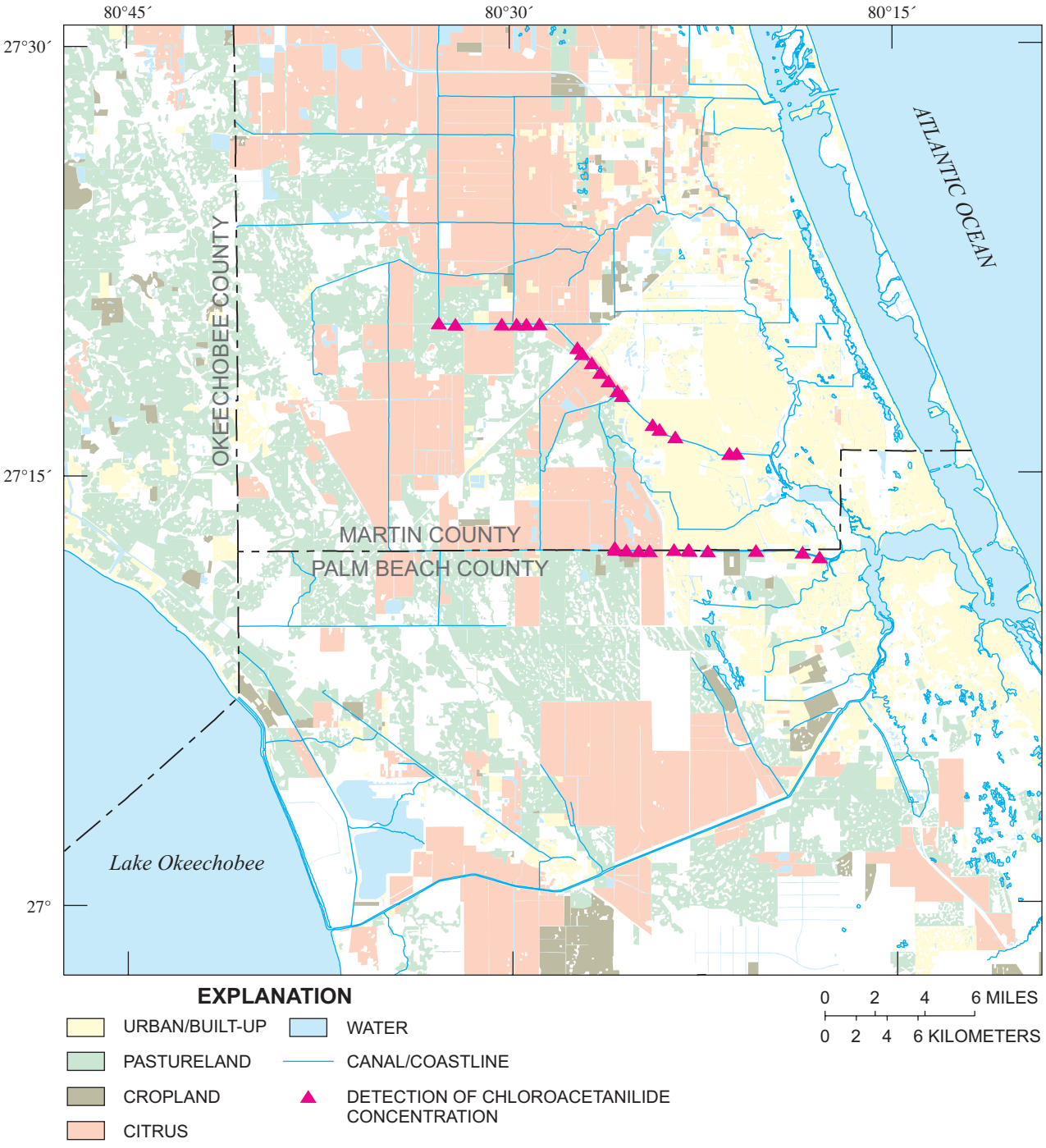

Figure 16. Spatial distribution of chloroacetanilides among various land uses in the St. Lucie River watershed.

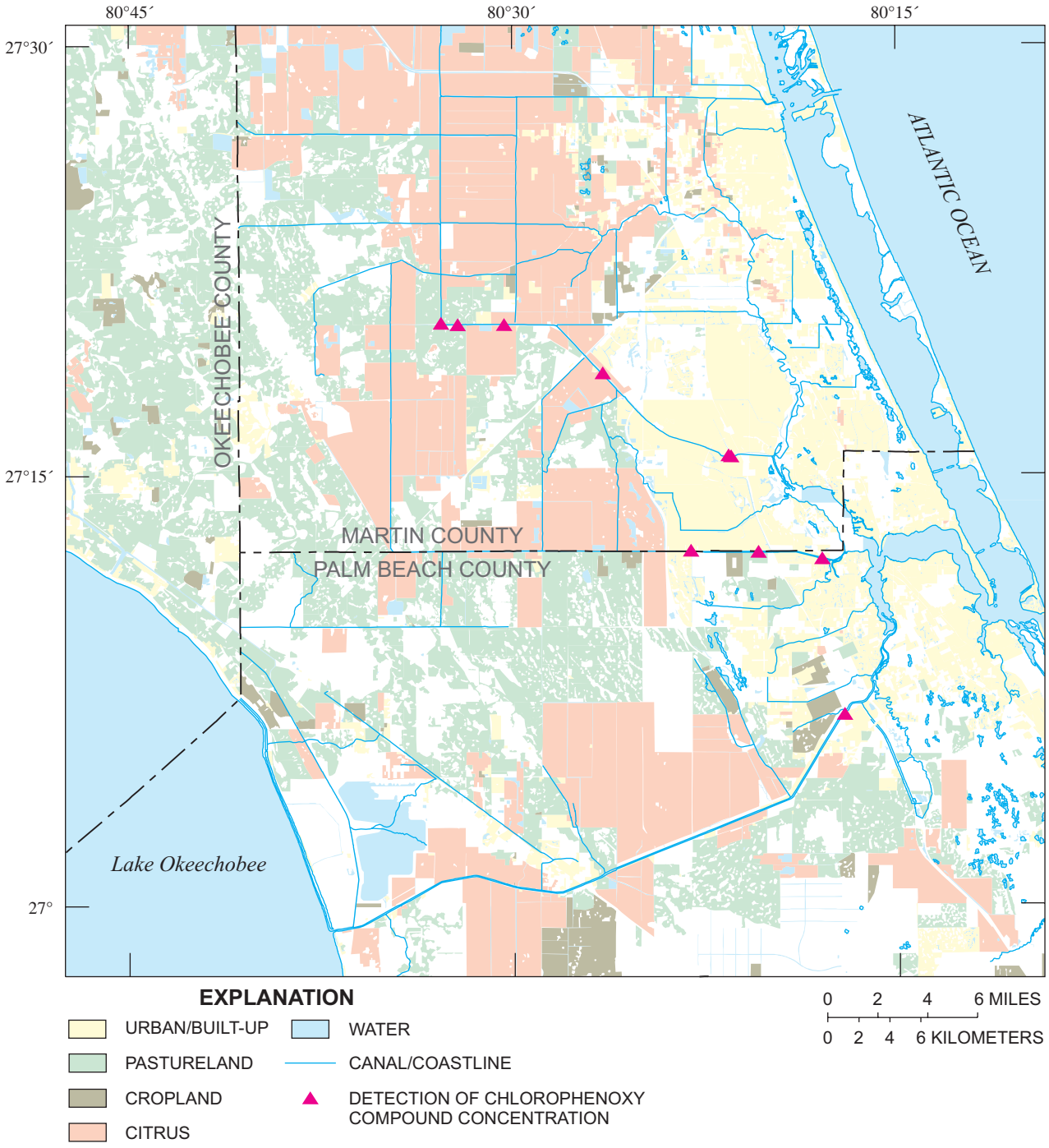

Figure 17. Spatial distribution of chlorophenoxy compounds among various land uses in the St. Lucie River watershed.

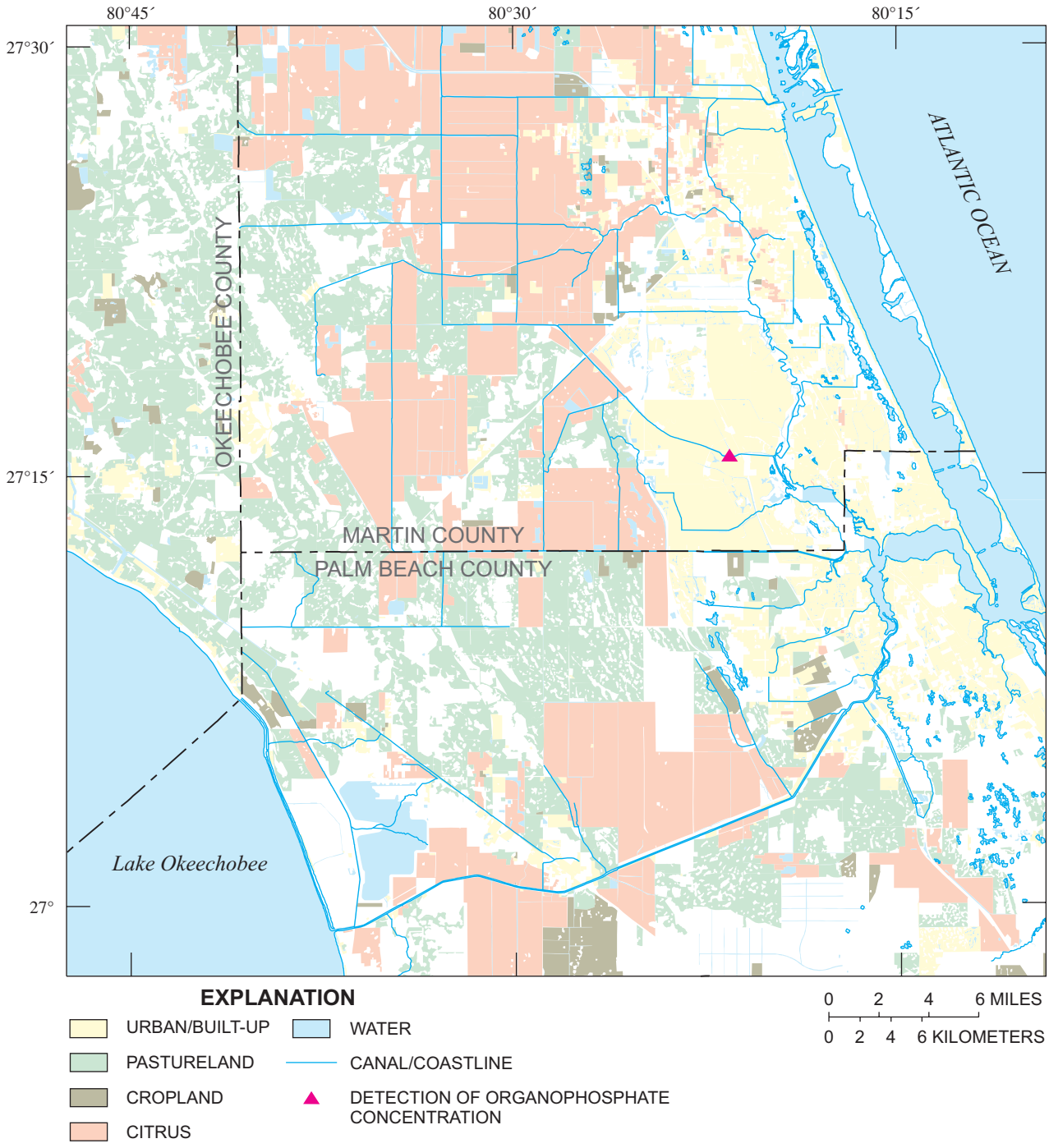

Figure 18. Spatial distribution of organophosphates among various land uses in the St. Lucie River watershed.

The spatial distribution and range of concentrations of the pesticide classes were determined based on the number of samples collected at all of the sampling sites and among land uses in the St. Lucie River watershed. The results are shown as boxplots in figures 19 and 20. Censored data values are reported as the MDL for the boxplots. Upper outside values represent concentrations greater than 1.5 times the interquartile range (25th to 75th percentile), and upper detached values represent concentrations greater than 3 times the interquartile range.

Based on the distribution of data from all samples collected, the boxplots showing triazine and chloroacetanilide concentration distributions have a narrow interquartile range with both upper outside and upper detached values (fig. 19A-B). The maximum triazine concentration was 0.63 µg/L, and the maximum chloroacetanilide concentration was 1.0 µg/L. The concentration distributions of chlorophenoxy compounds and organophosphates are shown as boxplots in figures 19C and 19D, respectively. Concentrations of chlorophenoxy compounds ranged from the MDL (0.70 µg/L) to 14 µg/L. Organophosphate was detected only once above the MDL (0.10 µg/L), with a concentration of 0.20 µg/L (fig. 19D).

The distribution and range of concentrations of triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates varied among the land-use categories in the St. Lucie River watershed. The highest triazine concentrations were 0.63 µg/L detected at site C-24-12W (fig. 7, site no. 23) and 0.57 µg/L detected at site C-24-9W (fig. 7, site no. 20)

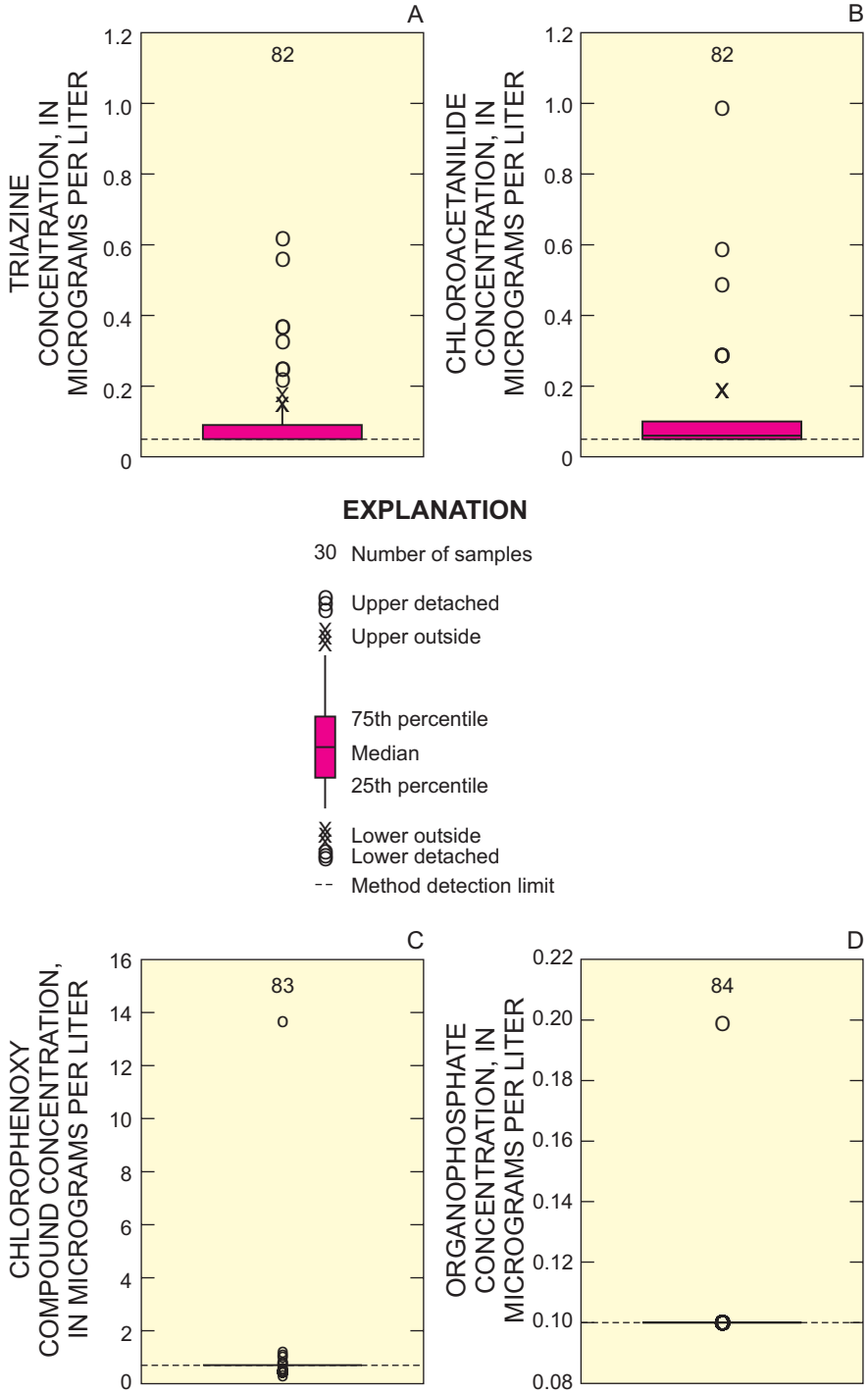

Figure 19. Distribution and range of concentrations of (A) triazines, (B) chloroacetanilides, (C) chlorophenoxy compounds, and (D) organophosphates based on number of samples collected at the sampling sites in the St. Lucie River watershed.

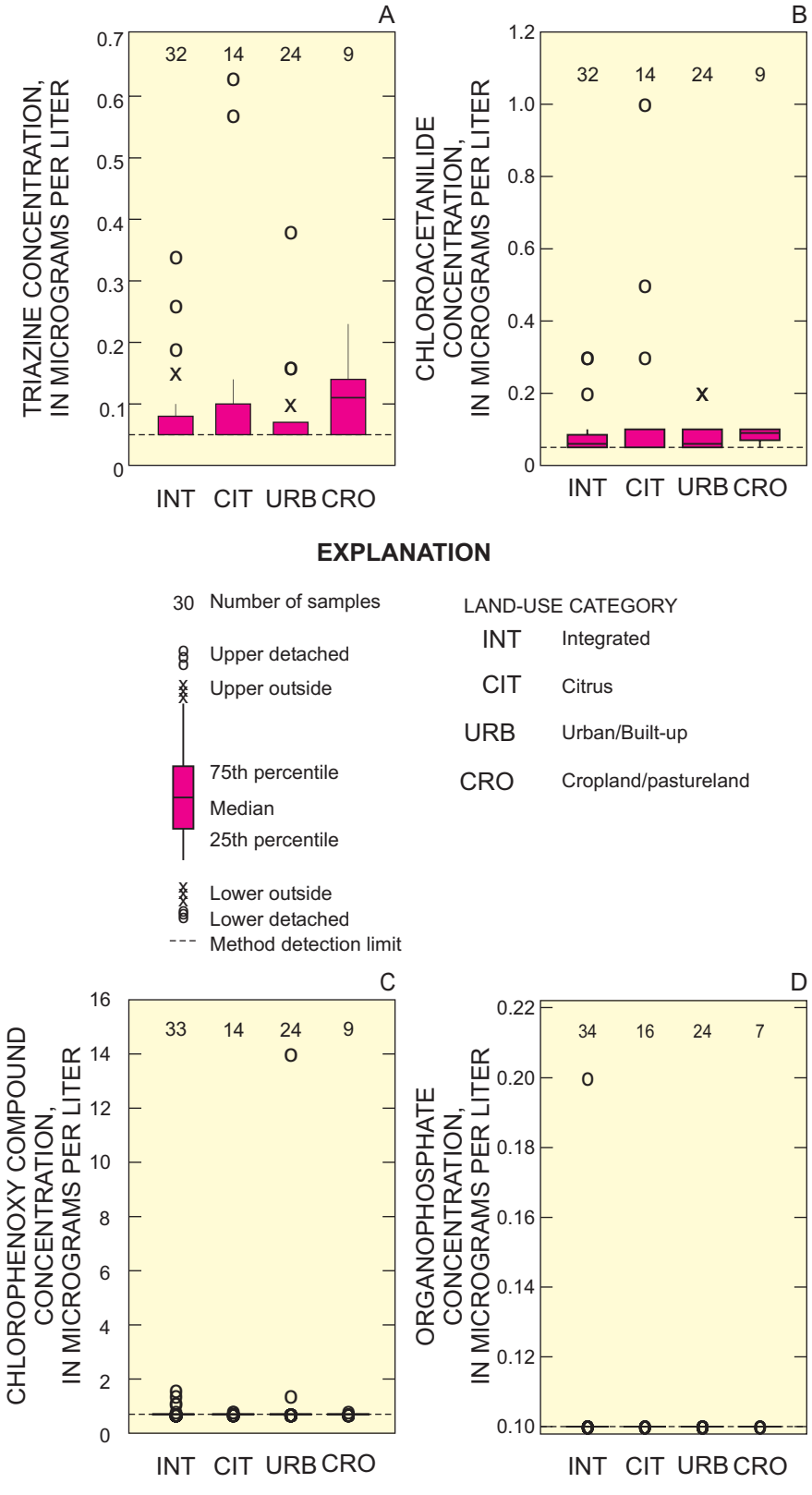

Figure 20. Distribution and range of concentrations of (A) triazines, (B) chloroacetanilides, (C) chlorophenoxy compounds, and (D) organophosphates among land uses in the St. Lucie River watershed.

in the citrus area (fig. 20A). Among the other land-use categories, the maximum triazine concentrations were 0.38 µg/L detected at site C-23-9E (fig. 7, site no. 8) in the urban/built-up area and 0.34 µg/L detected at integrated site S-48 UPS; the highest median concentration was detected in the cropland/pastureland area (fig. 20A).

At higher concentrations, triazine detections likely represent cross reactivity of the antibodies with simazine, which is used extensively in citrus applications within the watershed. Simazine was detected by GC/MS analysis. This selective triazine herbicide is used to control broadleaf weeds and annual grasses, has a soil half life of 28 to 149 days, and is poorly bound to soils with a K_{oc} of 130 mL/g (Extension Toxicology Network, 2002). In terms of percentages of detections, simazine ranked fourth highest in detections at structure S-80 within the SFWMD monitoring network where concentrations ranged from 0.02 to 1.2 µg/L and averaged 0.20 µg/L (table 2). According to the U.S. Department of Agriculture (2002), the estimated average annual agricultural use of simazine as an active ingredient in Florida is greater than 3.576 lb/mi^2 (pounds per square mile). Based on GC/MS analysis, simazine concentrations ranged from 0.02 to 0.95 µg/L. Samples analyzed by GC/MS also detected the triazine metabolites; namely, deethylatrazine and deisopropylatrazine (table 8).

As with triazines, the highest chloroacetanilide concentrations were detected in the citrus area, with a maximum concentration of 1.0 µg/L found at site C-24-12W (fig. 7, site no. 23). The second highest chloroacetanilide concentrations were detected in the inte

Table 8. Pesticides analyzed and detected by gas chromatography/ mass spectrometry analysis

[<, less than the value]

Pesticide	Detection	Concentration range (micrograms per liter)
Acetochlor	No	
Alachlor	No	
Ametryn	No	
Atrazine	Yes	<0.01-0.04
Butachlor	No	
Cyanazine	No	
Cyromazine	No	
Deethylatrazine	Yes	<0.01-0.01
Deisopropylatrazine	Yes	0.01-0.19
Metolachlor	No	
Metribuzin	No	
Prometon	No	
Prometryn	No	
Propachlor	No	
Propanil	No	
Propazine	No	
Simazine	Yes	0.02-0.95
Simetryn	No	
Terbutryn	No	

grated and urban/built-up areas; the highest median concentration was for the cropland/pastureland area (fig. 20B).

Important to understanding chloroacetanilide detections within the study area is the fact that metolachlor was not detected at any of the sites. However, at low concentrations, metolachlor antibodies are cross reactive with a number of structurally similar compounds, particularly metalaxyl (0.06 µg/L) used in the study area. Metalaxyl was detected north of the study area at structure S-99 along the C-25 Canal (fig. 1) where concentrations ranged from 0.15 to 0.21 µg/L and averaged 0.18 µg/L. This systemic benzenoid fungicide is used in mixtures as a foliar spray for tropical and subtropical crops. Metalaxyl has a half life of 7 to 170 days, a very high water solubility (7,100 mg/L at 20 °C), and a low K_{oc} of 50 (Extension Toxicology Network, 2002). According to the U.S. Department of Agriculture (2002), the average estimated annual agricultural use of metalaxyl in Florida is greater than 0.748 lb/mi^2.

Metalaxyl was not one of the compounds analyzed by GC/MS. Other chloroacetanilide herbicides that are cross reactive with metolachlor antibodies in the ELISA test were analyzed by GC/MS. These herbicides include acetochlor, butachlor, propachlor, and alachlor; however, none of these compounds were detected by GC/MS analysis (table 8). These herbicides, however, are not commonly used in the study area. Many of the chloroacetanilide detections in the St. Lucie River watershed actually may be detections of metolachlor metabolites, such as metolachlor ethane sulfonic acid (ESA) or metolachlor oxanilic acid (OA). In the Midwest, these metabolites have been found to exist in higher concentrations than the parent compound itself. In one study done in Iowa, more than 80 percent of the measured mass of chloroacetanilide compounds found in surface water was due to the presence of the metabolites (Kalkhoff and others, 1998). Individual metabolites also were detected from 2 to 100 times more than the parent compounds. Metolachlor ethane sulfonic acid (ESA) also has been detected in Joe Bay in southern Florida (Mark Zucker, U.S. Geological Survey, oral commun., 2002).

The distribution and range of concentrations of chlorophenoxy compounds and organophosphates were limited in the watershed. The highest chlorophenoxy compound concentrations were detected in the urban/built-up area, with a maximum concentration of 14.0 µg/L found at site C-24 E (fig. 7, site no. 11). The second highest chlorophenoxy compound concentrations were detected in the integrated area; only two detections each were found in the citrus and cropland/pastureland areas (fig. 20C). Only one detection of organophosphate was found in all of the land-use areas in the study area. Based on the ELISA screening for chlorpyrifos (and as previously mentioned), an organophosphate concentration of 0.20 µg/L was detected at integrated site S-49 UPS (fig. 20D).

The nonparametric Kruskal-Wallis test was employed to test for statistically significant (p-value less than 0.05) differences among medians for ELISA pesticide concentration data from the various land-use categories. The p-values were 0.21 for triazines, 0.08 for chloroacetanilides, 0.91 for chlorophenoxy compounds, and 0.71 for organophosphates. These results indicate no statistically significant differences were apparent at the 95-percent confidence level.

Herbicide/Metabolite Ratios and Geochemical Transport

The ratio of the concentration of the atrazine metabolite, deethylatrazine, to the parent compound atrazine (the DAR), has been used as an indicator of herbicide transport and ground-water and surface-water interaction in the environment. DAR values greater than 1.0 generally indicate atrazine transport through the unsaturated zone, whereas DAR values less than 1.0 usually indicate atrazine transport by means of surface runoff (Adams and Thurman, 1991). A DAR value less than 0.10 generally indicates herbicide transport by overland flow immediately following herbicide application, whereas a ratio ranging between 0.10 and 1.0 usually results from postapplication runoff. Deethylatrazine was detected in three water samples analyzed by GC/MS, and all concentrations were 0.01 µg/L. The DAR value ranged from 0.25 to 0.33, indicating that the most likely source of atrazine to the environment was postapplication runoff at the time of sampling.

Deisopropylatrazine is an atrazine metabolite as well as a metabolite of other structurally similar compounds, such as cyanazine and simazine. This metabolite is degraded rapidly in the unsaturated zone and is important in surface runoff (Thurman and others, 1991). Deisopropylatrazine and simazine were detected in all samples analyzed by GC/MS, with concentrations ranging from 0.01 to 0.19 µg/L and 0.02 to 0.95 µg/L, respectively. Of special importance to understanding the source of deisopropylatrazine to the environment is the D^2R, which is the deisopropylatrazine/deethylatrazine ratio (Meyer and others, 2001). The D^2R is important in determining if nonpoint sources of deisopropylatrazine may come from sources other than atrazine. Deethylation proceeds more rapidly than deisopropylation, and simazine degrades to deisopropylatrazine by means of deethylation as opposed to atrazine, which degrades to deisopropylatrazine by means of deisopropylation (Mills and Thurman, 1994). The D^2R, when due to atrazine degradation alone, has been shown to be constrained from 0.3 to 0.5 based on previous studies. For the present study, the D^2R ranged from 1 to 3, indicating simazine is a source of deisopropylatrazine to the environment at the time of sampling because simazine degrades rapidly and directly by deethylation to deisopropylatrazine. These analyses were made for samples collected at sites C-23-6W (fig. 7, site no. 4), C-23-8W (fig. 7, site no. 7), and S-49 UPS (fig. 7, site no. 34) on October 3-4, 2000, and at site S-97 UPS (fig. 7, site no. 37) on January 23, March 30, May 24, and July 11, 2001.

Comparison of Detected Pesticide Concentrations to Water-Quality Standards

To protect aquatic life, the USEPA has established water-quality guidelines for selected pesticides. These guidelines encompass criteria maximum concentrations (CMC) and criteria continuous concentrations (CCC). The CMC and CCC are respective estimates of the highest concentration of a substance in surface water to which an aquatic community can be exposed briefly or indefinitely without resulting in an unacceptable effect (U.S. Environmental Protection Agency, 1999). Chlorpyrifos is the only detected pesticide for which USEPA aquatic life criteria exist, with a freshwater CMC of 0.083 µg/L and a CCC of 0.041 µg/L. Only one detection for organophosphate (chlorpyrifos) at a concentration of 0.200 µg/L exceeded both standards; however, the minimum detection level of the ELISA test for chlorpyrifos is 0.100 µg/L, which is greater than both standards. Considering this fact and also the cross reactivity of the chlorpyrifos antibodies with structurally similar organophosphate analogues, these results should be interpreted cautiously.

No USEPA aquatic life guidelines exist for atrazine, metolachlor, or 2,4-D; however, there are Canadian aquatic life guidelines for atrazine and metolachlor. Assuming all the ELISA triazine detections were atrazine, none of the triazine concentrations exceeded the Canadian freshwater concentration standard of 1.8 µg/L for atrazine. Atrazine concentrations determined by GC/MS analysis ranged from less than 0.01 to 0.04 µg/L, also below the Canadian aquatic life guideline of 1.8 µg/L. Additionally, by assuming that all ELISA chloroacetanilide detections were metolachlor, none of the chloroacetanilide concentrations exceeded the Canadian freshwater concentration standard of 7.8 µg/L for metolachlor.

Quality Assurance Criteria

Quality assurance efforts included the collection of equipment blanks and duplicate samples for every 20 and 10 environmental samples collected, respectively. Results of the equipment blanks and Wilcoxon Rank Sum Test Statistic on the duplicate environmental samples are presented in table 9. Equipment blank test results had

Table 9. Equipment blank concentration ranges and results of Wilcoxon Rank Sum Test on duplicate data sets from Enzyme-Linked Immunosorbent Assay (ELISA) analysis

[Statistically significant if p-value is less than 0.025; <, less than the value]

Pesticide	Equipment blank concentration range	Duplicate environmental sample	
		Wilcoxon Rank Sum Test statistic	p-value (two-sided)
Triazines	<0.05 - <0.05	1	0.32
Chloroacetanilides	<0.05 - 0.07	-.20	.84
Chlorophenoxy compounds	<0.70 - <0.70	-1	.32
Organophosphates	<0.100 - <0.100	1	.32

detections below the MDL for triazines, chlorophenoxy compounds, and organophosphates. Chloroacetanilide concentrations ranged from the MDL (0.05 µg/L) to 0.07 µg/L. No statistically significant differences were found between duplicate environmental samples as determined by the Wilcoxon Rank Sum Test.

A further assessment of the quality assurance efforts involved the comparison of selected constituents determined by ELISA analysis with those obtained by GC/MS analysis. Atrazine is detected by the ELISA test at a MDL of 0.05 µg/L. Atrazine was detected in seven samples submitted for GC/MS analysis, and results of these analyses were compared with ELISA results obtained from the same samples. Many of the ELISA results were reported as less than the MDL (0.05 µg/L); therefore, these results were converted to the MDL (0.05 µg/L) or one-half the MDL (0.025 µg/L) for comparison purposes. When ELISA results are converted to the MDL, test results indicate statistically significant (p-value = 0.03) differences between triazines analyzed by ELISA and atrazine analyzed by GC/MS. There was, however, no statistically significant (p-value = 0.59) difference between triazines determined by ELISA and atrazine determined by GC/MS when ELISA results were converted to one-half the MDL. Simazine and deisopropylatrazine concentrations were not used in any of these comparisons because only two simazine concentrations were of sufficient magnitude (greater than 0.34 µg/L) to be detected by ELISA, and no deisopropylatrazine concentrations were of sufficient magnitude to be detected by ELISA.

SUMMARY

An extensive agricultural and urban drainage system in the St. Lucie River watershed transports pesticides by way of stormwater runoff from various land-use areas to the primary canal system and eventually to the St. Lucie River and estuary. Concern has been raised about pesticide concentrations exceeding aquatic life water-quality criteria in the St. Lucie River watershed. To address this issue, the U.S. Geological Survey, in cooperation with the Florida Department of Environmental Protection, initiated a project to undertake a pesticide reconnaissance within the watershed.

The reconnaissance involved collecting samples during 8 rainfall events at 37 sites in several land-use categories (urban/built-up, citrus, cropland/pastureland, and integrated) at inflow points to the primary canal system within the watershed. The citrus, urban/built-up, and cropland/pastureland categories were represented by area, and the integrated category was represented by specific sites. The integrated sites included gated control structures S-49, S-97, S-48 and S-80 along the C-24, C-23 and C-44 Canals, which discharge to the estuary. Although located in urban areas, these structures represent flow from various land-use categories, and hence are referred to as integrated sites. Numerous grab samples, including quality assurance/quality control samples, were collected and analyzed for selected pesticide residues (triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates) using Enzyme-Linked Immunosorbent Assay (ELISA) screening.

The tests were specific for three herbicides (atrazine, metolachlor, 2,4-D) and for one insecticide (chlorpyrifos); however, cross reactivity of the ELISA antibodies dictates that the results be reported as pesticide classes and not as individual compounds. A Quality Assurance Project Plan was developed and approved by the Florida Department of Environmental Protection. This plan required an equipment blank for every 20 environmental samples, a duplicate sample for every 10 environmental samples collected, and confirmation of 10 percent of ELISA results by gas chromatography/mass spectrometry (GC/MS) analysis. Results indicated that the occurrence of pesticide detections varied based on the number of samples collected and the total sites sampled. Based on the number of samples collected, detections for chloroacetanilides, triazines, chlorophenoxy compounds, and organophosphates were 57, 39, 14 and 1 percent, respectively.

Based on the total sites sampled, detections for chloroacetanilides, triazines, chlorophenoxy compounds, and organophosphates were 89, 68, 27 and 3 percent, respectively. The percentage of sites for one, two, three, and four classes of pesticides detected were 19, 73, 16 and 3 percent, respectively.

Results also indicated that the occurrence of pesticide detections varied among land-use categories. The highest to lowest percentages of detections of triazines were 64, 43, 36, and 29 percent for cropland/pastureland, citrus, integrated, and urban/built-up land uses, respectively. The highest to lowest percentages of detections for chloroacetanilides were 79, 71, 61, and 43 percent for cropland/pastureland, urban/built-up, integrated, and citrus land uses, respectively. The highest to lowest percentages of detections for chlorophenoxy compounds were 36, 15, 8 and 7 percent for cropland/pastureland, integrated, urban/built-up, and citrus land uses, respectively. The lower percentage of detections for the chlorophenoxy compounds is probably related to the higher method detection limit (MDL) of 0.7 µg/L compared to the MDL of 0.5 µg/L for triazines and chloroacetanilides. Organophosphates were detected only once at an integrated site (S-49). The highest percentages of detections for triazines, chloroacetanilides, and chlorophenoxy compounds were all from the cropland/pastureland land-use category.

Temporal variability within the watershed was assessed by collecting water samples at the integrated sites during different rainfall events between October 2000 and September 2001. Triazine concentrations varied from the MDL to 0.34 µg/L at site S-48 UPS. Triazines, chloroacetanilides, chlorophenoxy compounds, and organophosphates were detected in 32, 60, 17, and 3 percent, respectively, of all the samples collected at the integrated sites.

Compared to the other sites, triazine concentrations at S-80 UPS were detected most often above the MDL. Maximum triazine concentrations were detected in samples collected at sites S-48 UPS and S-97 UPS during a rainfall event in October 2000, and at sites S-49 UPS and S-80 UPS during a rainfall event in July 2001.

Chloroacetanilide concentrations ranged from the MDL to 0.30 µg/L at sites S-48 UPS and S-97 UPS. Compared to the other sites, most chloroacetanilide concentrations were detected most often above the MDL at site S-48 UPS. Maximum chloroacetanilide concentrations were detected at sites S-48 UPS and S-97 UPS in October 2000, at site S-80 UPS in July 200l, and at site S-49 UPS in January, July, and August 2001 (each date representing a rainfall event).

Chlorophenoxy compound concentrations ranged from the MDL to 1.6 µg/L at site S-49 UPS. At three of the integrated sites (S-80, S-49 UPS, S-97 UPS), detections were recorded only during a rainfall event in August 2001. At site S-48 UPS, detections were found in June and August 2001. One organophosphate concentration was detected above the MDL at site S-49 UPS (0.20 µg/L) during a rainfall event in March 2001. No organophosphate concentrations were above the MDL at the remaining three integrated sites.

The spatial distribution and range of concentrations of the pesticide classes were determined. For samples collected from all of the sites, the range in concentration was greatest for chlorophenoxy compounds (0.70 to 14 µg/L), and the range in concentration was greater for chloroacetanilides than for the triazines. The range in triazine concentrations, from highest to lowest, was found in the citrus, urban/built-up, integrated, and cropland/pastureland areas, respectively. The highest median concentration was detected in the cropland/pastureland area. The maximum triazine concentration of 0.63 µg/L was detected at a citrus site (C-24-12W) during a rainfall event in October 2000. Confirmation of triazines from samples analyzed by GC/MS indicated the presence of atrazine, simazine, and deethylatrazine and deisopropylatrazine (both triazine metabolites). Simazine is widely used in citrus areas.

The range in chloroacetanilide concentrations, from highest to lowest, was found in the citrus, integrated, the urban/built-up, and cropland/pastureland areas, respectively. The highest median concentration was found in the cropland/pastureland area. A maximum chloroacetanilide concentration of 1.0 µg/L was found at a citrus site (C-24-12W) during a rainfall event in October 2000. No detections for metolachlor were found in samples analyzed by GC/MS, even though the ELISA test indicated the presence of chloroacetanilides. No detections for acetochlor, butachlor, propachlor, or alachlor were found in samples analyzed by GC/MS. The chloroacetanilide detections by ELISA may be the result of antibody cross reactivity with metolachlor metabolites; namely, metolachlor ethane sulfonic acid (ESA) and metolachlor oxanilic acid (OA). Additionally, metalaxyl, a fungicide used in the area, is cross reactive at low concentrations with the metolachlor antibodies and

may contribute to the chloroacetanilide detections by ELISA.

The range in concentrations, from highest to lowest, for the chlorophenoxy compounds was detected in the urban/built-up, integrated, citrus, and cropland/pastureland areas, respectively. A maximum concentration of 14 µg/L was found at an urban/built-up site (C-24-1E) during a rainfall event in May 2001. The nonparametric Kruskal-Wallis test indicated no statistically significant differences were apparent in medians for any of the pesticide classes among the different land-use categories.

The atrazine metabolites deethylatrazine and deisopropylatrazine are important indicators for ascertaining the geochemical transport of atrazine in the environment. The deethylatrazine/atrazine ratio (DAR) may be used as an indicator of atrazine transport and ground- and surface-water interaction in the environment. DAR values greater than 1.0 probably result from atrazine transport through the unsaturated zone, whereas DAR values less than 1.0 indicate atrazine transport by surface-water runoff. A DAR value less than 0.10 usually indicates herbicide transport by overland flow immediately following herbicide application, whereas a ratio of 0.10 to 1.0 usually results from postapplication runoff. Deethylatrazine was detected in three water samples, and the DAR values ranged from 0.25 to 0.33, indicating that the most likely source of atrazine to the environment at the time of sampling was postapplication runoff.

Deisopropylatrazine is an atrazine metabolite as well as a metabolite of other structurally similar compounds, such as cyanazine and simazine. This metabolite is rapidly degraded in the unsaturated zone and is important in surface runoff. Deisopropylatrazine and simazine were found in all samples analyzed by GC/MS, ranging from 0.01 to 0.19 µg/L and from 0.02 to 0.95 µg/L, respectively. Deethylation proceeds more rapidly than deisopropylation, and simazine degrades rapidly to deisopropylatrazine by means of deethylation. The deisopropylatrazine/deethylatrazine ratio (D^2R) is an important indicator of nonpoint sources of deisopropylatrazine in the environment and ranged from 1 to 3 in this study, indicating simazine as a source of deisopropylatrazine at the time of sampling as opposed to atrazine alone.

The U.S. Environmental Protection Agency has not established aquatic life guidelines for atrazine or metolachlor; however, Canadian aquatic life criteria do exist. Assuming that ELISA concentrations for triazines and chloroacetanilides were all the result of atrazine and metolachlor detections, Canadian aquatic life guidelines for atrazine (1.8 µg/L) and metolachlor (7.8 µg/L) were not exceeded by any of the concentrations detected in the St. Lucie River watershed. A single organophosphate detection of 0.200 µg/L exceeded the U.S. Environmental Protection Agency guidelines that encompass criteria maximum concentrations (0.083 µg/L) and criteria continuous concentrations (0.041 µg/L).

Quality assurance efforts included the collection of equipment blanks and duplicate samples for every 20 and 10 environmental samples collected, respectively. All equipment blank test results showed concentrations below the MDL for triazines, chlorophenoxy compounds, and organophosphates. Chloroacetanilide concentrations ranged from the MDL to 0.07 µg/L. A further comparison was made between triazines detected by ELISA and atrazine detected by GC/MS. Because some of the ELISA detections were below the MDL, the data were converted to the MDL (0.05 µg/L) or one-half the MDL (0.025 µg/L). Statistically significant (p-value = 0.03) differences were found between triazines by ELISA and atrazine by GC/MS when ELISA data were at the MDL. No statistically significant (p-value = 0.59) differences were found between triazines determined by ELISA and atrazine determined by GC/MS when ELISA results were converted to one-half the MDL.

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U.S. Department of the Interior
U.S. Geological Survey
227 North Bronough Street
Suite 3015
Tallahassee, FL 32301-1372

–A.C. Lietz– –Occurrence and Distribution of Pesticides in the St. Lucie River Watershed, South-Central Florida, 2000-01, Based on Enzyme-Linked Immunosorbent Assay (ELISA) Screening– –USGS/WRIR 02-4304

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