# Water Quality and Evaluation of Pesticides in Lakes in the Ridge Citrus Region of Central Florida

By Anne F. Choquette and Sharon E. Kroening

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# Conversion Factors

| Multiply | By | To obtain |
|---|---|---|
| | Length | |
| inch (in.) | 2.54 | centimeter |
| foot (ft) | 0.3048 | meter |
| mile (mi) | 1.609 | kilometer |
| | Area | |
| acre (ac) | 4.047 | square meter |
| square mile (mi$^2$) | 2.590 | square kilometer |
| | Flow rate | |
| inch per hour (in/hr) | 0.0254 | meter per hour |
| inch per year (in/yr) | 25.4 | millimeter per year |
| | Temperature | |
| Fahrenheit (°F) | °C = (°F - 32) /1.8 | Celsius (°C) |
| Celsius (°C) | °F = (1.8 x °C) + 32 | Fahrenheit (°F) |

Vertical coordinate information is referenced to North American Vertical Datum of 1929 (NGVD 29).
Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).
Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius
   (µS/cm at ˚25 C).

# Abbreviations

| | |
|---|---|
| FDEP | Florida Department of Environmental Protection |
| IQR | interquartile range |
| $K_{oc}$ | organic carbon partition coefficient |
| LRL | laboratory reporting level |
| NAWQA | National Water-Quality Assessment |
| SD | standard deviation |
| SRL | standardized reporting level |
| SWFWMD | Southwest Florida Water Management District |
| TOC | total organic carbon |
| USEPA | U.S. Environmental Protection Agency |
| USGS | U.S. Geological Survey |
| AMPA | aminomethylphosphonic acid |
| DCPU | 3,4-dichlorophyenyl urea |
| DCPMU | 3(3,4-dichlorophenyl) methyl urea |
| DDA | didealkylatrazine, or chlordiamino-s-triazine (CAAT) |
| DEA | deethylatrazine, or 2-chloro-4-isopropylamino-6-amino-s-triazine (CIAT) |
| DIA | deisopropylatrazine, or chloro-6-ethylamino-4-amino-s-triazine (CEAT) |
| HA | hydroxyatrazine, or 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine 2-hydroxyatrazine (OIET) |
| HS | hydroxysimazine, or 2-hydroxy-4,6-diethylamino-s-triazine (OEET) |

# Other Abbreviated Units

| | |
|---|---|
| acre/ft | acre per foot |
| mg/L | milligram per liter |
| µg/L | microgram per liter |
| µS/cm | microsiemens per centimeter |
| L | liter |
| µm | micrometer |
| µL | microliter |
| µg/mL | microgram per milliliter |
| Pt-Co | platinum-cobalt unit |
| lb/acre | pound per acre |
| lbs | pounds |

# Water Quality and Evaluation of Pesticides in Lakes in the Ridge Citrus Region of Central Florida

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## Abstract

Water chemistry, including major inorganic constituents, nutrients, and pesticide compounds, was compared between seven lakes surrounded by citrus agriculture and an undeveloped lake on the Lake Wales Ridge (herein referred to as the Ridge) in central Florida. The region has been recognized for its vulnerability to the leaching of agricultural chemicals into the subsurface due to factors including soils, climate, and land use. About 40 percent of Florida's citrus cultivation occurs in "ridge citrus" areas characterized by sandy well drained soils, with the remainder in "flatwoods citrus" characterized by high water tables and poorly drained soils. The lakes on the Ridge are typically flow-through lakes that exchange water with adjacent and underlying aquifer systems. This study is the first to evaluate the occurrence of pesticides in lakes on the Ridge, and also represents one of the first monitoring efforts nationally to focus on regional-scale assessment of current-use pesticides in small- to moderate-sized lakes (5 to 393 acres). The samples were collected between December 2003 and September 2005.

The lakes in citrus areas contained elevated concentrations of major inorganic constituents (including alkalinity, total dissolved solids, calcium, magnesium, sodium, potassium, chloride, and sulfate), total nitrogen, pH, and pesticides compared to the undeveloped lake. Nitrate (as N) and total nitrogen concentrations were typically elevated in the citrus lakes, with maximum values of 4.70 and 5.19 mg/L (milligrams per liter), respectively. Elevated concentrations of potassium, nitrate, and other inorganic constituents in the citrus lakes likely reflect inputs from the surficial ground-water system that originated predominantly from agricultural fertilizers, soil amendments, and inorganic pesticides.

A total of 20 pesticide compounds were detected in the lakes, of which 12 compounds exceeded the standardized reporting level of 0.06 µg/L (microgram per liter). Those most frequently detected above the 0.06-µg/L level were aldicarb sulfoxide, diuron, simazine degradates hydroxysimazine and didealkylatrazine (DDA), bromacil, norflurazon, and demethyl norflurazon which occurred at detection rates ranging from 25 to 86 percent of samples, respectively. Typically, pesticide concentrations in the lake samples were less than 1 microgram per liter. The number of targeted pesticide compounds detected per lake in the citrus areas ranged from 9 to 14 compared to 3 compounds detected at trace levels in the undeveloped lake. Consistent detections of parents and degradates in quarterly samples indicated the presence of pesticide compounds in the lakes many months or years (for example, bromacil) after their application, signaling the persistence of some pesticide compounds in the lakes and/or ground-water systems. Pesticide degradate concentrations frequently exceeded parent concentrations in the lakes. This study was the first in the Ridge citrus region to analyze for glyphosate—widely used in citrus—and its degradate aminomethylphosphonic acid (AMPA), neither of which were detected, as well as a number of triazine degradates, including hydroxysimazine, which were detected.

The lake pesticide concentrations did not exceed current Federal aquatic-life benchmarks, available for 10 of the 20 detected pesticide compounds. Limited occurrences of bromacil, diuron, or norflurazon concentrations were within about 10 to 90 percent of benchmark guidelines for acute effects on nonvascular aquatic plants in one or two of the lakes. The lake pesticide concentrations for several targeted pesticides were relatively high compared to corresponding national stream-water percentiles, which is consistent with this region's vulnerability for pesticide leaching into water resources.

Several factors were evaluated to gain insight into the processes controlling pesticide transport and fate, and to assess their utility for estimating the relative likelihood of transport to the lakes for specific pesticides and for designing future pesticide sampling networks. These factors included variations in pesticide concentrations within the lake water column, indexes of pesticide usage estimates and chemical properties to identify pesticides prone to transport, comparisons between pesticide concentrations in the lakes and in adjacent ground water, and the relation between nitrate and pesticide concentrations. Further study is needed to better understand the role of pesticide inputs from ground-water and atmospheric sources, in-lake processes of pesticide breakdown, and the influence of the lakes on regional ground-water quality in this dynamic, closely linked ground-water/surface-water system.

# Introduction

Lakes are the dominant surface-water feature in the central Florida landscape. They represent an important component of the region's ecosystem, are a resource for recreation, and contribute aesthetic beauty to this region. About 70 percent of Florida's lakes are seepage lakes (Palmer, 1984), having no natural surface flow into or out of them, and are fed predominantly by ground-water inflow and rainfall. Due to its soils and climate, central Florida is also one of the most productive regions of the State for citrus agriculture.

Historically, citrus has been one of the top agricultural crops in Florida, accounting for 68 percent of the Nation's citrus production, and generating more than 1.5 billion dollars of revenue annually (U.S. Department of Agriculture, 2006). During the 1990s, citrus acreage in Florida increased by 64 percent (Gianessi and Silvers, 2000), but experienced a 15-percent decline between 2004 and 2006 related to the intensive 2004 and 2005 hurricane seasons, the spread of citrus pests and diseases, and urban sprawl (U.S. Department of Agriculture, 2007). Citrus cultivation in Florida occurs in two distinct environments, including (1) the "ridge citrus," which occurs on the ridges of central Florida and is characterized by well-drained sandy soils; and (2) the "flatwoods citrus," which occurs predominantly in coastal and southern Florida and is characterized by poorly drained, high water-table, flatwoods soils (Boman, 2002). The "ridge citrus" comprises about 40 percent of Florida's total citrus acreage (Paramasivam and Sajwan, 2001).

This study focuses on an area of central Florida recognized as susceptible to leaching of agrichemicals into the ground-water system. The combination of the seasonally high rainfall rates, highly permeable sandy soils prone to leaching, and the widespread use of agricultural chemicals in the region render the region's lakes potentially susceptible to the influx of these chemicals. In 2003, the U.S. Geological Survey (USGS) in cooperation with the Southwest Florida Water Management District (SWFWMD) and the Florida

Department of Environmental Protection (FDEP) initiated a study of citrus pesticides in small to moderately sized lakes on the Lake Wales Ridge (subsequently referred to as "the Ridge" in this report) in central Florida (fig. 1). Initiated as a companion study to a long-term ground-water monitoring project (Choquette and Sepulveda, 2000), this study was designed as a regional reconnaissance to evaluate the occurrence and variability of pesticides, pesticide degradates, and nitrate in lakes in citrus cultivation areas, and to compare water quality in the citrus lakes to that in an undeveloped lake in a relatively undisturbed area.

More than 200 lakes occur on the Ridge covering about 10 percent of its area (Barcelo and others, 1990). Citrus orchards (typically referred to as groves, in Florida) commonly are found in Ridge lake basins and often extend to lake shore areas (fig. 2). The Ridge lakes both receive water from and discharge water to the aquifers underlying the Ridge (Sacks and others, 1998) and, therefore, also are important for understanding the fate and transport of pesticides within the ground-water system.

This study represents the first evaluation of the occurrence and distribution of pesticides and their degradates in the Ridge lakes, and is one of the first monitoring studies nationally to evaluate the occurrence of current-use pesticides in small to moderately sized lakes.[1] Also, the occurrence of several pesticide degradates that have not been widely analyzed in water resources was examined.

## Purpose and Scope

This report summarizes the results of a reconnaissance water-quality study of eight lakes distributed across the Lake Wales Ridge, with an emphasis on pesticides and their degradates. Water chemistry was sampled seasonally in seven lakes surrounded predominantly by citrus groves (orchards) and in one lake in a relatively undisturbed area to: (1) evaluate the effects of citrus agriculture on water quality, and (2) assess potential factors influencing the occurrence of pesticides in the lakes. Spatial variations in water quality between the lakes and seasonal variability in pesticide and pesticide degradate concentrations were also evaluated.

A total of 36 samples was collected from the seven citrus lakes and one undeveloped "control" lake. Each lake was sampled quarterly for 1 year, and paired samples were collected at two depths from four of the lakes to compare pesticide concentrations within the lake water column. Water-quality analyses included pesticides, nutrients, major water chemistry, and field measurements of basic water chemistry (app. 1). The targeted pesticides included the major chemicals used in Florida citrus cultivation (Florida Agricultural Statistics

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[1]German and Adamski (2005) also analyzed pesticides in lakes in a region north of the Ridge study area.
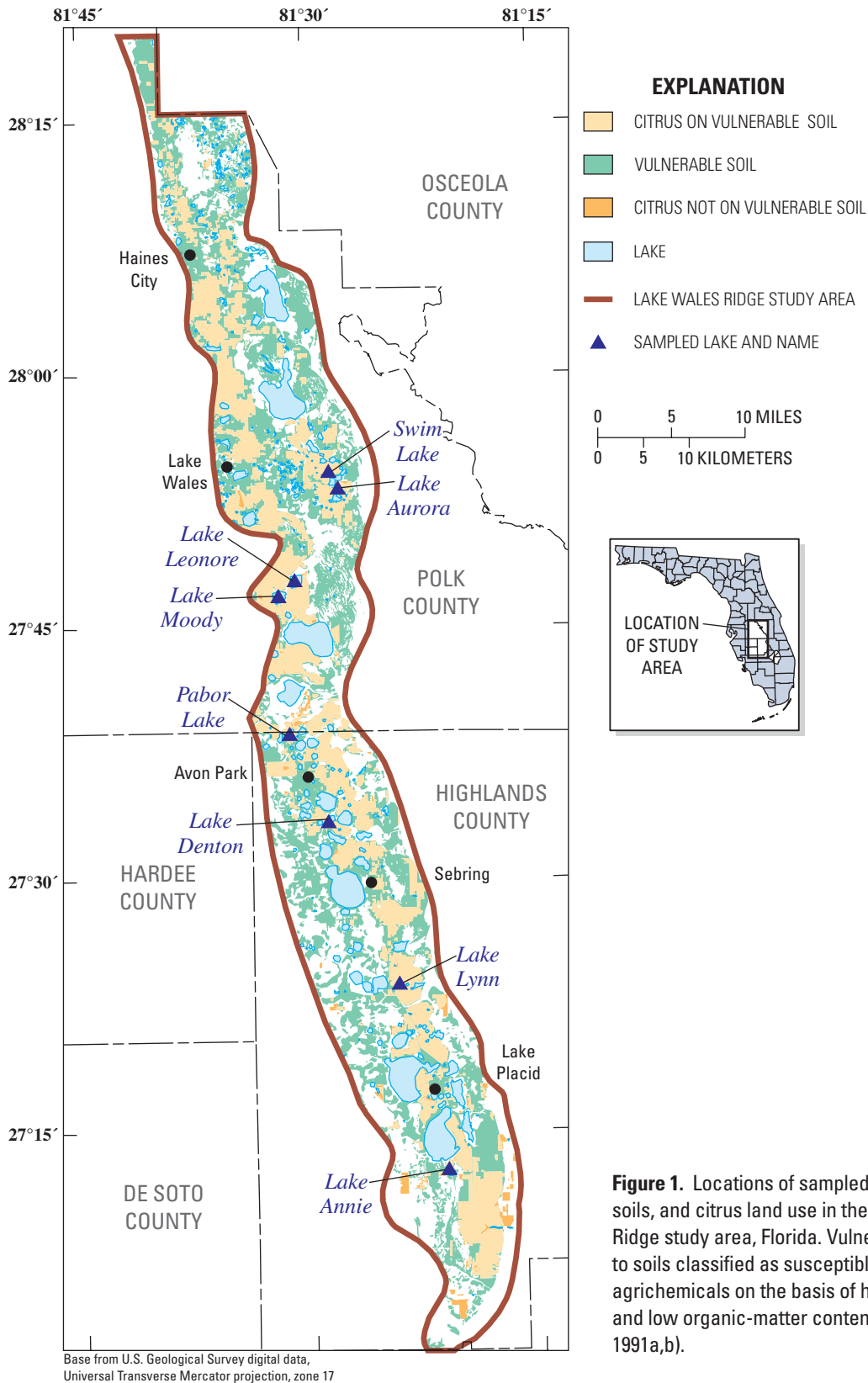
**Figure 1.** Locations of sampled lakes, vulnerable soils, and citrus land use in the Lake Wales Ridge study area, Florida. Vulnerable soils refer to soils classified as susceptible to leaching of agrichemicals on the basis of high permeability and low organic-matter content (Hurt and Obreza, 1991a,b).

**Figure 2.**  Lake Moody and nearby citrus land use. Citrus dominates the agricultural landscape of the Ridge, commonly found in close proximity to the lakes. Photograph courtesy of Sharon Kroening.

Service, 2000, 2004; Shahane, 2003). The pesticide concentrations were compared to aquatic-life and drinking-water benchmarks and to results of USGS surface-water sampling in other areas of the United States. Pesticide detections in the lakes were related to indexes of statewide agrichemical usage and pesticide properties to provide inferences regarding pesticide fate and transport in the region, and to assess the utility of these indexes for estimating the occurrence of pesticides in the lakes.

## Influences of Agrichemicals on Lake Systems

Assessment of agrichemicals in Ridge lakes is important for a number of reasons including: the presence of elevated nitrate and pesticides in ground water in the surficial aquifer system, which feeds the lakes; the connections between the lakes and the underlying Upper Floridan aquifer, which is the primary drinking-water supply; and the potential for adverse effects of elevated agrichemicals on lake biota and ecosystems. Much is unknown regarding the chronic toxicity of pesticides and their degradates, chemical mixtures, and nitrate to non-target organisms. Although pesticides have been documented in ground water underlying the Ridge (Choquette and others, 2005), there have been no studies to date to evaluate the potential transport of pesticides from ground water to the Ridge lakes, or to assess the influences of pesticides on the lake ecosystems.

The importance of pesticide and nitrate monitoring for protection of drinking water and ecosystems is supported by recent data indicating adverse effects of low concentrations of some pesticides on the endocrine systems of amphibians and other non-target organisms (Hayes and others, 2002; Gross and others, 2003; Barbash, 2004), and the incomplete removal of some pesticides from standard municipal water-filtration systems (Coupe and Blomquist, 2004; Carter and others, 2007). In addition, there is indirect theoretical evidence indicating the potential for increased human toxicity of simazine when combined with elevated nitrate concentrations (U.S. Department of Health and Human Services, 2004) and the possibility for endocrine disruption in biota upon exposure to elevated nitrate concentrations (Guillette and Edwards, 2005).

Several prior studies have focused on lake water budgets, ground-water/surface-water interactions, and the inorganic chemistry of the Ridge lake systems (Katz and others, 1995; Lee, 1996, Sacks and others, 1998; Swancar and others, 2000). Compared to non-citrus areas, the lakes in citrus areas generally contain elevated concentrations of dissolved nitrate (as N) and other inorganic agrichemicals including sulfate, chloride, potassium, and magnesium (Sacks and others, 1998; Romie, 2000; Kolasa and others, 2001). A statewide survey indicated that nitrate concentrations in citrus lakes on the Lake Wales Ridge exceeded those in 95 percent of lakes statewide (Romie, 2000). Median values of nitrate in Ridge citrus lakes ranged from about 0.5 to 8.4 mg/L as N (Sacks and others, 1998;

Kolasa and others, 2001); in contrast, nitrate concentrations were less than 0.002 mg/L in lakes located in undeveloped areas of the Ridge (Tihansky and Sacks, 1997).

Pesticide sampling in six golf-course ponds (Swancar, 1996) located in central Florida areas north of the Ridge yielded detections of at least one pesticide in 96 percent of samples. Nineteen of 41 targeted pesticide compounds were detected, some of which were not reported as being used on the golf courses, and were attributed to prior land uses at the sites (Swancar, 1996). Atrazine, the most frequently detected pesticide, was reported as not used at any of the golf courses where it was detected. Concentrations in the pond samples exceeded 1 µg/L for nine pesticides including simazine, diuron, and atrazine.

Results of ground-water sampling in citrus areas of the Ridge indicate a high potential for agrichemical transport into the subsurface. Concentrations of pesticides and nitrate in ground water underlying the Lake Wales Ridge were elevated compared to national USGS ground-water monitoring data, and exceedances of the Federal drinking-water standard for nitrate (10 mg/L) were common (Choquette and others, 2005). Twelve of 29 targeted pesticides and degradates have been detected in ground water from the Lake Wales Ridge ground-water network, with as many as eight different pesticides or degradates found in ground water from some of the wells. Pesticide concentrations in ground water often show significant short-term variability, and concentrations of some pesticides appear to be increasing over time (Choquette and others, 2005; Gilliom and others, 2006).

The high propensity for leaching of agricultural chemicals into ground water on Lake Wales Ridge is due to a combination of factors. The sandy soils are well drained promoting rapid infiltration rates and contain little organic matter to sorb or filter pesticide compounds. Among United States agricultural categories, citrus agriculture has been ranked as having the highest national rate of herbicide use and the third highest rate of insecticide use on the basis of active ingredient applied annually (Brandt, 1995; Barbash and Resek, 1996). The study area is located in Polk and Highlands Counties, which typically rank first and third, respectively, statewide in terms of total annual citrus production (National Agricultural Statistics Service, 2005). Due to the mild climate and long growing season in Florida, the number and frequency of pesticide applications annually exceeds that in many other regions of the United States. Additionally, low pH has been shown to enhance the persistence of some pesticides in the subsurface (Harkin and others, 1986; Barbask and Resek, 1996), and may also contribute to the elevated pesticide concentrations in ground water on the Ridge. The pH of ground water typically ranges from 4 to 6 in the surficial aquifer system on the Ridge (Sacks and others, 1998; Choquette and others, 2003).

Chemical properties of pesticides and pesticide usage are commonly used to identify pesticides prone to be transported into surface- and ground-water resources, and to select pesticides for water-quality monitoring (Buttler and others, 1993, 1998; Rao and Hornsby, 1993; Barbash and Resek,

1996). However, laboratory data on pesticide properties do not always accurately predict pesticide behavior in field settings (Katz, 1993; Warner and Morrow, 2007; Krutz and others, 2008). The Ridge lake study provided an opportunity to assess the accuracy of applying published data on pesticide properties and usage to derive estimates of transport potential, by comparing these estimates of transport potential to actual pesticide occurrence in the Ridge lakes.

In recent years, Federal and State laws and regulations have been developed to reduce leaching of agricultural chemicals into ground water and to protect drinking-water sources (National Association of State Departments of Agriculture Research Foundation, 2000; Boman, 2002). Guidelines and restrictions on agrichemical usage have been developed specifically for the sandy soils on the Ridge to minimize probability of leaching and protect water resources (State of Florida, 1995, 2002a,b; Aerts and Nesheim, 2000). In 2002, fertilizer best management practices were adopted specifically for Ridge citrus (State of Florida, 2002b) to minimize impacts to the ground-water system, and are being implemented by citrus growers on a voluntary basis. Reductions in nitrate concentrations in ground water have been observed in Ridge areas where these best management practices were implemented on a test basis (Lamb and others, 1999).

## Acknowledgments

## Description of Study Area

The study area is delineated by the Lake Wales Ridge in Polk and Highlands Counties (fig. 1) and covers an area of about 700 mi$^2$. The landscape, hydrology, and ecology of the Ridge are unique in a number of respects. The Ridge is the topographic crest and most prominent physiographic feature of peninsular Florida, consisting of a paleoisland remnant underlain by highly permeable Miocene-Holocene marine sands. Due in part to its geologic history, the Ridge supports one of the oldest ecosystems in Florida and contains one of the largest collections of rare and endangered species in the United States (Dobson and others, 1997) and one of the highest concentrations of endemic species in North America (Martin, 1998).

## Physical Setting, Climate, and Land Use

The Lake Wales Ridge is the most extensive ridge in a complex of several parallel northwest trending ridges in the physiographic province delineated as the Central Lakes District (Brooks, 1981). Elevations on the Ridge range from about 150 to 300 ft (NGVD of 1929). The Ridge contains numerous surface depressions and lakes that are typically formed by dissolution of underlying limestone and subsequent collapse of surficial sediments. Surface stream drainage is poorly developed or absent in most areas of the Ridge, although some surface-water flow occurs between lakes and on the flanks of the Ridge. Detailed descriptions of the study area and its hydrology can be found in Yobbi (1996), Sacks and others (1998), and Choquette and Sepulveda (2000).

Mean annual rainfall (1971-2000) in the vicinity of the Ridge ranges from about 48 to 51 in. and varies seasonally with about 60 percent of the annual rainfall occurring during June through September (National Oceanic and Atmospheric Administration, 2005). Rainfall amounts and intensity are highest during summer and early fall as a result of convective storms and hurricanes. Mean monthly rainfall during June through September ranges from about 5.5 to 8.5 in. compared with about 2 to 3 in. during other months. Mean monthly temperatures range from about 16 °C in January to 28 °C in July and August.

The geologic deposits underlying the Ridge form a layered, wedge-shaped sequence that thickens from north to south (Yobbi, 1996). The hydrogeologic units include the surficial aquifer system (50- to 300-ft layer of unconsolidated marine and dune sands), underlain by the intermediate confining unit/intermediate aquifer system (0- to 500-ft thick unit of heterogeneous clay, sands, and limestone), in turn underlain by the Upper Floridan aquifer (1,200- to 1,400-ft thick unit of limestone and dolomite). The Upper Floridan aquifer is the primary source of municipal drinking-water supply, but the surficial aquifer system and, locally, the intermediate aquifer system provide drinking water for rural domestic wells, particularly in the southern part of the Ridge where the Upper Floridan aquifer is as much as 600 ft below land surface (Tibbals, 1990; Tihansky and others, 1996). Water from the surficial aquifer system generally flows to, or recharges, the intermediate aquifer system and Upper Floridan aquifer (Yobbi, 1996). The water table in the surficial aquifer system appears to be less affected by topography than by hydraulic characteristics of the underlying deposits (Sacks and others, 1998; Daniel Moore, Florida Department of Agriculture and Consumer Services, written commun., 1998). Breaches in the underlying confining unit, seasonal changes in lake levels, local water-table gradients near lakes, and hydraulic head differences between the surficial aquifer system and underlying aquifer systems affect the horizontal and vertical ground-water flow in the surficial aquifer system.

Most of the Ridge is underlain by soils that have been classified as vulnerable to leaching of agrichemicals (fig. 1) on the basis of high permeability rates and low organic-matter content (State of Florida, 1995, 2002a; Hurt and

Obreza, 1991a,b; Wilson and others, 2002; Brown and others, 2003). The vulnerable soil types on the Ridge include the Candler, Astatula, and Paola Soil Series, which are entisols that exhibit minimal soil development, contain little organic matter, consist of about 97 to 99 percent sand-sized particles, and have high hydraulic conductivity, typically in the range of 24 to 51 in/hr throughout the soil profile (U.S. Department of Agriculture, 1989, 1990).

Land use on Lake Wales Ridge is predominantly agricultural, and citrus covers about 24 percent (787,600 acres) of the study area. The Ridge citrus represents about 14 percent of total citrus acreage statewide. Orange trees constitute about 93 percent of the citrus in Polk and Highlands Counties, and grapefruit represents the remainder (Shahane, 2003). The types and amounts of pesticides used in these citrus classes are similar. During the past 25 years, citrus acreage has been decreasing in Polk County and increasing in Highlands County due in part to increasing urban development in Polk County and to the southerly migration of citrus to avoid winter freezes (Choquette and Sepulveda, 2000). Most of the citrus groves in Polk and Highlands Counties are irrigated (93 and 98 percent of groves, respectively) (Florida Agricultural Statistics Service, 1998). Irrigation in the Ridge citrus is performed by a variety of methods including drip, microsprinkler, and overhead sprinkler systems.

## Agrichemical Usage

Statewide estimates of pesticide and fertilizer usage provide a general indication of the types, rates, and amounts of chemicals applied in Florida's citrus agriculture. The types and amounts of pesticides used in individual citrus groves, however, can vary widely, and the active ingredients applied can change over time due to a number of factors including the registration of new products, discontinuation of products, and the rotation of chemicals to avoid development of resistance to the chemicals, and reduced efficacy, for targeted pests (Jackson and Davies, 1999; Boman, 2002). In 2001, 59.3 million pounds (active ingredient) of pesticides were applied in citrus regions of Florida. The primary pesticide compounds used in Florida orange groves between 1995 and 2003 are shown in figure 3. Petroleum distillate (mineral oil), primarily used as an insecticide, was the most widely applied pesticide and was used in 84 to 93 percent of Florida's orange groves during these years (Florida Agricultural Statistics Service, 2002). Excluding petroleum distillate, pesticide usage in orange groves in terms of pounds of active ingredient per year is lead by herbicides (50 percent of total), insecticides (29 percent), and fungicides (21 percent). Herbicides, insecticides, and fungicides were applied in 95, 91, and 61 percent, respectively, of Florida orange groves in 2002-03 (Florida Agricultural Statistics Service, 2004).

Usage of several citrus pesticides, including 1,2-dibromoethane, bromacil, fenamiphos, and aldicarb, has been either restricted or prohibited in the vulnerable soils of the
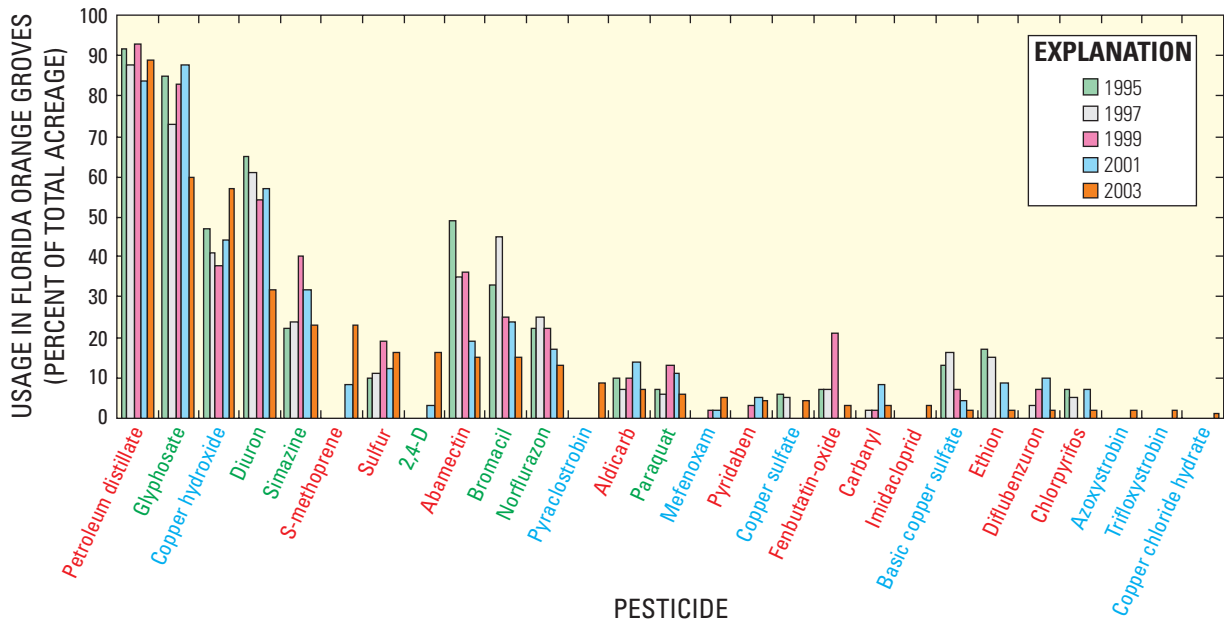
**Figure 3.** Primary pesticides applied in Florida orange groves from 1995 to 2003, showing usage as the percent of total bearing acreage receiving applications (Florida Agricultural Statistic Service, 2000, 2002, 2004). Pesticides are distinguished by colors as herbicides in green, insecticides in red, and fungicides in blue.

Ridge (State of Florida, 1995, 2002a; Aerts and Nesheim, 2000). Detections of bromacil in drinking-water wells led to the product being prohibited from use in most Ridge citrus areas in December 1994 (State of Florida, 1995), and it has subsequently been replaced by other herbicides including norflurazon and glyphosate. In Florida, aldicarb is classified as a "restricted-use pesticide" (State of Florida, 2002a), which indicates usage restrictions on the amounts, timing, and/or locations of applications. In citrus groves on sandy soils, aldicarb use is limited to one application per year at a maximum rate of 5 pounds (lbs) active ingredient per acre, applications must occur between January 1st and April 30th, and its usage is prohibited near potable wells.

Statewide annual average application rates in Florida orange groves, for 1997, 1999, 2001, and 2003, for selected pesticides of interest in this study are shown in figure 4 (Florida Agricultural Statistics Service, 2002, 2004). Local application rates on the Ridge may vary from these averages. The annual average application rate for these six pesticides in 2003 ranged from about 1.2 lbs/acre for bromacil to 3.9 lbs/acre for simazine, and increased during the 1997 to 2003 period for bromacil, diuron, norflurazon, simazine, and glyphosate. The 1997 application rate for the herbicide simazine was higher for citrus in Florida than for any other crop nationally, and was twice that used in California citrus (Gianessi and Silvers, 2000).
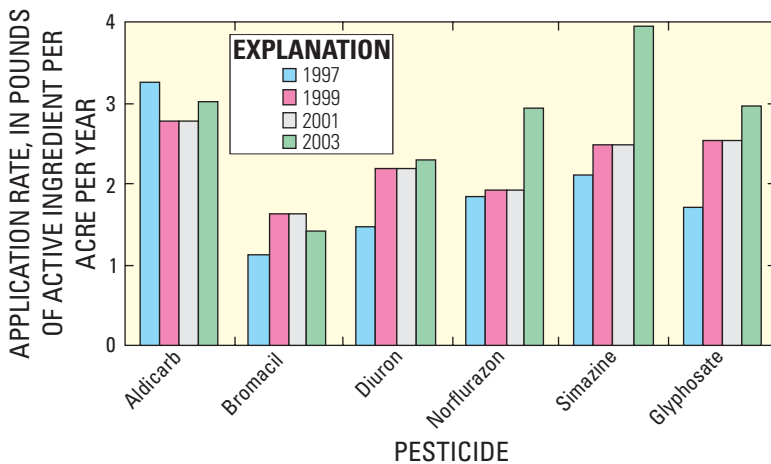


**Figure 4.** Statewide average application rates for selected pesticides in Florida orange groves between 1997 and 2003 (Florida Agricultural Statistics Service, 2002, 2004).

Due to the long growing season and warm climate, pesticides are often applied multiple times per year in Florida. Between 1997 and 2001, the herbicides norflurazon, diuron, and simazine were applied in orange groves on the average about 1.5 times per year (Florida Agricultural Statistics Service, 2002). Norflurazon, diuron, and simazine are applied prior to weed germination (pre-emergent) during spring and/or fall. Diuron, simazine, bromacil, norflurazon, and aldicarb were estimated to have been applied on the average at 59, 31, 27, 20, and 11 percent, respectively, of Florida orange groves statewide during this period.

Citrus cultivation on the Florida ridge soils often requires fertilization with nitrogen, phosphorus, potassium, and magnesium, along with lime amendments to maintain a moderately acidic soil (Stauffer, 1991). Annual average application rates for fertilizers in Florida orange groves in 1999 were 215 lbs/acre nitrogen, 213 lbs/acre potash, and 73 lbs/acre phosphate applied to 94, 94, and 71 percent of orange groves, respectively (Florida Agricultural Statistics Service, 2000). Nitrate fertilizers were applied an average 4.6 times per year in 1999, and potassium fertilizers were applied an average 4.3 times to orange groves in Florida (Florida Agricultural Statistics Service, 2000). Studies of the fate and transport of nitrate from citrus areas on sandy soils in central Florida indicate that fertilizer types (solubility), application rates, irrigation management, and soil organic carbon content can affect denitrification rates and leaching of nitrate into ground water (Graham and Alva, 1996; Wang and Alva, 1996; Paramasivam and others, 1999; Paramasivam and Sajwan, 2001).

## Hydrology of Ridge Seepage Lakes

The lakes in central Florida typically represent surface signatures of dissolution of limestone at depth in this karst region mantled by sand. A number of studies have focused on the geologic history, water budgets, and water quality of Florida's seepage lakes (Sacks and others,1998; Lee, 2002; Sacks, 2002; Swancar and Lee, 2003). Regional study of Ridge lakes indicated that nearly 70 percent of the 27 study lakes derived more than 50 percent of their total annual inflow (including precipitation) from ground water (Sacks, 2002). Direct runoff from the land surface into these lakes, with the exception of stormwater runoff in urban areas, is considered to be minimal because of the high permeability of the sandy soils in the area.

The lakes often exhibit complex hydraulic connections with the adjacent aquifer systems based on a number of factors including local hydrogeology, head gradients, and topography, as well as constructed controls on lake levels such as inter-lake drainage canals. Multiple episodes of subsidence and infilling of sediments can influence subsurface hydraulic connections (Tihansky and others, 1996). Sinkholes and subsidence features may also modify or breach the intermediate confining unit resulting in direct hydraulic connections between the surficial aquifer system and Upper Floridan aquifer (fig. 5).

Lake water budgets and hydrologic models of seepage lakes on Florida's central ridges have provided insight to the hydraulics of these lake systems. Hydraulic head is generally higher in the lakes than in the Upper Floridan aquifer, providing a constant potential for downward flow from the



NOT TO SCALE
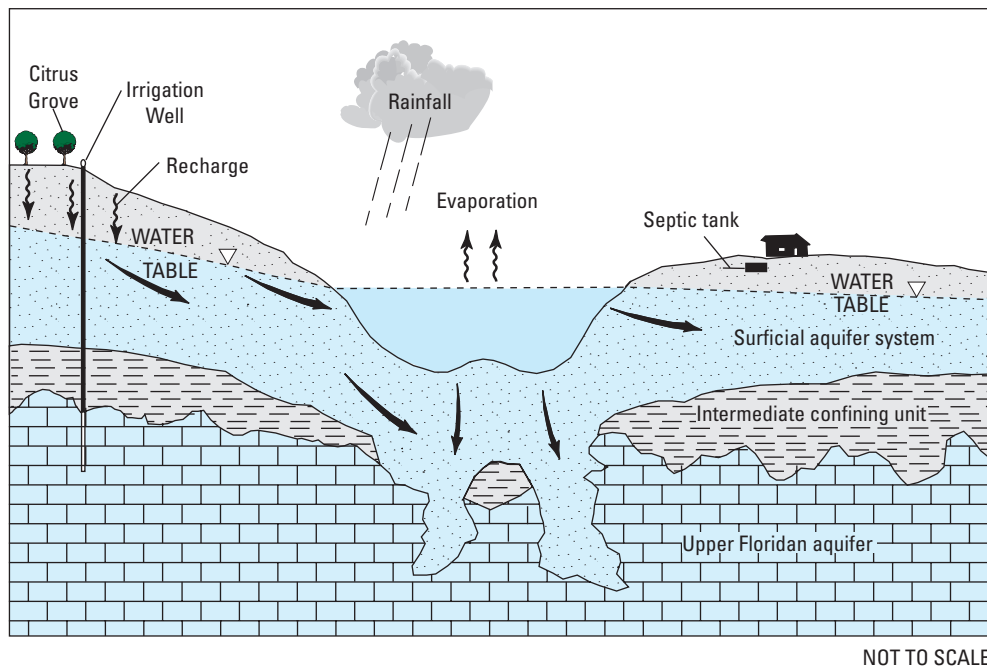
**Figure 5.** Generalized hydrogeologic section showing ground-water/surface-water interactions in the vicinity of Ridge seepage lakes. Arrows denote direction of water movement (from Sacks and others, 1998).

lakes to the Upper Floridan aquifer (Sacks and others, 1998), the principal drinking-water supply in the region (fig. 5). Many Ridge lakes consist of flow-through systems that both receive and disperse water to the adjacent surficial aquifer system, and often exhibit changes or reversals in ground-water flow directions in response to transient climatic events. Ground-water exchange rates (inflow and outflow) can vary considerably between lakes and over time.

The direction of lateral ground-water flow around lakes does not necessarily parallel the basin topography. For example, lateral ground-water outflow from one Ridge lake (Lake Starr) in topographically higher parts of the lake floor was attributed to preferential flow toward karstic features (Swancar and others, 2000). In the deeper parts of the lake, water typically flowed vertically into the Upper Floridan aquifer. Deep lakes tend to have higher rates of ground-water inflow and more delayed responses to recharge (rainfall) than lakes in shallow topographic basins (Sacks and others, 1998). Modeling studies indicate ground-water catchment areas for seepage lakes on the Ridge can be substantially smaller than the topographic drainage basins (Sacks and others, 1998; Lee, 2002).

Ground water and atmospheric inputs are the primary potential sources of elevated solutes and contaminants in most of the Ridge lake systems. Sacks and others (1998) inferred that the Ridge lakes typically are well mixed with respect to major inorganic solutes, on the basis of little lateral or vertical stratification of specific conductance, and that land use can alter lake water quality.

Lakes in undeveloped regions of the Ridge exhibited specific conductance (51 to 126 µS/cm) and pH (3.7 to 4.5) values that were considerably lower than lakes in residential and agricultural settings (Sacks and others, 1998). The Ridge lakes are naturally acidic due to low base cation concentrations and low acid neutralizing capacity in ground water and in rainfall (Canfield, 1983; Brenner and others, 1990; Sacks and others, 1998; National Atmospheric Deposition Program, 2008). Historical water-quality data for lakes in citrus areas of central Florida indicate nitrate (as N) concentrations ranging from about 0.5 to 21 mg/L (Sacks and others, 1998; Romie, 2000).

# Selection and Description of Sampled Lakes

The lakes sampled in the study included small- to medium-sized lakes (less than 400 acres) distributed across the Lake Wales Ridge from central Polk County to southern Highlands County (fig. 1). Criteria considered in selecting lakes included lake size and depth; citrus land use in the lake basin; elevated lake-water nitrate concentrations in historical sampling (Sacks and others, 1998; Romie, 2000; Kolasa and others, 2001); availability of information on adjacent ground-water flow paths from previous studies; absence of direct pesticide applications to the lake; and prior detections of pesticides in ground water within the surficial aquifer system in the vicinity of the lake (Choquette and others, 2005).

The seven citrus lakes included in the study were located in basins dominated by citrus agriculture and sandy, organic-poor soils considered to be vulnerable to leaching of agrichemicals (State of Florida, 1995, 2002a; Hooweg and Hornsby, 1998; Brown and others, 2003; Hurt and Obreza, 1991a,b). Four of the lake basins (Lakes Denton, Lynn, Pabor, and Leonore) included some residential development. An inactive industrial facility, which appeared to be a former citrus-processing plant, was located near Pabor Lake. The control lake (Lake Annie) was located within Archbold Biological Research Station, an ecological preserve in the southern part of the Lake Wales Ridge (fig. 1). Surface areas of the studied lakes ranged from 5 to about 393 acres, with estimated maximum depths ranging from about 20 to 65 ft (table 1). Geometry of the sampled lakes ranged from small deep lakes to large shallow lakes, with surface-to-depth ratios ranging from 0.2 to 19.7 acres/ft.

Four lakes with historical nitrate concentrations exceeding 4 mg/L were selected to increase the probability of sampling some lakes in which pesticides or pesticide degradates would be present. Elevated nitrate concentrations in the lake water may indicate higher concentrations of other soluble agrichemicals and higher rates of ground-water inflow (Sacks, 2002). Pesticides have been applied to selected lakes in Polk and Highlands Counties to control macrophyte growth (Florida Department of Environmental Protection, 2005). The eight pesticides registered for use (in 2003) in Florida lake waters included copper, diquat, endothall, fluridone, glyphosate, 2,4-dicholorophenoxyacetic acid (2,4-D), triclopyr, and imazapyr (University of Florida, 2003). County personnel confirmed that the studied lakes had not previously received any pesticide applications.

Lake bathymetry and dominant directions of ground-water inflow have been measured in two of the study lakes—Swim Lake and Lake Annie (Sacks and others, 1998). Both lakes were flow-through lakes exhibiting areas of ground-water inflow and areas of outflow. Swim Lake and Lake Annie

**Table 1.** Physical characteristics of the sampled lakes.

| Lake | Surface area (acres) | Approximate maximum depth (feet) | Lake surface/ depth ratio (acres per foot) |
|---|---|---|---|
| Swim | 5 | 30 | 0.2 |
| Lynn | 16 | 45 | .4 |
| Pabor | 40 | 20 | 2.0 |
| Denton | 57 | 48 | 1.2 |
| Annie ("control") | 92 | 65 | 1.4 |
| Aurora | 108 | 37 | 2.9 |
| Moody | 391 | 20 | 19.6 |
| Leonore | 393 | 20 | 19.7 |

were characterized by high monthly variability in net ground-water flow compared to the other lakes examined by Sacks and others (1998). In Swim Lake, monthly net ground-water flow was usually positive (inflow greater than outflow) during spring and summer, and negative (outflow greater than inflow) during winter and fall. In contrast, net flows in Lake Annie were consistently positive. Such differences indicate that inflow and outflow rates and residence times can vary between lakes (Sacks and others, 1998).

The control lake, Lake Annie, has been described as one of the most pristine bodies of water in southern Florida (Layne, 1979), although there have been some recent reductions in lake transparency and increases in dissolved nutrients (Swain and Gaiser, 2005). The 5.7-mi$^2$ area of the lake drainage basin is dominated by native vegetation, but also includes some areas of livestock grazing and citrus. Thermal stratification, which is uncommon in Florida lakes, has been observed at Lake Annie between spring and fall (March through October), and periodically during winter (Eckblad and others, 1974; McDiffett, 1978). The stratification has been attributed to the lake's small surface area, considerable depth, and protection from the mixing action of wind by a well-vegetated shoreline (McDiffett, 1978).

Prior to and during the sampling period, annual precipitation from 2003 through 2005 ranged from 54.8 to 66 in/yr at Archbold Biologic Research Station, and exceeded the 74-year, long-term mean of 53.8 in/yr (Nancy Deyrup, Archbold Biologic Research Station, written commun., 2003; National Oceanic and Atmospheric Administration, 2004, 2005). These precipitation conditions indicate average to above-average annual precipitation inputs to the lakes, and the likelihood of similarly high ground-water inflow to the lakes during the sampling period on the basis of lake water-budget studies in the region (Sacks and others, 1998; Lee, 2002; Swancar and Lee, 2003).

# Methods of Study

Sampling methods adhered to stringent parts-per-billion protocols and laboratory analyses for all pesticides and pesticide degradate concentrations were performed using high-performance liquid chromatography/mass spectrometry. Sampling protocols included quality assurance sampling and analyses. Interpretive analyses of pesticide results included methods for adjusting summary statistics and the use of a standardized reporting level to avoid potential bias due to varying laboratory reporting levels.

## Sampling and Laboratory Methods

Swim Lake, Lake Lynn, Lake Aurora, and Lake Denton were sampled quarterly during the first year of the study (December 2003 to September 2004), and Lake Moody,

Lake Leonore, Pabor Lake, and Lake Annie were sampled quarterly during the second year of the study (December 2004 to September 2005). Water samples were collected near the deepest part of each lake using a stainless-steel Kemmerer sampler. Approximately 5 to 8 L of water were composited in a Teflon churn splitter. Samples were collected from a depth of 5 ft below lake surface, with the exception of a subset of paired samples to compare water quality at different depths in the lake water column. During June 2004 in four of the lakes (Swim, Lynn, Denton, Aurora), paired samples were collected near the middle of each lake at a depth about 5 ft below lake surface and near the lake bottom.

Sample processing and equipment decontamination were performed according to USGS protocols (U.S. Geological Survey, 1997-2005). Samples collected for pesticide analysis were filtered through a 0.7-μm nominal pore size glass-micro-fiber filter, precombusted at 400 °C for at least 2 hours prior to use. Samples collected for analysis of calcium, magnesium, sodium, potassium, and orthophosphate concentrations were filtered through a 0.45-μm filter. Calcium, magnesium, potassium, and sodium samples were preserved with nitric acid to lower the pH to 2. Samples analyzed to determine total organic carbon, ammonia nitrogen, unfiltered orthophosphate, nitrite nitrogen, and total nitrogen concentrations were preserved with sulfuric acid to lower the pH to 2.

Water-quality analyses included 83 pesticides and pesticide degradates, major ions, nutrients, alkalinity, total dissolved solids, total suspended solids, turbidity, and water color (app. 1). The particular suites (laboratory schedules) of targeted pesticides analyzed in this study (table 2) include some pesticides not typically used in citrus agriculture because the suites originally were developed by the USGS for national pesticide analysis. Analyses of glyphosate, aminomethylphosphonic acid (AMPA), and glufosinate were not performed on samples collected during December 2003 and 2004, or during September 2004, due to cost constraints. Analyses of the diuron degradates 3,4-dichlorophenyl urea (DCPU) and 3(3,4-dichlorophenyl) methyl urea (DCPMU) and demethyl norflurazon were not performed during June and September 2005.

Appendix 1 includes documentation of laboratory methodology and reporting levels by constituent. Inorganic constituent concentrations were determined at the SWFWMD laboratory in Brooksville, Florida, using standard U.S. Environmental Protection Agency methods (Southwest Florida Water Management District, 2002). Pesticide concentrations were determined using high performance liquid chromatography and mass spectrometry at the USGS National Water-Quality and Organic Geochemistry Research Laboratories. Most pesticide and pesticide degradates concentrations were analyzed according to Furlong and others (2001). Most triazine pesticides and pesticide degradates and the phenylurea pesticides were analyzed according to Lee and others (2002b). Glyphosate and its degradate AMPA and glufosinate were analyzed according to Lee and others (2002a).

**Table 2.** Pesticides and pesticide degradates analyzed in the lake samples.

[Reporting levels and analytical methods appear in appendix 1. Pesticide degradates are shown in *italics*]

| Pesticide or degradate name | Pesticide or degradate name | Pesticide or degradate name |
|---|---|---|
| 2,4-D (2,4-Dicholorophenoxyacetic acid) | Cycloate | Norflurazon |
| 2,4-D methyl ester | Dacthal monoacid | *Demethyl norflurazon* |
| 2,4-DB | Dicamba | Oryzalin |
| 3-ketocarbofuran | Dichlorprop | Oxamyl |
| Acifluorfen | Dinoseb | Picloram |
| Aldicarb | Diphenamid | Prometon |
| *Aldicarb sulfone* | Diuron | Propazine |
| *Aldicarb sulfoxide* | *DCPMU [3-(3,4-dichlorophenyl) methyl urea]* | Propham |
| Atrazine | *DCPU [1-(3,4-dichlorophenyl) urea]* | Propiconazole |
| Bendiocarb | Fenuron | Propoxur |
| Benomyl | Flumetsulam | Siduron |
| Bensulfuron-methyl | Fluometuron | Simazine |
| Bentazon | *Demethyl fluometuron* | Sulfometuron-methyl |
| Bromacil | Glufosinate | Tebuthiuron |
| Bromoxynil | Glyphosate | Terbacil |
| Carbaryl | *Aminomethyl phosphonic acid (AMPA)* | ***Triazine[1] Degradates:*** |
| Carbofuran | Imazaquin | *DDA (CAAT): Didealkylatrazine, Chlordiamino-s-triazine* |
| *3-Hydroxycarbofuran* | Imazethapyr | *DIA (DES, CEAT): Deisopropylatrazine; Deethylsimazine; 2-Chloro-6-ethylamino-4-amino-s-triazine* |
| Chloramben, methyl ester | Imidacloprid | *DEA (CIAT): deethylatrazine; 2-Chloro-4-isopropylamino-6-amino-s-triazine* |
| Chlorimuron-ethyl | Linuron | *DEHA (HDEA; OIAT): Deethylhydroxy-atrazine; 2-hydroxy-4-isopropylamino-6-amino-s-triazine* |
| CPMU [3-(4-chlorophenyl)-1-methyl urea] | MCPA (2-methyl-4-chlorophenoxyacetic acid) | *DIHA (HDIA; OEAT): Deisopropylhydroxy-atrazine; 2-hydroxy-6-ethylamino-4-amino-s-triazine* |
| Chlorothalonil | MCPB (4-(2-methyl-4-chlorophenoxy) butyric acid | *HA (OIET): 2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine (2-hydroxyatrazine)* |
| Clopyralid | Metalaxyl | *HS (OEET): Hydroxysimazine; 2-hydroxy-4,6-diethylamino-s-triazine* |
| Cyanazine | Methiocarb | Tribenuron-methyl |
| *Cyanazine amide* | Methomyl | Triclopyr |
| *Cyanazine acid* | Metsulfuron methyl | Oxamyl |
| *Deethylcyanazine* | Neburon | Picloram |
| *Deethylcyanazine acid* | Nicosulfuron | |
| *Deethylcyanazine amid* | | |

[1]The triazine pesticides include atrazine, simazine, cyanazine, and propazine. Alternative abbreviations and nomenclature also are shown.
See appendix 5 for additional information on triazine parent pesticides and degradates, and degradation pathways.

## Quality Assurance

Quality assurance sampling included field blank samples, replicate samples, and matrix spike samples. Ten field blank samples were collected from December 2003 to September 2005 to evaluate potential for contamination. Four of these samples were analyzed for the suite of constituents determined according to Furlong and others (2001). Three of the samples were analyzed for the suite of constituents determined according to Lee and others (2002b), and three samples were analyzed for the suite of constituents determined according to Lee and others (2002a). Three constituents were detected in the field blank samples; caffeine was detected once at a concentration of 0.033 µg/L, propiconazole was detected once at a concentration of 0.0034 µg/L, and bromacil was detected once at a concentration of 0.06 µg/L.

One replicate sample was collected to evaluate the potential for variability between concurrently collected samples. This sample was collected from Lake Lynn in March 2004 and analyzed for the 21 pesticides and degradates determined according to Lee and others (2002b). Four constituents were detected in the replicate and environmental sample from this site—bromacil, deisopropylatrazine, didealkylatrazine, and hydroxysimazine. The relative standard deviation for each of these constituents was 2.7, 0, 8.3, and 20.2 percent, respectively.

Three samples were spiked with 200 µL of a pesticide mixture to determine the recovery of these pesticides in lake water. The spike solution contained 2.5 µg/mL of a solution containing all of the pesticides analyzed [according to Furlong and others (2001)] in appendix 1, except for demethyl norflurazon, DCPMU, and DCPU. The lake waters used to spike these samples were collected from Lake Leonore and Pabor Lake between December 2004 and September 2005, and these samples were analyzed according to Furlong and others (2001). The minimum, maximum, and mean matrix spike recoveries are listed in table 3. Mean percent recovery values ranged from 8.7 percent for aldicarb sulfone to 93.3 percent for 2,4-D.

## Analytical Methods

Analyses of water-quality data included descriptive summary statistics for both spatial (for example, by lake) and temporal groupings of data. To avoid bias due to censoring of pesticide concentrations, calculations of descriptive statistics for pesticides incorporated adjustments for censoring and standardized censoring levels. Descriptive statistics for censored data were determined on the basis of the log-likelihood method (Helsel and Cohn, 1988; Helsel, 2005) using S-Plus Software (Insightful Corporation, 2001). A minimum of three sample detections above laboratory reporting levels were required to determine summary statistics using the log-likelihood method (Helsel, 2005), which also incorporated adjustments to account for multiple censoring levels. Both parametric and non-parametric statistical methods were used to calculate summary statistics. Correlations were performed using the non-parametric Spearman's rho rank correlation coefficient (Helsel and Hirsch, 1992) using SAS software (SAS Institute Inc., 2008).

Duplicate analyses performed at different laboratories were available for some of the targeted pesticides based on the methods of Furlong and others (2001) performed at the USGS National Laboratory, and Lee and others (2002b) performed at the USGS Organic Geochemistry Laboratory (apps. 1 and 3). Duplicate analyses were performed for atrazine, bromacil, diuron, chlordiamino-s-triazine (DDA), chloro-6-ethylamino-4-amino-s-triazine (DIA), and 2-chloro-4-isopropylamino-6-amino-s-triazine (DEA). For summaries in this report, results from one of the duplicate analyses were selected on the basis of method performance, as indicated by laboratory quality assurance data on recovery and precision, and analytical resolution (lower reporting levels), and the analyzing laboratory is noted for these analytes in the summary tables.

For parent-degrade pairs or groupings, consistency of methods between the parent and degrade analyses also was desirable to avoid introducing extraneous variability by using multiple samples, laboratories, and analytical methods. Results based on Lee and others (2002b) were used as the primary source of information for the simazine degradates (DIA, DDA) and bromacil. Results based on Furlong and others (2001) were used as the primary source of information for diuron, atrazine, DEA, and hydroxyatrazine.

Both unadjusted pesticide detection frequencies, associated with differing laboratory reporting levels, and standardized detection frequencies, associated with a single "standardized" reporting level, were used to summarize results for censored concentration data. The unadjusted summaries provided information at the highest analytical resolution supplied by the laboratories. Standardized pesticide detection frequencies were calculated using a single reporting level of 0.06 µg/L, which was the lowest laboratory reporting level common to all detected compounds. The use of a standardized reporting level minimizes potential bias in comparisons between analytes with differing laboratory reporting levels. Such bias can also arise when reporting levels change over time, and when estimated concentrations below laboratory reporting levels are inconsistently reported for all of the samples, such as in the case of interference from the sample matrix or other effects. In comparisons using varying laboratory reporting levels, analytes having lower reporting levels are apt to be detected more often solely due to a higher resolution of detection.

The pesticide concentrations were compared to aquatic-life and drinking-water benchmark guidelines specified by the U.S. Environmental Protection Agency and the State of Florida, and to national pesticide monitoring by the USGS National Water-Quality Assessment (NAWQA) Program of surface waters that drained other land uses and crop types.

**Table 3.** Matrix spike recovery results for selected pesticides and pesticide degradates in the lake samples.

[The samples were analyzed according to Furlong and others (2001). Data represent results from three samples, except as noted]

| Analyte | Percent recovery | | | Analyte | Percent recovery | | |
|---|---|---|---|---|---|---|---|
| | Mean | Minimum | Maximum | | Mean | Minimum | Maximum |
| 2,4-D | 93.3 | 74.7 | 115.9 | Diuron | 76.4 | 50.2 | 121 |
| 2,4-D methyl ester | 36.3 | 2 | 96.2 | Fenuron | 56.2 | 39.2 | 82.9 |
| 2,4-DB | 52.4 | 33.6 | 77 | Flumetsulam | 87.5 | 65.4 | 128.4 |
| 3(4-chlorophenyl) methyl urea | 37.2 | 22.4 | 55.8 | Fluometuron | 52.3 | 48.4 | 119.9 |
| 3-Hydroxy carbofuran | 37 | 19.2 | 71.9 | Imazaquin | 77.2 | 37.4 | 129.1 |
| 3-Keto carbofuran | 11 | 0 | 33 | Imazethapyr | 56.2 | 35.5 | 79.2 |
| Acifluorfen | 58.7 | 11.2 | 96.7 | Imidacloprid | 89.1 | 65 | 127.1 |
| Aldicarb | 19.1 | 13.1 | 25.7 | Linuron | 76.7 | 46.7 | 135 |
| Aldicarb sulfone | 8.7 | 1.9 | 16.9 | MCPA | 51.8 | 33.6 | 77 |
| Aldicarb sulfoxide | 55.5 | 15.9 | 110.2 | MCPB | 57.3 | 37.4 | 84.4 |
| Bendiocarb | 25.7 | 0 | 77 | Metalaxyl | 90.6 | 61.4 | 139.4 |
| Benomyl | 35.1 | 21.5 | 55.2 | Methiocarb | 53.1 | 16 | 124.7 |
| Bensulfuron, methyl | 91.8 | 46.7 | 167.3 | Methomyl | 42.6 | 41.8 | 102.3 |
| Bentazon | 75.2 | 54.2 | 93.2 | Metsulfuron, methyl | 68.8 | 59.8 | 79.8 |
| Bromoxynil | 56.2 | 35.5 | 75.6 | Neburon | 55.8 | 18.7 | 128 |
| Caffeine | 60.5 | 44.3 | 90.2 | Nicosulfuron | 76.3 | 69.1 | 102.7 |
| Carbaryl | 45.6 | 14.9 | 99.4 | Norflurazon | 64.2 | 52.1 | 75 |
| Carbofuran | 38.5 | 36.1 | 103.3 | Oryzalin | 56.4 | 11.2 | 107.8 |
| Chloramben, methyl ester | 34.2 | 7.5 | 58 | Oxamyl | 42.2 | 3.7 | 117.4 |
| Chlorimuron, ethyl | 33.2 | 4.1 | 70.4 | Pichloram | 61.5 | 40.9 | 96.8 |
| Chlorothalonil[1] | 43.8 | 38.4 | 49.1 | Propham | 75.3 | 48.5 | 124.3 |
| Clopyralid | 19.5 | 7.5 | 26 | Propiconazole | 55.9 | 9.3 | 104.5 |
| Cycloate | 68 | 20.5 | 133.1 | Propoxur | 58.8 | 38.7 | 96.3 |
| Dacthal, monoacid | 67.3 | 46.7 | 99.4 | Siduron | 88 | 50.4 | 150.4 |
| Dicamba | 40.2 | 18.7 | 70.4 | Sulfometuron, methyl | 72.1 | 54.7 | 97.6 |
| Dichlorprop | 56.2 | 31.8 | 81.1 | Tebuthiuron | 51.5 | 37 | 74.1 |
| Dinoseb | 87.5 | 22.4 | 145.3 | Terbacil | 44.8 | 34.4 | 65.5 |
| Diphenamid | 76.4 | 54.2 | 119.2 | Triclopyr | 56.4 | 43 | 75.9 |

[1]Spike recovery based on two samples.

Several indices were used to compare pesticide chemical properties and usage to the occurrence of pesticides in the lakes. The comparisons provide an indication of the utility of these indexes for estimating pesticide occurrence in the lakes on the Ridge, and possibly in other regions, and the potential value of such indexes in the design of monitoring networks, such as selecting pesticides targeted for analysis.

The *leaching vulnerability index* (Schlosser and others, 2002), the *pesticide usage index*, and the *transport-potential index*, were defined as:

Equation 1:   *Leaching vulnerability index* $= K_{OC}/t_{1/2}$, where $K_{OC}$ is the organic carbon partition coefficient, and $t_{1/2}$ is the estimated half-life of the compound in soil; and is a measure of the propensity of the pesticide to leach from the soil into ground water.

Equation 2:   *Pesticide usage index* = the product of the percent of total crop area [by crop type[2]] in the area of interest and the application rate (in AI/acre/year), where AI is the active ingredient of pesticide.

Equation 3:   *Transport-potential index* = the ratio of the *pesticide usage index* to the *leaching vulnerability index*.

[2]Crop type corresponded to area of orange orchards in Florida.

The pesticide application estimates used to calculate the *pesticide usage index* were statewide averages for orange orchards in Florida, which comprise the major citrus crop in Polk and Highlands Counties (Florida Agricultural Statistics Service, 2002; Shahane, 2003). Usage in specific orchards may vary from these averages.

# Lake Water Quality

Lake water quality was evaluated in terms of spatial and seasonal variability, as well as comparison between the lakes in citrus areas versus the control (undeveloped) lake basin. Interpretive analyses of water quality focused on the occurrence of agricultural chemicals in the lakes. The water-quality data for agricultural chemicals were evaluated in terms of potential land-use impacts, aquatic life and human-health guidelines, pesticide degradation, concentrations relative to national stream samples, and factors related to the transport and fate of chemicals in the lakes. Field and laboratory results for the lake samples are listed in appendixes 2 and 3.

## Physical Properties and Major Constituents

Physical properties measured in lake water included field measurements of Secchi depth, water color, temperature, specific conductance, dissolved oxygen, and pH. Laboratory analyses included major ions, total organic carbon, total dissolved solids, and suspended sediment.

Water clarity, as measured by Secchi depth, ranged from 10 to 21 ft in lakes Denton, Swim, Lynn, and Aurora, in contrast to values generally between 1.5 and 5 ft in lakes Moody, Pabor, Leonore, and Annie (table 4 and app. 2). The lakes with greater water clarity were among the deeper lakes sampled and also were characterized by lower concentrations of total organic carbon (TOC) with median TOC values between 4.7 and 7.2 mg/L, compared to median values of 13.8 to 20.5 mg/L in the four lakes with lower clarity (table 4).

Water color was less than 21 Pt-Co units in samples from all lakes except the control lake, Lake Annie, which was highly colored, ranging from 100 to 175 Pt-Co units. The median TOC concentration in the control lake (18.4 mg/L) was similar to the median values in lakes Moody (20.5 mg/L), Leonore (13.8 mg/L), and Pabor (15.1 mg/L), which given their lack of color, suggests the organic matter in the control lake has different characteristics, such as a large amount of organic matter derived from lignin. Suspended solids concentration was less than 16 mg/L in all sampled lakes (table 4). The highest median suspended solids concentrations occurred in Lake Moody (13 mg/L), Pabor Lake (6.7 mg/L), and Lake Leonore (6 mg/L), which were the shallowest lakes in the study (depths generally less than 20 ft). The relatively higher suspended solids concentrations in these three lakes may reflect increased susceptibility to re-suspension of bottom sediments (for example, by wind or precipitation) as a result of their shallow depths.

The sampled lakes typically did not exhibit strong thermal stratification. Median temperatures in the lakes ranged from 24.7 to 25.8 °C with seasonal extremes ranging from 14 to 30 °C (table 4). The temperature difference between the top and bottom of the water column in the lakes was less than 2.0 °C in more than 50 percent of the sampling events. The largest temperature gradient was a difference of about 11 °C measured in Lake Annie (during June 2005 and September 2005) and in Pabor Lake (June 2005), with higher temperatures observed at the top of the water column.

Alkalinity and total dissolved solids, calcium, magnesium, sodium, potassium, chloride, and sulfate concentrations were greater in all seven sampled citrus lakes compared to the control lake (table 4). Elevated concentrations of inorganic constituents in lakes in citrus areas as compared to undeveloped areas are consistent with other central Florida results from Sacks and others (1998) and Stauffer (1991). Similarly, elevated concentrations of calcium, magnesium, potassium, and sulfate have also been observed in streams draining residential and agricultural land use compared to undeveloped basins in areas underlain by sand and gravel deposits in New Jersey (Morgan and Good, 1988).

Increased concentrations of potassium and other inorganic constituents measured in lakes in this study likely reflect inputs to the lakes from the surficial aquifer system, which has been affected by the use of agricultural chemicals in citrus areas. Fertilizers are likely a source of increased potassium, sodium, chloride, and sulfate concentrations to the lake water because fertilizers have been applied as potassium nitrate, potassium chloride, or sulfate salts (Stauffer, 1991). Citrus pesticides that contain sulfur, sulfate, and chloride (fig. 3) may also contribute to elevated concentrations of sulfate and chloride in the lakes.

The water in Pabor Lake was more mineralized compared to the other sampled lakes with higher concentrations of total dissolved solids, alkalinity, and dissolved sodium and potassium. Sodium and potassium were the predominant cations in the water in Pabor Lake and comprised about 65 percent of the sum of cations. In contrast, sodium and potassium typically comprised between 20 and 46 percent of the sum of cations in the other sampled lakes.

The sampled lakes generally had a near neutral pH and dissolved oxygen concentrations greater than 5 mg/L (table 4). The pH in the control lake was substantially lower than the citrus lakes, with a median value of 5.9 compared to medians ranging from 7.1 to 7.7 units for the citrus lakes. Undisturbed lakes in this part of Florida typically are acidic due to low acid neutralizing capacity in the water recharging the lakes from the surficial aquifer system (Canfield, 1983). The higher pH values in most lakes sampled in this study may result from increased concentrations of anions in the ground water due to the fertilization and to liming of citrus groves, in which calcium carbonate is added in order to neutralize acidic soils.

**Table 4.** Summary statistics for major inorganic constituent concentrations in the sampled lakes.

[The summary includes four samples per lake which were collected quarterly over a 1-year period at a depth of 5 feet below lake surface. All units are in milligram per liter, except as noted; nd, not determined; µS/cm, microsiemens per centimeter; <, less than]

| Constituent and units | Statistic | Lake | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Annie ("control") | Aurora | Denton | Leonore | Lynn | Moody | Pabor | Swim |
| Total dissolved solids | Minimum | 42 | 127 | 149 | 190 | 190 | 220 | 303 | 151 |
| | Median | 47 | 136 | 166 | 202 | 191 | 230 | 313 | 169 |
| | Maximum | 50 | 136 | 171 | 225 | 199 | 256 | 316 | 179 |
| Dissolved calcium | Minimum | 2.43 | 16.7 | 20.5 | 21.9 | 21.8 | 25.9 | 19.2 | 24.1 |
| | Median | 2.59 | 18.1 | 21.9 | 22.8 | 22.3 | 28.1 | 20.75 | 27.8 |
| | Maximum | 2.76 | 18.3 | 22.1 | 24.9 | 22.6 | 30.1 | 21.5 | 28.4 |
| Dissolved magnesium | Minimum | .69 | 7.25 | 11.8 | 14.3 | 15.9 | 15.2 | 7.83 | 7.44 |
| | Median | .75 | 7.62 | 12.4 | 14.85 | 16.1 | 16.7 | 8.2 | 8.45 |
| | Maximum | .76 | 7.78 | 12.4 | 16.2 | 16.3 | 17.9 | 8.32 | 8.72 |
| Dissolved sodium | Minimum | 2.85 | 5.2 | 4.73 | 6.81 | 6.79 | 7.33 | 42.5 | 4.66 |
| | Median | 3.03 | 5.2 | 4.83 | 7.13 | 6.96 | 8.08 | 44.2 | 5.04 |
| | Maximum | 3.2 | 5.41 | 4.91 | 8.16 | 7.08 | 8.99 | 45.4 | 5.26 |
| Dissolved potassium | Minimum | .59 | 11.2 | 12.8 | 12.9 | 14.3 | 12.5 | 47.5 | 11.2 |
| | Median | .69 | 11.7 | 13.2 | 13.25 | 14.4 | 13.3 | 48.8 | 12.3 |
| | Maximum | .82 | 12 | 13.7 | 15 | 14.7 | 14.3 | 50.8 | 13.1 |
| Alkalinity, as calcium carbonate | Minimum | 1.85 | 27.8 | 35.22 | 34.6 | 39.5 | 47.88 | 163.43 | 16.04 |
| | Median | 2.37 | 29.58 | 35.4 | 41.49 | 41.61 | 49.42 | 166.21 | 31.7 |
| | Maximum | 3.69 | 61.21 | 38.37 | 55.59 | 46.42 | 56.73 | 185.83 | 32.79 |
| Dissolved sulfate | Minimum | 1.11 | 36.03 | 41.4 | 55.6 | 61.8 | 67.22 | 47.88 | 50.73 |
| | Median | 2.43 | 39.76 | 42.8 | 56.51 | 62.07 | 72.54 | 48.02 | 57 |
| | Maximum | 2.94 | 38.3 | 44.12 | 59.7 | 64.83 | 84.16 | 50.21 | 57.82 |
| Dissolved chloride | Minimum | 2.97 | 17.36 | 25.15 | 25.02 | 27.05 | 26 | 16.5 | 13.91 |
| | Median | 5.79 | 18.7 | 26.4 | 26.2 | 27.6 | 27.02 | 16.72 | 15.7 |
| | Maximum | 6.07 | 19.78 | 27.53 | 28.51 | 28.65 | 28.9 | 16.81 | 16.23 |
| Total organic carbon | Minimum | 15.3 | 4.6 | 4.5 | 5 | 3.8 | 9.9 | 13.4 | 4.5 |
| | Median | 18.4 | 7 | 7.2 | 13.8 | 4.7 | 20.5 | 15.1 | 5.9 |
| | Maximum | 36.8 | 10 | 9.7 | 29.6 | 5 | 47 | 31.5 | 8.5 |
| Water color, in platinum-cobalt units | Minimum | 100 | <5 | <5 | 10 | <5 | 10 | 15 | <5 |
| | Median | 138 | <5 | <5 | 15 | <5 | 12.5 | 15 | <5 |
| | Maximum | 175 | <5 | <5 | 20 | <5 | 15 | 15 | <5 |
| Secchi depth[1], in feet | Minimum | 2.8 | 12 | 15 | 1.6 | 9.6 | 1.5 | 2.2 | 12 |
| | Median | ND | ND | ND | ND | ND | ND | ND | ND |
| | Maximum | 5.0 | 12.5 | 21 | 7.8 | 18 | 1.6 | 3.6 | 19 |
| Suspended solids | Minimum | 1.3 | .5 | .7 | 1.3 | .9 | 9.9 | 3.7 | .6 |
| | Median | 1.3 | 1.2 | .8 | 6 | 1.4 | 13 | 6.7 | .9 |
| | Maximum | 2 | 1.3 | 1.2 | 10.8 | 1.5 | 15.9 | 9.2 | 1.2 |
| pH, field, in standard units | Minimum | 5.2 | 6.9 | 7.3 | 6.1 | 6.7 | 7 | 7.3 | 6.4 |
| | Median | 5.9 | 7.2 | 7.65 | 7.35 | 7.1 | 7.45 | 7.5 | 7.15 |
| | Maximum | 7 | 7.5 | 7.8 | 7.7 | 8.2 | 7.9 | 7.5 | 7.3 |
| Dissolved oxygen | Minimum | 5.4 | 7.1 | 7.8 | 7.5 | 7.2 | 6.8 | 6.4 | 6.2 |
| | Median | 5.95 | 8.3 | 8.7 | 7.8 | 8.1 | 8.35 | 7.05 | 8.4 |
| | Maximum | 8.7 | 8.3 | 9.6 | 8.1 | 8.9 | 10.3 | 9.9 | 8.9 |
| Specific conductance, µS/cm at 25 degrees Celsius | Minimum | 37 | 218 | 279 | 311 | 327 | 339 | 474 | 257 |
| | Median | 37.5 | 222 | 283.5 | 329 | 329 | 352.5 | 487.5 | 284.5 |
| | Maximum | 39 | 238 | 303 | 343 | 343 | 383 | 495 | 296 |
| Temperature, in degrees Celsius | Minimum | 18.6 | 19.4 | 20.4 | 14 | 20.5 | 15.1 | 17.7 | 19.1 |
| | Median | 25.75 | 25.1 | 24.9 | 24.7 | 25 | 24.95 | 25.3 | 25.25 |
| | Maximum | 29.2 | 29.5 | 29.2 | 29.5 | 29.7 | 29.1 | 29.4 | 30 |

[1]Includes two to three measurements per lake.

The dissolved oxygen in the lake samples from the shallow zone of the water column ranged from 5.4 to 10.3 mg/L (table 4). Dissolved oxygen concentrations generally were lower near the bottom of the sampled lakes, especially during the summer months. In Lake Lynn, the bottom of the water column (depths about 35 to 45 ft) was virtually devoid of oxygen (less than 0.1 mg/L) during most sampling events, compared to dissolved oxygen concentration greater than 10 mg/L near the bottom of the water column (about 45 ft) at Lake Denton.

## Nutrients

The nutrients included nitrate nitrogen, nitrite nitrogen, ammonia nitrogen, total phosphorus, and total nitrogen. Many of the sampled lakes were characterized by high nitrate concentrations and low phosphorus concentrations. Nitrate concentrations ranged from less than 0.001 mg/L (as N) in Lake Annie and Pabor Lake, to 4.70 mg/L in Swim Lake (table 5). Maximum nitrate concentrations were highest in Swim Lake (4.7 mg/L), Lake Denton (3.45), and Lake Leonore (3.56) and were lowest in Lake Annie (0.16) and Pabor Lake (0.04). Increased nitrate concentrations in citrus lakes on the Lake Wales Ridge have been attributed to fertilizer use because nitrogen isotope analyses indicate that nitrate in the surficial ground water typically is of inorganic or fertilizer origin (Tihansky and Sacks, 1997).

Ammonia and nitrite concentrations were low in the study lakes. Total ammonia concentrations ranged from minimum values of about 0.1 mg/L in several of the lakes

to maximum values of 0.4 to 0.5 mg/L in Lake Moody and Pabor Lake (table 5). Nitrite concentrations in the lake samples ranged from less than 0.01 to 0.05 mg/L. Total nitrogen concentration ranged from 0.86 to 5.19 mg/L in the citrus lakes compared to 0.4 to 0.68 mg/L in the control lake (table 5).

Although the range in *total* nitrogen concentrations in Pabor Lake was similar to that observed in the other citrus lakes, Pabor's nitrate concentrations were markedly lower, ranging from less than 0.001 to 0.04 mg/L compared with 0.4 to 4.7 mg/L in the other citrus lakes (table 5). The low nitrate concentrations in Pabor may reflect differing sources of nitrogen or fertilizer application practices, a lower proportion of ground-water inflow compared to the other study lakes, biogeochemical conditions more conducive to denitrification (such as organic carbon in water), or higher inputs of organic nitrogen relative to inorganic forms, and possibly a combination of these factors. The elevated total nitrogen and low nitrate concentrations in Pabor indicate the relative proportion of organic to total nitrogen may be higher in Pabor Lake compared to the other citrus lakes (table 5).

Phosphorus generally was not detected in Lake Aurora, Lake Denton, and Lake Lynn. Low phosphorus concentrations previously have been noted in lakes in the citrus agricultural areas of central Florida (Stauffer, 1991), and occur despite the application of phosphorus fertilizers at citrus farms an average of 3.1 times per year at a rate of 23 lbs/acre in 1999 (Florida Agricultural Statistics Service, 2000). Previous studies have attributed the low phosphorus concentrations in the lakes in citrus agricultural areas of central Florida to efficient phosphorus retention in the soil (Stauffer, 1991).

**Table 5.** Summary statistics for nutrient concentrations in the sampled lakes.

[The summary includes four samples per lake which were collected quarterly over a 1-year period at a depth of 5 feet below lake surface. All units are in milligram per liter; <, less than]

| Constituent and units | Statistic | Lake | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | Annie ("control") | Aurora | Denton | Leonore | Lynn | Moody | Pabor | Swim |
| Total nitrate (as N) | Minimum | <0.001 | 0.97 | 2.71 | 1.36 | 1.01 | 0.4 | <0.001 | 2.87 |
| | Median | .06 | 1.16 | 3.2 | 2.91 | 1.53 | .48 | .01 | 3.65 |
| | Maximum | .16 | 1.49 | 3.45 | 3.56 | 1.81 | .99 | .04 | 4.7 |
| Total nitrogen | Minimum | .4 | 1.35 | 2.98 | 2.39 | 1.53 | 2.31 | .86 | 3.33 |
| | Median | .48 | 1.76 | 3.78 | 4.01 | 2.05 | 2.63 | 1.41 | 4.79 |
| | Maximum | .68 | 2 | 3.82 | 4.14 | 2.21 | 2.96 | 1.84 | 5.19 |
| Total ammonia (as N) | Minimum | .014 | .017 | .010 | .012 | .016 | .026 | .014 | <.010 |
| | Median | .021 | .021 | .020 | .026 | .067 | .153 | .024 | .025 |
| | Maximum | .082 | .033 | .175 | .161 | .147 | .377 | .459 | .042 |
| Total phosphorus | Minimum | .01 | <.01-.02 | | <.01 | | .02 | .01 | <.01-<.02 |
| | Median | .015 | <.01 | <.01-<.02 | .015 | <.01-<.02 | .02 | .02 | <.01 |
| | Maximum | .02 | .011 | | .03 | | .04 | .03 | .01 |

Some characteristics of inorganic water chemistry unique to Pabor Lake, previously discussed, may signify sources of nitrogen species and denitrification or redox processes in Pabor that differ from the other citrus lakes. Pabor Lake exhibited markedly higher concentrations of sodium, potassium, alkalinity, total dissolved solids, and specific conductance and slightly lower median dissolved oxygen concentration, and was among three lakes with elevated total organic carbon concentration (table 4). One potential source of nitrogen is wastewater (for example, septic tank leachate from nearby residential development), which could also explain the elevated sodium and potassium concentrations in Pabor. Another potential influence on the water chemistry in Pabor Lake may be the currently inactive industrial facility in the basin; further study would be necessary to confirm the source(s) of these water-quality differences between Pabor Lake and the other citrus lakes.

## Pesticides and Pesticide Degradates

The sampling design of the Ridge lake study provides baseline data documenting spatial and short-term temporal variability of pesticide concentrations in the lakes. Variations in concentration and degradate-parent ratios were examined within and between the lakes, and seasonally in the year sampled. The pesticide concentrations in lake samples were compared to benchmark guidelines, pesticide concentrations in other areas of the United States, and leaching "risk factors" including pesticide chemical properties and citrus pesticide usage data.

Regional-scale field monitoring of pesticides in water resources is limited, compared to traditional inorganic water-quality monitoring, due primarily to the high costs associated with sampling and laboratory analyses of organic constituents that typically occur at "parts-per-billion" concentrations. However, monitoring data are critical for documenting and understanding the behavior of pesticides in the environment under a variety of application practices and variable field conditions (for example, climate and soil), and for providing realistic concentrations for use in ecotoxicity laboratory studies. Results of the lake pesticide study provide important information for the potential for leaching of the targeted compounds into water resources in other regions and land uses, protection of drinking-water resources, potential impacts to the Ridge lake biota and ecosystems, the utility of using chemical and usage data to predict risks of pesticide leaching into water resources, and guidance in designing future monitoring networks.

## Occurrence of Pesticides

Of the 83 pesticide compounds evaluated in the analysis (table 2), 20 pesticide compounds (12 parent pesticides and 8 degradates) were detected at or above laboratory reporting levels (LRLs) in the 28 samples from the 7 lakes in citrus areas (fig. 6; table 6). Laboratory results for the pesticide samples are presented in appendix 3. In addition, the atrazine degradate DEA was observed below the LRL in one sample (Lake Lynn), at an estimated concentration of 0.006 µg/L. Herbicides and their degradates were the class of compounds most frequently detected in the lake samples followed by insecticides and fungicides, which is consistent with their usage in Florida's
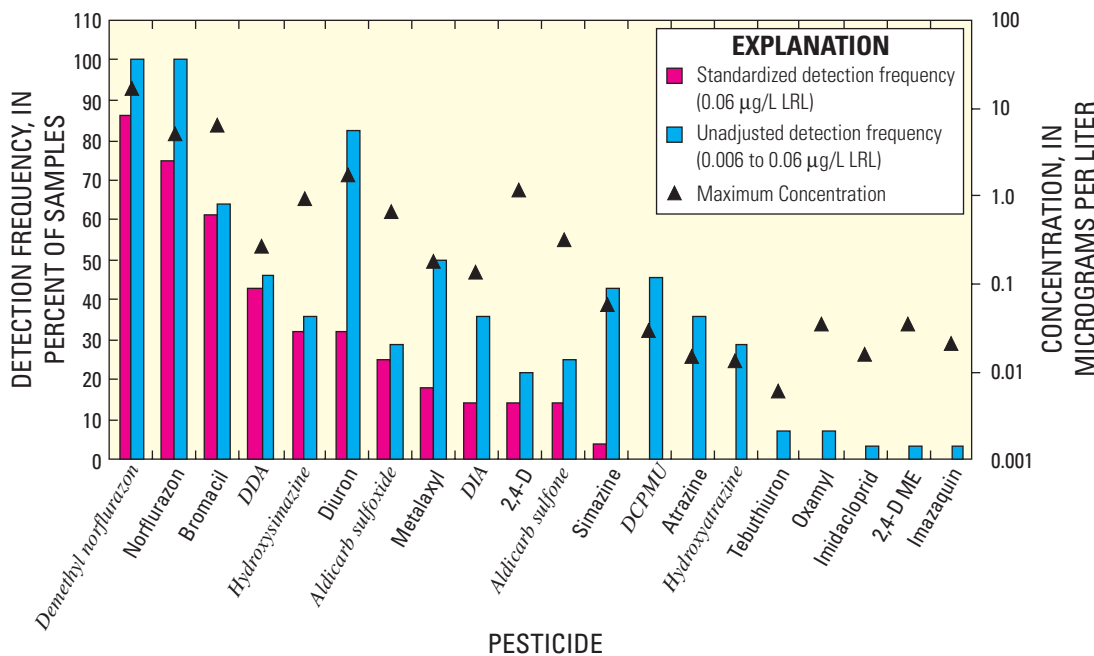


**Figure 6.** Frequency of pesticides and degradates detected in samples from the seven lakes in citrus areas. Degradates are shown in *italics*. The laboratory reporting levels (LRL) for the unadjusted detection frequencies ranged from 0.006 to 0.06 µg/L (microgram per liter). The summary includes 28 samples for most compounds, and excludes the deep water-column samples collected in four of the lakes. Pesticide acronyms are defined in table 2.

**Table 6.** Summary statistics for concentrations of pesticides and degradates detected in the seven sampled citrus lakes.

[The summary includes quarterly samples collected 5 feet below the lake surface. Statistics were calculated using the log-probability method and included adjustments to account for multiple reporting levels (Helsel, 2005). Concentrations are in microgram per liter (µg/L). Pesticide degradates are *italicized*. >, greater than; ND, not determined; SD, standard deviation; CV, coefficient of variation; LRL, laboratory reporting level; SRL, standardized reporting level of 0.06 µg/L]

| Compound | Mean | SD | CV (percent) | Percentiles | | | | | Maxi-mum | Inter-quartile range (IQR) | IQR/median (percent) | Number of samples | | Number of lakes with detections >LRL (>SRL) |
| | | | | 10 | 25 | 50 | 75 | 90 | | | | Total | Concen-tration > LRL (>SRL) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Herbicides and degradates** | | | | | | | | | | | | | | |
| 2,4-D | 0.062 | 0.218 | 350 | 0.001 | 0.003 | 0.010 | 0.024 | 0.113 | 1.16 | 0.021 | 206 | 28 | 6 (4) | 2 (2) |
| 2,4-D Methyl ester | ND | ND | ND | ND | ND | ND | ND | ND | .036 | ND | ND | 28 | 1 (0) | 1 (0) |
| Atrazine | .006 | .003 | 48 | .003 | .004 | .005 | .007 | .011 | .015 | .003 | 53 | 28 | 10 (0) | 5 (0) |
| *Hydroxyatrazine* | .008 | .002 | 29 | .005 | .006 | .008 | .009 | .012 | .013 | .003 | 40 | 28 | 8 (0) | 3 (0) |
| Bromacil | .754 | 1.40 | 186 | .008 | .026 | .175 | .723 | 2.78 | 6.29 | .697 | 398 | 28 | 18 (17) | 5 (5) |
| Diuron | .101 | .332 | 328 | .009 | .015 | .040 | .068 | .081 | 1.79 | .052 | 130 | 28 | 23 (9) | 7 (4) |
| *DCPMU* | .013 | .007 | 49 | .006 | .009 | .012 | .018 | .022 | .030 | .010 | 81 | 22 | 10 (0) | 6 (0) |
| Imazaquin | ND | ND | ND | ND | ND | ND | ND | ND | .021 | ND | ND | 28 | 1 (0) | 1 (0) |
| Norflurazon | .619 | 1.17 | 188 | .013 | .058 | .180 | .656 | 2.37 | 5.30 | .598 | 333 | 28 | 28 (21) | 7 (6) |
| *Demethyl norflurazon* | 2.14 | 4.68 | 219 | .038 | .154 | .336 | 1.07 | 12.3 | 17.1 | .917 | 273 | 22 | 22 (19) | 7 (7) |
| Simazine | .029 | .011 | 40 | .015 | .020 | .026 | .040 | .041 | .060 | .020 | 77 | 28 | 12 (1) | 5 (1) |
| *DDA* | .085 | .069 | 81 | .020 | .033 | .056 | .138 | .187 | .270 | .104 | 188 | 28 | 13 (12) | 4 (3) |
| *DIA* | .030 | .037 | 125 | .003 | .006 | .014 | .030 | .101 | .140 | .024 | 167 | 28 | 10 (4) | 4 (2) |
| *Hydroxysimazine* | .127 | .210 | 165 | .004 | .011 | .034 | .190 | .464 | .940 | .179 | 530 | 28 | 10 (9) | 6 (5) |
| *DEA* | ND | ND | ND | ND | ND | ND | ND | ND | .006E | ND | ND | 28 | 1 (0) | 1 (0) |
| Tebuthiuron | ND | ND | ND | ND | ND | ND | ND | ND | .006 | ND | ND | 28 | 2 (0) | 2 (0) |
| **Insecticides and degradates** | | | | | | | | | | | | | | |
| *Aldicarb sulfone* | .032 | .078 | 240 | <.001 | .001 | .004 | .019 | .117 | .330 | .018 | 465 | 28 | 7 ( 4 ) | 2 (2) |
| *Aldicarb sulfoxide* | .066 | .159 | 241 | <.001 | .001 | .006 | .062 | .216 | .670 | .061 | 978 | 28 | 8 ( 7 ) | 3 (2) |
| Imidacloprid | ND | ND | ND | ND | ND | ND | ND | ND | .016 | ND | ND | 28 | 1 (0) | 1 (0) |
| Oxamyl | ND | ND | ND | ND | ND | ND | ND | ND | .036 | ND | ND | 28 | 2 (0) | 2 (0) |
| **Fungicides:** | | | | | | | | | | | | | | |
| Metalaxyl | .037 | .043 | 117 | .005 | .009 | .018 | .048 | .112 | .180 | .039 | 212 | 28 | 14 ( 5 ) | 4 (2) |

citrus groves (fig. 3; Florida Agricultural Statistics Service, 2004). Based on statewide usage for all crops, 6 of the parent compounds detected in the Ridge lakes were ranked within the top 21 pesticides applied in Florida between 1999 and 2002: diuron, 2,4-D, simazine, aldicarb, norflurazon, and bromacil, with estimated agricultural usage ranging from 283,000 to 934,000 pounds of active ingredient annually (Shahane, 2003).

Parent pesticides and degradates were detected during all seasons of the year, indicating the persistence of pesticide compounds in the lake systems for several months or longer after application. The pesticide degradates (and associated parent compounds) detected in lake samples include: demethyl norflurazon (norflurazon); DDA, DIA, DEA, hydroxysimazine, and hydroxyatrazine (simazine and atrazine); aldicarb sulfoxide and aldicarb sulfone (aldicarb); and DCPMU (diuron). The degradates detected more frequently, and often at

higher concentrations, than their respective parent compounds included demethyl norflurazon, DDA, hydroxysimazine, DIA, aldicarb sulfone, and aldicarb sulfoxide (fig. 6). The pesticide degradates are discussed later.

Maximum concentrations of detected compounds in the citrus lakes ranged from 0.006 (tebuthiuron) to 17.1 µg/L (demethyl norflurazon) (table 6). Summary statistics for the pesticide compounds in citrus lake samples showed that most concentrations were less than 1 µg/L; the 90th percentile concentrations were less than 1 µg/L for all detected target pesticides and degradates except for bromacil, norflurazon, and demethyl norflurazon. Variability in pesticide concentrations (table 6), as measured by the standard deviation (SD), ranged from 0.002 µg/L (hydroxyatrazine) to 4.68 µg/L (demethyl norflurazon). The inter-quartile range (IQR) ranged from 0.003 µg/L (hydroxyatrazine and atrazine) to 0.92 µg/L (demethyl norflurazon).

The total number of pesticide compounds detected (at or above their LRLs) per lake ranged from 9 to 14 in the citrus lakes (fig. 7). In the control lake, only three pesticide compounds were detected (tebuthiuron, diuron, and atrazine) at concentrations less than 0.04 µg/L. All of the citrus lakes yielded detections of norflurazon, demethyl norflurazon, and diuron at or above their LRLs, and six of the seven citrus lakes yielded detections of DCPMU (diuron degradate) and hydroxysimazine at or above their LRLs (table 6 and fig. 8).

Of the 20 pesticide compounds detected in the citrus lake samples at concentrations above LRLs, 12 compounds were detected at or exceeding the 0.06 µg/L standardized reporting level (SRL) (fig. 6). The most frequently detected pesticide compounds at the 0.06-µg/L SRL in the citrus lakes were (in decreasing order) demethyl norflurazon, norflurazon, bromacil, DDA, hydroxysimazine, diuron, and aldicarb sulfoxide with respective sample detection frequencies ranging from 86 to 25 percent (fig. 6). Norflurazon, demethyl norflurazon, and diuron were detected above LRLs in all citrus lakes; hydroxysimazine, DCPMU, bromacil, simazine, and atrazine were detected in five or more of the seven citrus lakes.
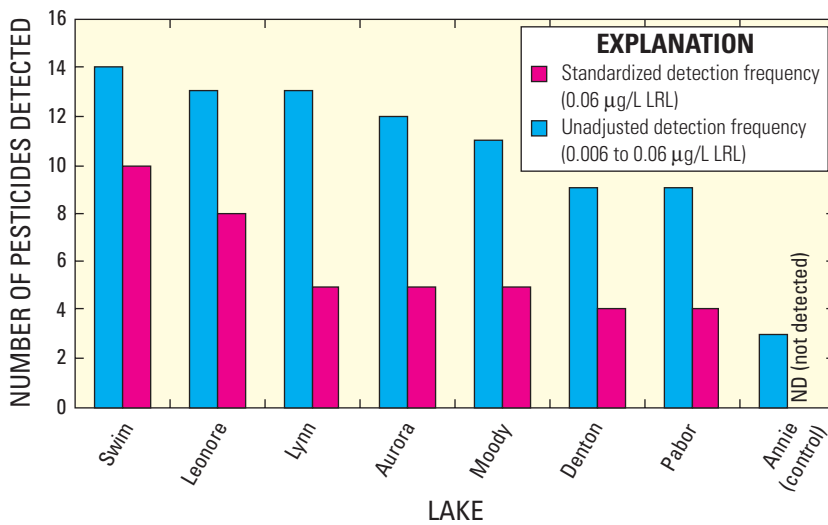


**Figure 7.** Total number of pesticides and degradates detected in each of the lakes sampled quarterly over a year. The unadjusted detection frequency refers to laboratory reporting levels (LRL) that varied by pesticide compound from 0.006 to 0.06 µg/L (microgram per liter).
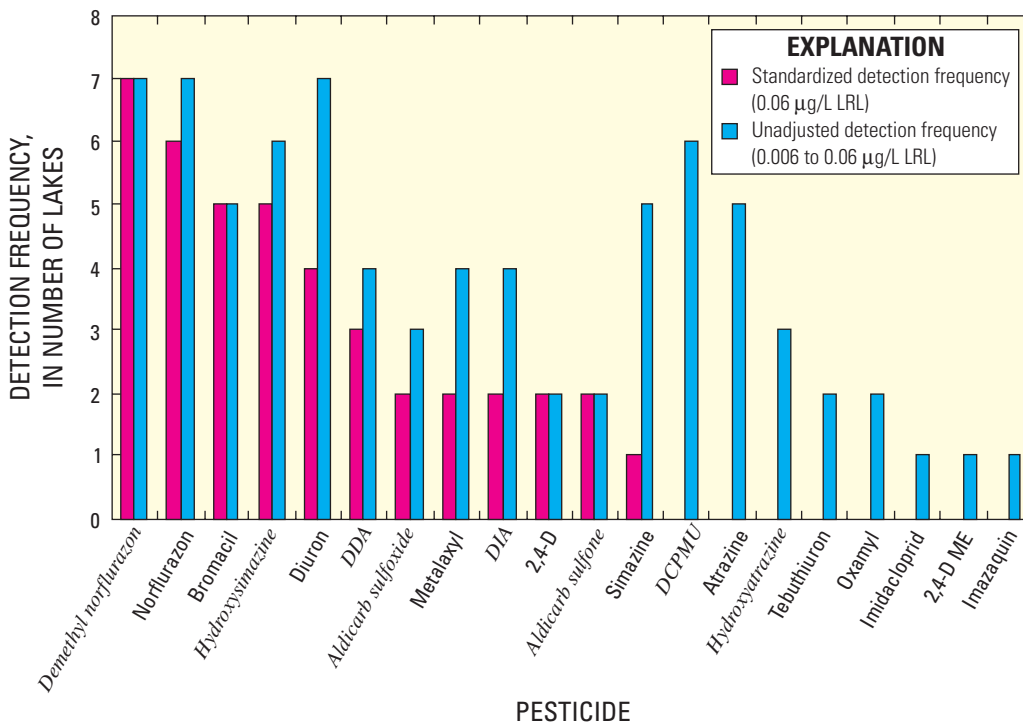


**Figure 8.** Number of citrus lakes in which targeted pesticide compounds were detected in one or more quarterly samples. The unadjusted detection frequency refers to laboratory reporting levels (LRLs) that varied by pesticide compound from 0.006 to 0.06 µg/L (microgram per liter). Pesticide degradates are shown in *italics*. Pesticide acronyms are defined in table 2.

Although DCPMU, atrazine, hydroxyatrazine, and tebuthiuron were detected in more than 25 percent of samples, these compounds were not detected at concentrations equal to or exceeding the 0.06-µg/L SRL. The detection frequencies by lake (fig. 8), which indicate detections in one or more of the samples collected per lake, tend to be somewhat higher than the sample detection frequencies (fig. 6) due to temporal fluctuations in concentrations and/or reporting levels.

Some of the most commonly detected pesticides in the lake samples included pesticides that have not been widely used since 1994 (bromacil), and degradates of commonly used pesticides (simazine, diuron, norflurazon); by contrast, some commonly used pesticides and their degradates were not detected (glyphosate and AMPA). Bromacil continues to be detected in the Ridge lakes and in ground water (surficial aquifer system) at least 11 years after the prohibition on its use in most Ridge source areas, indicating bromacil's persistence in Ridge water resources (Choquette and others, 2005; Gilliom and others, 2006). Bromacil was detected in five of the seven citrus lakes (fig. 8) and in more than 60 percent of lake samples (fig. 6). Bromacil has not been used in most Ridge citrus groves since the 1994 usage restriction (State of Florida, 1995), and its usage in non-citrus areas of the Ridge is reported to be insignificant (Danny Moore, Florida Department of Agriculture and Consumer Services, oral commun., 2003). Therefore, bromacil sources appear to be residues stored in soils, the surficial aquifer system, and perhaps lake sediments.

Glyphosate and its primary degradate AMPA were not detected in any of the lake samples in spite of the fact that glyphosate is one of the most widely applied herbicides in Florida citrus (figs. 3 and 4). Its absence is possibly due to high sorption potential (organic carbon partition coefficient) and relatively short half-life in soil and in water; however, the lack of detections also may reflect the higher LRL for glyphosate and its degradate AMPA (0.1 µg/L) relative to the LRLs for the detected pesticide compounds, which ranged from 0.006 to 0.03 µg/L.

Tebuthiuron, detected at trace concentrations in two of the sampled lakes including the control lake, is typically a non-crop herbicide (Oregon State University, 1996b), and is not a major pesticide used in citrus areas (Shahane, 2003). Tebuthiuron was among the pesticides most frequently detected nationally in stream and ground-water sampling in urban/suburban and agricultural settings (Gilliom and others, 2006), indicating broad usage nationally and a propensity for transport into water resources.

The nitrate concentration in the study lakes increased with the total number of pesticide compounds detected (fig. 9). The low nitrate concentrations in Pabor Lake (the outlier in fig. 9), and unusual inorganic water chemistry of the lake compared to the other citrus lakes, as previously discussed, indicate that nitrogen sources and perhaps denitrification processes in this basin differed from the other six citrus lakes. Similarly, total pesticide concentration (sum of quarterly samples for each lake) also increased with median nitrate concentration, except for Pabor Lake due to its low nitrate values (fig. 10). These relations suggest that elevated nitrate concentration may be an indicator of pesticide occurrence in the Ridge lakes, but the Pabor Lake data show that pesticides also may be present in lakes with low nitrate concentrations.

## Comparisons to Benchmark Values

Concentrations of pesticides and degradates in the Ridge lake samples were compared to Federal aquatic-life benchmarks compiled by Gilliom and others (2006) (table 7) which were specified for 10 of the 20 pesticide compounds detected in the citrus lakes. Drinking-water criteria (U.S. Environmental Protection Agency, 2006), Florida guidance values for drinking water, and Florida's Brownfields target cleanup levels for surface water (Florida Department of Environmental Protection, 2004) also are included in table 7 for comparison. However, the lakes typically are not used directly as drinking-water sources. The benchmark comparison was intended to identify and prioritize potential needs for
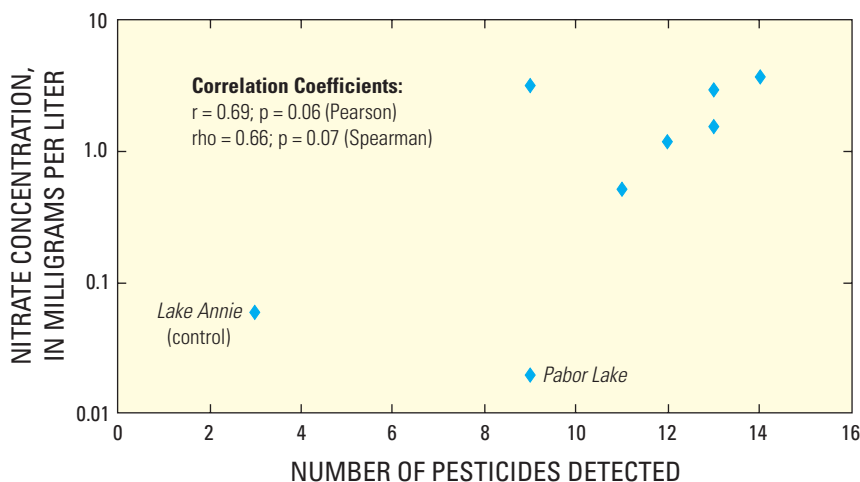


**Figure 9.** Median nitrate concentration related to number of pesticides detected above laboratory reporting levels in each sampled lake. Medians are based on four samples from each lake.

NITRATE CONCENTRATION, IN MILLIGRAMS PER LITER

TOTAL PESTICIDE CONCENTRATION, IN MICROGRAMS PER LITER

Lake Annie (control)

Pabor Lake
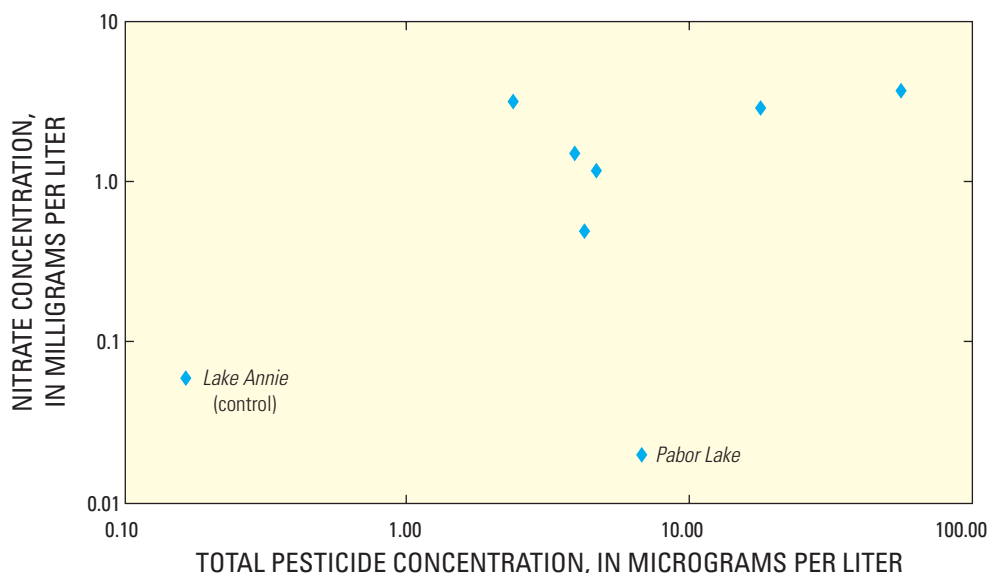
**Figure 10.** Median nitrate concentration related to total concentration of pesticides and degrades in quarterly samples summed over one year in each lake. Medians are based on four samples from each lake.

**Table 7.** Pesticide concentrations in lake samples compared to aquatic-life and human-health benchmark values.

[The summary includes samples from all of the study lakes. The selected aquatic benchmark values correspond to those associated with the lowest concentrations listed in Gilliom and others (2006). A complete listing of the benchmarks is available at *http://water.usgs.gov/nawqa/pnsp/*. BM, benchmark; LRL, laboratory reporting level; ND, not detected above laboratory reporting level; NL, not listed, USEPA, U.S. Environmental Protection Agency; >, greater than; µg/L, microgram per liter]

| Compound | Benchmarks (µg/L) | | | | Maximum concentration in lake samples (µg/L) | Total number of lake samples [3] | Number of samples with concentration greater than the LRL | Number of samples (and number of lakes) with concentrations exceeding specified USEPA aquatic-life criteria | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | USEPA drinking water | Florida drinking water guidance value [1] | Florida surface-water cleanup target [2] | USEPA aquatic life | | | | > BM | > 0.5 of the BM value to the BM | > 0.1 to 0.5 of the BM value |
| 2,4-D | [1,5]70 | 70 | 80 | [8]299.2 | 1.16 | 36 | 6 | 0 | 0 | 0 |
| Aldicarb | [4,6]7, [5]3 | [6]7 | .9 | [9].46 | ND | 36 | 0 | ND | ND | ND |
| Aldicarb sulfone | [4,6]7, [5]2 | [6]7 | 46 | [10]140 | .33 | 36 | 7 | 0 | 0 | 0 |
| Aldicarb sulfoxide | [4,6]7, [5]4 | [6]7 | 4.2 | [10]21.5 | .67 | 36 | 8 | 0 | 0 | 0 |
| Atrazine | [4]3 | 3 | 1.9 | [11]17.5 | .015 | 36 | 12 | 0 | 0 | 0 |
| Bromacil | [7]90 | 70 | 97 | [12]6.8 | 6.29 | 36 | 21 | 0 | 2 (1 lake) | 6 (2 lakes) |
| Diuron | [7]10 | 14 | 8 | [12]2.4 | [13]1.79 | 36 | 25 | 0 | 1 | 0 |
| Norflurazon | NL | 280 | NL | [12]13 | 5.30 | 36 | 28 | 0 | 0 | 3 (1 lake) |
| Oxamyl | [4]200 | 200 | 8.5 | [10]90 | .036 | 36 | 2 | 0 | 0 | 0 |
| Simazine | [4]4 | 4 | 7.3 | [12]36 | .06 | 36 | 12 | 0 | 0 | 0 |

[1] Values associated with ground-water cleanup targets under State of Florida (2004), which are used by the Florida Department of Environmental Protection as non-regulated guidelines for drinking water.

[2] State of Florida (2004).

[3] Includes the samples collected quarterly at a depth of 5 feet below lake surface from each of the eight study lakes, and the water-column samples collected near the lake bottom from four study lakes during one sampling event.

[4] USEPA Maximum Contaminant Level (U.S. Environmental Protection Agency, 2006).

[5] USEPA Maximum Contaminant Level, stayed effective date (U.S. Environmental Protection Agency, 2006).

[6] The benchmark specifies that the sum for any combination of two or more of these three chemicals is not to exceed this amount, due to similar mode of action.

[7] USEPA Lifetime Health Advisory (HAL).

[8] USEPA acute vascular plants (each individual sample).

[9] Chronic fish (60-day mean).

[10] USEPA acute invertebrates (each individual sample).

[11] USEPA chronic aquatic community (average for 60-day period).

[12] USEPA acute nonvascular plants (each individual sample).

[13] Duplicate analysis yielded a concentration of 3.81 µg/L (app. 3), which exceeds the associated USEPA aquatic benchmark for nonvascular plants.

further monitoring or investigation, and was not intended as a risk assessment, which would include more detailed assessment of factors such as frequency, duration, and routes of exposure, and lethal and sublethal effects.

The aquatic-life benchmarks included acute and chronic effects on fish, invertebrates, nonvascular and vascular plants, and aquatic communities. Benchmarks have not yet been specified for all these aquatic-risk categories for each of the 10 pesticide compounds in table 7. Also, these benchmarks do not take into consideration possible cumulative or interactive effects (synergistic or antagonistic) of pesticide mixtures.

Sample concentrations in the Ridge lakes were compared to the aquatic benchmark (table 7) that had the lowest concentration. The lowest benchmarks for the insecticides generally corresponded to acute effects on invertebrates, and for the herbicides generally corresponded to acute effects on plants or, in the case of atrazine, chronic effects on aquatic communities.

None of the observed concentrations in the Ridge lakes exceeded the aquatic-life benchmarks, with the exception of one duplicate sample in which diuron exceeded the guideline for acute effects on nonvascular plants (sample concentration of 3.8 µg/L compared to guideline of 2.4 µg/L, table 7). In a few of the lake samples, concentrations of diuron, bromacil, and norflurazon approached the respective aquatic-life benchmarks (acute effects for nonvascular plants). Expressed as a percentage of the benchmark value, the maximum concentrations of diuron, bromacil, and norflurazon in lake samples were 75 percent, 71 percent, and 42 percent, respectively, of the benchmarks (table 7).

Table 7 lists the number of sample concentrations that exceeded 10 percent of the benchmark concentrations for the respective compound detected. Diuron concentration exceeded 50 percent of the benchmark in one sample (Pabor Lake). Bromacil concentrations exceeded 50 percent of the benchmark in two samples (Lake Leonore), and were within 10 to 50 percent of the benchmark in six samples (two samples from Lake Leonore and four samples from Lake Aurora). Norflurazon concentrations were within 10 to 50 percent of the benchmark in three samples (Swim Lake).

Some of the sample concentrations more closely approached the human-health benchmarks than the aquatic-life benchmarks. The maximum sampled concentrations of aldicarb sulfone and aldicarb sulfoxide were each 17 percent of the proposed Federal drinking-water maximum contaminant level[3], and 5 to 10 percent of the current Federal and Florida drinking-water guidance values (table 7). Two samples from Swim Lake yielded concentrations of aldicarb sulfone and aldicarb sulfoxide (app. 3), exceeding 10 percent of the

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[3]The proposed U.S. Environmental Protection Agency maximum contaminant levels for aldicarb and its degradates are "under administrative stay" and, therefore, are not enforced. The U.S. Environmental Protection Agency health advisory level is used as Florida's drinking-water guidance value for aldicarb and its degradates.

national guideline. The maximum concentration of diuron (1.79 µg/L) was 13 and 18 percent of the Federal and State drinking-water benchmarks, respectively.

## Areal and Seasonal Variations

More than half of the 20 detected pesticides were detected in at least four of the seven citrus lakes, and norflurazon, demethyl norflurazon, diuron, hydroxysimazine, and DCPMU were detected above their minimum LRLs in six or more of the citrus lakes (fig. 8 and app. 4). Inferences about seasonality in the lake pesticide results are exploratory because sampling spanned only 1 year in a small number of lakes.

The amount of seasonal variation between pesticide concentrations in quarterly samples often exceeded one order of magnitude and was sometimes as high as two orders of magnitude (fig. 11). In the control lake, pesticide concentrations were generally near or less than reporting levels (fig. 11). No regionally consistent seasonal patterns were evident in the number of pesticides detected above the 0.06-µg/L level, although slightly more pesticides were detected during spring and/or winter than during summer or fall in lakes Swim, Leonore, Aurora, and Pabor (fig. 12). Norflurazon was the only pesticide that indicated a possible seasonal pattern showing lower concentrations in summer (June) compared to the other quarterly samples (fig. 11A). Concentrations of demethyl norflurazon indicated a similar, but less pronounced, seasonal pattern on the basis of a limited number of summer analyses of this compound available for three of the seven citrus lakes.

Because this study was a reconnaissance, the actual causes of differences in pesticide occurrence between lakes are unknown, but contributing factors would probably include pesticide usage practices in the basins; lake geometry, local hydrogeology (controlling lateral and vertical ground-water/lake-water exchange), and the residence time of water in the lakes; and the ages, rates and amounts of ground-water flow into the lakes.

Lake geometry can be a general indicator of differences between lakes in ground-water input (Sacks and others, 1998), and also of the processes that may affect pesticide breakdown within the lake water column. For example, comparing lakes of similar area, shallower lakes would be expected to capture a larger proportion of precipitation in their source water, and deeper lakes would have the potential to intercept more ground-water inflow due to increased exposure to the surficial aquifer system. For lakes of similar depth, the larger lakes would have proportionally greater solar exposure, which would, in turn, increase the potential for water temperature changes, evaporative losses, and photodegradation of chemicals as well as mixing from wind and atmospheric delivery of agrichemicals.

In spite of differences in lake geometry and size, the total number of pesticides and degradates detected did not differ widely between the study lakes (fig. 7). In addition, there
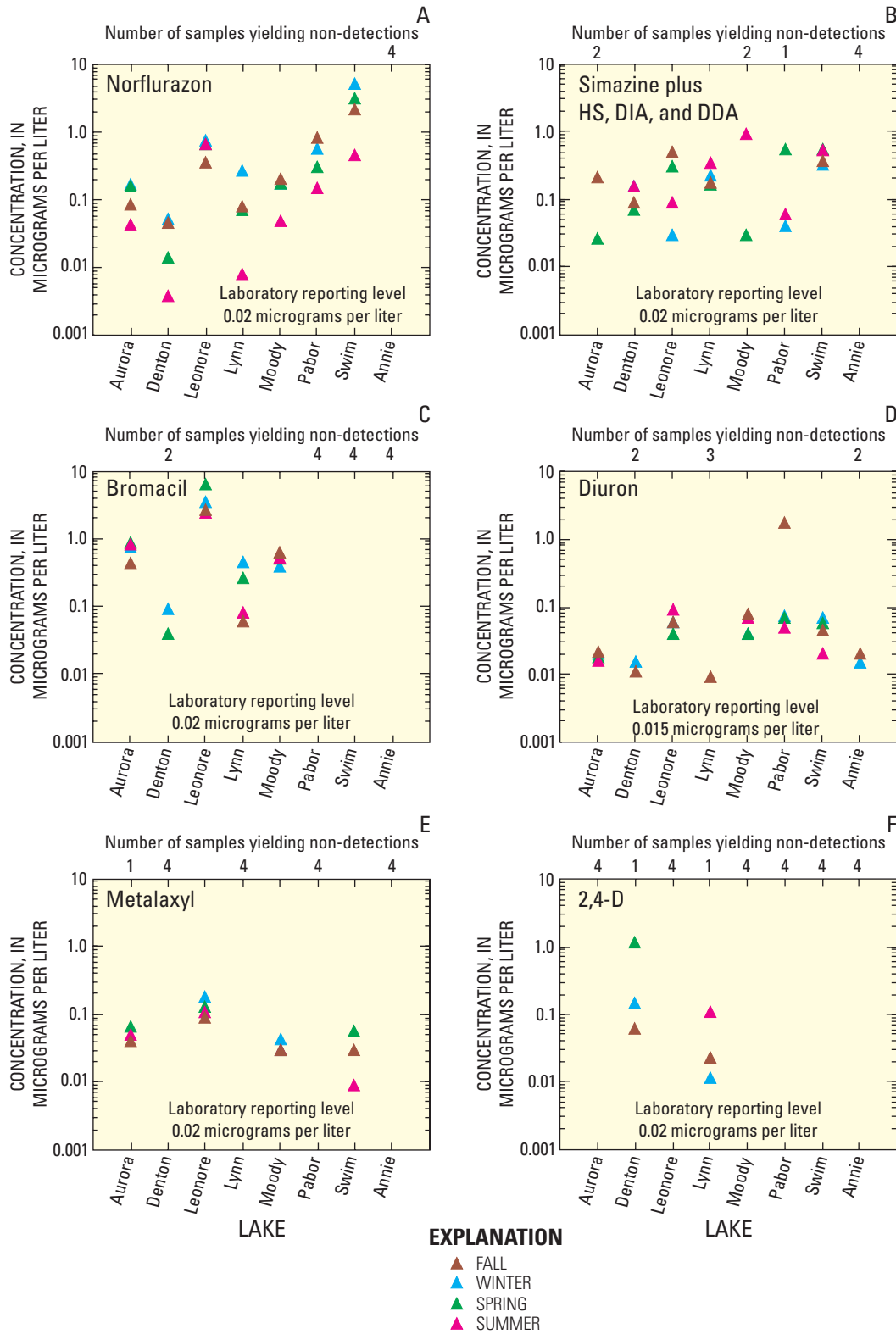
**Figure 11.** Variations in concentrations of selected pesticides seasonally within and between sampled lakes. Values below the laboratory reporting level are estimated concentrations. Pesticide acronyms are defined in table 2.

**Figure 12.** Number of pesticide compounds detected seasonally in each of the citrus lakes. SRL represents standardized reporting level.

was no consistent difference in concentrations of pesticides and degradates in the deeper lakes (Lakes Lynn and Denton) compared to the shallow lakes (Lakes Leonore, Moody, and Pabor) (fig. 11). Swim Lake, with the lowest surface/depth ratio of sampled lakes (table 1), yielded some of the highest concentrations and the highest number of pesticides detected; however, Lake Leonore, which was one of the shallowest lakes sampled, yielded a similar number of pesticide compounds and high concentrations of norflurazon, bromacil, and metalaxyl compared to the other lakes (figs. 11 and 12). The concentrations of degradates relative to parent pesticides generally were consistent between lakes as discussed in the next section.

## Comparisons of Parent Pesticides and Degradates

Analysis of lake water samples (fig. 6) indicated that some pesticide degradates were more commonly detected than their respective parent pesticides. Comparison of relative concentrations of parent pesticides and their degradates over time in the lakes where both were detected provides information regarding pesticide transport and fate in the lake/groundwater systems, and on seasonal variability.

### Norflurazon and Degradate

The median concentration of demethyl norflurazon in samples from the citrus lakes (0.34 µg/L) was nearly twice that of norflurazon (0.18 µg/L) based on detections in all samples from the citrus lakes (table 6). On average, concentrations of demethyl norflurazon were 3.27 times those of norflurazon in samples; degradate to parent ratios ranged from 0.73 to 10.15. Of the 26 samples in which norflurazon

and desmethyl norflurazon were analyzed and detected, 23 of the samples (88 percent) yielded higher concentrations of degradate than the parent. Concentrations of demethyl norflurazon in samples from all the citrus lakes, except for Lake Leonore, were consistently higher than the parent compound throughout the year. This pattern is evident in samples from Lake Aurora and Swim Lake (fig. 13). Although strong seasonal patterns were not apparent in concentrations of each of these compounds, concentrations during summer (June) were typically lower than during fall, winter, and spring (figs. 11A and 13). In Lake Leonore, norflurazon exceeded demethyl norflurazon concentrations during the quarters in which analyses were available for both compounds (December and March; fig. 13C), which suggests that higher concentrations of the parent relative to the degradate were transported to this lake and/or less rapid rates of norflurazon breakdown in Lake Leonore compared to the other lakes.

### Simazine, Atrazine, and Degradates

In the citrus lakes, the triazine pesticide degradates hydroxysimazine, DDA, and DIA were detected more frequently at concentrations exceeding the 0.06-µg/L SRL than the parent simazine (figs. 6 and 8). In samples from Lake Lynn and Swim Lake (fig. 14), where simazine and its degradates were frequently detected, concentrations of hydroxysimazine, DDA, and DIA consistently exceeded those of the parent simazine. Trace concentrations of atrazine (less than 0.007 µg/L) also were detected in each of the four samples from Lake Lynn (fig. 14). In most of the samples, DDA concentrations exceeded those of DIA, and both simazine and hydroxysimazine were detected at higher concentrations and more frequently in Swim Lake. Similar seasonal patterns in the parent-degradate concentrations were not evident between
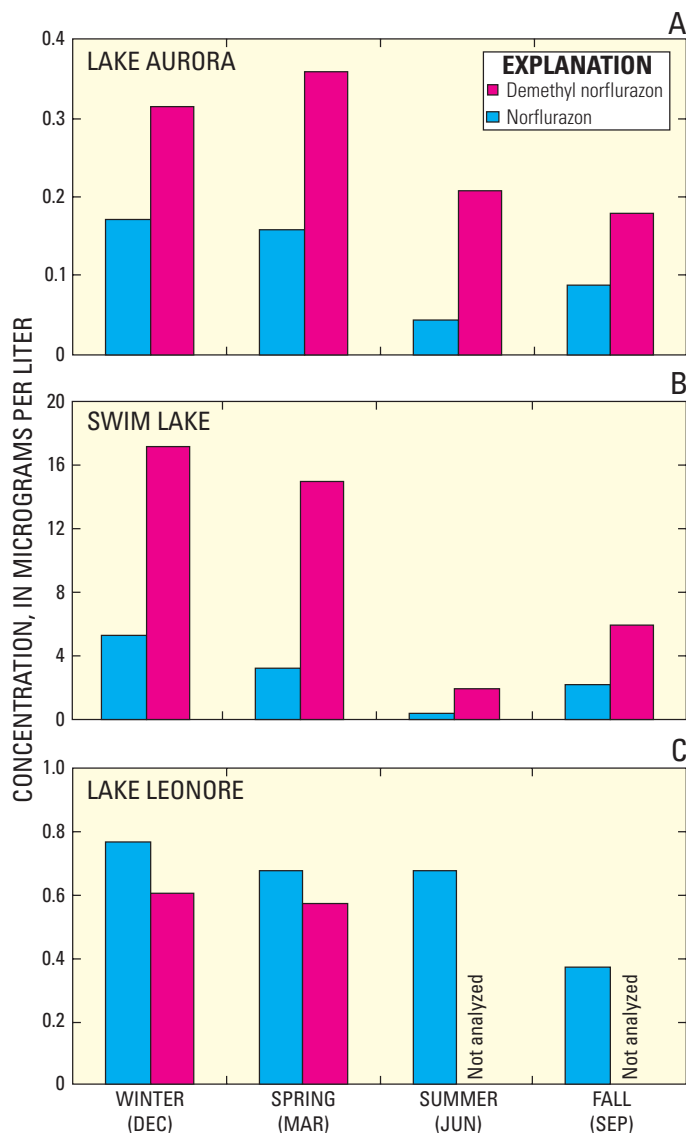
**Figure 13.** Seasonal variations in concentrations of norflurazon and demethyl norflurazon in samples from Lake Aurora, Swim Lake, and Lake Leonore.

these lakes. Hydroxysimazine was a dominant degradate in Swim Lake, occurring in three of four samples, but it was detected at relatively low concentrations in only one of the four samples from Lake Lynn. In both lakes, DDA concentrations exceeded those of DIA (fig. 14).

Evaluation of the triazine degradates is complicated by shared parent pesticides (fig. 15 and app. 5; Scribner and others, 1999), but several factors indicate that simazine is the primary source of the triazine degradates hydroxysimazine, DDA, and DIA in the Ridge citrus lakes. Simazine is the only triazine pesticide applied to Florida citrus, although several of its degradates also can originate from atrazine, cyanazine,

and propazine. Neither cyanazine, banned in the United States since 2002, nor propazine are likely sources for these degradates on the Ridge according to their past or current labeled usages. Limited atrazine use may occur in non-citrus areas of the Ridge, such as to control weeds in residential areas.

The pesticide results in this study are consistent with minimal atrazine use in the lake basins, because atrazine was only detected at very low concentrations (0.015 µg/L maximum), and concentrations of its degradates hydroxyatrazone and DEA, which are not shared with simazine, also were very low (less than 0.014 µg/L). In contrast, detections of simazine, its degradate hydroxysimazine, and its shared degradates with atrazine (DDA and DIA) occurred at higher concentrations in lake samples and were more frequently detected (table 6; figs. 6 and 8).

### Diuron and Degradates

Diuron occurred at higher concentrations and detection frequencies than its degradates DCPU and DCPMU (fig. 6 and table 6). The primary degradate, 3,4-dichloroaniline (Giacomazzi and Cochet, 2004), was not analyzed as part of this study, and reporting levels varied between these three compounds. Generally, the LRLs were 0.015 µg/L for diuron, 0.06 µg/L for DCPU, and 0.03 µg/L for DCPMU. Diuron was detected in all of the study lakes, and DCPMU was detected in six of the study lakes. DCPU was not detected in any of the lake samples above LRLs ranging from 0.03 to 0.06 µg/L (app. 3). Concentrations of DCPMU were consistently lower than those of the parent in all samples where both were detected (app. 3). Concentrations of diuron in Lake Aurora and Swim Lake were lowest during summer sampling, and seasonal differences were more pronounced in Swim Lake than in Lake Aurora (fig. 16). DCPU was not detected in any lake samples; however, in these samples the DCPU reporting level was significantly higher than that of both diuron and DCPMU.

### Aldicarb and Degradates

Aldicarb was not detected in any lake samples (table 7); however, one or both of its degradates, aldicarb sulfone and aldicarb sulfoxide, were detected in three of the citrus lakes. The lack of aldicarb detections likely reflects its relatively rapid degradation rate (estimated 7- to 30-day half-life in soil; Hornsby and others, 1996; U.S. Environmental Protection Agency, 2007), usage restrictions on its application (one application allowed per year; State of Florida, 2002a), and the higher laboratory reporting level for aldicarb (0.04 µg/L) compared to the degradates (0.0022 to 0.02 µg/L, app. 1). Additionally, the low recovery of aldicarb (mean value, 19 percent) may also have contributed to its lack of detection (table 3). Concentrations and detection frequencies of aldicarb sulfoxide, the first-order degradation product of aldicarb, exceeded those of aldicarb sulfone (table 6), a second-order aldicarb degradation product formed by the breakdown of aldicarb sulfoxide (Barbash and Resek, 1996).
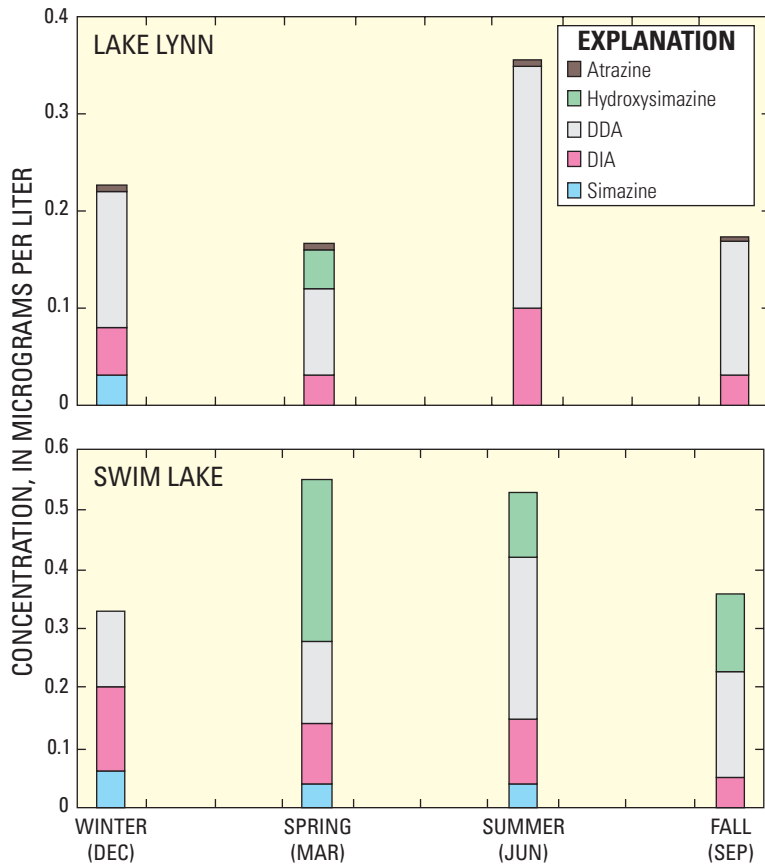
**Figure 14.** Seasonal variations in concentrations of simazine and its degradates in samples from Lake Lynn and Swim Lake. Pesticide acronyms are defined in table 2.
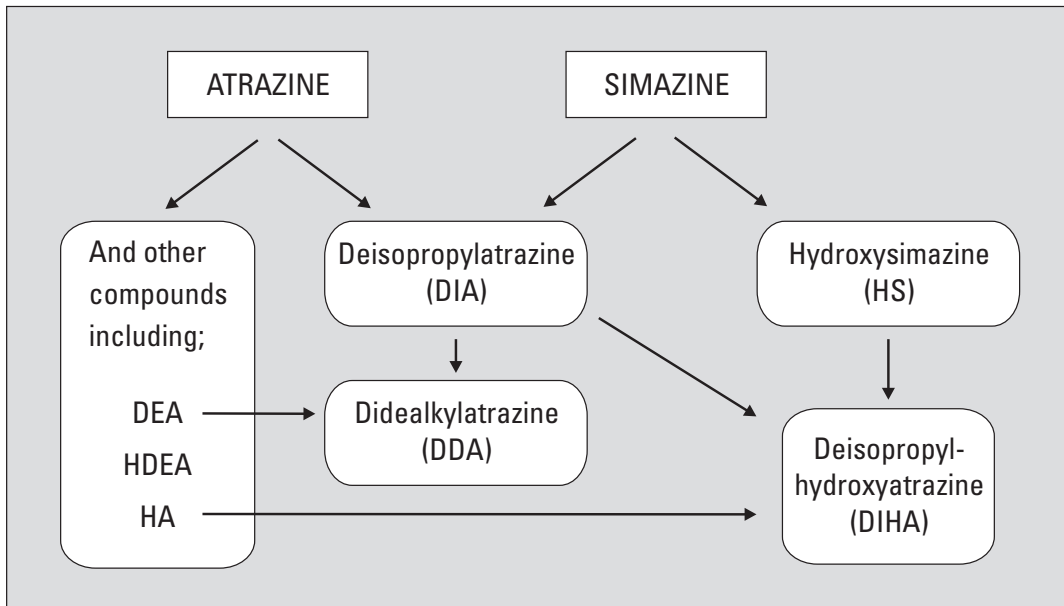


**Figure 15.** Generalized chemical degradation pathways and sources for simazine degradates (Scribner and others, 1999; M.T. Meyer, U.S. Geological Survey, written commun., 2009). Some simazine degradates may also originate from atrazine, cyanazine, and propazine as well as from some of their degradational products (appendix 1). Atrazine is not registered for use, or applied, in Florida's citrus groves. Pesticide acronyms are defined in table 2.
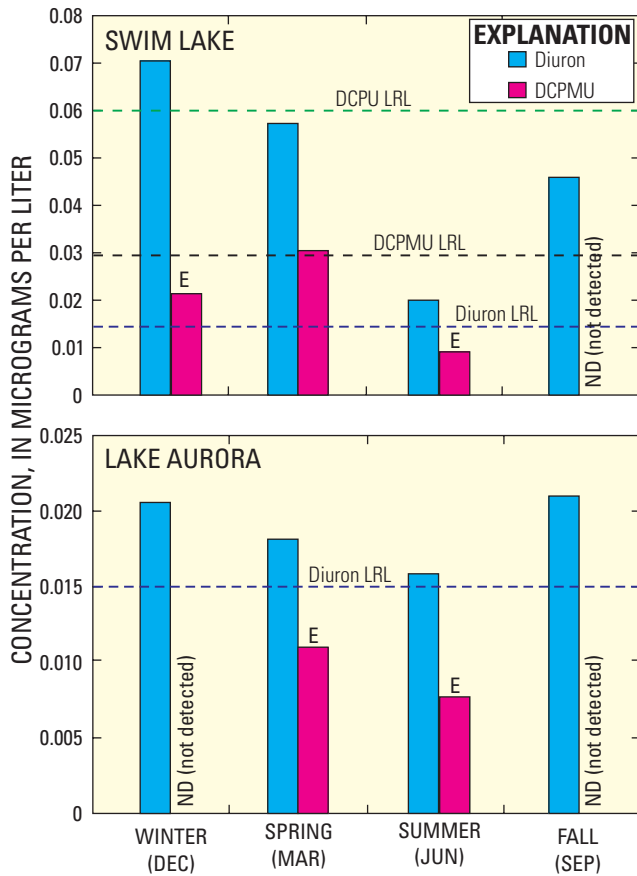
Both degradates degrade more slowly than the parent, and exhibit lower sorption potential. The occurrence of aldicarb sulfoxide as the primary degradate has been noted in other studies of soil water and ground water (Jones and others, 1987; Hornsby and others, 1990; and Morgan and others, 1993). Laboratory reporting levels for aldicarb sulfoxide were at times lower than those for aldicarb sulfone (app. 3), and average laboratory recoveries for aldicarb sulfoxide were considerably higher than those for aldicarb sulfone (56 and 9 percent, respectively) (table 3).

Aldicarb sulfone was detected in two of the three lakes where aldicarb sulfoxide was detected. In the lakes where both degradates were detected, Lake Leonore and Swim Lake, concentrations of aldicarb sulfoxide were consistently higher, typically about double those of aldicarb sulfone during all quarters (fig. 17). Concentrations of the aldicarb degradates in Swim Lake were considerably higher in samples

**Figure 16.** Seasonal variations in concentrations of diuron and its degradates in samples from Swim Lake and Lake Aurora. The diuron degradate DCPU was not detected above the 0.06 microgram per liter laboratory reporting level (LRL) in the lake samples. Pesticide acronyms are defined in table 2. Estimated (E) concentrations below laboratory reporting level.
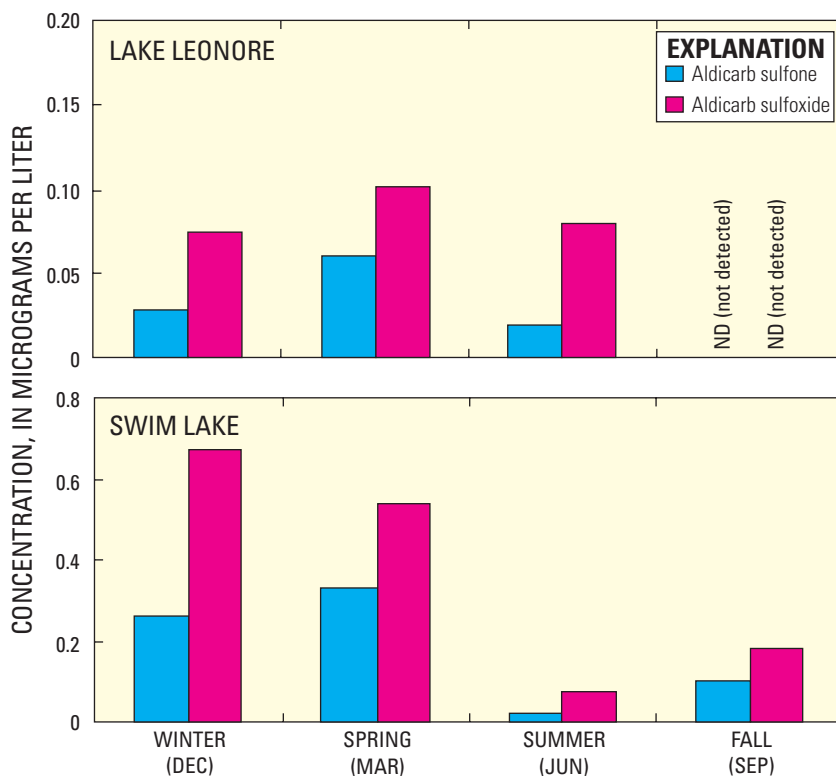


**Figure 17.** Seasonal variations in concentrations of aldicarb degradates in samples from Lake Leonore and Swim Lake. The parent compound aldicarb was not detected in any samples above its laboratory reporting level of 0.04 microgram per liter.

collected during winter and spring than in samples collected during summer and fall. The high concentrations observed in December were somewhat unexpected given that aldicarb usage is restricted to the period January to April, and would indicate multiseasonal persistence of the degradates in ground water and/or the lake, assuming that application of aldicarb in the basin occurred within the restricted time period.

## Variations within the Lake Water Column

Several factors related to depth of sample within the lake water column could influence pesticide concentrations and degradation rates, such as concentration differences within source waters (rainfall and ground water), physicochemical characteristics of the water (temperature, light penetration, and dissolved oxygen concentrations), biologic communities and population densities (to degrade chemicals), and proximity to the sediment-water interface (influencing suspended-sediment concentrations, availability of organic matter and biota for

sorption and chemical breakdown). Because many Ridge lakes exhibit high clarity (University of Florida, 2005b; University of South Florida, 2008), there is potential for chemical breakdown by photolysis in the shallow zone of the lake water column. Although the number of water-column comparisons in the study were limited, these results may be useful for directing future research and sampling designs, especially given the sparse information on variability of pesticide concentrations within lake environments.

Comparisons between shallow and deep water-column samples were possible only when at least one of the sample concentrations exceeded LRLs. In the 8 depth samples collected (4 sample pairs), a total of 14 pesticide compounds were detected one or more times above LRLs (table 8), including 6 parent pesticides and 9 degradates. Results included 1 to 4 sample pairs per compound, and a total of 29 sample pairs. Pesticide concentrations in deep samples exceeded those in shallow samples for 19 of the 29 sample pairs (table 8).

**Table 8.**  Comparison between pesticide concentrations in shallow and deep samples from the lake water column.

[Paired samples were collected from four lakes at depths of about 5 feet below the lake surface and near the lake bottom. The comparison is limited to pairs that yielded detectable concentrations in the shallow and/or deep sample. µg/L, microgram per liter; >, greater than; <, less than; =, equal to]

| Analyte | Number of sample pairs with one or more detections | Number of sample pairs | | | Concentration ratios (deep /shallow), in µg/L | Concentration difference (deep minus shallow), in µg/L |
|---|---|---|---|---|---|---|
| | | Concentration in deep sample > shallow sample | Concentration in deep sample = shallow sample | Concentration in deep sample < shallow sample | | |
| **Parent compounds** | | | | | | |
| 2,4-D | 2 | 2 | 0 | 0 | [1]>1.27 to 2.10 | [1]>0.024 to .029 |
| Bromacil | 3 | 3 | 0 | 0 | [1]>1.14 to 2.5 | [1]>.005 to .12 |
| Diuron | 2 | 1 | 0 | 1 | .88 to 1.14 | -.002 to .003 |
| Metalaxyl | 2 | 1 | 0 | 1 | .97 to 1.13 | -.002 to .001 |
| Norflurazon | 4 | 4 | 0 | 0 | 1.72 to 16.05 | .005 to .330 |
| Simazine | 1 | 0 | 1 | 0 | 1 | 0 |
| **Total** | 14 | 11 | 1 | 2 | | |
| **Degradates** | | | | | | |
| Aldicarb sulfone | 1 | 1 | 0 | 0 | 1.39 | .007 |
| Aldicarb sulfoxide | 1 | 1 | 0 | 0 | 1.49 | .036 |
| DDA | 3 | 1 | 0 | 2 | .56 to 1.27 | -.11 to .04 |
| DIA | 2 | 0 | 0 | 2 | .50 to .91 | -.05 to -.01 |
| DCPMU | 1 | 0 | 0 | 1 | .91 | -.001 |
| Demethyl norflurazon | 4 | 4 | 0 | 0 | 1.30 to 9.04 | .02 to .66 |
| Hydroxysimazine | 1 | 0 | 1 | 0 | 1 | 0 |
| Hydroxyatrazine | 2 | 1 | 0 | 1 | .85 to 2.00 | -.002 to .007 |
| **Total** | 15 | 8 | 1 | 6 | | |
| **Overall total** | 29 | 19 | 2 | 8 | | |

[1] The low value in the range is a minimum estimate, because concentration in the shallow sample was below the laboratory reporting level.

Except for norflurazon and its degradate, there was insufficient evidence to suggest pronounced differences in pesticide concentrations within the lake water column. The observed differences in concentrations between the water-column samples were generally less than 0.1 µg/L (table 8). Although bromacil and 2,4-D concentrations were consistently greater in the deep samples, the concentration differences were small, and the limited number of detections (2 to 3 sample pairs) was insufficient to evaluate the significance of these differences.

The results for norflurazon and its degradate, given that photolysis is an important mechanism for their chemical breakdown, indicate the possibility that concentrations and perhaps degradation rates can vary with depth in the water column. Secchi depths were 12.5, 18, 19, and 21 ft for Lake Aurora, Lake Lynn, Swim Lake, and Lake Denton, respectively, at the time that the water-column samples were collected (app. 2), which are comparable to Secchi-depth values measured in these lakes in other studies (Sacks and others, 1998; University of Florida, 2005b; University of South Florida, 2008). These Secchi depths extend into the top one-third to one-half of the respective maximum depths of these lakes, and indicate the high potential for sunlight exposure at the 5-ft depth where the shallow samples were collected.

In the four sampled lakes, water temperature was 0.3 to 5.8 ºC cooler in deep samples compared to shallow samples. Between deep and shallow samples, values were comparable for specific conductance, pH, and dissolved oxygen concentrations (within 16 µS/cm² , 0.5 units, and 3 mg/L, respectively) with the exception of Lake Lynn, which had very low dissolved oxygen in the deep (0.8 mg/L) versus shallow (7.8 mg/L) zones sampled in the water column.

The degradation rates of both norflurazon and demethyl norflurazon appeared to decrease with depth in the lake water column on the basis of concentration comparisons in and between the lakes. Both norflurazon and demethyl norflurazon concentrations were greater in the deep samples compared to shallow samples in all four lakes sampled (app. 3). Concentrations of norflurazon ranged from 1.7 to 16 times higher in deep samples compared to shallow samples, and concentrations of demethyl norflurazon ranged from 1.3 to 9 times higher in the deep versus shallow samples (table 8). Differences in concentrations between shallow and deep samples ranged from 0.005 to 0.33 µg/L for norflurazon and from 0.02 to 0.66 µg/L for demethyl norflurazon.

The relative difference in total norflurazon plus demethyl norflurazon concentrations between deep and shallow samples, calculated as the ratio of the difference (concentration in deep minus shallow samples) to the mean concentration of the two depth samples, increased with the vertical distance between sampling points (fig. 18). Further, the degradate/parent ratios for norflurazon were greater in shallow compared to deep samples in three of the four study lakes, indicating degradation had proceeded further in shallow than in deep samples (fig. 19). Also, the magnitude of differences between degradate/parent ratios in shallow samples compared to deep samples increased with the depth interval between samples (lake depth) (fig. 19), consistent with decreasing degradation rates with depth in the water column. These inferences regarding degradation are based on the assumption that the lakes are well mixed with respect to source waters including ground-water inflows, which presumably contain a higher proportion of parent compared to degradate concentrations. The lack of observable differences in the norflurazon
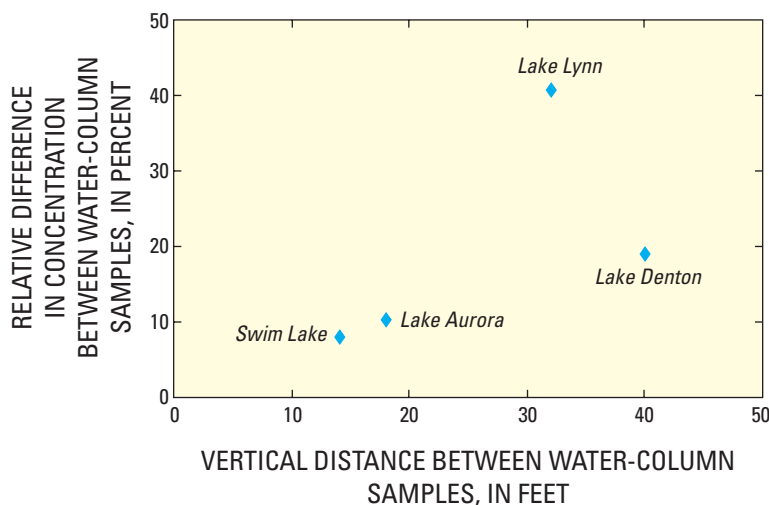


**Figure 18.** Relative difference in the concentrations of norflurazon plus demethyl norflurazon in water-column samples compared to the vertical distance between the samples. Relative difference is concentration in deep sample minus shallow sample/mean concentration of paired samples for each lake.
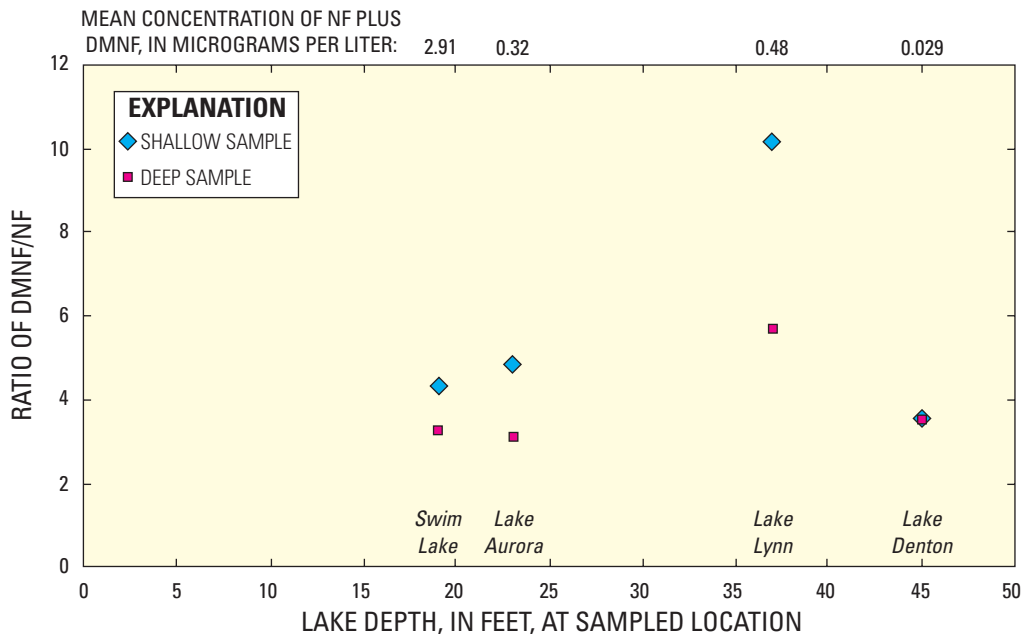
**Figure 19.** Ratio of demethyl norflurazon (DMNF) concentration to norflurazon (NF) concentration in water-column samples related to lake depth at the sampled location.

degradate/parent ratios in the Lake Denton samples may be associated with difficulty in quantification of the very low concentrations of norflurazon and demethyl norflurazon (0.004 to 0.03 µg/L) in this lake, one to two orders of magnitude lower than concentrations in the other sampled lakes, and near their laboratory reporting levels.

Due to the limited number of samples, additional sampling is needed to confirm the inference of more rapid degradation of norflurazon and its degradate in shallow depths of the Ridge citrus lakes.

## Comparison to National Studies

Several of the pesticides and degradates targeted in the Ridge lake study have been analyzed by the USGS-NAWQA Program in streams and ground water throughout the United States. Although lakes were not sampled in the NAWQA Program, many conditions affecting pesticide transport and fate in streams also occur in lake environments, and differ from ground-water environments. Some of these conditions include potential for chemical breakdown through exposure to sunlight and aquatic biota, availability of organic matter and sediment on which pesticides may sorb, exposure to air for volatilization, and ground-water sources of inflow. The NAWQA pesticide data consisted of more than 1,468 samples collected from about 80 sampling sites on streams draining agricultural lands (Gilliom and others, 2006), in addition to more than 1,400 pesticide samples

collected from streams draining non-agricultural land uses such as urban, mixed (combination of urban, agricultural, and/or undeveloped), and undeveloped. The NAWQA data are referred to as "national" data in the remainder of the report.

Concentrations of many of the pesticides detected in the citrus lakes were higher than those observed in streams nationally, and included pesticides associated with agricultural use (norflurazon and aldicarb degradates), as well as some pesticides associated nationally with urban land use (diuron, simazine, 2,4-D, bromacil, and tebuthiuron) (Gilliom and others, 2006). The 90th percentile (Q90) concentrations for Ridge lake samples exceeded the national Q90 for agricultural land use for 6 of the 11 pesticides analyzed in both studies (table 9). Norflurazon and bromacil, the two most frequently detected compounds in Ridge citrus lakes, were detected in less than 5 percent of national samples in any land-use class.

Norflurazon, bromacil, aldicarb sulfoxide, and aldicarb sulfone were detected at higher concentrations (maximum and Q90) in the Ridge lakes than in the national samples from agricultural lands, and the Ridge Q90 concentrations of diuron and 2,4-D exceeded the national Q90 values for agricultural areas (table 9). The elevated concentrations of pesticides in Ridge surface waters relative to national values for agricultural land use are consistent with comparisons of Ridge ground-water pesticide concentrations, with national ground-water values (Choquette and others, 2003) highlighting the vulnerability of the Ridge to transport of agricultural chemicals into ground and surface waters.

**Table 9.** Pesticide results for the sampled Ridge citrus lakes compared to U.S. Geological Survey national surface-water monitoring data.

[The comparison includes target pesticides common to both the Ridge and the U.S. Geological Survey National Water-Quality Assessment (USGS NAWQA) Program surface-water monitoring networks. The NAWQA data summaries are from Gilliom and others (2006). All concentrations are in micrograms per liter; ND, not determined; LTRL, long-term laboratory reporting level]

| Compound | Lake Wales Ridge Citrus Lakes[1] | | | USGS NAWQA surface-water sampling, 1992-2001 | | | | | | | |
| | | | | Agricultural land use | | | | Detection frequency[2] in other land-use classes (percent of samples) | | | |
| | Detection frequency[2] (percent of samples) | 90th percentile concentration | Maximum concentration | Detection frequency[2] (percent of samples) | 90th percentile concentration | Maximum concentration | No. of sites (samples) | NAWQA maximum LTRL | Urban[3] | Mixed[4] | Undeveloped[5] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Norflurazon | 100 | 2.37 | 5.30 | 4.2 | <0.021 | 1.24 | 62 (1,468) | 0.021 | 0 | 0.06 | 1.8 |
| Diuron | 82 | .081 | 1.79 | 13 | .040 | 14 | 62 (1,469) | .06 | 22 | 8.4 | 4.2 |
| Bromacil | 64 | 2.78 | 6.29 | 1.68 | <.040 | 1.9 | 62 (1,470) | .04 | 1.6 | .03 | .85 |
| Simazine | 43 | .041 | .060 | 58 | .074 | 5.76 | 83 (2,009) | .006 | 65 | 63 | 24 |
| Atrazine | 36 | .011 | .015 | 90 | .800 | 201 | 83 (2,009) | .004 | 71 | 85 | 54 |
| Aldicarb sulfoxide | 29 | .216 | .67 | .13 | <.140 | 1.91 | 62 (1,470) | .14 | 0 | .05 | 0 |
| Aldicarb sulfone | 25 | .117 | .33 | 0 | <.100 | <.100 | 62 (1,469) | .1 | 0 | 0 | 0 |
| 2,4-D | 21 | .113 | 1.16 | 13 | .110 | 15 | 62 (1,465) | .08 | 13 | 6.4 | .38 |
| Oxamyl | 7 | ND | .036 | .57 | <.080 | .16 | 62 (1,469) | .08 | 0 | 0 | 0 |
| Tebuthiuron | 7 | ND | .006 | 21 | .013 | 6.33 | 83 (1,983) | .008 | 30 | 29 | 21 |
| DEA | 4 | ND | .006 | 79 | .128 | 3.03 | 83 (2,000) | .003 | 42 | 72 | 47 |

[1] Includes 7 sites (lakes) and 28 samples.

[2] Detections above laboratory reporting levels.

[3] Includes 19 to 30 sites and 523 to 812 samples, depending on compound.

[4] Includes 36 to 65 sites and 798 to 1385 samples, depending on compound.

[5] Includes 5 to 8 sites and 100 to 144 samples, depending on compound.

The maximum concentrations of bromacil (6.29 µg/L) and norflurazon (5.30 µg/L) in the Ridge lakes were higher than the national maximums (1.9 and 1.24 µg/L, respectively) in streams draining agricultural lands (table 9). The Q90 concentration of diuron in the Ridge lakes (0.081 µg/L) was twice the national Q90 (0.040 µg/L). The Ridge Q90 concentration for 2,4-D (0.113 µg/L) was similar to the national Q90 for agricultural basins (0.110 µg/L). In contrast, the Ridge Q90 for simazine (0.041) was about half of the national Q90 (0.074 µg/L). Atrazine concentrations in the Ridge lakes (maximum = 0.015 µg/L) were considerably lower than national concentrations in streams draining agricultural land use (maximum = 201 µg/L, Q90 = 0.80 µg/L), and reflect the lack of atrazine usage in Florida citrus (Florida Agricultural Statistics Service, 2000; 2002).

The pesticides diuron, simazine, 2,4-D, atrazine, bromacil, and tebuthiuron were detected nationally in urban and mixed land uses at similar or higher frequencies as in agricultural areas (table 9). Notably, national detection frequencies in urban areas for simazine (65 percent) and

diuron (22 percent) were higher than in agricultural areas (58 and 13 percent, respectively). Simazine and atrazine were also detected nationally in mixed land use (63 and 85 percent of samples, respectively) and in undeveloped areas (24 and 54 percent of samples). National detection frequencies for 2,4-D were similar between agricultural and urban areas (13 percent of samples) (table 9).

The relatively frequent detection of tebuthiuron and atrazine (and its degradate DEA) in undeveloped areas nationally and their detection in the undeveloped control lake on the Ridge (app. 3) suggest non-agricultural usage and/or atmospheric transport as possible sources of low-level concentrations of these compounds in the Ridge lakes. Tebuthiuron, a broad spectrum herbicide typically used in non-cropland areas to control weeds, was detected at trace concentrations in all samples from the Ridge control lake and in 21 percent of national samples from undeveloped areas (table 9). Atrazine was also detected in two of four samples from the control lake on the Ridge and was detected nationally in urban, mixed, and undeveloped land use (71, 85, and 54 percent of samples,

respectively). Atrazine and DEA also were detected at trace levels in a nearly pristine lake in Orange County, Florida (German and Adamski, 2005). Atmospheric transport of atrazine has been documented in a number of studies (Richards and others, 1987; Goolsby and others, 1994; Muir and others, 2004; Scribner and others, 2005), and estimated atmospheric emissions of atrazine from agricultural source areas near the Ridge are identified in Cohen and others (1997). Atmospheric transport of atrazine in rainfall over large distances and its deposition in lakes located hundreds of kilometers from atrazine source areas has been documented in areas of the northern United States and in Canada (Stamer and others, 1998; Muir and others, 2004).

## Relation of Chemical Properties and Usage to Pesticide Occurrence

Estimates of pesticide chemical properties and usage were compiled for selected target pesticides on the basis of published data and were used to define indices related to pesticide transport into water resources (table 10). The indexes of leaching, pesticide usage, and pesticide transport are defined in the "Analytical Methods" section.

Lower values of the *leaching vulnerability index* (Schlosser and others, 2002) indicate increased propensity for the pesticide to leach from soils into ground water. The leaching

**Table 10.**  Indexes of leaching vulnerability, pesticide usage, and transport potential for selected pesticides targeted in the Ridge lake study.

[The indexes are shown in shaded column. Pesticides are ranked according to the leaching "vulnerability index" (Schlosser and others, 2002). Lower values are indicative of increased potential to leach based on these properties. Sources for pesticide properties were obtained from Hornsby and others (1996), except where noted. AI, active ingredient; I, insecticide; H, herbicide; N, nematicide; F, fungicide; d, degradate; Ac, acaricide; mL/g, milliliter per gram; acre/yr, acre per year; ND not determined; NA, not available; lb, pounds; mg/L, milligram per liter]

| Pesticide (or degradate) | Soil organic carbon partition coefficient, $K_{OC}$ (mL/g) | Soil half-life, $t_{1/2}$ (days) | Leaching vulnerability index[1] ($K_{OC}/t_{1/2}$) | Solubility in water[2] (mg/L) | Pesticide class | Percent of Florida orange orchards[3] | Annual application rates in Florida orange orchards[3] (lb AI/acre/yr) | Pesticide usage index for Florida orange orchards[4] | Ranking by usage for major crops in Florida (lb AI/ crop year)[5] | Transport-potential index (usage index/ vulnerability index) |
|---|---|---|---|---|---|---|---|---|---|---|
| Tebuthiuron | 80 | 360 | 0.22 | 2,500 | H | NA | NA | NA | NA | ND |
| Aldicarb sulfone | 10 | 20 | .50 | 10,000 | d | [6]14 | [6]2.78 | 38.9 | [6]15 | 78 |
| Bromacil[7] | 32 | 60 | .53 | 700 | H | 24 | 1.61 | 38.6 | 21 | 72 |
| Metalaxyl | 50 | 70 | .71 | 8,400 | F | NA | ND | NA | 69 | ND |
| Aldicarb | 30 | 30 | 1.00 | 6,000 | I, Ac, N | 14 | 2.78 | 38.9 | 15 | 39 |
| Bentazon | [8]34 | [8]20 | 1.70 | [8]2,300,000 | H | NA | NA | NA | 47 | ND |
| 2,4-D | [9]20 | [9]10 | 2.00 | [9]890 | H | 3 | .31 | .9 | 10 | .47 |
| Simazine | 130 | 60 | 2.17 | 6.2 | H | 32 | 2.47 | 79.0 | 12 | 36 |
| Methomyl | 72 | 30 | 2.40 | 58,000 | I | NA | NA | NA | 29 | ND |
| Imidacloprid | [10]203 | [10]50 | 4.06 | [10]510 | I | NA | NA | NA | 76 | ND |
| Diuron | 480 | 90 | 5.33 | 42 | H | 57 | 2.18 | 124.3 | 10 | 23 |
| Oxamyl | 25 | 4 | 6.25 | 282,000 | I, Ac, N | NA | NA | NA | 81 | ND |
| Norflurazon | 700 | 30 | 23.33 | 28 | H | 17 | 1.91 | 32.5 | 18 | 1.4 |
| Benomyl | 1,900 | 67 | 28.36 | 2 | F | <1 | .86 | <.86 | 54 | .03 |
| Oryzalin | 600 | 20 | 30.00 | 2.5 | H | NA | NA | NA | 114 | ND |
| Glyphosate | [11]24,000 | [11]47 | 510.64 | [11]900,000 | H | 88 | 2.52 | 221.8 | 17 | .43 |

[1] Schlosser and others (2002).

[2] Within range of 20 to 25 degrees Celsius.

[3] Percent by area, Florida Agricultural Statistics Service (2002); Shahane (2003).

[4] The product of usage area (percent of total crop area) and application rate (AI/acre/yr).

[5] Includes pesticides used for 32 major crop types in Florida, 2001 (Shahane, 2003).

[6] Parent pesticide, aldicarb.

[7] Bromacil has been prohibited from use in Ridge citrus orchards located on sandy well drained soils since December 1994.

[8] Chemical properties associated with formulation bentazon sodium salt.

[9] Chemical properties associated with formulation 2,4-D acid.

[10] Source: Oregon State University ExToxNet (Extension Toxicology Network), available online at *http://extoxnet.orst.edu/*

[11] Chemical properties associated with formulation glyphosate isopropylamine salt.

vulnerability index ranged from 0.22 (tebuthiuron) to 510 (glyphosate) for the pesticides listed in table 10, and values were less than about 5 for most of the pesticides detected in the Ridge lakes. Published values of aldicarb soil half-life varied from 7 to 30 days (Hornsby and others, 1996; U.S. Environmental Protection Agency, 2007). The lack of aldicarb detections in the Ridge ground water (Choquette and others, 2005) and lake samples, in light of concurrent detections of its degradates, suggests that aldicarb breakdown rates in the Ridge region may correspond to the lower (more rapid) values in this range.

Pesticide usage data were available for eight of the parent compounds listed in table 10 (Shahane, 2003). The *pesticide usage index* (table 10) was indicative of the areal extent of usage and application rate. Highest rankings of the pesticide usage index were associated with glyphosate (222), diuron (124), and simazine (79), followed by aldicarb (39), bromacil (39), and norflurazon (33) (table 10). The bromacil value reflects average usage in citrus statewide; however, in Ridge citrus, the usage index for bromacil should be near zero because its use is prohibited in nearly all of the Ridge citrus areas (State of Florida, 1995; Choquette and Sepulveda, 2000). The *transport potential index* is determined by leaching potential and pesticide usage, and higher values indicate increased potential of a pesticide to be transported by way of ground water to the lakes (table 10).

Most of the pesticides that were detected in two or more of the lakes, including norflurazon, diuron, simazine, bromacil, metalaxyl, aldicarb degradates, 2,4-D, oxamyl (fig. 8), exhibited either a leaching index less than about 5, or a moderate to high usage index greater than about 30 (table 10). The high leaching index (23.33) for norflurazon, relative to the other compounds, did not suggest a high propensity for leaching of this compound, contrary to the high frequency of norflurazon detections in the lake samples, and in ground-water sampling (Choquette and others, 2005). Also, the lower relative solubility of simazine (6.2 mg/L) and norflurazon (28 mg/L) compared to the other detected compounds (42 to 282,000 mg/L) does not appear to be a limiting factor in their transport to the Ridge lakes.

The transport-potential index provided a generally accurate estimate of occurrence (or absence) of the pesticides glyphosate, atrazine, benomyl, alicarb sulfoxide, and diuron in the lakes on the basis of standardized detection frequencies (figs. 6 and 8). However, the transport-potential index underestimated the occurrence of bromacil, norflurazon, and 2,4-D, and overestimated the occurrence of aldicarb, aldicarb sulfone, and simazine in the lake samples. Bromacil detections in the lake samples indicate that bromacil persists much longer in the environment than expected on the basis of its chemical properties, based on the assumption that it has not been used in most Ridge citrus areas since 1994 (discussed in the "Agrichemical Usage" section). The transport-potential index for norflurazon significantly underestimated its occurrence in the Ridge lakes relative to other pesticides given

that it was the most frequently occurring pesticide and was detected in all of the lake samples (fig. 8). This result suggests that norflurazon's propensity to leach was underestimated by the chemical properties in the index, and/or the statewide usage averages were lower than its actual usage on the Ridge. Comparing median pesticide concentrations in Swim Lake and Lakes Lynn and Leonore with the transport-potential index for selected pesticides (fig. 20) indicates patterns similar to the regional results, and highlights the strengths and limitations of using this approach for estimating the occurrence of pesticide compounds in the lakes.

The transport-potential and the leaching vulnerability indexes indicated that aldicarb sulfone should be detected at about twice the rate of aldicarb sulfoxide; however, the standardized detection rate of aldicarb sulfoxide (above the 0.06 µg/L level) was 25 percent compared to 10 percent for aldicarb sulfone. The lower laboratory recoveries for aldicarb sulfone and aldicarb (table 3), as previously discussed, may account for their lower than expected frequency of detection. The lack of aldicarb detections in any of the lake samples and in few Ridge ground-water samples (Choquette and others, 2005) indicates that it degrades rapidly in the Ridge environment.

The lack of detection of the target pesticide glyphosate and its primary degradate AMPA in lake samples, despite the widespread application of glyphosate in citrus (table 10 and fig. 4), is consistent with its chemical properties. Glyphosate, moderately persistent with an average soil half life of 47 days and highly soluble, has a strong tendency to sorb to soils, as indicated by its high organic-carbon partition coefficient ($K_{oc}$), even those with low organic and low clay content (Oregon State University, 1996a).

Some factors that may limit the utility of chemical properties to predict propensity for pesticide transport into ground water and surface water include preferential transport of water into and through the subsurface (resulting in more rapid transport rates than expected based solely on soil or lithologic properties), and variations in pesticide behavior due to differences in chemical, physical, and biological conditions between controlled laboratory environments and the field (Barbash and Resek, 1996). Recent study of pesticide degradation indicates higher than expected rates of degradation as well as changes in degradation pathways in soils adapted to the application of the pesticide (Krutz and others, 2008). The limitations of the transport potential index for estimating relative pesticide occurrence in the lake samples also could be due to differences between pesticide usage in Ridge groves compared to statewide averages for citrus. The low organic content in the sandy soils and geologic deposits underlying the Ridge may limit the utility of $K_{oc}$ (organic carbon partition coefficient) and, hence, the leaching vulnerability index, for identifying compounds having a propensity to leach into ground water and lakes in this region.

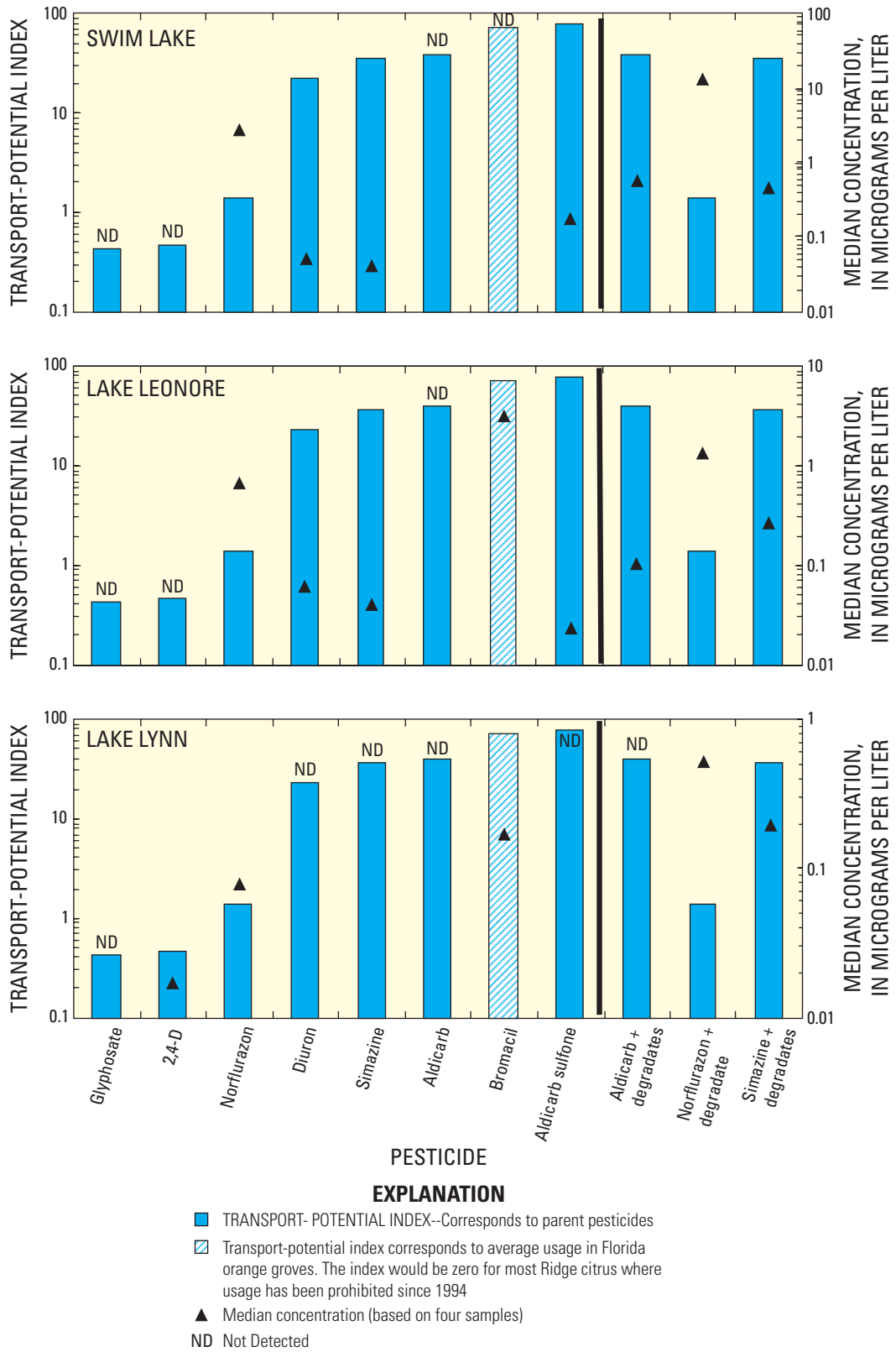**Figure 20.** Pesticide transport-potential indexes compared to median pesticide concentrations in Swim Lake, Lake Leonore, and Lake Lynn. Higher values of the transport-potential index indicate higher likelihood of transport into ground and surface water. The application of bromacil has been prohibited in most Ridge citrus orchards since 1994. The median concentrations correspond to four samples collected over a year at each lake.

## Discussion of Pesticide Transport and Fate

The Ridge lake study, although intended as a reconnaissance, also provides some insight into the transport and fate of pesticides and their degradates in the surficial aquifer system and citrus lakes. Land use, soils, and climate were similar among the citrus study basins and, therefore, these factors are not expected to significantly contribute to spatial differences observed in pesticide occurrence between the study lakes. Given the limited availability of field data on pesticides in surface water and ground water, the transport and fate processes indicated by the Ridge results may be useful for future studies in the Ridge or in other field settings.

The high incidence of norflurazon and demethyl norflurazon detections and typically higher concentrations of demethyl norflurazon in more than 90 percent of the lake samples that yielded norflurazon detections (fig. 6 and app. 4) are consistent with ground-water sources contributing to lake inflow and with the in-lake processes influencing the breakdown of norflurazon. Photodegradation has been identified as the probable primary route of degradation for norflurazon (U.S. Environmental Protection Agency, 1996).

Norflurazon degradation can occur after its application at land surface in soils and as it moves through the unsaturated zone and into the aquifer, and also while ground water moves through the subsurface and into the lakes. Norflurazon has been described as a relatively mobile compound that is expected to be persistent in surface waters due to its resistance to abiotic hydrolysis, low volatilization potential, and relatively low susceptibility to degradation under aerobic conditions, and is even more persistent in anaerobic environments (U.S. Environmental Protection Agency, 1996). Although less is known about the properties of norflurazon's primary degradate, demethyl norflurazon, it too is persistent in aerobic and anaerobic conditions and has been reported to be more persistent than norflurazon (U.S. Environmental Protection Agency, 1996). Both norflurazon and demethyl norflurazon exhibit low soil/water partitioning, indicating that their mass in surface waters would likely be dissolved in the water column rather than adsorbed to suspended and bottom sediment.

Norflurazon in water irradiated in sunlight has an estimated half-life of 2 to 3 days (compared to 130 days and 6-8 months in non-irradiated soils and sediment, respectively) (U.S. Environmental Protection Agency, 1996). The clarity of lakes in the Lake Wales Ridge region would provide an environment for photolysis. The Secchi depths of lakes on the Ridge typically range from about 3.5 to 13 ft, averaging between about 6 and 9 ft (Romie, 2000), and (as previously described) has been measured at 15 to 21 ft in some of the sampled lakes (Sacks and others, 1998; University of Florida, 2005b; University of South Florida, 2008).

The possibility of photodegradation in shallow zones of the lake water column more directly exposed to sunlight was supported by consistently lower concentrations of norflurazon and its degradate in shallow versus deep zones, and larger concentrations of the degradate than the parent in shallow

versus deep zones. Low dissolved oxygen concentrations (Lake Lynn only) and cooler water temperatures in deeper zones of the lake water column also could contribute to slower degradation rates at depth. The typically higher concentrations of norflurazon and demethyl norflurazon in ground water compared to lakes sampled in Ridge citrus areas (Choquette and Kroening, 2006) may in part reflect photodegradation of these compounds after they enter the lakes.

Widespread detections of atrazine and bromacil in the lakes (fig. 8) were not anticipated on the basis of minimal usage in Ridge citrus. Atrazine has no historic use in Florida citrus, but was detected at trace concentrations (less than 0.016 µg/L) in five of the citrus lakes and in the control lake (app. 3), which may be indicative of atmospheric transport of atrazine into Ridge lakes or applications in non-citrus source areas.

The occurrence of bromacil in the lakes, at relatively high concentrations compared to other compounds (table 6), was consistent with recent bromacil detections in Ridge ground water (Choquette and others, 2005) and, as previously discussed, may originate from residual bromacil because its use has been prohibited in most Ridge citrus since 1994. In ground water, detections of bromacil have decreased slightly with time, whereas detections of one of its replacements, norflurazon, are increasing (Choquette and others, 2005; Gilliom and others, 2006). Given the significant ground-water inflow to the Ridge lakes, this result suggests the possibility of such temporal trends in bromacil and norflurazon in the lakes.

Neither glyphosate, which is widely used in Florida citrus orchards (fig. 3), nor its degradate AMPA were detected above the LRL (0.1 µg/L) in any of the lake samples (app. 3). The lack of detections of glyphosate and its degradate AMPA, despite widespread usage, is likely due to its relatively short half-life in water of 7 to 14 days (Giesy and others, 2000) and high potential to sorb to phosphate binding sites, iron and aluminum oxides, clay, and organic matter (Sprankle, 1975; Hance, 1976; and Hornsby and others, 1996). The presence of glyphosate in ground water on the Ridge has not been evaluated. In contrast, Battaglin and others (2005) documented moderate to high detection rates of glyphosate and AMPA in streams of the midwestern United States.

The variation in pesticide compounds detected among the citrus lakes suggests that differences in usage practices and amounts of ground-water inflow contribute to pesticide occurrence in the study lakes. Positive correlations have been observed between the amount of ground-water inflow into Ridge lakes and nitrate concentration indicating the importance of ground-water transport of agricultural chemicals into the lakes (Kolasa and others, 2001). The seasonal variations in pesticide concentrations in the lakes may reflect local differences in the timing, types, and rates of pesticide applications; differences in ground-water flow path lengths; ages of ground water flowing into the lakes; and the residence time of water in the lakes.

Comparison of the lake pesticide results to Ridge ground-water sampling indicated that median concentrations of most pesticides and degradates were lower in lakes than in ground water (Choquette and Kroening, 2006). This pattern is likely due to increased opportunity for biogeochemical degradation (including photolysis), sorption, and dilution of pesticides both within the lakes and during the transport of ground water to the lakes. The ratios of degradate-to-parent pesticide concentrations were typically higher in lakes than in ground water, which is consistent with degradation occurring as ground water moves through the subsurface into the lakes and with chemical breakdown within the lake systems. The detections of parent pesticides in the lakes may reflect relatively rapid ground-water transit times, slow chemical breakdown and/or sorption and subsequent desorption of pesticides within the lakes, and possible atmospheric deposition of pesticides.

# Summary

This report presents the first assessment of pesticides in lakes on the Lake Wales Ridge, central Florida, and is one of the first pesticide studies in the Nation focused on small- to moderate-sized lakes. The sampled lakes included seven lake basins characterized predominately by citrus agriculture and one undeveloped ("control") lake basin, which ranged in area from 5 to 393 acres with maximum depths ranging from 20 to 65 ft. Quarterly water-quality samples were collected over a 1-year period from each of the lakes, along with a single sampling event to compare water quality in shallow and deep zones in four of the lakes. Water-quality data included field properties, and laboratory analyses of major inorganic constituents, nutrients, and 83 selected pesticides and degradates.

Compared to the control lake, the citrus lakes typically exhibited elevated pH, and elevated concentrations of dissolved solids, major inorganic constituents (including calcium, magnesium, sodium, potassium, chloride, and sulfate), nitrate, and pesticide compounds. The elevated concentrations of the major inorganic constituents and pesticides in the citrus basins likely reflect inputs from citrus agrichemcials that have leached into the surficial aquifer system which feeds the lakes. Atmospheric transport may also contribute these constituents to the lakes, but it is likely a less important source of these constituents than ground water. The median pH of the citrus lakes ranged from 7.1 to 7.7, in contrast to 5.9 in the control lake. These differences in pH likely reflect the increased concentrations of anions in the ground water due to fertilization and liming in citrus groves, the acidic pH of rainfall in Florida, and the low acid-neutralizing capacity of the surficial aquifer system.

Median nitrate (as N) concentrations in the citrus lakes generally ranged from 0.6 to 3.7 mg/L, and median total nitrogen in the citrus lakes ranged from 1.41 to 4.79 mg/L compared to 0.48 mg/L in the control lake. One of the citrus lakes, Pabor Lake, exhibited low nitrate concentrations (less than 0.06 mg/L); however, total nitrogen in the lake was similar to the other citrus lakes, indicating that the nitrogen in Pabor Lake may consist predominantly of organic nitrogen.

A total of 20 pesticide compounds (12 parent compounds and 8 degradates) were detected above laboratory reporting levels in the study lakes. Herbicides and their degradates accounted for most (75 percent) of these pesticide compounds, followed by insecticides and one fungicide. The number of pesticide compounds detected in each of the citrus lakes ranged from 9 to 14. Trace concentrations of three pesticides were detected in the control lake.

Of the 20 pesticides detected above LRLs, 12 were detected at concentrations equal to or exceeding the 0.06-µg/L SRL. The compounds with the highest standardized detection frequencies included, in decreasing order of detection, demethyl norflurazon, norflurazon, bromacil, simazine degradates (DDA and hydroxysimazine), diuron, and aldicarb sulfoxide, which occurred in 86 to 25 percent of the samples from the citrus lakes. Other compounds detected in less than 20 percent of samples at or above the 0.06-µg/L level included metalaxyl, DIA, aldicarb sulfone, and simazine. This study was one of the first to evaluate the occurrence of hydroxysimazine in surface waters of the United States.

Pesticide concentrations in the lakes did not exceed any currently specified (2007) Federal aquatic-life benchmarks, which were available for 10 of the 20 detected pesticides, with the exception of one duplicate sample in which diuron slightly exceeded a guideline for aquatic plants. The concentrations of diuron, bromacil, and norflurazon in a few samples approached the benchmarks for acute effects on nonvascular plants. None of the lake samples yielded pesticide concentrations that exceeded State or Federal human-health guidance values for drinking water. Potential impacts of agrichemical mixtures on aquatic life cannot be assessed until criteria for such mixtures are developed.

Maximum pesticide concentrations were less than 1 µg/L for 15 of the 20 detected compounds, and ranged, by compound, from 0.006 to 17.1 µg/L. Summary statistics for concentrations of the pesticide compounds detected in the citrus lakes were calculated using the log-likelihood method. The coefficient of variation (standard deviation/ mean) of concentrations, by compound, ranged from 29 to 363 percent (median 133 percent); the ratio of the interquartile range to the median, a nonparametric measure of variability, ranged from 41 to 813 percent (median 205 percent).

Atrazine, which is not a citrus pesticide, was detected in six of the eight study lakes, including the control lake, at trace concentrations (less than 0.016 µg/L); its degradates hydroxyatrazine and DEA also were detected at low concentrations in some samples. Atmospheric transport may be a source of atrazine in the study lakes, but atrazine may also originate from usage in non-citrus source areas in the basins.

In the citrus lakes, pesticide degradates were detected more frequently and at higher concentrations than the parent concentrations for most parent-degradate combinations analyzed. Norflurazon and its degradate demethyl norflurazon were detected in all of the lake samples in which both compounds were analyzed, and 88 percent of these samples yielded higher concentrations of the degradate than the parent. The simazine degradates hydroxysimazine, DDA, and DIA were detected more frequently than simazine in the lake samples above the 0.06-µg/L level. The degradates aldicarb sulfone and aldicarb sulfoxide were detected in 25 and 29 percent of the samples, respectively, but aldicarb was not detected in any of the samples. Laboratory recoveries differed between these compounds and mean recoveries in matrix spikes were low (8.7 to 55 percent) compared to other targeted analytes. Diuron, in contrast to other parent-degradate results, occurred at higher concentrations and detection frequencies than its degradates DCPMU and DCPU, although its primary degradate, 3,4-dichloroaniline, was not analyzed as part of this study.

Preliminary analysis indicated that norflurazon and demethyl norflurazon degradation rates may be higher in shallow zones and decrease with depth in the lake water column, presumably due to increased sunlight penetration near the lake surface, but additional sampling is needed to confirm these results. These data are consistent with prior studies indicating photodegradation is an important process for breakdown of norflurazon and its degradate.

Concentrations of pesticides detected in the Ridge study were compared to those detected in national (USGS NAWQA) monitoring at 2,868 sites on streams. The 90th percentile concentrations for Ridge lake samples exceeded or were similar to the national 90th percentiles for agricultural land use for 6 of the 11 target pesticides analyzed in both the lake study and national monitoring, indicating that the concentrations in the Ridge lakes are relatively high in a national context. Some of the pesticides detected in the Ridge lakes occurred more frequently in "urban" or "mixed" land-use settings nationally than in agricultural settings, including diuron, simazine, 2,4-D, and tebuthiuron.

The lake pesticide detections were compared to an index of pesticide leachability, and other indexes representing pesticide usage and transport potential. The transport-potential index underestimated the relative occurrence of bromacil, norflurazon, and 2,4-D, and overestimated the occurrence of aldicarb, aldicarb sulfone, and simazine in the lake samples. The discrepancies between expected and observed detection frequencies indicate that field monitoring is critical for assessing agrichemical transport into water resources and to verify the accuracy of such estimates in specific regions. For example, bromacil detections in the lakes and in ground water on the Ridge more than 10 years since the prohibition of its use in most Ridge citrus suggest that bromacil persists much longer in this environment than expected on the basis of its chemical properties.

Agrichemical usage practices implemented to protect water resources on the Ridge include the prohibition on bromacil usage, restrictions on aldicarb applications, and establishment of voluntary fertilizer "best management practices." These changes are anticipated to result in reductions in nitrate and pesticide concentrations in ground water over time, which may, in turn, result in future reductions of their concentrations in the Ridge lakes.

This study indicates that parent pesticides as well as their degradates persist in the Ridge lakes, despite contributions via relatively slow ground-water transport and opportunity for chemical breakdown, dilution, and sorption in the lake environments. The typically lower pesticide concentrations in Ridge lakes compared to ground water suggest that in-lake processes may be important for reducing agrichemical concentrations in lake waters discharging to the surficial aquifer system and Upper Floridan aquifer. Considerations for future studies include periodic monitoring to evaluate temporal trends of pesticides in the lakes, bioassessment of aquatic communities in the lakes to evaluate potential effects of pesticides and pesticide mixtures, and measurement of atmospheric contributions of agrichemicals to the lakes. Local-scale ground-water flow-path studies could provide information on the processes and hydrogeologic factors controlling the transport and fate of pesticides in the lakes and in adjacent aquifers, and help to determine the influence of the lakes on regional water quality in this dynamic, closely linked ground-water/surface-water system.

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**Appendix 1.** Constituents, analytical methods, and reporting levels for water-quality samples analyzed in the lake samples.

[Units are in micrograms per liter, except as noted. IC, ion chromatography; ICP-AES, inductively coupled plasma—atomic emission spectroscopy; HPLC-MS, high performance liquid chromatography—mass spectrometry; SPE, solid phase extraction; USEPA, U.S. Environmental Protection Agency]

| Constituent | Reporting level | Analysis method | Reference |
|---|---|---|---|
| Filtered calcium | 0.25 mg/L | ICP-AES | USEPA (2001) (Method 200.7) |
| Filtered magnesium | .25 mg/L | ICP-AES | USEPA (2001) (Method 200.7) |
| Filtered sodium | .25 mg/L | ICP-AES | USEPA (2001) (Method 200.7) |
| Filtered potassium | .25 mg/L | ICP-AES | USEPA (2001) (Method 200.7) |
| Filtered chloride | .25 mg/L | IC | USEPA (1993a) (Method 300.0) |
| Filtered sulfate | .48 mg/L | IC | USEPA (1993a) (Method 300.0) |
| Filtered fluoride | .08 mg/L | Ion selective electrode | Greenberg (1992) (Method 4500F-C) |
| Unfiltered ammonia nitrogen | .02 mg/L as nitrogen | Spectroscopy | Greenberg (1992) (Method 4500NH3-H) |
| Unfiltered nitrite plus nitrate nitrogen | .01 mg/L as nitrogen | Spectroscopy | USEPA (1993b) (Method 353.2) |
| Unfiltered nitrogen | .1 mg/L as nitrogen | Spectroscopy | USEPA (1993b) (Method 353.2) |
| Filtered orthophosphate | .0125 mg/L | Spectroscopy | Greenberg (1992) (Method 4500-P) |
| Unfiltered phosphate | .0125 mg/L | Spectroscopy | USEPA (1993c) (Method 365.1) |
| Unfiltered organic carbon | 1.0 mg/L | High temperature combustion | Greenberg (1992) (Method 5310B) |
| Unfiltered alkalinity | | Titration | USEPA (1978) (Method 310.1) |
| Turbidity | | Nephelometry | Greenberg (1992) (Method 2130B) |
| Total suspended solids | | Gravimetric | Greenberg (1992) (Method 2540D) |
| Total dissolved solids | | Gravimetric | Greenberg (1992) (Method 2540C) |
| 2,4-D (2,4-Dicholorophenoxyacetic acid) | .0218[1], .0218[2], .038[2] | HPLC-MS/SPE | Furlong and others (2001) |
| 2,4-D ME (2,4-D methyl ester) | .0086[1], .0086[2], .016[2] | HPLC-MS/SPE | Furlong and others (2001) |
| 2,4-DB | .016[1], .016[2], 0.020[2] | HPLC-MS/SPE | Furlong and others (2001) |
| 3-ketocarbofuran | 1.5[1], .014[2], .02[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Acifluorfen | .0066[1], .0066[2], .028[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Aldicarb | .04[1], .04[2], .04[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Aldicarb sulfone | .02[1], .02[2], .018[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Aldicarb sulfoxide | .0082[1], .0082[2], .0022[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Atrazine | .009[1], 0.009[2], 0.008[3] | HPLC-MS/SPE | Furlong and others (2001) |
| | .025 | HPLC/MS | Lee and others (2002b) |
| Bendiocarb | .0252[1], .0252[2], .020[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Benomyl | .0038[1], .0038[2], .0022[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Bensulfuron-methyl | .0158[1], .0158[2], .018[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Bentazon | .011[1], .011[2], .012[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Bromacil | .033[1], .033[2], .018[3] | HPLC-MS/SPE | Furlong and others (2001) |
| | .025 | HPLC-MS | Lee and others (2002b) |
| Bromoxynil | .017[1], .017[2], .028[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Caffeine | .0096[1], .0096[2], .018[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Carbaryl | .0284[1], .0284[2], .018[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Carbofuran | .0056[1], .0056[2], .016[3] | HPLC-MS/SPE | Furlong and others (2001) |
| 3-Hydroxycarbofuran | .0058[1], .0058[2], .008[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Chloramben, methyl ester | .018[1], .018[2], .024[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Chlorimuron-ethyl | .0096[1], .0096[2], .032[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Chlorothalonil | .035[1], .035[2], .035[3] | HPLC-MS/SPE | Furlong and others (2001) |

**Appendix 1.** Constituents, analytical methods, and reporting levels for water-quality samples analyzed in the lake samples.—Continued

[Units are in micrograms per liter, except as noted. IC, ion chromatography; ICP-AES, inductively coupled plasma—atomic emission spectroscopy; HPLC-MS, high performance liquid chromatography—mass spectrometry; SPE, solid phase extraction; USEPA, U.S. Environmental Protection Agency]

| Constituent | Reporting level | Analysis method | Reference |
|---|---|---|---|
| Clopyralid | .0138[1], .0138[2], .024[3] | HPLC-MS/SPE | Furlong and others (2001) |
| CPMU (3-(4-chlorophenyl)-1-methyl urea) | .0242[1], .0242[2], .036[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Cyanazine | .025 | HPLC-MS | Lee and others (2002b) |
| Cyanazine amide | .025 | HPLC-MS | Lee and others (2002b) |
| Cyanazine acid | .025 | HPLC-MS | Lee and others (2002b) |
| Deethylcyanazine | .025 | HPLC-MS | Lee and others (2002b) |
| Deethylcyanazine acid | .025 | HPLC-MS | Lee and others (2002b) |
| Deethylcyanazine amid | .025 | HPLC-MS | Lee and others (2002b) |
| Cycloate | .013[1], .013[2], .014[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Dacthal monoacid | .0116[1], .0116[2], .028[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Dicamba | .0128[1], .0128[2], .036[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Dichlorprop | .0138[1], .0138[2], .028[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Dinoseb | .012[1], .012[2], .038[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Diphenamid | .0264[1], .0264[2], .010[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Diuron | .015[1], .015[2], .015[3] | HPLC-MS/SPE | Furlong and others (2001) |
|  | .20 | HPLC-MS | Lee and others (2002b) |
| DCPMU: 3(3,4-Dichlorophenyl) methyl urea | .0242[6], .036[7] | HPLC-MS/SPE | Furlong and others (2001) |
| DCPU: 3,4-Dichlorophenylurea | .06 | HPLC-MS/SPE | Furlong and others (2001) |
| Fenuron | .0316[1], .0316[2], .019[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Flumetsulam | .011[1], .011[2], .040[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Fluometuron | .031[1], .031[2], .016[3] | HPLC-MS/SPE | Furlong and others (2001) |
|  | .20 | HPLC-MS | Lee and others (2002b) |
| Demethylfluometuron | .20 | HPLC-MS | Lee and others (2002b) |
| Glufosinate | .10 | HPLC-MS | Lee and others (2002a) |
| Glyphosate | .10 | HPLC-MS | Lee and others (2002a) |
| Aminomethylphosphonic acid (AMPA) | .10 | HPLC-MS | Lee and others (2002a) |
| Imazaquin | .016[1], .016[2], .036[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Imazethapyr | .017[1], .017[2], .038[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Imidacloprid | .0068[1], .0068[2], .020[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Linuron | .0144[1], .0144[2], .014[3] | HPLC-MS/SPE | Furlong and others (2001) |
|  | .20 | HPLC-MS | Lee and others (2002b) |
| MCPA | .0162[1], .0162[2], .030[3] | HPLC-MS/SPE | Furlong and others (2001) |
| MCPB | .015[1], .015[2], .010[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Metalaxyl | .02[1], .02[2], .012[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Methiocarb | .008[1], .008[2], .010[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Methomyl | .0044[1], .0044[2], .020[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Metsulfuron methyl | .025[1], .025[2], .025[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Neburon | .012[1], .012[2], .012[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Nicosulfuron | .013[1], .013[2], .04[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Norflurazon | .016[1], .016[2], .020[3] | HPLC-MS/SPE | Furlong and others (2001) |
| De(s)methyl norflurazon | .03 | HPLC-MS/SPE | Furlong and others (2001) |
| Oryzalin | .0176[1], .0176[2], .012[3] | HPLC-MS/SPE | Furlong and others (2001) |

**Appendix 1.** Constituents, analytical methods, and reporting levels for water-quality samples analyzed in the lake samples.—Continued

[Units are in micrograms per liter, except as noted. IC, ion chromatography; ICP-AES, inductively coupled plasma—atomic emission spectroscopy; HPLC-MS, high performance liquid chromatography—mass spectrometry; SPE, solid phase extraction; USEPA, U.S. Environmental Protection Agency]

| Constituent | Reporting level | Analysis method | Reference |
|---|---|---|---|
| Oxamyl | .0122[1], .0122[2], .030[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Picloram | .0198[1], .0198[2], .032[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Prometon | .025 | HPLC-MS | Lee and others (2002b) |
| Propazine | .025 | HPLC-MS | Lee and others (2002b) |
| Propham | .0096[1], .0096[2], .030[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Propiconazole | .021[1], .021[2], .010[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Propoxur | .008[1], .008[2], .008[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Siduron | .0168[1], .0168[2], .020[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Simazine | .025 | HPLC-MS | Lee and others (2002b) |
| Sulfometuron-methyl | .0088[1], .0088[2], .038[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Tebuthiuron | .0062[1], .0062[2], .026[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Terbacil | .0098[1], .0098[2], .016[3] | HPLC-MS/SPE | Furlong and others (2001) |
| *Triazine Degradates*[5]**:** | | | |
| DDA (CAAT): | .01[1], .044[2], .04[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Didealkylatrazine; Chlordiamino-s-triazine; Deethyldeisopropylatrazine | .025 | HPLC-MS | Lee and others (2002b) |
| DIA (CEAT; DES): | .044[1], .01[2], .08[3] | HPLC-MS/SPE | Furlong and others (2001) |
| Deisopropylatrazine; 2-Chloro-6-ethyl-amino-4-amino-s-triazine; Deethylsimazine | .025 | HPLC-MS | Lee and other (2002b) |
| DEA (CIAT): | .0282[1], .0282[2], .028[2] | HPLC-MS/SPE | Furlong and others (2001) |
| Deethylatrazine; 2-Chloro-4-isopropyl-amino-6-amino-s-triazine | .025 | HPLC-MS | Lee and others (2002b) |
| DEHA (HDEA): | .025 | HPLC-MS | Lee and others (2002b) |
| Deethylhydroxyatrazine | | | |
| DIHA (OEAT; HDIA): | .025 | HPLC-MS | Lee and others (2002b) |
| Deisopropylhydroxyatrazine; 2-hydroxy-6-ethylamino-4-amino-s-triazine | | | |
| HA (OIET): | .008[1], .008[2], .032[3] | HPLC-MS/SPE | Furlong and others (2001) |
| 2-hydroxyatrazine; 2-Hydroxy-4-isopropyl-amino-6-ethylamino-s-triazine | .025 | HPLC-MS | Lee and others (2002b) |
| HS (OEET): | .025 | HPLC-MS | Lee and others (2002b) |
| Hydroxysimazine; 2-hydroxy-4,6-diethyl-amino-s-triazine | | | |
| Tribenuron-methyl | .088[1], .088[4] | HPLC-MS/SPE | Furlong and others (2001) |
| Triclopyr | .0224[1], .0224[2], .026[3] | HPLC-MS/SPE | Furlong and others (2001) |

[1]Reporting level from December 1, 2004 – June 30, 2004.

[2]Reporting level from July 1, 2004 – September 30, 2004.

[3]Reporting level from October 1, 2004 – September 30, 2005.

[4]Reporting level from July 1, 2004 – August 3, 2005.

[5]Depending on the degradate, possible parent compounds may include atrazine, simazine, propazine, cyanazine, or cyanazine degradates. Triazine degradation pathways and details regarding analytical methods are described in Scribner and others (1999), and in appendix 5. Simazine degradation is depicted in figure 15.

[6]Reporting level from December 1, 2003 – September 30, 2004.

[7]Reporting level from October 1, 2004 – September 30, 2005.

**Appendix 2.** Field measurements and laboratory results for major water-quality constituents and nutrients in the lake samples.

[Includes samples collected at a depth of 5 feet below lake surface. All values in milligrams per liter, except as noted; ºC, degrees Celsius; NA, not analyzed; E, estimated value; NTU, nephelometric turbidity units; µs/cm, microsiemens per centimeter; < , less than]

| Station identifier | Station name | Date | Time | Color (platinum-cobalt units) | pH, field (standard units) | Temperature, field (ºC) | Specific conductance, field (µS/cm) | Dissolved oxygen, field | Secchi depth (feet) | Total alkalinity[1], as CaCO3 | Suspended sediment | Total organic carbon | Dissolved calcium |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 02266923 | Swim Lake near Alcoma | 12/09/03 | 1120 | NA | 7.2 | 19 | 283 | 8.9 | NA | NA | NA | NA | NA |
| 02266923 | Swim Lake near Alcoma | 03/23/04 | 1050 | < 5 | 6.4 | 22 | 286 | 8.7 | NA | 31.7 | .60 | 8.5 | 28.4 |
| 02266923 | Swim Lake near Alcoma | 06/08/04 | 1130 | < 5 | 7.3 | 30 | 296 | 8.1 | 19 | 32.79 | .87 | 4.5 | 27.8 |
| 02266923 | Swim Lake near Alcoma | 09/15/04 | 1005 | < 5 | 7.1 | 28 | 257 | 6.2 | 12 | 16.04 | 1.23 | 5.9 | 24.1 |
| 02270655 | Lake Lynn near De Soto City | 12/08/03 | 1155 | NA | 7.5 | 21 | 327 | 8.9 | NA | NA | NA | NA | NA |
| 02270655 | Lake Lynn near De Soto City | 03/22/04 | 1050 | < 5 | 6.7 | 20.5 | 328 | 8.4 | NA | 39.5 | .88 | 3.8 | 22.6 |
| 02270655 | Lake Lynn near De Soto City | 06/07/04 | 1010 | < 5 | 6.7 | 29.5 | 343 | 7.8 | 18 | 41.61 | 1.52 | 5 | 22.3 |
| 02270655 | Lake Lynn near De Soto City | 09/14/04 | 1035 | < 5 | 8.2 | 29 | 330 | 7.2 | 9.6 | 46.42 | 1.40 | 4.7 | 21.8 |
| 02270700 | Lake Annie near Lake Placid | 12/20/04 | 1015 | 175 | 7 | 18.5 | 38 | 6.3 | 2.8 | 2.64 | 1.32 | 15.3 | 2.74 |
| 02270700 | Lake Annie near Lake Placid | 03/23/05 | 1150 | 125 | 5.2 | 22.5 | 37 | 8.7 | NA | 1.85 | 1.29 | 20.7 | 2.43 |
| 02270700 | Lake Annie near Lake Placid | 06/22/05 | 1300 | 100 | 5.8 | 29 | 39 | 5.6 | 5.0 | 2.09 | 1.38 | 16 | 2.43 |
| 02270700 | Lake Annie near Lake Placid | 09/06/05 | 1400 | 150 | 6 | 29 | 37 | 5.4 | 3.2 | 3.69 | 2.00 | 36.8 | 2.76 |
| 273323081290800 | Lake Denton near Avon Park | 12/08/03 | 1505 | NA | 7.7 | 20.5 | 284 | 9.4 | NA | NA | NA | NA | NA |
| 273323081290800 | Lake Denton near Avon Park | 03/22/04 | 1440 | < 5 | 7.6 | 21 | 283 | 9.6 | NA | 35.4 | .66 | 9.7 | 22.1 |
| 273323081290800 | Lake Denton near Avon Park | 06/07/04 | 1350 | < 5 | 7.8 | 29 | 303 | 8 | 21 | 35.22 | .84 | 4.5 | 21.9 |
| 273323081290800 | Lake Denton near Avon Park | 09/14/04 | 1355 | < 5 | 7.7 | 26 | 287 | 11.2 | 15 | 38.37 | 1.21 | 7.2 | 20.5 |
| 273850081310800 | Pabor Lake near Avon Park | 12/20/04 | 1420 | 15 | 7.5 | 17.5 | 490 | 7.3 | 2.3 | 185.83 | 4.54 | 13.4 | 21.5 |
| 273850081310800 | Pabor Lake near Avon Park | 03/23/05 | 0815 | 15 | 7.3 | 21.5 | 474 | 9.9 | NA | 164.83 | 9.00 | 31.5 | 20.9 |
| 273850081310800 | Pabor Lake near Avon Park | 06/22/05 | 0850 | 15 | 7.5 | 29 | 495 | 6.4 | 2.2 | 167.58 | 9.21 | 14.9 | 20.6 |
| 273850081310800 | Pabor Lake near Avon Park | 09/07/05 | 1300 | 15 | NA | 29.5 | 485 | 6.8 | 3.6 | 163.43 | 3.73 | 15.3 | 19.2 |
| 274648081315100 | Lake Moody near Frostproof | 12/21/04 | 0920 | 15 | 7.9 | 15 | 383 | 8.8 | 1.5 | 56.73 | 13.75 | 27.9 | 30.1 |
| 274648081315100 | Lake Moody near Frostproof | 03/22/05 | 1310 | 10 | 7.6 | 21 | 350 | 10.3 | NA | 48.35 | 12.18 | 9.9 | 28.2 |
| 274648081315100 | Lake Moody near Frostproof | 06/21/05 | 1400 | 10 | 7.3 | 29 | 355 | 7.9 | 1.6 | 50.49 | 15.94 | 13.1 | 28 |
| 274648081315100 | Lake Moody near Frostproof | 09/06/05 | 0930 | 15 | 7 | 29 | 339 | 6.8 | 1.5 | 47.88 | 9.88 | 47 | 25.9 |
| 274744081304200 | Lake Leonore near Frostproof | 12/21/04 | 1200 | 20 | 7.7 | 14 | 343 | 8.1 | 1.6 | 55.59 | 10.84 | 21.1 | 24.9 |
| 274744081304200 | Lake Leonore near Frostproof | 03/22/05 | 0930 | 10 | 7.2 | 21 | 340 | 7.6 | NA | 37.08 | 1.31 | 29.6 | 23.5 |
| 274744081304200 | Lake Leonore near Frostproof | 06/21/05 | 0900 | 10 | 6.1 | 29.5 | 318 | 7.5 | 7.8 | 34.6 | 1.32 | 5 | 21.9 |
| 274744081304200 | Lake Leonore near Frostproof | 09/07/05 | 0850 | 20 | 7.5 | 28.5 | 311 | 8 | 1.8 | 45.89 | 10.60 | 6.5 | 22.1 |
| 275256081275900 | Lake Aurora at Hesperides | 12/09/03 | 0900 | NA | 6.9 | 19.5 | 220 | 8.3 | NA | NA | NA | NA | NA |
| 275256081275900 | Lake Aurora at Hesperides | 03/23/04 | 0805 | < 5 | 7.4 | 21.5 | 224 | 8.3 | NA | 27.8 | < .50 | 10 | 18.3 |
| 275256081275900 | Lake Aurora at Hesperides | 06/08/04 | 0815 | < 5 | 7.1 | 29.5 | 238 | 8.3 | 12.5 | 29.58 | 1.28 | 4.6 | 18.1 |
| 275256081275900 | Lake Aurora at Hesperides | 09/15/04 | 0810 | < 5 | 7.5 | 28.5 | 218 | 7.1 | 12 | 61.21 | 1.20 | 7 | 16.7 |

**Appendix 2.** Field measurements and laboratory results for major water-quality constituents and nutrients in the lake samples.—Continued

[Includes samples collected at a depth of 5 feet below lake surface. All values in milligrams per liter, except as noted; ºC, degrees Celsius; NA, not analyzed; E, estimated value; NTU, nephelometric turbidity units; μs/cm, microsiemens per centimeter; < , less than]

| Station identifier | Dissolved magnesium | Dissolved sodium | Dissolved potassium | Dissolved calcium | Dissolved sulfate | Fluoride | Total dissolved solids | Turbidity (NTUs) | pH lab (standard units) | Nutrients | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Total nitrogen[1], as N | Ammonia[1], as N | Nitrite[1], as N | Nitrite plus nitrate[1], as N | Nitrate[1,2], as N | Total phosphorus, as P | Dissolved orthophosphate, as P |
| 02266923 | NA | NA | NA | NA | NA | NA | NA | NA | 7.21 | NA | < 0.01 | < 0.01 | 2.9 | 2.89 | < 0.02 | NA |
| 02266923 | 8.72 | 5.04 | 13.1 | 15.7 | 57 | .090 | 179 | .46 | 7.14 | 4.79 | .02 | .029 | 4.44 | 4.41 | .011 | < .01 |
| 02266923 | 8.45 | 5.26 | 12.3 | 16.23 | 57.82 | .074 | 169 | .114 | 7.46 | 5.19 | .03 | .049 | 4.75 | 4.70 | < .01 | < .01 |
| 02266923 | 7.44 | 4.66 | 11.2 | 13.91 | 50.73 | .066 | 151 | .9 | 6.82 | 3.33 | .04 | .028 | 2.90 | 2.87 | < .01 | < .01 |
| 02270655 | NA | NA | NA | NA | NA | NA | NA | NA | 7.45 | NA | .11 | .010 | 1.40 | 1.39 | < .02 | NA |
| 02270655 | 16.3 | 6.79 | 14.7 | 27.6 | 61.8 | .040 | 199 | .61 | 7.97 | 2.21 | .02 | .015 | 1.82 | 1.81 | < .01 | < .01 |
| 02270655 | 16.1 | 7.08 | 14.4 | 28.65 | 64.83 | .031 | 191 | .339 | 8.27 | 2.05 | .02 | .019 | 1.69 | 1.67 | < .01 | < .01 |
| 02270655 | 15.9 | 6.96 | 14.3 | 27.05 | 62.07 | .039 | 190 | .02 | 7.28 | 1.53 | .15 | .015 | 1.03 | 1.01 | < .01 | < .01 |
| 02270700 | .74 | 3.01 | .66 | 2.97 | 1.11 | .031 | 48 | .09 | 5.51 | .68 | .08 | .005 | .12 | .11 | .014 | .01 |
| 02270700 | .75 | 3.05 | .72 | 5.93 | 2.63 | .036 | 42 | 4.21 | 5.2 | .54 | .01 | .007 | .16 | .15 | .017 | < .01 |
| 02270700 | .76 | 3.2 | .82 | 6.07 | 2.94 | .02 | 46 | .145 | 5.8 | .42 | .02 | < .005 | .01 | E .004 | .011 | < .01 |
| 02270700 | .69 | 2.85 | .59 | 5.64 | 2.22 | .0208 | 50 | .08 | NA | .40 | .02 | .007 | .01 | .001 | .015 | < .01 |
| 273323081290800 | NA | NA | NA | NA | NA | NA | NA | NA | 7.67 | NA | .01 | .020 | 3.00 | 2.98 | < .02 | NA |
| 273323081290800 | 12.4 | 4.83 | 13.7 | 26.4 | 42.8 | .27 | 166 | .43 | 7.31 | 3.82 | .18 | .028 | 3.45 | 3.42 | < .01 | < .01 |
| 273323081290800 | 12.4 | 4.91 | 13.2 | 27.53 | 44.12 | .258 | 171 | .111 | 7.89 | 3.78 | .03 | .034 | 3.48 | 3.45 | < .01 | < .01 |
| 273323081290800 | 11.8 | 4.73 | 12.8 | 25.15 | 41.4 | .239 | 149 | .02 | 7.36 | 2.98 | .01 | .023 | 2.73 | 2.71 | < .01 | < .01 |
| 273850081310800 | 8.32 | 45.4 | 47.6 | 16.63 | 50.21 | .142 | 316 | 5.98 | 7.63 | 1.84 | .46 | .009 | .05 | .04 | .02 | < .01 |
| 273850081310800 | 8.18 | 44.1 | 47.5 | 16.8 | 48.13 | .107 | 313 | 8.7 | NA | 1.47 | .01 | < .005 | .03 | E .025 | .032 | < .01 |
| 273850081310800 | 8.21 | 44.3 | 50 | 16.5 | 47.88 | .098 | 312 | 6.99 | NA | 1.36 | .03 | < .005 | .01 | E .001 | .015 | < .01 |
| 273850081310800 | 7.83 | 42.5 | 50.8 | 16.81 | 47.91 | .095 | 303 | 3.72 | NA | .86 | .02 | < .005 | .00 | E .001 | .016 | < .01 |
| 274648081315100 | 17.9 | 8.99 | 14.3 | 28.9 | 84.16 | .196 | 256 | 11.3 | 7.17 | 2.96 | .38 | .010 | .41 | .40 | .020 | < .01 |
| 274648081315100 | 16.9 | 8.27 | 13.4 | 27.38 | 73.07 | .180 | 232 | 14 | NA | 2.88 | .03 | .007 | 1.00 | .99 | .037 | < .01 |
| 274648081315100 | 16.5 | 7.88 | 13.2 | 26.65 | 72 | .174 | 220 | 17.8 | NA | 2.37 | .03 | .007 | .42 | .41 | .021 | < .01 |
| 274648081315100 | 15.2 | 7.33 | 12.5 | 26 | 67.22 | .151 | 227 | 13.9 | NA | 2.31 | .28 | .006 | .56 | .55 | .017 | < .01 |
| 274744081304200 | 16.2 | 8.16 | 15 | 28.51 | 57.25 | .101 | 225 | 11.2 | 7.21 | 3.98 | .16 | .009 | 2.29 | 2.28 | .018 | < .01 |
| 274744081304200 | 15.2 | 7.39 | 13.3 | 26.77 | 59.7 | .101 | 204 | 2.82 | NA | 4.14 | .01 | .021 | 3.58 | 3.56 | .015 | < .01 |
| 274744081304200 | 14.5 | 6.86 | 12.9 | 25.02 | 55.77 | .092 | 190 | 2.25 | NA | 4.03 | .04 | .014 | 3.56 | 3.55 | < .01 | < .01 |
| 274744081304200 | 14.3 | 6.81 | 13.2 | 25.63 | 55.6 | .111 | 199 | 12.7 | NA | 2.39 | .02 | .009 | 1.38 | 1.37 | .025 | < .01 |
| 275256081275900 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | .02 | < .010 | .98 | E .97 | < .02 | NA |
| 275256081275900 | 7.62 | 5.2 | 12 | 18.7 | 38.3 | .060 | 136 | .57 | 7.02 | 2.00 | .02 | .011 | 1.50 | 1.49 | .011 | < .01 |
| 275256081275900 | 7.78 | 5.41 | 11.7 | 19.78 | 39.76 | .053 | 136 | .112 | 6.65 | 1.76 | .02 | .015 | 1.35 | 1.34 | < 0.1 | < .01 |
| 275256081275900 | 7.25 | 5.2 | 11.2 | 17.36 | 36.03 | .051 | 127 | .2 | 6.92 | 1.35 | .03 | .006 | .9874 | .98 | < 0.1 | < .01 |

[1] Unfiltered.
[2] Calculated as [(nitrite plus nitrate) – nitrite].

**Appendix 3.** Laboratory results for detected pesticides and degradates in the lake samples.

[All values in micrograms per liter. Shaded columns indicate duplicate analyses conducted at separate laboratories that typically were not included in summaries in the report. Full chemical names for abbreviated pesticide compounds are listed in table 2. Degradates are shown in italics. NL, USGS National Water Quality Laboratory; KS, USGS Organic Geochemistry Research Lab; NA, not analyzed; E, estimated value; L., Lake; ft, feet; < less than]

| Station identifier | Station name | Short name | Date | Time | Depth[1] | 2,4-D | 2,4-D Methyl Ester | *Aldicarb sulfone* | *Aldicarb sulfoxide* | Atrazine-NL | Atrazine-KS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 02266923 | Swim Lake near Alcoma | Swim L. | 12/09/03 | 1120 | Top | < 0.0218 | <0.0086 | E 0.26 | E 0.67 | E 0.004 | 0.025 |
| 02266923 | Swim Lake near Alcoma | Swim L. | 03/23/04 | 1050 | Top | <.0218 | <.0086 | E .33 | E .54 | <.009 | <.025 |
| 02266923 | Swim Lake near Alcoma | Swim L. | 06/08/04 | 1125 | Bottom (19 ft) | <.0218 | <.0086 | E .025 | E .11 | <.009 | <.025 |
| 02266923 | Swim Lake near Alcoma | Swim L. | 06/08/04 | 1130 | Top | <.0218 | <.0086 | E .018 | E .074 | <.009 | <.025 |
| 02266924 | Swim Lake near Alcoma | Swim L. | 09/15/04 | 1005 | Top | <.0218 | <.0086 | E .101 | E .18 | <.009 | <.025 |
| 02270655 | Lake Lynn near De Soto City | L. Lynn | 12/08/03 | 1155 | Top | E .0113 | <.0086 | <.02 | E .026 | E .0063 | <.025 |
| 02270655 | Lake Lynn near De Soto City | L. Lynn | 03/22/04 | 1050 | Top | <.0218 | <.0086 | <.02 | <.0082 | E .0067 | <.025 |
| 02270655 | Lake Lynn near De Soto City | L. Lynn | 06/07/04 | 1000 | Bottom (37 ft) | .138 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 02270655 | Lake Lynn near De Soto City | L. Lynn | 06/07/04 | 1010 | Top | .109 | <.0086 | <.02 | <.0082 | E .0056 | <.025 |
| 02270656 | Lake Lynn near De Soto City | L. Lynn | 09/14/04 | 1035 | Top | .023 | <.0086 | <.02 | <.0082 | E .0046 | <.025 |
| 02270700 | Lake Annie near Lake Placid | L. Annie | 12/20/04 | 1015 | Top | <.038 | <.016 | <.018 | <.022 | <.008 | <.025 |
| 02270700 | Lake Annie near Lake Placid | L. Annie | 03/23/05 | 1150 | Top | <.04 | <.016 | <.02 | <.022 | E .007 | <.025 |
| 02270700 | Lake Annie near Lake Placid | L. Annie | 06/22/05 | 1300 | Top | <.04 | <.016 | <.02 | <.022 | <.008 | <.025 |
| 02270700 | Lake Annie near Lake Placid | L. Annie | 09/06/05 | 1400 | Top | <.04 | <.016 | <.02 | <.022 | E .005 | <.025 |
| 273323081290800 | Lake Denton near Avon Park | L. Denton | 12/08/03 | 1505 | Top | .144 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 273323081290800 | Lake Denton near Avon Park | L. Denton | 03/22/04 | 1440 | Top | 1.16 | .0359 | <.02 | <.0082 | <.009 | <.025 |
| 273323081290800 | Lake Denton near Avon Park | L. Denton | 06/07/04 | 1345 | Bottom (45 ft) | .0458 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 273323081290800 | Lake Denton near Avon Park | L. Denton | 06/07/04 | 1350 | Top | <.0218 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 273323081290800 | Lake Denton near Avon Park | L. Denton | 09/14/04 | 1355 | Top | .0621 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 273850081310800 | Pabor Lake near Avon Park | Pabor L. | 12/20/04 | 1420 | Top | <.038 | <.016 | <.018 | <.022 | <.008 | <.025 |
| 273850081310800 | Pabor Lake near Avon Park | Pabor L. | 03/23/05 | 815 | Top | <.04 | <.016 | <.02 | <.022 | E .015 | <.025 |
| 273850081310800 | Pabor Lake near Avon Park | Pabor L. | 06/22/05 | 850 | Top | <.04 | <.016 | <.02 | <.022 | .011 | <.025 |
| 273850081310800 | Pabor Lake near Avon Park | Pabor L. | 09/07/05 | 1300 | Top | <.04 | <.016 | <.02 | <.022 | E .013 | <.025 |
| 274648081315100 | Lake Moody near Frostproof | L. Moody | 12/21/04 | 920 | Top | <.038 | <.016 | <.018 | <.022 | <.008 | <.025 |
| 274648081315100 | Lake Moody near Frostproof | L. Moody | 03/22/05 | 1310 | Top | <.04 | <.016 | <.02 | <.022 | <.008 | <.025 |
| 274648081315100 | Lake Moody near Frostproof | L. Moody | 06/21/05 | 1400 | Top | <.04 | <.016 | <.02 | <.022 | <.008 | <.025 |
| 274648081315100 | Lake Moody near Frostproof | L. Moody | 09/06/05 | 930 | Top | <.04 | <.016 | <.02 | <.022 | E .004 | <.025 |
| 274744081304200 | Lake Leonore near Frostproof | L. Leonore | 12/21/04 | 1200 | Top | <.038 | <.016 | .028 | .075 | <.008 | <.025 |
| 274744081304200 | Lake Leonore near Frostproof | L. Leonore | 03/22/05 | 930 | Top | <.04 | <.016 | .06 | .102 | <.008 | <.025 |
| 274744081304200 | Lake Leonore near Frostproof | L. Leonore | 06/21/05 | 900 | Top | <.04 | <.016 | E .02 | .079 | <.008 | <.025 |
| 274744081304200 | Lake Leonore near Frostproof | L. Leonore | 09/07/05 | 850 | Top | <.04 | <.016 | <.02 | <.022 | <.008 | <.025 |
| 275256081275900 | Lake Aurora at Hesperides | L. Aurora | 12/09/03 | 900 | Top | <.0218 | <.0086 | <.02 | <.0082 | E .0038 | <.025 |
| 275256081275900 | Lake Aurora at Hesperides | L. Aurora | 03/23/04 | 805 | Top | <.0218 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 275256081275900 | Lake Aurora at Hesperides | L. Aurora | 06/08/04 | 810 | Bottom (23 ft) | <.0218 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 275256081275900 | Lake Aurora at Hesperides | L. Aurora | 06/08/04 | 815 | Top | <.0218 | <.0086 | <.02 | <.0082 | <.009 | <.025 |
| 275256081275900 | Lake Aurora at Hesperides | L. Aurora | 09/15/04 | 810 | Top | <.0218 | <.0086 | <.02 | <.0082 | <.009 | <.025 |

[1]Top samples were collected about 5 feet below the lake surface. Bottom samples were collected near the lake bottom at depth shown.

**Appendix 3.** Laboratory results for detected pesticides and degradates in the lake samples—Continued.

[All values in micrograms per liter. Shaded columns indicate duplicate analyses conducted at separate laboratories that typically were not included in summaries in the report. Full chemical names for abbreviated pesticide compounds are listed in table 2. Degradates are shown in italics. NL, USGS National Water Quality Laboratory; KS, USGS Organic Geochemistry Research Lab; NA, not analyzed; E, estimated value; L., Lake; ft, feet; < less than]

| Short name | Bromacil-NL | Bromacil-KS | CPMU | Diuron-NL | Diuron-KS | *DCPU* | *DCPMU* | Imazquin | Imidacloprid | Metalaxyl | Norflurazon | *Demethyl-norflurazon* | Oxamyl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Swim L. | E 0.062 | < .025 | < 0.02 | 0.07 | < 0.2 | < 0.06 | E 0.0215 | < 0.016 | < 0.0068 | < 0.02 | E 5.3 | E 17.1 | < 0.012 |
| Swim L. | E .042 | < .025 | < .02 | .057 | < .2 | < .06 | .0301 | < .016 | < .0068 | .0564 | E 3.3 | E 14.97 | < .012 |
| Swim L. | E .018 | < .025 | < .02 | .023 | < .2 | < .06 | E .008 | < .016 | < .0068 | E .0102 | E .79 | 2.58 | < .012 |
| Swim L. | E .018 | < .025 | < .02 | .02 | < .2 | < .06 | E .0088 | < .016 | < .0068 | E .009 | E .46 | 1.99 | < .012 |
| Swim L. | < .033 | < .025 | < .02 | .046 | < .2 | < .06 | < .03 | < .016 | .0162 | .03 | E 2.27 | E 5.99 | < .012 |
| L. Lynn | E .31 | .45 | < .02 | < .131 | < .2 | < .03 | < .06 | < .016 | < .0068 | < .02 | E .27 | .858 | < .012 |
| L. Lynn | E .21 | .26 | < .02 | < .015 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .074 | .629 | < .012 |
| L. Lynn | E .15 | .2 | < .02 | < .015 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .13 | .743 | < .012 |
| L. Lynn | E .046 | .08 | < .02 | < .015 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .008 | .082 | < .012 |
| L. Lynn | E .066 | .06 | < .02 | E .009 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .081 | .262 | < .012 |
| L. Annie | < .018 | < .025 | < .04 | .015 | < .2 | < .06 | < .03 | < .036 | < .02 | < .012 | < .02 | < .03 | < .03 |
| L. Annie | < .02 | < .05 | < .04 | < .01 | < .2 | < .06 | < .03 | < .04 | < .02 | < .01 | < .02 | < .03 | < .03 |
| L. Annie | < .02 | < .025 | < .04 | < .01 | < .2 | NA | NA | < .04 | < .02 | < .01 | < .02 | NA | < .03 |
| L. Annie | < .02 | < .025 | < .04 | .02 | < .2 | NA | NA | < .04 | < .02 | < .01 | < .02 | NA | < .03 |
| L. Denton | E .091 | .09 | < .02 | .015 | < .2 | < .06 | E .004 | < .016 | < .0068 | < .02 | E .052 | .038 | < .012 |
| L. Denton | E .034 | .04 | < .02 | < .015 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .014 | .038 | < .012 |
| L. Denton | E .026 | .03 | < .02 | < .015 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .009 | .031 | < .012 |
| L. Denton | E .017 | < .025 | < .02 | < .015 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .004 | .014 | < .012 |
| L. Denton | E .037 | < .025 | < .02 | E .011 | < .2 | < .06 | < .03 | < .016 | < .0068 | < .02 | E .047 | .078 | < .012 |
| Pabor L. | < .018 | < .025 | < .04 | .075 | < .2 | < .06 | E .021 | E .021 | < .02 | < .012 | .582 | E 1.16 | < .03 |
| Pabor L. | < .02 | < .05 | < .04 | .07 | < .2 | < .06 | E .018 | < .04 | < .02 | < .01 | .31 | 1.04 | < .03 |
| Pabor L. | < .02 | < .025 | < .04 | .05 | < .2 | NA | NA | < .04 | < .02 | < .01 | .15 | NA | < .03 |
| Pabor L. | < .02 | < .025 | < .04 | 1.79 | 3.81 | NA | NA | < .04 | < .02 | < .01 | .83 | NA | < .03 |
| L. Moody | .247 | .39 | < .04 | .041 | < .2 | < .06 | < .03 | < .036 | < .02 | .042 | .179 | .230 | E .036 |
| L. Moody | .34 | .51 | < .04 | .04 | < .2 | < .06 | E .0094 | < .04 | < .02 | .03 | .18 | .302 | < .03 |
| L. Moody | .38 | .52 | < .04 | .07 | < .2 | NA | NA | < .04 | < .02 | .03 | .05 | NA | < .03 |
| L. Moody | .71 | .61 | < .04 | .08 | < .2 | NA | NA | < .04 | < .02 | .03 | .21 | NA | < .03 |
| L. Leonore | 4.87 | 3.53 | < .04 | .06 | < .2 | < .06 | < .033 | < .036 | < .02 | .18 | .771 | .606 | < .03 |
| L. Leonore | < .02 | 6.29 | < .04 | .04 | < .2 | < .06 | E .016 | < .04 | < .02 | .13 | .68 | .575 | < .03 |
| L. Leonore | E 3.35 | 2.48 | < .04 | .09 | < .2 | NA | NA | < .04 | < .02 | .11 | .68 | NA | < .03 |
| L. Leonore | E 3.86 | 2.7 | < .04 | E .06 | < .2 | NA | NA | < .04 | < .02 | E .09 | .37 | NA | < .03 |
| L. Aurora | E .52 | .76 | < .02 | .021 | < .2 | < .03 | < .03 | < .016 | < .0068 | < .02 | E .17 | .315 | < .012 |
| L. Aurora | E .71 | .88 | < .02 | .018 | < .2 | < .06 | E .011 | < .016 | < .0068 | .0665 | E .16 | .358 | E .009 |
| L. Aurora | E .67 | .95 | < .02 | E .014 | < .2 | < .06 | < .03 | < .016 | < .0068 | .0484 | E .092 | .287 | < .012 |
| L. Aurora | E .84 | .83 | < .02 | .016 | < .2 | < .06 | E .0077 | < .016 | < .0068 | .0499 | E .043 | .208 | < .012 |
| L. Aurora | E .366 | .43 | < .02 | .021 | < .2 | < .06 | < .03 | < .016 | < .0068 | .04 | E .088 | .178 | < .012 |

**Appendix 3.** Laboratory results for detected pesticides and degradates in the lake samples.—Continued

[All values in micrograms per liter. Shaded columns indicate duplicate analyses conducted at separate laboratories that typically were not included in summaries in the report. Full chemical names for abbreviated pesticide compounds are listed in table 2. Degradates are shown in italics. NL, USGS National Water Quality Laboratory; KS, USGS Organic Geochemistry Research Lab; NA, not analyzed; E, estimated value; L., Lake; ft, feet; < less than]

| Short name | Simazine-KS | Tebuthiuron | Hydroxyatrazine-NL (OIET) | Hydroxyatrazine-KS (OIET) | DEA-NL (CIAT) | DEHA-KS (HDEA) | Hydroxysimazine-KS (HS) | DDA-KS (CAAT) | DDA-NL (CAAT) | DIA-KS (CEAT) | DIA-NL (CEAT) | DIHA-KS (HDIA) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Swim L. | 0.06 | <0.0062 | <0.008 | < 0.025 | < 0.028 | < 0.025 | < 0.025 | 0.13 | < 0.01 | 0.14 | E 0.071 | < 0.025 |
| Swim L. | .04 | <.0062 | <.008 | < .025 | < .028 | < .025 | .27 | .14 | E .02 | .1 | E .051 | < .025 |
| Swim L. | .04 | <.0062 | <.008 | < .025 | < .028 | < .025 | .11 | .24 | E .034 | .1 | E .061 | < .025 |
| Swim L. | .04 | <.0062 | <.008 | < .025 | < .028 | < .025 | .11 | .27 | E .03 | .11 | E .069 | < .025 |
| Swim L. | < .025 | <.0062 | <.008 | < .025 | < .0282 | < .025 | .13 | .18 | E .043 | .05 | E .022 | < .025 |
| L. Lynn | .03 | <.0062 | E .01 | < .025 | < .028 | < .025 | < .025 | .14 | E .009 | .05 | E .026 | < .025 |
| L. Lynn | < .025 | <.0062 | E .0093 | < .025 | < .028 | < .025 | .04 | .09 | E .034 | .03 | E .017 | < .025 |
| L. Lynn | < .025 | <.0062 | E .013 | < .025 | < .028 | < .025 | < .025 | .14 | E .014 | .05 | E .016 | < .025 |
| L. Lynn | < .025 | <.0062 | E .0065 | < .025 | E .0056 | < .025 | < .025 | .25 | E .019 | .1 | E .028 | < .025 |
| L. Lynn | < .025 | <.0062 | E .012 | < .025 | < .0282 | < .025 | < .025 | .14 | E .043 | .03 | E .017 | < .025 |
| L. Annie | < .025 | .03 | <.032 | < .025 | < .028 | < .025 | < .025 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Annie | < .025 | .039 | <.032 | < .025 | < .03 | < .025 | < .05 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Annie | < .025 | .027 | <.032 | < .025 | < .03 | < .025 | < .025 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Annie | < .025 | E .023 | <.032 | < .025 | < .03 | < .025 | < .025 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Denton | < .025 | <.0062 | <.008 | < .025 | < .028 | < .025 | < .025 | .12 | < .01 | .03 | E .017 | < .025 |
| L. Denton | < .025 | <.0062 | <.008 | < .025 | < .028 | < .025 | < .025 | .07 | E .01 | < .025 | E .008 | < .025 |
| L. Denton | < .025 | <.0062 | <.008 | < .025 | < .028 | < .025 | < .025 | .19 | E .02 | < .025 | E .014 | < .025 |
| L. Denton | < .025 | <.0062 | <.008 | < .025 | < .028 | < .025 | < .025 | .15 | E .022 | < .025 | E .011 | < .025 |
| L. Denton | < .025 | <.0062 | <.008 | < .025 | < .0282 | < .025 | < .025 | .09 | E .044 | < .025 | E .007 | < .025 |
| Pabor L. | .04 | <.026 | <.032 | < .025 | < .028 | < .025 | < .025 | < .025 | < .04 | < .025 | <.08 | < .025 |
| Pabor L. | .04 | <.026 | <.032 | < .025 | < .03 | < .025 | .5 | < .025 | < .04 | < .025 | E .02 | < .025 |
| Pabor L. | .03 | <.026 | <.032 | < .025 | < .03 | < .025 | < .025 | < .025 | < .04 | .03 | E .02 | < .025 |
| Pabor L. | < .025 | <.026 | <.032 | < .025 | < .03 | < .025 | < .025 | < .025 | < .04 | < .025 | NA | < .025 |
| L. Moody | < .025 | <.026 | E .013 | < .025 | < .028 | < .025 | < .025 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Moody | .03 | <.026 | E .009 | < .025 | < .03 | < .025 | < .05 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Moody | .025 | <.026 | <.032 | < .025 | < .03 | < .025 | .94 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Moody | .025 | <.026 | <.032 | < .025 | < .03 | < .025 | < .025 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Leonore | .03 | E .006 | <.032 | < .025 | < .028 | < .025 | < .025 | < .025 | < .04 | < .025 | < .08 | < .025 |
| L. Leonore | .05 | <.026 | <.032 | < .025 | < .03 | < .025 | .26 | < .025 | < .04 | < .025 | E .01 | < .025 |
| L. Leonore | .04 | <.026 | <.032 | < .025 | < .03 | < .025 | < .025 | .05 | < .04 | < .025 | E .01 | < .025 |
| L. Leonore | .04 | <.026 | <.032 | < .025 | < .03 | < .025 | .46 | < .025 | < .04 | < .025 | E .01 | < .025 |
| L. Aurora | < .025 | E .0038 | <.008 | < .025 | < .028 | < .025 | < .025 | < .025 | < .01 | < .025 | <.044 | < .025 |
| L. Aurora | < .025 | <.0062 | E .009 | < .025 | < .028 | < .025 | .26 | < .025 | < .01 | < .025 | <.044 | < .025 |
| L. Aurora | < .025 | <.0062 | E .011 | < .025 | < .028 | < .025 | < .025 | < .025 | < .04 | < .025 | <.01 | < .025 |
| L. Aurora | < .025 | <.0062 | E .013 | < .025 | < .028 | < .025 | < .025 | < .025 | < .04 | < .025 | <.01 | < .025 |
| L. Aurora | < .025 | <.0062 | <.01 | < .025 | < .0282 | < .025 | .21 | < .025 | < .04 | < .025 | E .004 | < .025 |

**Appendix 4.** Summary statistics of detected pesticide and degradate concentrations by lake.

[The samples were collected at a depth of 5 feet below the lake surface. Four samples were analyzed per lake for all compounds, except where noted. NL, U.S. Geological Survey National Water-Quality Laboratory; LRL, laboratory reporting level; ND, not determined; KS, U.S. Geological Survey Organic Geochemistry Laboratory]

| Compound | Summary of samples yielding detectable concentrations (micrograms per liter) | | | | |
| --- | --- | --- | --- | --- | --- |
| | No. of samples with detections | Sum of detected concentrations | Median detected concentration | Minimum detected concentration | Maximum detected concentration |
| **Lake Annie ("control")** | | | | | |
| Atrazine-NL | 2 | 0.012 | ND | 0.005 | 0.007 |
| Diuron-NL | 2 | .035 | ND | .015 | .020 |
| Tebuthiuron | 4 | .119 | .029 | .023 | .039 |
| **Lake Aurora[2]** | | | | | |
| Atrazine-NL | 1 | .004 | ND | ND | ND |
| Bromacil-KS | 5 | 3.85 | .83 | .43 | .95 |
| Bromacil-NL | 5 | 3.11 | .670 | .366 | .840 |
| DIA-NL | 1 | .004 | ND | ND | ND |
| DCPMU-NL | 2 | .019 | ND | .008 | .011 |
| Diuron-NL | 5 | .090 | .018 | .014 | .021 |
| Demethyl norflurazon | 5 | 1.35 | .287 | .178 | .358 |
| Hydroxysimazine-KS | 2 | .470 | ND | .210 | .260 |
| Metalaxyl | 4 | .205 | .049 | .04 | .067 |
| Norflurazon | 5 | .553 | .092 | .043 | .170 |
| HA-NL | 3 | .033 | .011 | .009 | .013 |
| Oxamyl | 1 | .009 | ND | ND | ND |
| Tebuthiuron | 1 | .004 | ND | ND | ND |
| **Lake Denton[2]** | | | | | |
| 2,4-D | 4 | 1.41 | .103 | .046 | 1.16 |
| 2,4-D Methyl ester | 1 | .036 | ND | ND | ND |
| Bromacil-NL | 5 | .205 | .034 | .017 | .091 |
| Bromacil-KS | 3 | .16 | .04 | .03 | .09 |
| DDA-KS | 5 | .62 | .12 | .07 | .19 |
| DIA-NL | 5 | .057 | .011 | .007 | .017 |
| DCPMU-NL | 1 | .004 | ND | ND | ND |
| Diuron-NL | 2 | .026 | ND | .011 | .015 |
| Demethyl norflurazon | 5 | .198 | .038 | .014 | .078 |
| Norflurazon | 5 | .126 | .014 | .004 | .052 |
| **Lake Leonore** | | | | | |
| Aldicarb sulfone | 3 | .108 | .028 | .02 | .06 |
| Aldicarb sulfoxide | 3 | .256 | .079 | .075 | .102 |
| Bromacil-NL | 3 | 12.1 | 3.86 | 3.35 | 4.87 |
| Bromacil-KS | 4 | 15.0 | 3.12 | 2.48 | 6.29 |
| DDA-KS | 1 | .05 | ND | ND | ND |
| DIA-NL | 3 | .03 | .01 | .01 | .01 |
| DCPMU-NL | [1]1 | .016 | ND | ND | ND |
| Diuron-NL | 4 | .25 | .06 | .04 | .09 |
| Demethyl norflurazon | [1]2 | 1.18 | ND | .575 | .606 |
| Hydroxysimazine-KS | 2 | .72 | ND | .26 | .46 |
| Metalaxyl | 4 | .51 | .12 | .09 | .18 |
| Norflurazon | 4 | 2.50 | .68 | .37 | .771 |
| Simazine-KS | 4 | .16 | .04 | .03 | .05 |
| Tebuthiuron | 1 | .006 | ND | ND | ND |
| **Lake Lynn[2]** | | | | | |
| 2,4-D | 4 | .281 | .066 | .011 | .138 |
| Aldicarb sulfoxide | 1 | .026 | ND | ND | ND |
| Atrazine-NL | 4 | .023 | .006 | .005 | .007 |
| Bromacil-NL | 5 | .782 | .15 | .046 | .31 |
| Bromacil-KS | 5 | 1.05 | .20 | .06 | .45 |
| DDA-KS | 5 | .76 | .14 | .09 | .25 |
| DIA-NL | 5 | .104 | .017 | .016 | .028 |

**Appendix 4.** Summary statistics of detected pesticide and degradate concentrations by lake.—Continued

[The samples were collected at a depth of 5 feet below the lake surface. Four samples were analyzed per lake for all compounds, except where noted. NL, U.S. Geological Survey National Water-Quality Laboratory; LRL, laboratory reporting level; ND, not determined; KS, U.S. Geological Survey Organic Geochemistry Laboratory]

| Compound | Summary of samples yielding detectable concentrations (micrograms per liter) | | | | |
| --- | --- | --- | --- | --- | --- |
| | No. of samples with detections | Sum of detected concentrations | Median detected concentration | Minimum detected concentration | Maximum detected concentration |
| DEA-NL | 1 | .006 | ND | ND | ND |
| Diuron-NL | 1 | .009 | ND | ND | ND |
| Demethyl norflurazon | 5 | 2.57 | .629 | .082 | .858 |
| Hydroxysimazine-KS | 1 | .04 | ND | ND | ND |
| Norflurazon | 5 | .563 | .081 | .008 | .270 |
| HA-NL | 5 | .050 | .01 | .007 | .013 |
| Simazine-KS | 1 | .03 | ND | ND | ND |
| **Lake Moody** | | | | | |
| Atrazine-NL | 1 | .004 | ND | ND | ND |
| Bromacil-NL | 4 | 1.68 | .36 | .247 | .71 |
| Bromacil-KS | 4 | 2.03 | .515 | .39 | .61 |
| DCPMU-NL | [1]1 | .009 | ND | ND | ND |
| Diuron-NL | 4 | .231 | .056 | .04 | .08 |
| Demethyl norflurazon | [1]2 | .532 | ND | .23 | .302 |
| Hydroxysimazine-KS | 1 | .94 | ND | ND | ND |
| Metalaxyl | 4 | .132 | .03 | .03 | .042 |
| Norflurazon | 4 | .619 | .180 | .05 | .210 |
| HA-NL | 2 | .022 | ND | .009 | .013 |
| Oxamyl | 1 | .036 | ND | ND | ND |
| Simazine-KS | 1 | .03 | ND | ND | ND |
| **Parbor Lake** | | | | | |
| Atrazine-NL | 3 | .039 | .013 | .011 | .015 |
| DIA-NL | 2 | .04 | ND | .020 | .020 |
| DCPMU-NL | [1]2 | .039 | ND | .018 | .021 |
| Diuron-NL | 4 | 1.99 | .073 | .05 | 1.79 |
| Demethyl norflurazon | [1]2 | 2.20 | ND | 1.04 | 1.16 |
| Hydroxysimazine-KS | 1 | .50 | ND | ND | ND |
| Imazaquin | 1 | .021 | ND | ND | ND |
| Norflurazon | 4 | 1.87 | .446 | .15 | .830 |
| Simazine-KS | 3 | .11 | .04 | .03 | .04 |
| **Swim Lake[2]** | | | | | |
| Aldicarb sulfone | 5 | .734 | .101 | .018 | .33 |
| Aldicarb sulfoxide | 5 | 1.57 | .180 | .074 | .67 |
| Atrazine-NL | 1 | .004 | ND | ND | ND |
| Bromacil-NL | 4 | .14 | .03 | .018 | .062 |
| DDA-KS | 5 | .96 | .18 | .13 | .27 |
| DIA-NL | 5 | .274 | .061 | .022 | .071 |
| DCPMU-NL | 4 | .068 | .015 | .008 | .03 |
| Diuron-NL | 5 | .216 | .046 | .020 | .07 |
| Demethyl norflurazon | 5 | 42.6 | 5.99 | 1.99 | 17.1 |
| Hydroxysimazine-KS | 4 | .62 | .12 | .11 | .27 |
| Imidacloprid | 1 | .016 | ND | ND | ND |
| Metalaxyl | 4 | .106 | .020 | .009 | .056 |
| Norflurazon | 5 | 12.1 | 2.27 | .46 | 5.30 |
| Simazine-KS | 4 | .18 | .04 | .04 | .06 |

[1]A total of two samples were analyzed for this compound.

[2]A total of five samples were analyzed for each compound, including two samples, collected in the shallow and in the deep zone of the lake water column, during one sampling event.

**Appendix 5.**  Summary of parent pesticides and order of degradation for triazine pesticide degradates.

[Degradation pathways from Scribner and others (1999); see fig. 15 for generalized schematic of pathways]

| Triazine pesticide degradate [abbreviations, chemical name, alternative name(s)] | Parent pesticide compound | Order of degradation |
|---|---|---|
| Hydroxyatrazine (HA, OIET): 2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine | Atrazine | 1st |
| Deethylatrazine (DEA, CIAT): 2-Chloro-4-isopropylamino-6-amino-s-triazine | Atrazine, propazine | 1st |
| Deisopropylatrazine  (DIA, DES, CEAT): Deethylsimazine; 2-Chloro-6-ethylamino-4-amino-s-triazine | Atrazine, simazine, cyanazine (and several cyanazine degradates) | 1st |
| Hydroxysimazine (HS, OEET): 2-hydroxy-4,6-diethylamino-s-triazine | Simazine | 1st |
| Didealkylatrazine (DDA, CAAT ): Deethyldeisopropylatrazine; Chlordiamino-s-triazine | DIA, DEA, and the cyanazine degradates DCAC and CAC [indirectly, atrazine, simazine, propazine, and cyanazine] | 2nd to 4th |
| Deethylhydroxyatrazine (DEHA, HDEA, OIAT): 2-hydroxy-4-isopropylamino-6-amino-s-triazine | DEA, HA [indirectly, atrazine, propazine] | 2nd |
| Deisopropylhydroxyatrazine (DIHA, HDIA, OEAT): 2-hydroxy-6-ethylamino-4-amino-s-triaxine | DIA, HA, HS [indirectly, atrazine, simazine, and cyanazine] | 2nd |