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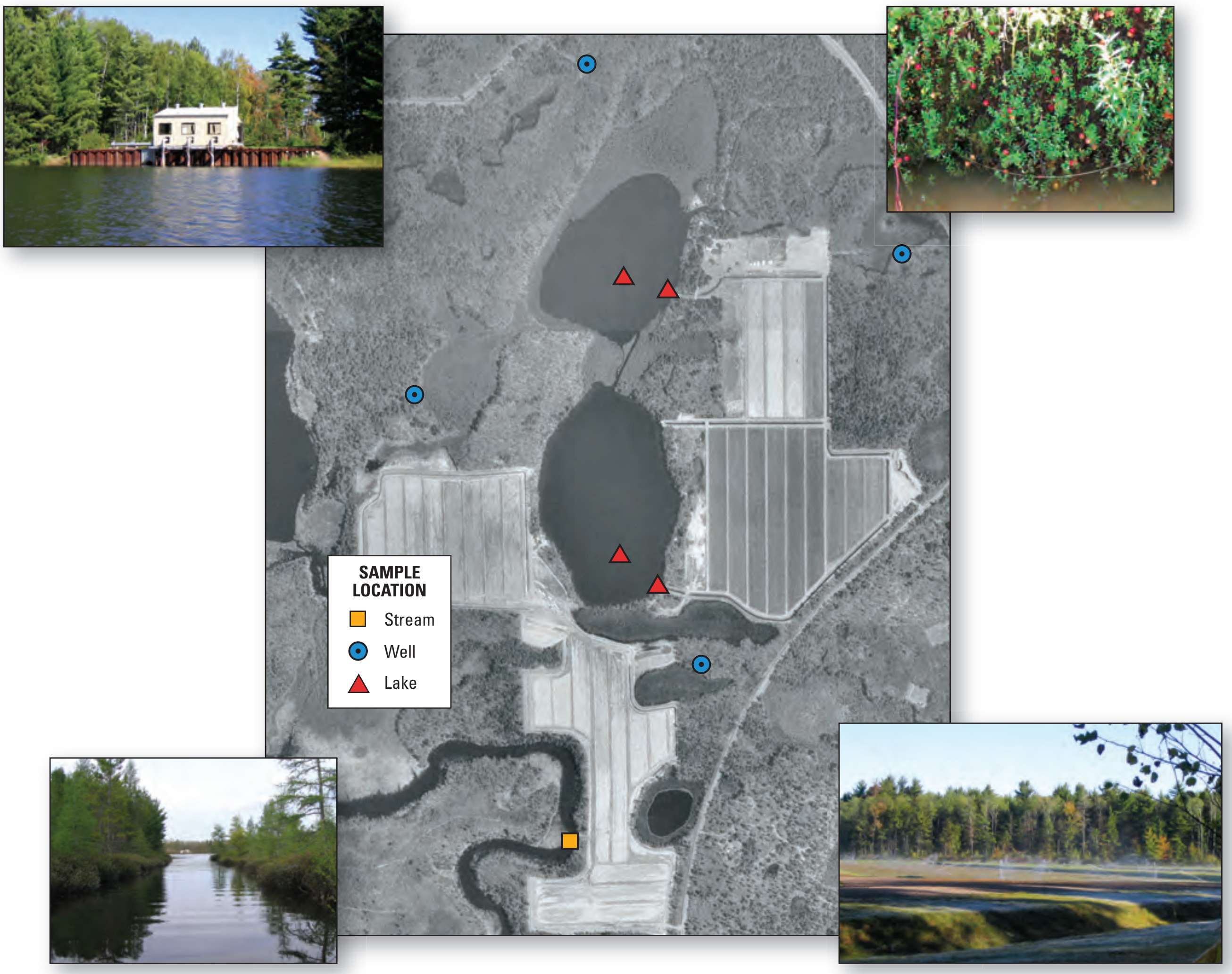
Pesticides in Surface Water, Bed Sediment, and Ground Water Adjacent to Commercial Cranberry Bogs, Lac du Flambeau Reservation, Vilas County, Wisconsin



Scientific Investigations Report 2005–5262

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

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By David A. Saad

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Gale A. Norton, Secretary

U.S. Geological Survey
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Cover photos:
Large aerial photo – U.S. Geological Survey aerial photograph from May 2000
Upper left – pump station
Upper right – cranberries
Lower right – cranberry bogs being irrigated for frost protection
Lower left – channel between Great and Little Corn Lakes looking south

Small photos taken by David A. Saad.

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Conversion Factors, Vertical Datum, and Abbreviated Units of Measurement

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
	Volume	
gallon (gal)	3.785	liter (L)
	Flow rate	
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year (m^3/yr)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram (kg)

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

°F=(1.8×°C)+32

Vertical coordinate information is referenced to sea level. In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929) – a geodetic datum derived from a general adjustment of the first-order level of both the United States and Canada, formerly called Sea Level Datum of 1929.

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

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

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

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L). Concentrations of chemical constituents in sediment are given either in grams per kilograms (g/kg) or micrograms per kilogram (µg/kg).

Pesticides in Surface Water, Bed Sediment, and Ground Water Adjacent to Commercial Cranberry Bogs, Lac du Flambeau Reservation, Vilas County, Wisconsin

By David A. Saad

Abstract

Pesticides commonly used on cranberries were detected in lakes, lake-bed sediment, and ground water of the Lac du Flambeau Reservation, Wisconsin adjacent to commercial cranberry bogs. Additionally, pesticides not typically used on cranberries were also detected.

In water samples from Little Trout and the Corn Lakes, which are adjacent to commercial cranberry bogs, five targeted pesticides commonly used on cranberries (2,4-D, carbaryl, diazinon, napropamide, and norflurazon) were detected. No targeted pesticides were detected in Ike Walton Lake (the reference lake), which is not adjacent to commercial cranberry bogs. The non-targeted pesticide atrazine (not commonly used on cranberries) was detected in all lakes during all sample periods, with precipitation the likely source. Non-targeted pesticides metolachlor and oryzalin were also detected in samples from Ike Walton and the Corn Lake, but the sources are not apparent. Pesticide concentrations measured in lake samples were far below levels considered lethal to fish.

In samples from the Trout River, which is used as a source of water to maintain lake levels in the Corn Lakes, the only pesticides detected were the non-targeted compounds atrazine and deethyl atrazine, indicating it was not a source of targeted compounds detected in the Corn Lakes. Only two pesticides (chlorpyrifos and metolachlor) were detected in bed-sediment samples collected from the lakes; chlorpyrifos from Little Trout Lake and metolachlor from the Corn Lakes. Four pesticides (the targeted compounds napropamide and norflurazon and the non-targeted compounds atrazine and deethyl atrazine) were detected in ground-water samples from two of four sampled monitor wells. The highest ground-water concentrations (up to 0.14 μg/L napropamide and 0.56 μg/L norflurazon) were measured in samples from the monitoring well located directly downgradient from the Corn Lakes and commercial cranberry operations. No pesticides were detected in samples from the reference well located upgradient from the Corn Lakes and cranberry operations. Further study is needed to identify additional pesticides as well as chronic effects on aquatic organisms to determine whether cranberry-related pesticides affect the lake ecosystems of the Lac du Flambeau Reservation.

Introduction

The Lac du Flambeau Indian Reservation is located in northern Wisconsin, covering parts of Vilas, Iron, and Oneida Counties, in an area known for its abundance of lakes (fig. 1). The Lac du Flambeau Band of Lake Superior Chippewa Indians are interested in maintaining the quality of the lakes in and around the Reservation and understanding which anthropogenic activities may have an effect on that quality because the health of the lakes is important to the economic and cultural health of the Tribe. In addition to being used for a variety of recreational purposes, the lakes of the Reservation support culturally important plant and animal species.

Three lakes of interest to the Tribe are Great and Little Corn Lakes and Little Trout Lake adjacent to commercial cranberry operations (fig. 1). The Tribe has designated these lakes and surrounding areas for protection because culturally important plants are collected from those locations (Gretchen Watkins, Lac du Flambeau Water-Resources Program, written commun., October 13, 2005). The Tribe is concerned that pesticides used in commercial cranberry operations are affecting the water quality and biology of these lakes as well as downgradient lakes and streams. Additionally, the Tribe is concerned that pesticides may be moving into ground water adjacent to commercial cranberry bogs.

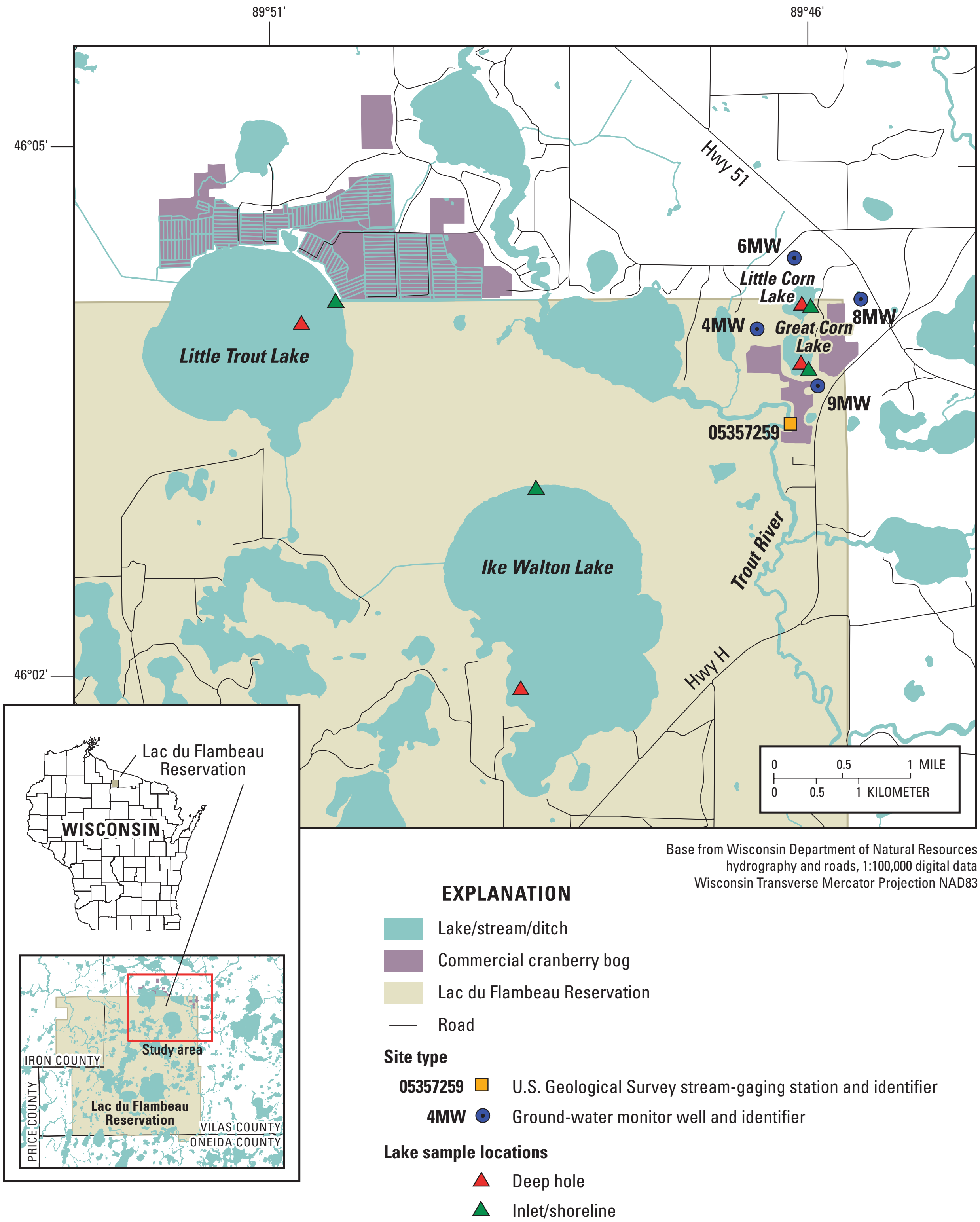

Figure 1. Lake, stream, and ground-water sample locations in the study area, Lac du Flambeau Reservation and vicinity, Vilas County, Wis.

During the fall of 2004 and spring of 2005, the U.S. Geological Survey (USGS), in cooperation with the Lac du Flambeau Band of Lake Superior Chippewa Indians, collected water and bed-sediment samples from four lakes, and water samples from the Trout River, and shallow ground-water monitor wells adjacent to commercial cranberry operations near the northeastern corner of the Reservation. Water and bed-sediment samples were analyzed for an extensive list of pesticides including those that are commonly used in commercial cranberry operations (referred to as targeted pesticides in this report). The objective of this study was to quantify targeted pesticide concentrations in lakes, bed sediments, and ground water adjacent to commercial cranberry operations. A reference lake (Ike Walton Lake) and a reference ground-water well (6MW) (sites away or upgradient from commercial cranberry bogs) (fig. 1) were included in this study to identify potential atmospheric or non-cranberry-related pesticide sources and measure background concentrations.

Purpose and Scope

This report summarizes the water- and bed-sediment-quality data collected for this study during fall 2004 and spring 2005. Pesticide data described in this report will focus on those pesticides that were detected in at least one sample. Pesticides included in analyses are listed in appendixes 1, 2, and 3.

Lake water-quality samples were collected during September and November 2004, and May 2005. These sampling times corresponded approximately to early harvest (lake water used to flood bogs creating low lake levels), post-harvest (flood waters returned to lakes creating high lake levels), and late spring (period after spring flooding associated with a variety of spring and pre-bloom pesticide applications and variable lake levels), respectively. Each lake-sampling time represents a period during which there was an exchange of water (and possibly pesticide residues) between the lakes of interest and the cranberry bogs.

Lake bed-sediment samples were collected during September 2004 and ground-water samples were collected during October 2004. Water from the Trout River is sometimes pumped into the Corn Lakes to maintain the lake levels during the flooding of the adjacent bogs and is a potential source of pesticides to the lakes. Stream samples from the Trout River were collected during November 2004 and May 2005.

Description of Study Area, Water Use and Movement, and Pesticide Use

The study area is located in the northeastern corner of the Lac du Flambeau Reservation in Vilas County, Wisconsin (fig. 1). Land surface in the study area is relatively flat to undulating and ranges in altitude from approximately 1,600 to 1,710 ft above sea level. Lake-surface altitude of the sampled lakes ranges from 1,616 ft for Ike Walton and the Corn Lakes, to 1,610 ft for Little Trout Lake. Land cover in the study area is mainly forests, lakes, wetlands, and commercial cranberry bogs. The area is underlain by Precambrian bedrock and approximately 100 to 200 ft of glacial deposits (Batten and Lidwin, 1996). The glacial deposits in the study area are mostly sand and gravel, and along with a relatively shallow water table (generally less than 10 ft below land surface), make the ground-water system potentially vulnerable to contamination from chemicals (such as pesticides) applied at the land surface.

Commercial cranberry growers require large amounts of water to grow and harvest cranberries. Water needs for commercial cranberry growing have been estimated to be 6 acre-feet per year per acre of planted vines (Roper and Planer, 1996). The water is used for a variety of purposes including irrigation, harvest, and frost protection. In the study area, growers utilize lakes and streams as their primary sources of water. Water is moved from lakes and streams to cranberry bogs using pump stations. Once in the bogs, a large amount of water is lost to evaporation and seepage to the ground-water system (Sentz and others, 2000). After use in the bogs, the remaining water drains back to the lakes and streams through the pump stations and drainage ditches (Sentz and others, 2000; Roper and Planer, 1996).

In 1999, the U.S. Army Corps of Engineers (Army Corps) conducted a detailed study of the Corn Lakes (Sentz and others, 2000). The study included a detailed water budget and lake-level monitoring of the Corn Lakes. The water budget is complex, but generally indicates that the Corn Lakes were the main water supply for the cranberry bogs east of the lakes and the Trout River (which flows north to northwest near the study area) was the main supply of water for the bogs south and west of the Corn Lakes (fig. 2). After use, water from the east bogs drains back to the Corn Lakes through pump stations along the east shorelines of Great and Little Corn Lakes. Water from the south and west bogs drains to adjacent wetlands to the west and to the Trout River. Water from the Trout River is also pumped into Great Corn Lake (through the south and west cranberry bogs) to maintain lake levels during cranberry production.

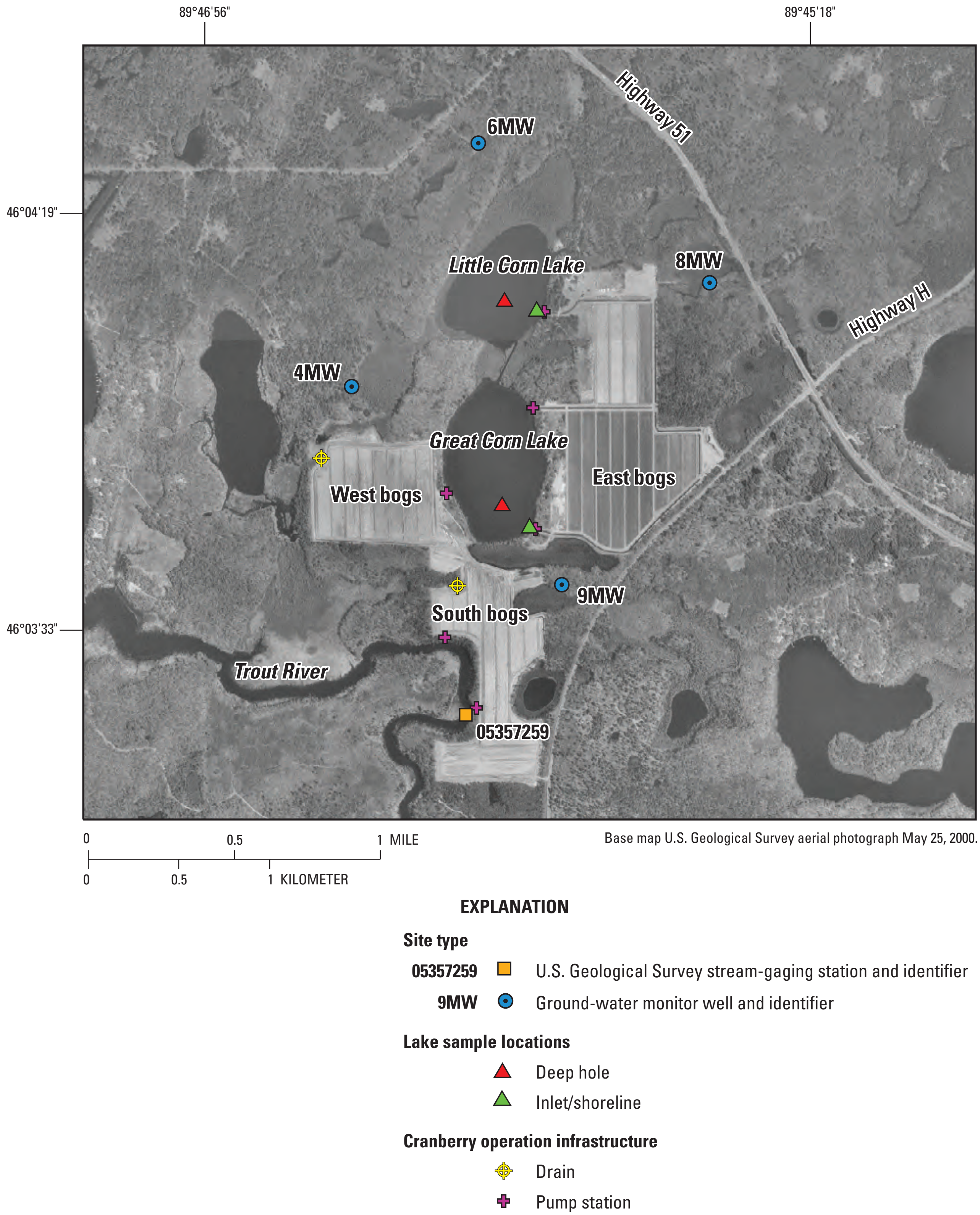

Figure 2. Lake, stream, and ground-water sample locations near the Corn Lakes, Vilas County, Wis.

The Corn Lakes water balance for 1999 showed that inflows to the lakes were mainly from cranberry bog return water and Trout River pumping (34.8 and 33.7 percent, respectively). The remaining inflows were from ground water (20.8 percent) and precipitation (10.7 percent). Most of the outflow from the lake was from pumpage into the cranberry bogs (68.9 percent). Other outflows included seepage to ground water and evaporation (23.0 and 8.1 percent, respectively).

The lake-level data collected during the Army Corps study helped to determine when large volumes of water flowed between the Corn Lakes and the cranberry bogs. This information (along with an understanding of the pesticide-application schedule) was important for determining when to sample the lakes. It was expected that if pesticide residues remained in the cranberry bogs for some time after application (weeks and months), measurable concentrations in the lakes would most likely be found during periods after the large volumes of used water was returned to the lakes (identified by lake-level increases). For the Corn Lakes in 1999, large decreases in lake levels corresponded to multiple spring flooding of the cranberry bogs during March and April, fall harvest flooding in October, and winter flooding in December. Large increases in lake levels generally corresponded to numerous spring flood returns and post-harvest flood returns in the fall. Additionally, pumping from the Trout River into the Corn Lakes accounted for numerous increases in lake levels during 1999.

A similar water budget was estimated for Little Trout Lake based on long-term average conditions (Sentz and others, 1996). Inflows were mainly from precipitation and cranberry bog returns (45 and 40 percent, respectively). Outflows were mainly from pumpage into cranberry bogs and evaporation (60 and 34 percent, respectively). Ground water provided the remaining inflows (15 percent) and outflows (6 percent).

The pesticides of most interest to the Tribe include those that are commonly used or were historically used in commercial cranberry production to control weeds, insects, and fungus. Some of these pesticides can be toxic to fish and other aquatic biota (Pesticide Action Network, 2005). It was expected that pesticide concentrations in the lakes would vary temporally, being associated with pesticide-use patterns and the periods of water exchange between the lakes and cranberry bogs. Pesticides are used on cranberries primarily during spring and summer (Mahr and others, 2005). Herbicides are applied to control a variety of weeds in late spring and throughout the summer as needed. Post-harvest herbicides are also applied for some weeds. Insecticides are used on cranberries primarily during spring and summer, with the exception of the blossom period to protect the pollinating insects. In Wisconsin, the blossom period begins in late June to early July and lasts 3 to 4 weeks (Roper and Planer, 1996). Fungicides are applied typically during the blossom period. Many of these pesticide applications require irrigation of the bogs soon after pesticide application. For some of the pesticides it is also recommended that applications not be done within 30 to 60 days of harvest (Mahr and others, 2005).

Sampling Locations, Strategy, and Methods

Sampling Locations

Sampling locations for this study included four lakes, a stream, and four ground-water monitor wells (figs. 1 and 2). Three of the lakes (Great Corn, Little Corn, and Little Trout) were selected because of their proximity and hydraulic connection to commercial cranberry operations. The fourth lake (Ike Walton) was chosen as a reference lake (not affected by cranberry operations) that was comparable in size and setting to Little Trout Lake. The Trout River (USGS stream-gaging station 05357259) was included in the study because it is an important source of water to the Corn Lakes and a potential source of contamination. Monitor wells around the Corn Lakes were sampled to determine if seepage from the cranberry bogs or the Corn Lakes was adding pesticides to the shallow ground-water system. Three of the monitor wells (4MW, 8MW, and 9MW) are downgradient from the Corn Lakes and one (9MW) is also directly downgradient from the cranberry bogs. One monitor well (6MW) is upgradient from the bogs and lakes and was selected as a reference well to represent ground-water quality conditions unaffected by cranberry operations.

Great and Little Corn Lakes are the smallest lakes sampled as part of this study and are connected by a small channel (fig. 2). The Corn Lakes are considered seepage lakes as there are no natural inlets or outlets and natural recharge and discharge from the lakes is by ground-water flow. Both lakes are connected to cranberry bogs by pump-station inlets at various locations along the shorelines. Little Corn Lake is upgradient from Great Corn Lake and covers an area of 26.0 acres with a maximum depth of 26 ft. Great Corn Lake covers an area of 32 acres with a maximum depth of 28 ft (Wisconsin Department of Natural

Table 1. Well depth, water levels, and lithology information for sampled monitor wells in the study area, Lac du Flambeau Reservation and vicinity, Vilas County, Wis.

[pvc, polyvinyl chloride; location of wells are shown in figure 1]

Well name	Well depth, in feet	Water level, in feet below land surface (October 12–13, 2004)	Well-construction materials	General lithology
4MW	10.5	4.97	steel	Fine to medium, silty, gravelly, sand
6MW	11.3	4.88	pvc	Fine to medium sand with gravel
8MW	18.0	6.55	pvc	Fine to medium sand
9MW	13.0	6.19	pvc	Fine to medium sand

Resources, 1995). Commercial cranberry development began in 1993 near the Corn Lakes. As of 1999, approximately 100 acres of commercial cranberry bogs surrounded the east, south, and west sides of the Corn Lakes (fig. 2; Sentz and others, 2000). Water samples from both lakes were collected at the deep hole (3.3 ft from top and 3.3 ft from bottom) and at 3.3-ft depth near pump station inlets near the southeastern corner of each lake. Bed-sediment samples were also collected near the southeastern corner of each lake near pump-station inlets.

Little Trout Lake is the deepest lake (maximum depth 98 ft) sampled as part of this study and covers about 978 acres (Wisconsin Department of Natural Resources, 1995). Little Trout Lake is considered a seepage lake although it has a small inlet and outlet. Much of the north shoreline of the lake is adjacent to approximately 880 acres of commercial cranberry bogs, the first of which were established in the 1940s. Pump stations and drainage ditches along this part of the lake allow water to flow between the bogs and the lake. Wetlands and forest surround the western, southern, and eastern parts of the lake. Water samples from Little Trout Lake were collected from the deep hole (3.3 ft from top and 3.3 ft from bottom) and at 3.3-ft depth near the inlet of a large drainage ditch along the northeastern corner of the lake (fig. 1). A bed-sediment sample was also collected near the inlet.

Ike Walton Lake was included in this study as a reference lake (not directly adjacent to, or downgradient from, commercial cranberry bogs). Ike Walton Lake is larger than Little Trout Lake (1,424 acres) but not as deep (maximum depth 61 ft; Wisconsin Department of Natural Resources, 1995). Ike Walton is also a seepage lake and is surrounded mostly by forest and wetland. There are no commercial cranberry bogs in the Ike Walton Lake watershed. The nearest commercial cranberry bogs are more than 1 mi away from the lake and are not hydraulically connected. Water samples from Ike Walton Lake were collected from the deep hole (3.3 ft from top and 3.3 ft from bottom) and at 3.3-ft depth near the north shore of the lake (fig. 1). The north shore was chosen for sampling because there were no representative inlets to the lake and this location was the closest to commercial cranberry operations. A bed-sediment sample was also collected near the north shore.

The Trout River was sampled near USGS streamgaging station 05357259 and adjacent to the pump-station intake that provides the water for maintaining the Corn Lakes water levels (fig. 2). At this location, the river is approximately 30 ft wide and 6 ft deep. Depth-integrated samples were collected from near the midpoint of the stream

Ground-water monitor wells sampled for this study (fig. 1) were installed in September and October 1998 by the Army Corps (Sentz and others, 2000). The wells ranged in depth from 10.5 to 18 ft and were constructed of polyvinyl chloride or steel (table 1). Depth to ground water ranged from 4.88 to 6.55 ft below land surface. A groundwater contour (water table) map for the Corn Lakes area was constructed by the Army Corps (Sentz and others, 2000). The water table varies depending on the level of water in the lakes and adjacent cranberry bogs, but indicates that the direction of ground-water flow is generally north to south through the Corn Lakes as well as east and west from the lakes. Monitor well 9MW is directly downgradient and adjacent to the cranberry bogs near Great Corn Lake. Wells 4MW and 8MW are located laterally downgradient from the Corn Lakes and are adjacent to the cranberry bogs (fig. 2). Water from these wells may show some effects from the commercial cranberry operations or from the nearby pesticide use through lake seepage. Well 6MW (the reference well) is located upgradient from the Corn Lakes and the cranberry bogs.

Table 2. Great Corn Lake stage measured intermittently during the period from September 2004 to May 2005 in the study area.

Date	Great Corn Lake stage, in feet above an arbitrary datum	Comments
9/28/04	5.85	
9/29/04	5.6	Lowered lake level due to irrigation for frost protection of bogs
10/13/04	5.02	Harvest period, bogs flooded with lake water
11/1/04	6.25	Post-harvest, water returned to lakes
5/25/05	5.1	

Sampling Strategy

The lakes sampled for this study were chosen to represent locations that were potentially affected and unaffected by commercial cranberry operations. Additionally, because pesticide use and water exchange between the lakes and cranberry bogs varies throughout the year, and because lakes can be stratified or mixed at different times during the year (fig. 3), lake-water samples were collected multiple times (September and November 2004, and May 2005) to provide a temporal view of water quality. Lake samples collected in late September were expected to represent lake-water quality before the post-harvest flood returns from the cranberry bogs. During this time, it was assumed that the lakes would still be stratified; therefore, samples were collected from all four lakes at the deep hole (top and bottom) and near the inlet/shoreline. Lake samples collected in early November were expected to represent lake-water quality after the post-harvest flood returns. Lakes were expected to be unstratified at this time, so samples were only collected from the deep hole (top) and near the inlets/shoreline. Samples were not collected from Little Corn Lake in November and May in an effort to conserve samples for the spring sampling period. September samples indicated that Great Corn Lake samples represented both Corn Lakes. At the Corn Lakes, cranberry harvest had been completed by the time of November sampling (Richard Teske, Teske Rayala Cranberry Co., oral commun., November 1, 2004) and lake levels had increased (lake levels intermittently monitored using the Great Corn Lake pump-station inlet gage, table 2). Therefore, the November lake samples represented water quality that was potentially affected by flood returns, Trout River pumping, or a combination of both. Late-spring samples in May were expected to represent post-spring flood return and pre-bloom pesticide applications. Because the lakes were expected to be re-stratified by late spring, May lake samples were collected from the deep hole (top and bottom) and near the inlets/shoreline from Great Corn, Little Trout, and Ike Walton Lakes.

Bed sediments, consisting of fine-grained particles and organic matter, are natural accumulators of hydrophobic organic contaminants, which include many pesticides (Shelton and Capel, 1994). Additionally, pesticides are generally more persistent in bed sediments because they are exposed to less sunlight (and, therefore, less photochemical reactions) and are less accessible for biotransformations (Barbash, 2003). For these reasons, the quality of bed sediments in the lakes was expected to have less temporal variability than lake-water quality. Bed-sediment samples were collected once from each of the four lakes during September 2004.

Water from the Trout River is used to flood the bogs south and west of the Corn Lakes, and also used to maintain the level of the lakes during the harvest. For these reasons, the Trout River was a potential source of pesticides to the Corn Lakes and was sampled in November 2004 and May 2005.

Similar to the lakes, monitor wells sampled for this study were chosen to represent locations that were potentially affected and unaffected by commercial cranberry operations. Ground-water quality can vary temporally, but ground-water movement is relatively slow compared to surface water. It was expected that ground-water quality would not vary as much, or as rapidly, as the lakes; therefore, monitor wells were only sampled once during October 2004.

Methods of Sample Collection

Lake-water samples for this study were typically collected using a Teflon Kemmerer sampler (Shelton, 1994). One lake sample, collected June 1, 2005, by Lac du Flambeau personnel to replace a sample destroyed during shipment to the lab, was collected directly into a sample bottle held approximately 2 ft below the lake surface. Stream-water samples were collected using a DH-81 sampler with a 1-L Teflon sample bottle (with a 5/16-in. nozzle).

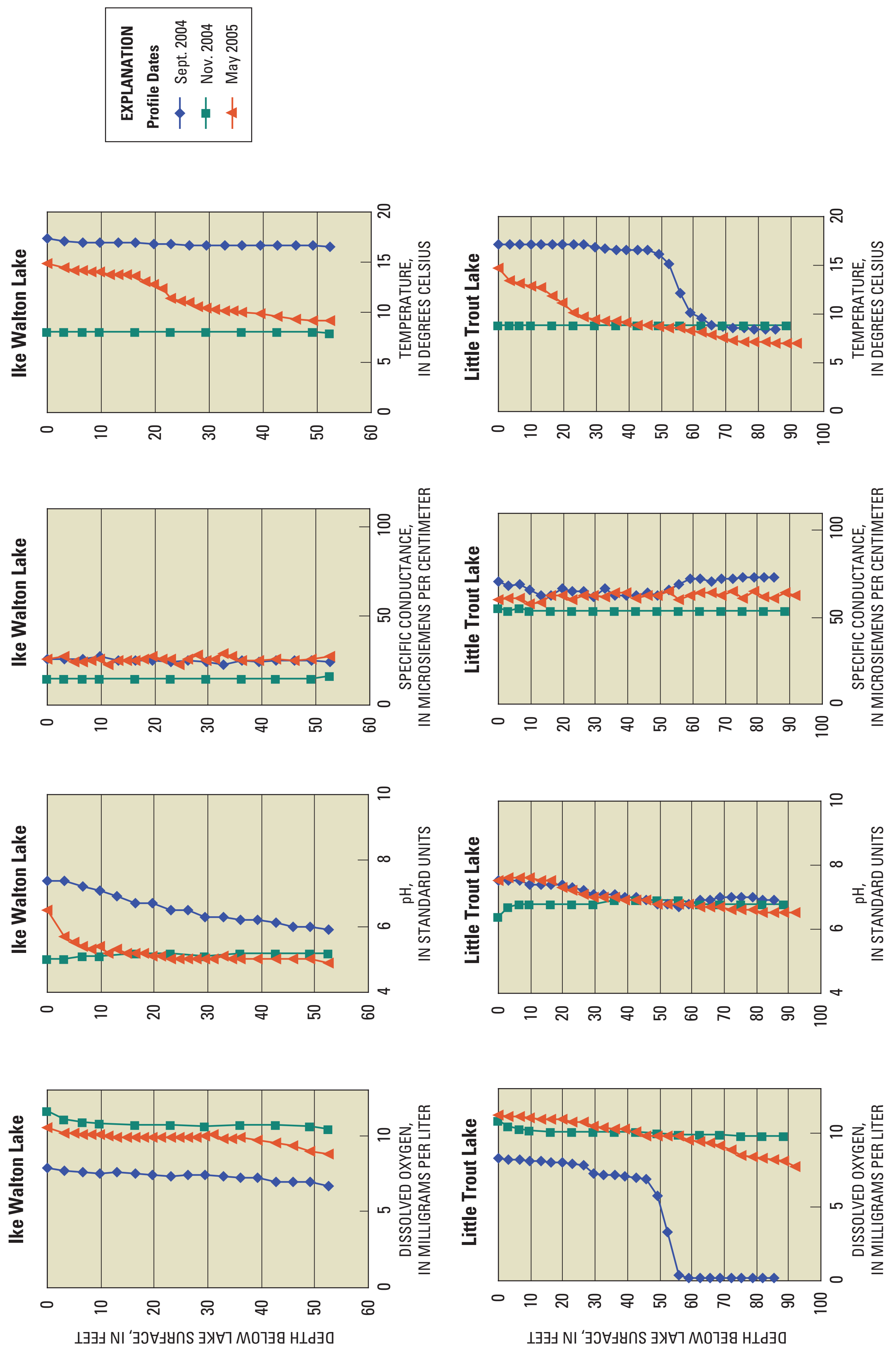

Figure 3. Vertical distribution of dissolved oxygen, pH, specific conductance, and temperature in Ike Walton, Little Trout, Little Corn, and Great Corn Lakes, Vilas County, Wis.

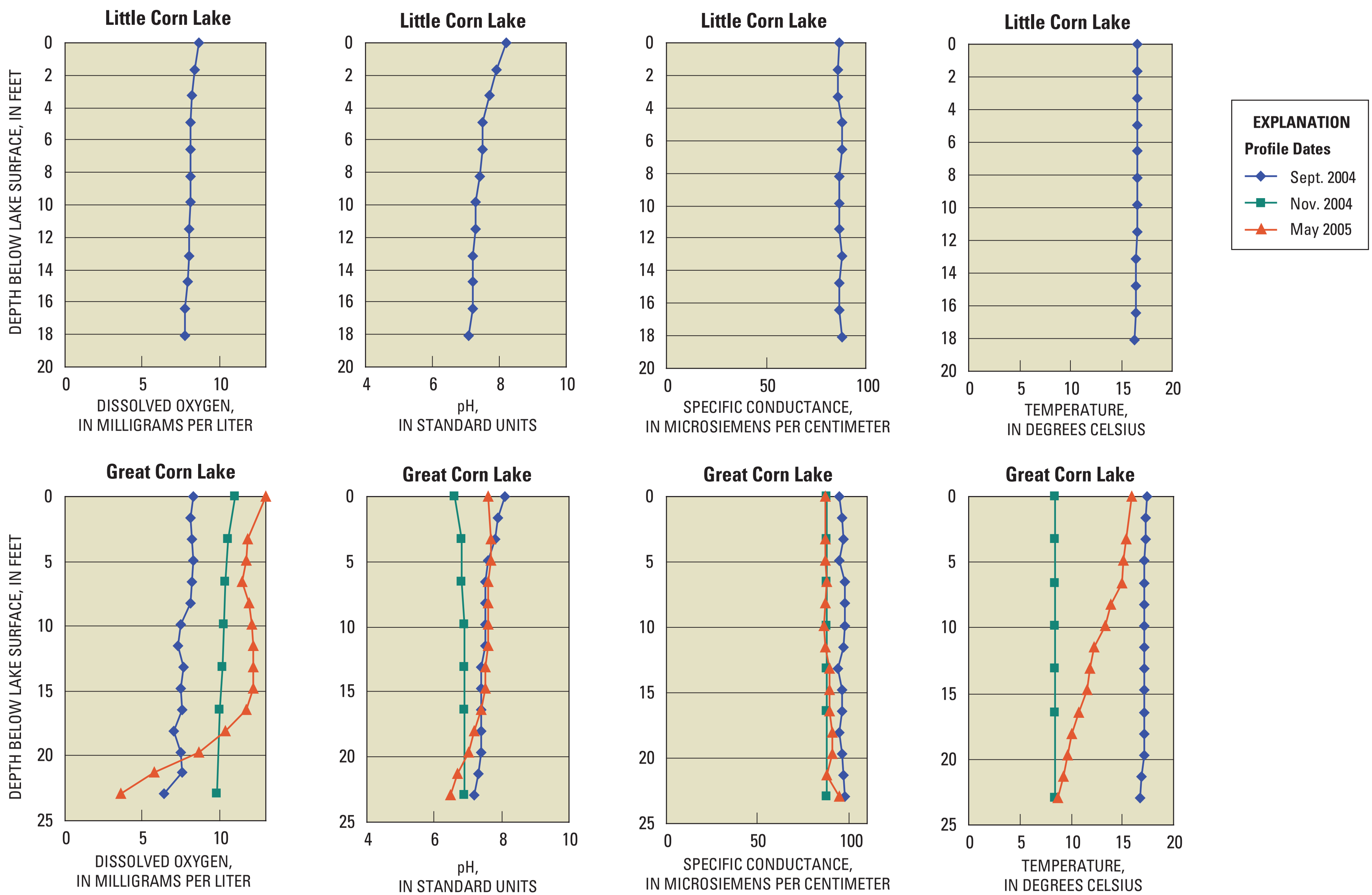

Figure 3. Vertical distribution of dissolved oxygen, pH, specific conductance, and temperature in Ike Walton, Little Trout, Little Corn, and Great Corn Lakes, Vilas County, Wis.—Continued

Table 3. Laboratory methods used for pesticide analyses in this study.

[%, percent; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory]

Pesticide schedule (medium)	Analysis method	Reference
Schedule 2001 (water)	C-18 solid-phase extraction and analysis using gas chromatography/mass spectrometry	Zaugg and others (1995); Madsen and others (2003)
Schedule 2060 (water)	Graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry	Furlong and others (2001)
Schedule 5503 (bed sediment)	Extraction of analytes from solids using 25% acetone in dichloromethane under pressure, followed by C-18 solid-phase extraction and analysis using gas chromatography/mass spectrometry	William Foreman, USGS, NWQL (written commun., August 10, 2005); Zaugg and others (1995); Sandstrom and others (2001)

Stream water was collected using a single depth-integrated sample at the approximate centroid of flow near the middle of the stream (Webb and others, 1999). Lake-bed sediment samples were collected using a Petite Ponar dredge sampler (Radtke, 1997). Three bed-sediment samples were collected from each inlet/shoreline location and composited into a stainless-steel pan. The bed-sediment material was then filtered through a 0.08-in. stainless-steel mesh screen using a stainless-steel spatula. Approximately 0.5 L of representative bed-sediment material was then placed in a 1-L wide-mouth jar using a stainless-steel spoon. Ground-water samples were collected using positive displacement pumps constructed of stainless steel and Teflon. Ground-water samples were collected after three casing volumes of water were removed and continuously monitored field parameters (dissolved oxygen, pH, specific conductance, and water temperature) stabilized (Koterba and others, 1995).

Sample equipment was cleaned, after each lake was sampled and between the collection of each well or stream sample, following USGS protocols for cleaning equipment used to collect organic compounds (Wilde, 2004). Sample equipment was initially cleaned using a solution of non-phosphate soap, followed by rinses with tap water and deionized water. Equipment was then rinsed with pesticide-grade methanol followed by a final rinse with pesticide-grade blank water. Equipment was wrapped in aluminum foil and stored in clean plastic bags between sites.

All water samples were poured or pumped directly into 1-L baked glass bottles and immediately chilled. Samples were shipped overnight to the USGS National Water Quality Laboratory (NWQL) within 2 days of collection. Bed-sediment samples were frozen prior to shipping. All water samples were filtered at the laboratory prior to analysis. Samples were collected, stored, and shipped using NWQL chain-of-custody protocols (U.S. Geological Survey, 2005).

Methods of Water-Quality Analysis

Field parameters (dissolved oxygen, pH, specific conductance, and water temperature) were measured using a Hydrolab water-quality sonde (Hach Environmental, 2005), calibrated daily. Field-parameter profiles were measured at the deep hole location in each lake at 1.7, 3.3, or 6.6 ft intervals depending on lake depth and amount of stratification. Lake-water clarity was measured using a Secchi disk.

The pesticides or metabolites of most interest to the Tribe include those that are commonly, or were historically, used on cranberries including azinphos-methyl, ethylenethiourea, 2,6-dichlorobenzamide, carbaryl, carbofuran, chlorothalonil, chlorpyrifos, diazinon, dichlobenil, napropamide, norflurazon, p,p’-DDT, p,p’-DDE, 2,4-D, glyphosate, sethoxydim, acephate, piperonyl butoxide, pyrethrins, copper hydroxide, and triforine. This targeted list includes the most heavily used pesticides on cranberries in Wisconsin (Wisconsin Agricultural Statistics Service, 1986, 1991, 1997). The group of targeted pesticides analyzed for was limited to only those that were included in USGS NWQL analytical schedules 2001, 2060, and 5503 (table 3, and appendixes 1, 2, and 3). Targeted pesticides from Schedule 2001 include azinphos-methyl, carbaryl, carbofuran, chlorpyrifos, diazinon, napropamide, and p,p’-DDE. Targeted pesticides from schedule 2060 include 2,4-D, carbaryl, carbofuran, chlorothalonil, and norflurazon. Schedule 5503 is for bed-sediment samples and includes azinphos-methyl, carbaryl, chlorpyrifos, and diazinon from the targeted list. Schedule 5503 is not an approved method by the USGS NWQL but it is currently (2005) going through the approval process. To aid in the analysis of pesticides in bed sediment, carbon content (total and inorganic, with organic being determined by difference) was measured using NWQL analytical schedule 2503 (Brenton, 1998).

Reporting levels for total and inorganic carbon are 0.1 and 0.2 g/kg, respectively. Pesticide and carbon data, for those constituents that were detected in at least one water or bed-sediment sample, are shown in tables 4 and 5.

Quality-assurance and quality-control samples were also collected as part of this study. These samples included two field blanks and a field spike for schedules 2001 and 2060. Additionally, one replicate each was collected for schedules 2001, 2060, and 5503. Field blank samples (consisting of pesticide-grade blank water passed through the cleaned sampling equipment) were collected after the September 2004 sampling of Little Trout Lake, and after the October 2004 sampling of monitor well 9MW. There were no pesticides detected in either of the field blank samples indicating that the cleaning process was sufficient.

Replicate lake samples were collected from Great Corn Lake (deep hole, top) during November 2004. Replicate bed-sediment samples were collected from Great Corn Lake (near the southeast inlet) during September 2004. Concentrations of most compounds in replicate samples were less than the reporting limit. Differences in detected compounds for replicate lake samples ranged from 0 to 15.4 percent and from 5.3 to 8.7 percent for replicate bed-sediment samples.

A replicate lake sample, collected during September 2004 from the deep hole (top) of Little Corn Lake, was spiked with known quantities of the pesticides included in schedules 2001 and 2060. Spike recoveries for all of the schedule-2001 compounds averaged 90 percent. Schedule-2001 recoveries averaged 125 percent for targeted compounds and 97 percent for compounds detected in water samples. Of the schedule-2001 targeted compounds, only azinphos-methyl (182 percent), carbaryl (144 percent) and carbofuran (144 percent) were outside of the typical recovery range (from 70 to 130 percent) for pesticides. Of the schedule-2001 compounds detected in water samples, only deethyl atrazine (27 percent) and carbaryl (144 percent) were outside of the typical recovery range. Spike recoveries for the schedule 2060 compounds averaged 97 percent. Schedule-2060 recoveries averaged 106 percent for targeted compounds and 116 percent for compounds detected in water samples. Of the schedule-2060 targeted compounds, only 2,4-D (159 percent), norflurazon (139 percent), and chlorothalonil (12 percent) recoveries were outside of the typical range. Of the compounds detected in water samples, only 2,4-D and norflurazon recoveries were outside the typical range. Concentrations given in this report were not adjusted on the basis of spike recoveries. However, results listed in table 4 for pesticides with a history of poor recoveries (such as deethyl atrazine and norflurazon) are marked with an “E” (estimated). Other estimated values shown in table 4 represent constituents that were detected at concentrations less than the NWQL reporting level, but greater than the laboratory detection limit (which is usually half of the reporting level) (Oblinger and others, 1999).

Pesticides in Surface Water, Bed Sediment, and Ground Water

Ten pesticides or metabolites plus caffeine were detected in water samples collected for this study (table 4). Two pesticides (chlorpyrifos and metolachlor) were detected in lake bed-sediment samples (table 5). Eight of the pesticides or metabolites detected in water samples are herbicides and two (carbaryl and diazinon) are insecticides. Of the pesticides detected in water samples, five are targeted compounds (2,4-D, carbaryl, diazinon, napropamide, and norflurazon) commonly used in commercial cranberry operations. One of the pesticides detected in bed-sediment samples is a targeted compound (chlorpyrifos, an insecticide), the other is a non-targeted herbicide (metolachlor) not commonly used in these operations.

Several non-target compounds detected in water samples are herbicides that are commonly used on corn (atrazine and metolachlor) or apple trees, strawberries, and raspberries (oryzalin) in Wisconsin (Wisconsin Agricultural Statistics Service, 1986, 1991, and 1997; National Center for Food and Agricultural Policy, 2005; Mahr and others, 2005). Atrazine, metolachlor, and oryzalin were detected in at least one sample collected from Ike Walton Lake (the reference lake). Atrazine or one of its metabolites (deethyl and hydroxyl atrazine) was detected in nearly all samples from the lakes and the Trout River and in two of the four ground-water samples (table 4). Atrazine concentrations were relatively uniform in all surface-water samples (fig. 4) and slightly lower than concentrations measured in rainfall (from 0.05 to 0.10 μg/L) near the study area in 1991 (Stamer and others, 1998). The uniform concentrations and widespread detections indicate that the likely source of atrazine detected in water samples from the study area is precipitation. Sources of metolachlor and oryzalin are not apparent and concentrations were only detected in water samples from Ike Walton and the Corn Lakes. Metolachlor has been detected in rainfall (Majewski and Capel, 1995; Stamer and others, 1998), but no rainfall data are available for oryzalin. In addition to agricultural uses, metolachlor and oryzalin are also known to be used

Table 4. Field measurements and concentrations of detected water-quality constituents for water samples collected from the study area.

[y, year; m, month; d, day; mg/L, milligrams per liter; --, no data or not applicable; µS/cm, microsiemens per centimeter; C, Celsius; µg/L, micrograms per liter; <, less than; E, estimated; CAS, Chemical Abstract Service registry number; locations of sampling stations are shown in figure 1; shaded areas highlight data from deep-hole bottom samples]

Station name	Sample date (yyyymmdd)	Sample time	Station number	Sampling depth (feet)	Depth of well (feet below land surface)	Depth to water level (feet below land surface)	Altitude of land surface (feet)	Transparency, water, Secchi disc (feet)	Dissolved oxygen, water, unfiltered (mg/L)
Ike Walton Lake, deep hole	20040927	1110	460142089484301	3.3	--	--	1616	--	7.7
	20041101	1100		3.3	--	--	1616	9.2	11.1
	20050524	1100		3.3	--	--	1616	17.7	10.2
	20040927	1120		49.0	--	--	1616	--	7.0
	20050524	1110		52.5	--	--	1616	--	8.8
Ike Walton Lake, north shore	20040927	1150	460259089483401	3.3	--	--	1616	--	8.1
	20050524	1120		3.3	--	--	1616	--	10.3
Little Trout Lake, deep hole	20040927	1400	460402089504301	3.3	--	--	1610	--	8.2
	20041101	1520		3.3	--	--	1610	11.2	10.5
	20050524	1320		3.3	--	--	1610	10.2	11.1
	20040927	1410		82.0	--	--	1610	--	0.2
	20050524	1330		91.9	--	--	1610	--	7.7
Little Trout Lake, northeast inlet	20040927	1430	460410089502401	3.3	--	--	1610	--	8.6
	20041101	1600		3.3	--	--	1610	--	10.5
	20050524	1340		3.3	--	--	1610	--	11.9
	20050601	1341		2.0	--	--	1610	--	6.5
Great Corn Lake, deep hole	20040928	1310	460346089460801	3.3	--	--	1616	--	8.2
	20041101	1330		3.3	--	--	1616	10.5	10.6
	20050525	900		3.3	--	--	1616	16.4	11.8
	20040928	1320		23.0	--	--	1616	--	6.4
	20050525	910		23.0	--	--	1616	--	3.6
Great Corn Lake, southeast inlet	20040928	1330	460344089460401	3.3	--	--	1616	--	8.6
	20041101	1400		3.3	--	--	1616	--	10.5
	20050525	920		3.3	--	--	1616	--	10.7
Little Corn Lake, deep hole	20040928	1020	460409089460801	3.3	--	--	1616	--	8.2
	20040928	1040		18.0	--	--	1616	--	7.8
Little Corn Lake, southeast inlet	20040928	1100	460408089460301	3.3	--	--	1616	--	8.5
Trout River	20041101	1200	05357259	--	--	--	1605	--	9.6
	20050524	1330		--	--	--	1605	--	10.9
Well 6MW	20041012	1110	460426089461201	--	11.3	4.88	1621	--	3.2
Well 8MW	20041012	1230	460411089453501	--	18.0	6.55	1619	--	.2
Well 9MW	20041012	1330	460337089455901	--	13.0	6.19	1617	--	.2
Well 4MW	20041013	1010	460359089463201	--	10.5	4.97	1619	--	.4

Table 4. Field measurements and concentrations of detected water-quality constituents for water samples collected from the study area–Continued.

[y, year; m, month; d, day; mg/L, milligrams per liter; --, no data or not applicable; µS/cm, microsiemens per centimeter; C, Celsius; µg/L, micrograms per liter; <, less than; E, estimated; CAS, Chemical Abstract Service registry number; locations of sampling stations are shown in figure 1; shaded areas highlight data from deep-hole bottom samples]

Station name	Sample date (yyyymmdd)	pH, water, unfiltered, field, standard units	Specific conductance, water (µS/cm at 25 degrees C)	Water temperature (degrees C)	2,4-D, water, filtered, recoverable (µg/L) (CAS 94-75-7)	Deethyl atrazine, water, filtered, recoverable (µg/L) (CAS 6190-65-4)	Hydroxy atrazine, water, filtered, recoverable (µg/L) (CAS 2163-68-0)	Atrazine, water, filtered, recoverable (µg/L) (CAS 1912-24-9)
Ike Walton Lake, deep hole	20040927	7.4	26	17.1	<0.02	E0.009	E0.019	0.029
	20041101	5.0	15	8.0	<.04	E.009	E.016	.027
	20050524	5.7	27	14.4	<.04	E.006	E.014	.021
	20040927	6.0	25	16.6	<.02	E.009	<.017	.025
	20050524	4.9	27	9.1	<.04	E.006	E.013	.019
Ike Walton Lake, north shore	20040927	5.8	25	16.5	<.02	E.008	<.020	.025
	20050524	5.6	24	16.0	<.04	E.007	E.013	.022
Little Trout Lake, deep hole	20040927	7.5	68	17.2	<.07	E.012	<.018	.036
	20041101	6.7	54	8.9	.05	E.010	<.032	.041
	20050524	7.6	61	13.4	.05	E.009	<.032	.034
	20040927	6.9	73	8.4	.08	E.008	E.014	.028
	20050524	6.5	63	7.0	.04	E.009	<.032	.029
Little Trout Lake, northeast inlet	20040927	6.3	67	15.6	<.05	E.010	<.013	.035
	20041101	6.7	55	8.5	.04	E.011	<.032	.035
	20050524	7.7	60	15.3	--	E.010	--	.033
	20050601	6.7	52	18.4	<.04	<.03	<.032	.017
Great Corn Lake, deep hole	20040928	7.8	97	17.3	<.02	E.007	E.010	.026
	20041101	6.8	88	8.5	<.04	E.006	<.032	.028
	20050525	7.7	87	15.4	<.04	<.006	<.032	.02
	20040928	7.2	98	16.8	<.02	E.006	E.008	.023
	20050525	6.5	95	8.7	<.04	<.006	<.032	.018
Great Corn Lake, southeast inlet	20040928	7.9	97	17.6	<.02	E.007	E.006	.026
	20041101	7.3	88	8.5	<.04	E.006	<.032	.025
	20050525	7.0	93	15.4	<.04	<.006	<.032	.021
Little Corn Lake, deep hole	20040928	7.7	86	16.6	<.02	E.007	E.013	.031
	20040928	7.1	88	16.3	<.02	E.008	<.012	.032
Little Corn Lake, southeast inlet	20040928	7.9	86	16.5	<.02	E.007	E.011	.032
Trout River	20041101	6.8	92	7.3	--	E.005	<.032	.021
	20050524	7.6	96	18.4	<.04	E.004	<.032	.020
Well 6MW	20041012	5.5	28	10.0	<.04	<.006	<.032	<.007
Well 8MW	20041012	5.6	41	8.2	<.04	E.005	<.032	<.007
Well 9MW	20041012	5.8	64	9.5	<.04	E.006	<.032	.009
Well 4MW	20041013	5.9	78	8.9	<.04	<.006	<.032	<.007

Table 4. Field measurements and concentrations of detected water-quality constituents for water samples collected from the study area–Continued.

[y, year; m, month; d, day; mg/L, milligrams per liter; --, no data or not applicable; µS/cm, microsiemens per centimeter; C, Celsius; µg/L, micrograms per liter; <, less than; E, estimated; CAS, Chemical Abstract Service registry number; locations of sampling stations are shown in figure 1; shaded areas highlight data from deep-hole bottom samples]

Station name	Sample date (yyyymmdd)	Caffeine, water, filtered, recoverable, (µg/L) (CAS 58-08-2)	Carbaryl, water, filtered (0.7 micron glass fiber filter), recoverable (µg/L) (CAS 63-25-2)	Diazinon, water, filtered, recoverable (µg/L) (CAS 333-41-5)	Metolachlor, water, filtered, recoverable (µg/L) (CAS 51218-45-2)	Napropamide, water, filtered (0.7 micron glass fiber filter), recoverable (µg/L) (CAS 15299-99-7)	Norflurazon, water, filtered (0.7 micron glass fiber filter), recoverable (µg/L) (CAS 27314-13-2)	Oryzalin, water, filtered (0.7 micron glass fiber filter), recoverable (µg/L) (CAS 19044-88-3)
Ike Walton Lake, deep hole	20040927	<0.010	<0.041	<0.005	<0.013	<0.007	<0.02	<0.02
	20041101	<.018	<.041	<.005	<.006	<.007	<.02	<.01
	20050524	<.018	<.041	<.005	<.006	<.007	<.02	<.01
	20040927	<.010	<.041	<.005	<.013	<.007	<.02	E.02
	20050524	<.018	<.041	<.005	<.006	<.007	<.02	<.01
Ike Walton Lake, north shore	20040927	<.010	<.041	<.005	<.013	<.007	<.02	<.02
	20050524	<.018	<.041	<.005	E.003	<.007	<.02	<.01
Little Trout Lake, deep hole	20040927	<.010	<.041	.030	<.013	<.007	E.07	<.02
	20041101	<.018	E.009	.021	<.006	<.007	.12	<.01
	20050524	<.018	<.041	.013	<.006	<.007	.09	<.01
	20040927	<.010	<.041	.009	<.013	<.007	E.14	<.02
	20050524	<.018	<.041	.015	<.006	<.007	.10	<.01
Little Trout Lake, northeast inlet	20040927	<.010	<.041	.031	<.013	<.007	E.08	<.02
	20041101	<.018	E.018	.018	<.006	.026	.49	<.01
	20050524	--	<.041	.014	<.006	<.007	--	--
	20050601	.077	--	--	--	--	.07	<.01
Great Corn Lake, deep hole	20040928	<.010	<.041	<.005	E.004	<.007	E.43	<.02
	20041101	<.018	<.041	<.005	<.006	<.007	E2.74	.05
	20050525	<.018	<.041	<.005	<.006	<.007	E1.67	<.01
	20040928	<.010	<.041	<.005	E.003	<.007	E.42	<.02
	20050525	<.018	<.041	<.005	<.006	<.007	E2.21	<.01
Great Corn Lake, southeast inlet	20040928	<.010	<.041	<.005	E.003	<.007	E.40	<.02
	20041101	<.018	<.041	<.005	<.006	<.007	E2.50	.06
	20050525	<.018	<.041	<.005	<.006	<.007	E2.42	<.01
Little Corn Lake, deep hole	20040928	<.010	<.041	<.005	E.004	<.007	E.70	<.02
	20040928	.011	<.041	<.005	<.013	<.007	E.63	<.02
Little Corn Lake, southeast inlet	20040928	<.010	<.041	<.005	E.004	<.007	E.60	<.02
Trout River	20041101	<.018	<.041	<.005	<.006	<.007	<.02	<.01
	20050524	<.018	<.041	<.005	<.006	<.007	<.02	<.01
Well 6MW	20041012	<.018	<.041	<.005	<.006	<.007	<.02	<.01
Well 8MW	20041012	<.018	<.041	<.005	<.006	.018	E.09	<.01
Well 9MW	20041012	<.018	<.041	<.005	<.006	.137	E.56	<.01
Well 4MW	20041013	<.018	<.041	<.005	<.006	<.007	<.02	<.01

Table 5. Concentrations of detected bed-sediment-quality constituents for samples collected from the study area.

[y, year; m, month; d, day; <, less than; mm, millimeters; g/kg, grams per kilogram; µg/kg, micrograms per kilogram; CAS, Chemical Abstract Service registry number]

Station name	Sample date, yyyymmdd	Sample time	Station number	Sampling depth (feet)	Total carbon, bed sediment <2 mm (g/kg)	Inorganic carbon, bed sediment <2 mm (g/kg)	Organic carbon, bed sediment <2 mm (g/kg)	Chlorpyrifos, solids (µg/kg) (CAS 2921-88-2)	Metolachlor, solids (µg/kg) (CAS 51218-45-2)
Ike Walton Lake, north shore	20040927	1210	460259089483401	3.2	51.21	<0.2	51.086	<1	<10.0
Little Trout Lake, northeast inlet	20040927	1440	460410089502401	3.2	5.985	<.2	5.95	1.1	<1.40
Little Corn Lake, southeast inlet	20040928	1110	460408089460301	3.2	195.1	.491	194.609	<1	15.5
Great Corn Lake, southeast inlet	20040928	1350	460344089460401	3.2	19.71	<.2	19.667	<1	3.29

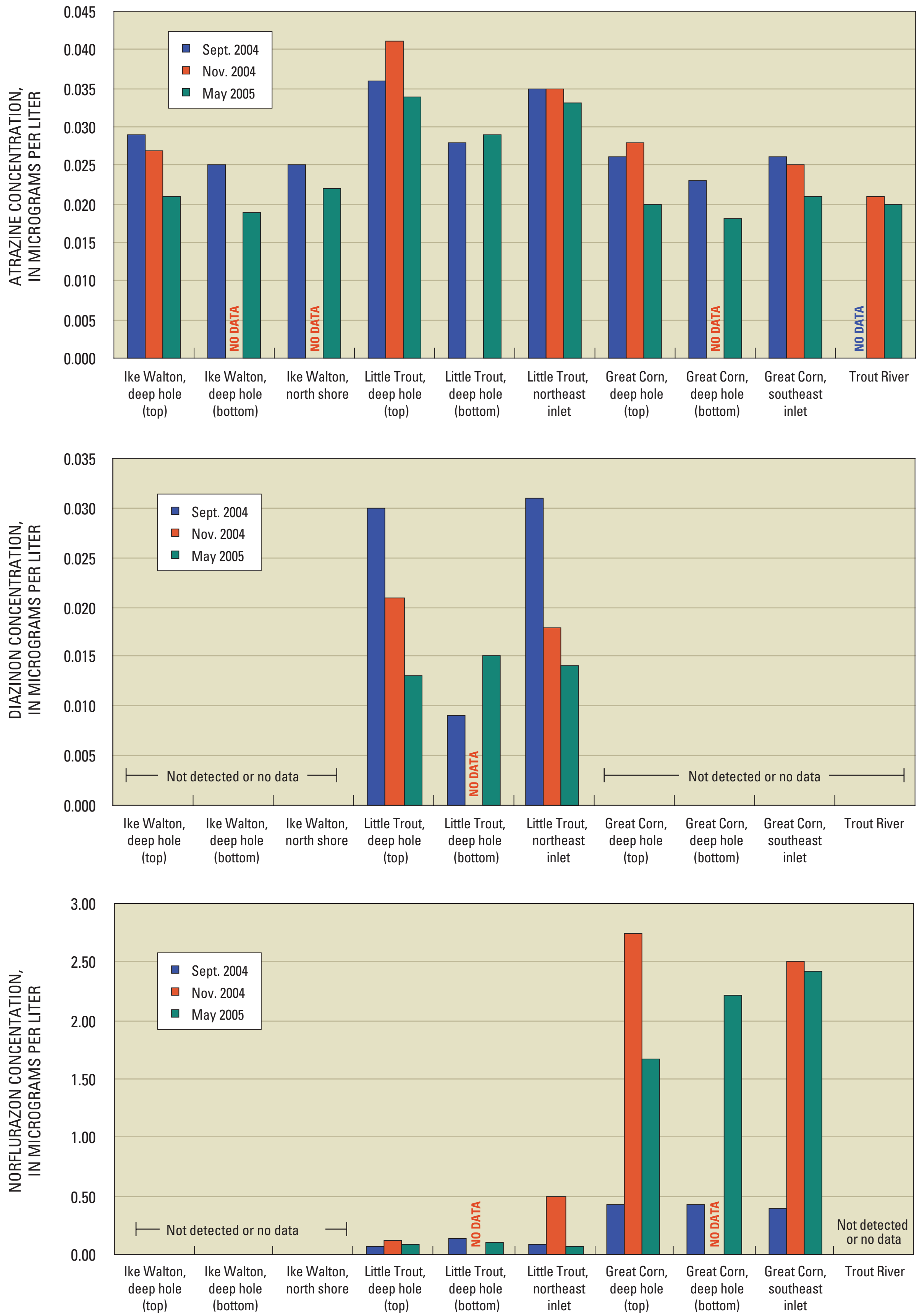

Figure 4. Temporal variability in atrazine, diazinon, and norflurazon concentrations from lake and river samples collected September and November 2004, and May 2005, Lac du Flambeau Reservation and vicinity, Vilas County, Wis.

for clearing weeds and grasses from roads and other rights-of-way (Pesticide Action Network, 2005). Metolachlor and oryzalin are not identified as commonly used pesticides for growing cranberries, but they could be used for road or ditch maintenance as part of commercial cranberry operations or for maintenance of roads and other rights-of-way throughout the study area.

Caffeine was detected in one sample each from Little Trout and Little Corn Lakes. Caffeine is not a pesticide, but its presence in the lakes indicates an anthropogenic source such as wastewater (Barnes and others, 2002).

Lakes

Five of the 10 pesticides or metabolites detected in lake-water samples are targeted compounds (2,4-D, carbaryl, diazinon, napropamide, and norflurazon) commonly used to control weeds and insects in commercial cranberry operations. Eight of the pesticides or metabolites detected are herbicides and two (carbaryl and diazinon) are insecticides.

The most commonly detected pesticide in lake-water samples was the non-target herbicide, atrazine, detected in 100 percent of lake-water samples. Deethyl atrazine and hydroxy atrazine were also detected in a high percentage of lake samples (85 and 42 percent, respectively), but typically at lower concentrations than the parent compound (table 4). As noted above, the widespread detections and uniform concentrations make precipitation the likely source of atrazine in the lakes.

The most commonly detected target pesticide was norflurazon. Norflurazon was not detected in samples from Ike Walton Lake (the reference lake), but was detected in 100 percent of the other lake samples. Norflurazon was also the pesticide detected at the highest concentrations in lake samples (up to 2.7 µg/L) from Great Corn Lake (figs. 4 and 5). The lowest detected concentrations were from Little Trout Lake. Actual norflurazon concentrations may be slightly lower than those given in this report based on high recoveries measured in spiked samples collected during this study. Where comparisons could be made between the three sample periods (September, November, and May) measured concentrations were highest in November (fig. 4). The recommended application time for norflurazon is in the spring for controlling weeds (Mahr and others, 2005). Norflurazon can be persistent in the environment (U.S. Environmental Protection Agency, 2005a). The half-life of norflurazon (half-life is defined as the time required for half of the parent pesticide present after an application to break down into metabolites) in soil is 90 to 130 days and 240 to 2,650 days in water (Pesticide Action Network, 2005; U.S. Environmental Protection Agency, 2005a). The high concentrations measured in November samples could represent norflurazon residue from spring applications flushed from the bogs into the lakes from the post-harvest flood-return water.

Three pesticides (2,4-D, carbaryl, and diazinon) were only detected in Little Trout Lake samples. Carbaryl and 2,4-D were detected at concentrations near or lower than the USGS NWQL reporting limits. Carbaryl was only detected in lake-water samples collected in November. 2,4-D was detected in Little Trout Lake samples from September, November, and May with fairly uniform concentrations from each sample period. Diazinon was detected in all Little Trout Lake samples at concentrations up to six times the reporting limit. The highest diazinon concentrations were measured in shallow lake-water samples collected in September (fig. 4). Metolachlor and oryzalin were detected in a few samples from Ike Walton and the Corn Lakes, but at concentrations near or lower than the reporting limit. Napropamide was detected in only one lake-water sample from Little Trout Lake in November.

Only two of the detected pesticides in lake-water samples from this study (2,4-D and atrazine) have maximum contaminant level (MCL) guidelines for drinking water (70 and 3 µg/L, respectively) as described in the USEPA Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 2005b). The lakes sampled for this study are not used as a source of drinking water, but these guidelines can be used for relative comparison purposes. Concentrations detected in lake samples are from 2 to 3 orders of magnitude lower than the drinking-water standards for these constituents. Drinking-water standards are based on toxicity studies associated with human health. Studies of toxic effects of contaminants on plants and animals are also done and results are commonly described in terms of acute toxicity (adverse health effects from a single, short-term exposure [hours and days]) and chronic toxicity (adverse health effects from repeated, lower-level exposure over a long period of time [years]). Results of chronic-toxicity studies of pesticides on plants and animals native to the study area are not readily available and may limit the ability to describe all of the effects pesticides can have on the ecology of the lakes. Results of acute toxicity studies of several fish native to the area are available and toxicity ratings relative to measured pesticide concentrations are summarized in the following sections.

The pesticides detected in lake-water samples can be acutely toxic to fish, but only at much higher concentrations than those measured in samples collected during this

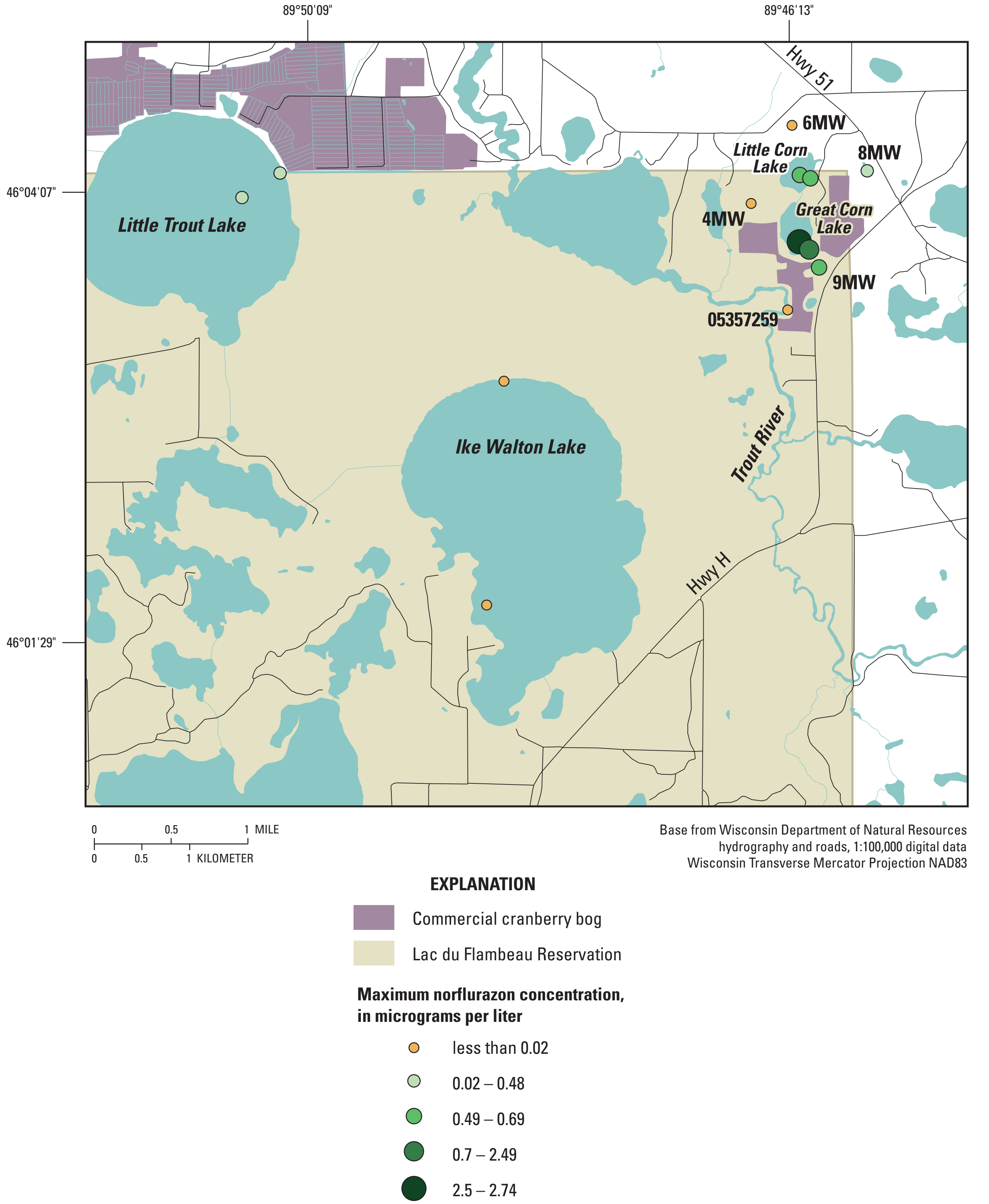

Figure 5. Maximum norflurazon concentration by location for lake, stream, and ground-water samples collected for this study, Lac du Flambeau Reservation and vicinity, Vilas County, Wis. Type of sampling site shown in figure 1.

Table 6. Average LC_{50} concentrations for selected fish for pesticides detected in lake samples from the study area.

[µg/L, micrograms per liter; --, no data; data compiled from Pesticide Action Network Pesticides Database (Pesticide Action Network, 2005)]

Pesticide	Fathead minnow		Bluegill		Largemouth bass		Smallmouth bass	
	Average LC_{50}* (µg/L)	Number of studies	Average LC_{50} (µg/L)	Number of studies	Average LC_{50} (µg/L)	Number of studies	Average LC_{50} (µg/L)	Number of studies
2,4-D	191,500	9	176,000	9	129,000	4	3,100	1
Atrazine	15,000	2	38,100	11	--	--	--	--
Carbaryl	11,500	33	10,700	54	8,500	5	--	--
Diazinon	5,800	22	237	27	--	--	--	--
Metolachlor	8,200	1	10,000	1	--	--	--	--
Napropamide	--	--	12,000	1	--	--	--	--
Norflurazon	--	--	16,300	1	--	--	--	--
Oryzalin	--	--	2,880	1	--	--	--	--

* LC_{50} is the concentration of pesticide in water that is lethal to 50 percent of the test fish in a study within a stated period of time. Average LC_{50} is an average value based on the number of studies shown.

study. Acute-toxicity ratings of the pesticides detected in the lakes ranged from not-acutely toxic to highly toxic to minnows, bluegills, and bass (table 6; Pesticide Action Network, 2005; U.S. Environmental Protection Agency, 2005c), fish that are known to be present in the study lakes (Wisconsin Department of Natural Resources, 1995). The acute-toxicity rating of pesticides to fish was based on the LC_{50} (LC_{50} is the concentration of pesticide in water that is lethal to 50 percent of the test fish in a toxicity study within a stated time period, typically 24-96 hours) according to Kamrin (1997). LC_{50} concentrations for pesticides detected in this study ranged from 237 to 191,500 µg/L (table 6). Very highly toxic pesticide LC_{50} concentrations are less than 100 µg/L, highly toxic pesticides range from 100 to 1,000 µg/L; moderately toxic from 1,000 to 10,000 µg/L; slightly toxic from 10,000 to 100,000 µg/L; and not-acutely toxic are greater than 100,000 µg/L. The pesticide 2,4-D is moderately toxic to smallmouth bass, but not acutely toxic to minnows, bluegills, and largemouth bass. Atrazine, carbaryl, metolachlor, napropamide, and norflurazon are slightly toxic to bluegills, whereas oryzalin is moderately toxic and diazinon is highly toxic to bluegills. Atrazine, carbaryl, diazinon, and metolachlor are slightly to moderately toxic to minnows and carbaryl is moderately toxic to largemouth bass. Concentrations of pesticides detected in lake-water samples (table 4) were from 5 to 8 orders of magnitude lower than the LC_{50} concentrations listed in table 6 and, therefore, were not considered toxic to fish.

Trout River

The only pesticides detected in Trout River samples were the non-targeted compounds atrazine and deethyl atrazine, with higher concentrations of the parent compound than the metabolite. Concentrations varied minimally between November and May and were similar to those measured in lake-water samples. Atrazine concentrations measured in Trout River samples were from 6 to 7 orders of magnitude lower than the average LC_{50} concentrations for minnows and bluegills shown in table 6. As noted above, the source of atrazine is likely precipitation. Trout River water also does not appear to be the source of the targeted compounds detected in the Corn Lakes.

Bed Sediment

Only two pesticides were detected in bed-sediment samples collected from the lakes (table 5). Chlorpyrifos (a targeted insecticide) was detected at concentrations near the NWQL reporting limit (1.0 µg/kg) in the Little Trout Lake sample. Metolachlor (a non-targeted herbicide) was detected at concentrations ranging from 3.3 to 15.5 µg/kg in sediment samples from Great Corn and Little Corn Lakes, respectively. Pesticide analysis of bed sediment was affected by interference problems possibly caused by organic matter in the samples (William Foreman, U.S. Geological Survey, National Water Quality Laboratory, written commun., August 10, 2005). Interference makes detection and quantification of constituents difficult and possibly limited the number of schedule 5503 constituents that were detected. Organic-carbon content of the sediment samples ranged from 6 g/kg in Little Trout Lake to 195 g/kg in Little Corn Lake (table 5).

Ground Water

Four pesticides (the targeted compounds napropamide and norflurazon and non-targeted compounds atrazine and deethyl atrazine) were detected in ground-water samples collected for this study (table 4). Pesticides were detected in samples from monitor wells 8MW and 9MW, with the highest concentrations (up to 0.14 µg/L napropamide and 0.56 µg/L norflurazon) being measured in samples from monitor well 9MW (table 4), which is directly downgradient from the Corn Lakes and commercial cranberry operations. No pesticides were detected in samples from monitor well 4MW and reference well 6MW.

Deethyl atrazine concentrations detected in ground-water samples were similar to concentrations measured in surface-water samples, whereas concentrations of atrazine measured in ground water were lower than those measured in surface water. Measured ground-water concentrations of norflurazon were within the range of measured surface-water concentrations, but napropamide concentrations from well 9MW were higher than concentrations measured in surface-water samples. The source of atrazine and deethyl atrazine in ground water is likely from precipitation or lake seepage. The sources of napropamide and norflurazon are likely associated with commercial cranberry operations, either directly from upgradient cranberry bogs or by way of seepage from the lakes.

Summary and Conclusions

During the fall of 2004 and spring of 2005, the U.S. Geological Survey, in cooperation with the Lac du Flambeau Band of Lake Superior Chippewa Indians, collected water and bed sediment from four lakes (Great Corn, Little Corn, Little Trout, and Ike Walton Lakes), the Trout River, and shallow ground-water wells adjacent to commercial cranberry operations near the northeastern corner of the Lac du Flambeau Reservation, Wisconsin. Water and bed-sediment samples were analyzed for an extensive list of pesticides including those that are commonly used in commercial cranberry operations to better understand the quality of the lakes and ground water in the Reservation. Six pesticides commonly used on cranberries were detected in lakes, lake-bed sediment, or ground-water samples. Five pesticides or metabolites not typically used on cranberries were also detected.

Five targeted pesticides (2,4-D, carbaryl, diazinon, napropamide, and norflurazon) were detected in lake-water samples from Little Trout and the Corn Lakes. No targeted pesticides were detected in Ike Walton Lake (the reference lake). The non-targeted pesticide atrazine was detected in all lakes during all sample periods, with precipitation the likely source. Non-targeted pesticides metolachlor and oryzalin were also detected in samples from Ike Walton and the Corn Lakes, but the sources are not apparent. Measured concentrations of 2,4-D and atrazine were below drinking-water standards and concentrations of all detected pesticides were also far below levels considered lethal to fish.

The only pesticides detected in Trout River samples were the non-targeted compounds atrazine and deethyl atrazine. Concentrations varied minimally between November and May and were similar to those measured in lake-water samples. No targeted pesticides were detected in Trout River water, indicating that it is not a source of those compounds detected in the Corn Lakes.

Only two pesticides (chlorpyrifos and metolachlor) were detected in bed-sediment samples collected from the lakes. Chlorpyrifos was detected at concentrations near the USGS National Water Quality Laboratory reporting limit (1.0 µg/kg) in the Little Trout Lake sample. Metolachlor was detected at concentrations ranging from 3.3 to 15.5 µg/kg in sediment samples from Great Corn and Little Corn Lakes, respectively.

Four pesticides or metabolites (targeted compounds napropamide and norflurazon and non-targeted compounds atrazine and deethyl atrazine) were detected in ground-water samples from monitor wells 8MW and 9MW. The highest ground-water concentrations (up to 0.14 µg/L napropamide and 0.56 µg/L norflurazon) were measured in samples from monitor well 9MW, which is directly downgradient from the Corn Lakes and commercial cranberry operations. No pesticides were detected in samples from monitor well 4MW and the reference well 6MW.

Data collected for this study indicate that cranberry-related pesticides are entering lakes and ground water adjacent to commercial cranberry operations in northern Wisconsin. Measured concentrations were below U.S. Environmental Protection Agency drinking-water standards and levels considered lethal to fish; however, this result does not conclude that pesticides have no effect on the lakes and aquatic biology. Further study is needed to identify additional pesticides as well as chronic effects on aquatic organisms to determine whether cranberry-related pesticides affect the lake ecosystems of the Lac du Flambeau Reservation.

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Appendixes

Appendix 1. U.S. Geological Survey National Water Quality Laboratory Schedule 2001 analyte list.

[NWQL, National Water Quality Laboratory; µg/L, micrograms per liter; pct, percent]

Analyte	NWQL Parameter code	Reporting level	Reporting units
alpha-HCH	34253	0.005	µg/L
Acetochlor	49260	.006	µg/L
Alachlor	46342	.005	µg/L
2,6-Diethylaniline	82660	.006	µg/L
Atrazine	39632	.007	µg/L
Azinphos-methyl	82686	.05	µg/L
Benfluralin	82673	.01	µg/L
Butylate	04028	.004	µg/L
Carbaryl	82680	.041	µg/L
Carbofuran	82674	.02	µg/L
Chlorpyrifos	38933	.005	µg/L
cis-Permethrin	82687	.006	µg/L
Cyanazine	04041	.018	µg/L
Dacthal	82682	.003	µg/L
2-Chloro-4-isopropylamino-6-amino-s-triazine (Deethyl atrazine)	04040	.006	µg/L
Diazinon	39572	.005	µg/L
Diazinon-d10 (surrogate)	91063	.1	pct
Dieldrin	39381	.009	µg/L
Disulfoton	82677	.021	µg/L
EPTC	82668	.004	µg/L
Ethalfluralin	82663	.009	µg/L
Ethoprophos	82672	.005	µg/L
Desulfinylfipronil amide	62169	.029	µg/L
Fipronil sulfide	62167	.013	µg/L
Fipronil sulfone	62168	.024	µg/L
Desulfinylfipronil	62170	.012	µg/L
Fipronil	62166	.016	µg/L
Fonofos	04095	.003	µg/L
alpha-HCH-d6 (surrogate)	91065	.1	pct
Lindane	39341	.004	µg/L
Linuron	82666	.035	µg/L
Malathion	39532	.027	µg/L
Parathion-methyl	82667	.015	µg/L
Metolachlor	39415	.013	µg/L
Metribuzin	82630	.006	µg/L
Molinate	82671	.003	µg/L
Napropamide	82684	.007	µg/L
p,p’-DDE	34653	.003	µg/L
Parathion	39542	.01	µg/L
Pebulate	82669	.004	µg/L

Appendix 1. U.S. Geological Survey National Water Quality Laboratory Schedule 2001 analyte list—Continued.

[NWQL, National Water Quality Laboratory; µg/L, micrograms per liter; pct, percent]

Analyte	NWQL Parameter code	Reporting level	Reporting units
Pendimethalin	82683	0.022	µg/L
Phorate	82664	.011	µg/L
Prometon	04037	.005	µg/L
Propyzamide	82676	.004	µg/L
Propachlor	04024	.025	µg/L
Propanil	82679	.011	µg/L
Propargite	82685	.023	µg/L
Simazine	04035	.005	µg/L
Tebuthiuron	82670	.016	µg/L
Terbacil	82665	.034	µg/L
Terbufos	82675	.017	µg/L
Thiobencarb	82681	.01	µg/L
Triallate	82678	.002	µg/L
Trifluralin	82661	.009	µg/L

Appendix 2. U.S. Geological Survey National Water Quality Laboratory Schedule 2060 analyte list.

[NWQL, National Water Quality Laboratory; µg/L, micrograms per liter; pct, percent]

Analyte	NWQL Parameter code	Reporting level	Reporting units
2,4,5-T (surrogate)	99958	0.1	pct
2,4-D	39732	.0218	µg/L
2,4-D methyl ester	50470	.0086	µg/L
2,4-DB	38746	.016	µg/L
2-Hydroxy-4-isopropylamino-6-ethylamino-s-triazine (Hydroxy atrazine)	50355	.008	µg/L
3(4-Chlorophenyl)-1-methyl urea	61692	.0242	µg/L
3-Ketocarbofuran	50295	1.5	µg/L
Acifluorfen	49315	.0066	µg/L
Aldicarb	49312	.04	µg/L
Aldicarb sulfone	49313	.02	µg/L
Aldicarb sulfoxide	49314	.0082	µg/L
Chloramben, methyl ester	61188	.018	µg/L
Atrazine	39632	.009	µg/L
Barban	90640	.1	pct
Bendiocarb	50299	.0252	µg/L
Benomyl	50300	.0038	µg/L
Bensulfuron-methyl	61693	.0158	µg/L
Bentazon	38711	.011	µg/L
Bromacil	04029	.033	µg/L
Bromoxynil	49311	.017	µg/L
Caffeine	50305	.0096	µg/L
Caffeine-C13 (surrogate)	99959	.1	pct
Carbaryl	49310	.0284	µg/L
Carbofuran	49309	.0056	µg/L
3-Hydroxycarbofuran	49308	.0058	µg/L
Chlorimuron-ethyl	50306	.0096	µg/L
Chlorothalonil	49306	.035	µg/L
Clopyralid	49305	.0138	µg/L
Cycloate	04031	.013	µg/L
Dacthal monoacid	49304	.0116	µg/L
2-Chloro-4-isopropylamino-6-amino-s-triazine (Deethyl atrazine)	04040	.0282	µg/L
Chlordiamino-s-triazine	04039	.01	µg/L
2-Chloro-6-ethylamino-4-amino-s-triazine (Deisopropyl atrazine)	04038	.044	µg/L
Dicamba	38442	.0128	µg/L
Dichlorprop	49302	.0138	µg/L
Dinoseb	49301	.012	µg/L
Diphenamid	04033	.0264	µg/L
Diuron	49300	.015	µg/L

Appendix 2. USGS National Water Quality Laboratory Schedule 2060 analyte list—Continued.

[NWQL, National Water Quality Laboratory; µg/L, micrograms per liter; pct, percent]

Analyte	NWQL Parameter code	Reporting level	Reporting units
Fenuron	49297	0.0316	µg/L
Flumetsulam	61694	.011	µg/L
Fluometuron	38811	.031	µg/L
Imazaquin	50356	.016	µg/L
Imazethapyr	50407	.017	µg/L
Imidacloprid	61695	.0068	µg/L
Linuron	38478	.0144	µg/L
MCPA	38482	.0162	µg/L
MCPB	38487	.015	µg/L
Metalaxyl	50359	.02	µg/L
Methiocarb	38501	.008	µg/L
Methomyl	49296	.0044	µg/L
Metsulfuron methyl	61697	.025	µg/L
Neburon	49294	.012	µg/L
Nicosulfuron	50364	.013	µg/L
Norflurazon	49293	.016	µg/L
Oryzalin	49292	.0176	µg/L
Oxamyl	38866	.0122	µg/L
Picloram	49291	.0198	µg/L
Propham	49236	.0096	µg/L
Propiconazole	50471	.021	µg/L
Propoxur	38538	.008	µg/L
Siduron	38548	.0168	µg/L
Sulfometuron-methyl	50337	.0088	µg/L
Tebuthiuron	82670	.0062	µg/L
Terbacil	04032	.0098	µg/L
Tribenuron-methyl	61159	.0088	µg/L
Triclopyr	49235	.0224	µg/L

Appendix 3. U.S. Geological Survey National Water Quality Laboratory Schedule 5503 analyte list.

[NWQL, National Water Quality Laboratory; µg/kg, micrograms per kilogram; pct, percent]

Analyte	NWQL Parameter code	Reporting level	Reporting units
1-Naphthol	63240	10	µg/kg
2-Chloro-2,6-diethylacetanilide	63246	1	µg/kg
2-Ethyl-6-methylaniline	63247	30	µg/kg
3,4-Dichloroaniline	63248	75	µg/kg
4-Chloro-2-methylphenol	63255	10	µg/kg
Acetochlor	63257	1	µg/kg
Alachlor	63258	1	µg/kg
2,6-Diethylaniline	63243	30	µg/kg
Atrazine	63262	1	µg/kg
Azinphos-methyl	63263	5	µg/kg
Azinphos-methyl-oxon	63264	30	µg/kg
Benfluralin	63265	1	µg/kg
Carbaryl	63269	2	µg/kg
Chlorpyrifos	63273	1	µg/kg
Chlorpyrofos, oxygen analog	63274	30	µg/kg
cis-Permethrin	63365	5	µg/kg
Cyfluthrin	63279	20	µg/kg
Cypermethrin	63281	20	µg/kg
Dacthal	63282	1	µg/kg
2-Chloro-4-isopropylamino-6-amino-s-triazine (Deethyl atrazine)	63283	2	µg/kg
Diazinon	63284	1	µg/kg
Diazinon, oxygen analog	63285	5	µg/kg
Diazinon-d10 (surrogate)	90740	0.1	pct
Dichlorvos	63286	30	µg/kg
Dicrotophos	63288	3	µg/kg
Dieldrin	63289	2	µg/kg
Dimethoate	63291	2	µg/kg
Ethion	63302	2	µg/kg
Ethion monoxon	63303	2	µg/kg
Sum of Fenamiphos + Fenamiphos sulfone + Fenamiphos sulfoxide	63308	50	µg/kg
Fenamiphos	63305	30	µg/kg
Fenamiphos sulfone	63306	10	µg/kg
Fenamiphos sulfoxide	63307	10	µg/kg
Desulfinylfipronil amide	63317	1	µg/kg
Fipronil sulfide	63314	1	µg/kg
Fipronil sulfone	63315	1	µg/kg
Desulfinylfipronil	63316	1	µg/kg
Fipronil	63313	1	µg/kg
Fonofos	63319	1	µg/kg
Fonofos, oxygen analog	63320	5	µg/kg

Appendix 3. U.S. Geological Survey National Water Quality Laboratory Schedule 5503 analyte list—Continued.

[NWQL, National Water Quality Laboratory; µg/kg, micrograms per kilogram; pct, percent]

Analyte	NWQL Parameter code	Reporting level	Reporting units
Hexazinone	63321	1	µg/kg
Iprodione	63322	10	µg/kg
Isofenphos	63323	2	µg/kg
Malaoxon	63326	5	µg/kg
Malathion	63327	2	µg/kg
Metalaxyl	63328	1	µg/kg
Methidathion	63329	2	µg/kg
Parathion-methyl	63351	2	µg/kg
Metolachlor	63332	1	µg/kg
Metribuzin	63333	4	µg/kg
Myclobutanil	63335	1	µg/kg
Paraoxon-methyl	63349	5	µg/kg
Pendimethalin	63353	1	µg/kg
Phorate	63354	5	µg/kg
Phorate oxon	63355	7	µg/kg
Prometon	63359	2	µg/kg
Prometryn	63360	2	µg/kg
Propyzamide	63369	2	µg/kg
Simazine	63370	2	µg/kg
Tebuthiuron	63376	3	µg/kg
Terbufos	63380	3	µg/kg
Terbufos-O-analogue sulfone	63383	5	µg/kg
Terbuthylazine	63384	1	µg/kg
trans-Permethrin	63366	5	µg/kg
Trifluralin	63390	1	µg/kg

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