

Water Quality in the Arthur R. Marshall Loxahatchee National Wildlife Refuge— Trends and Spatial Characteristics of Selected Constituents, 1974-2004

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Conversion Factors, Acronyms, and Abbreviations

Multiply	By	To obtain
acre	0.4047	hectare (ha)
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
foot per year (ft/yr)	0.3048	meter per year (m/yr)
acre-foot (acre-ft)	1,233	cubic meter (m ³)
acre-foot (acre-ft)	0.001233	cubic hectometer (hm ³)
degrees Fahrenheit (°F)	$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$	degrees Celsius (°C)

EAA	Everglades Agricultural Area (north and west of the Loxahatchee NWR)
ENR	Everglades Nutrient Removal
LOESS	locally weighted scatter-plot smoothing—a technique for drawing a line through data points to help visualize the trend in the data
MRL	minimum reporting level
NAWQA	National Water-Quality Assessment Program
NWIS	National Water Information System—a computer data base maintained by the U.S. Geological Survey and available online
NWR	National Wildlife Refuge
SFWMD	South Florida Water Management District
SOFIA	South Florida Information Access web site at http://sofia.usgs.gov .
STA	Stormwater Treatment Area
USGS	U.S. Geological Survey
WCA	Water Conservation Area
kg	kilogram
mg/L	milligram per liter
Pt-Co units	platinum-cobalt units
µg/kg	micrograms per kilogram
µg/L	micrograms per liter
µS/cm °C	microsiemens per centimeter at 25 degrees Celsius

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

Water Quality in the Arthur R. Marshall Loxahatchee National Wildlife Refuge—Trends and Spatial Characteristics of Selected Constituents, 1974-2004

By Ronald L. Miller and Benjamin F. McPherson

Abstract

Water quality in the interior marsh of the Arthur R. Marshall Loxahatchee National Wildlife Refuge is characterized by low concentrations of major ions, principally sodium and chloride, and is affected primarily by natural seasonal processes, such as evapotranspiration, rainfall, and biological activity. During the dry season, evapotranspiration exceeds precipitation, and specific conductance and conservative ion concentrations at marsh background sites typically increase by 40-70 percent between the end of the rainy season in September and the end of the dry season in May.

Water enters the Refuge mainly from rainfall and perimeter canals. Water is pumped into the perimeter canals from large pumping stations, such as S-5A and S-6. In recent years, much of the water pumped into the Refuge passes through Stormwater Treatment Areas (STAs) before being released into the perimeter canals that surround the Refuge. Since 2001, water at S-6 has been diverted south toward STA-2, away from the Refuge perimeter canals. Water from S-5A and S-6 flows through agricultural lands with intense agricultural activity and typically contains relatively high concentrations of major ions, nutrients, and pesticides. Specific conductance, major-ion concentrations, and nutrient concentrations are an order of magnitude higher at S-5A and S-6 canal sites than at interior marsh sites. Water quality in the marsh bordering the canals can be affected substantially by the canal water, and these effects can extend several miles or more into the marsh depending on location in the Refuge and on the water level in the canals. As canal water flows into the marsh, processes such as uptake by periphyton and rooted vegetation and settling of particulate matter reduce the concentrations of nutrients to a greater extent than conservative ions such as chloride.

Long- and short-term trends for specific conductance, chloride ion, sulfate ion, total phosphorus, and total nitrogen at five sites were evaluated primarily using an uncensored seasonal Kendall test with a water-level adjustment to reduce the effects of long wet or dry periods. Significant long-term trends (1974-2003) for specific conductance, chloride, total phosphorus, and total nitrogen at canal sites S-5A and S-6

were generally downward. Of the five sites, S-5A had the most pronounced decline for specific conductance at about -340 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), followed by S-6 with a decline of about -280 $\mu\text{S}/\text{cm}$. The two internal marsh sites, LOX8 and LOX13, had significant long-term trends in specific conductance of about +37 and -36 $\mu\text{S}/\text{cm}$, respectively. Long-term trends for other constituents at the two internal marsh sites were generally small in magnitude or not measurable between 1978 and 2003. Marsh site LOX15 near the Hillsboro Canal showed no long-term trends, although specific conductance and sulfate concentration increased about 560 $\mu\text{S}/\text{cm}$ and 30 milligrams per liter, respectively, from 1998 to 2002. Site LOX15 is influenced strongly by intrusions of canal water, and increases in specific conductance and sulfate at this site coincided with increased canal-water inflows from STA-1W between 2001 and 2003. Median concentrations at LOX13 and S-5A were used to represent background and canal concentrations, respectively. Based on these values, the median chloride concentration at LOX15 indicates that the water is typically about 31 percent canal water and 69 percent “natural” background water. Using median sulfate concentrations, similarly to chloride, the fraction of water at LOX15 was estimated to be 17 percent from canals and 83 percent from “natural” background water. This finding suggests that in the low sulfate environment of the Refuge, sulfate is not conservative and only about half of the sulfate from canal water typically reaches LOX15; the rest presumably is removed by marsh plants, algae, and bottom sediments.

Concentrations of pesticides and other organic compounds were measured at inflow pumping stations S-5A and S-6. The most commonly detected pesticides in water were atrazine, metolachlor, simazine, ametryn, ethoprop, tebuthiuron, and hexazinone. The most commonly detected pesticides in bed sediment were p,p'-DDD, p,p'-DDE, ametryn, p,p'-DDT, and atrazine, with a maximum concentration of 390 micrograms per kilogram for p,p'-DDE measured at S-6. Only two water samples from the Refuge marsh had been analyzed for pesticides and neither contained detectable concentrations.

Even if the water quality of inflows to the Refuge improves overall as a result of management actions, concentrations of many constituents in canal water probably will remain substantially different from concentrations in the background water of the marsh. Changes in the timing or location of inflows associated with Everglades restoration could adversely affect water quality over greater expanses of marsh, especially if these changes result in canal-water intrusion farther into the Refuge marsh. Inflows from the STAs, even with relatively low nutrient concentrations, may adversely affect water quality in the marsh interior if the inflows contain high concentrations of pesticides or major ions. Major ions, such as calcium and bicarbonate, are not easily removed in STAs. Together with pH, these ions control periphyton species composition and can create an imbalance within the naturally low ionic-strength, soft-water marsh ecosystem.

Introduction

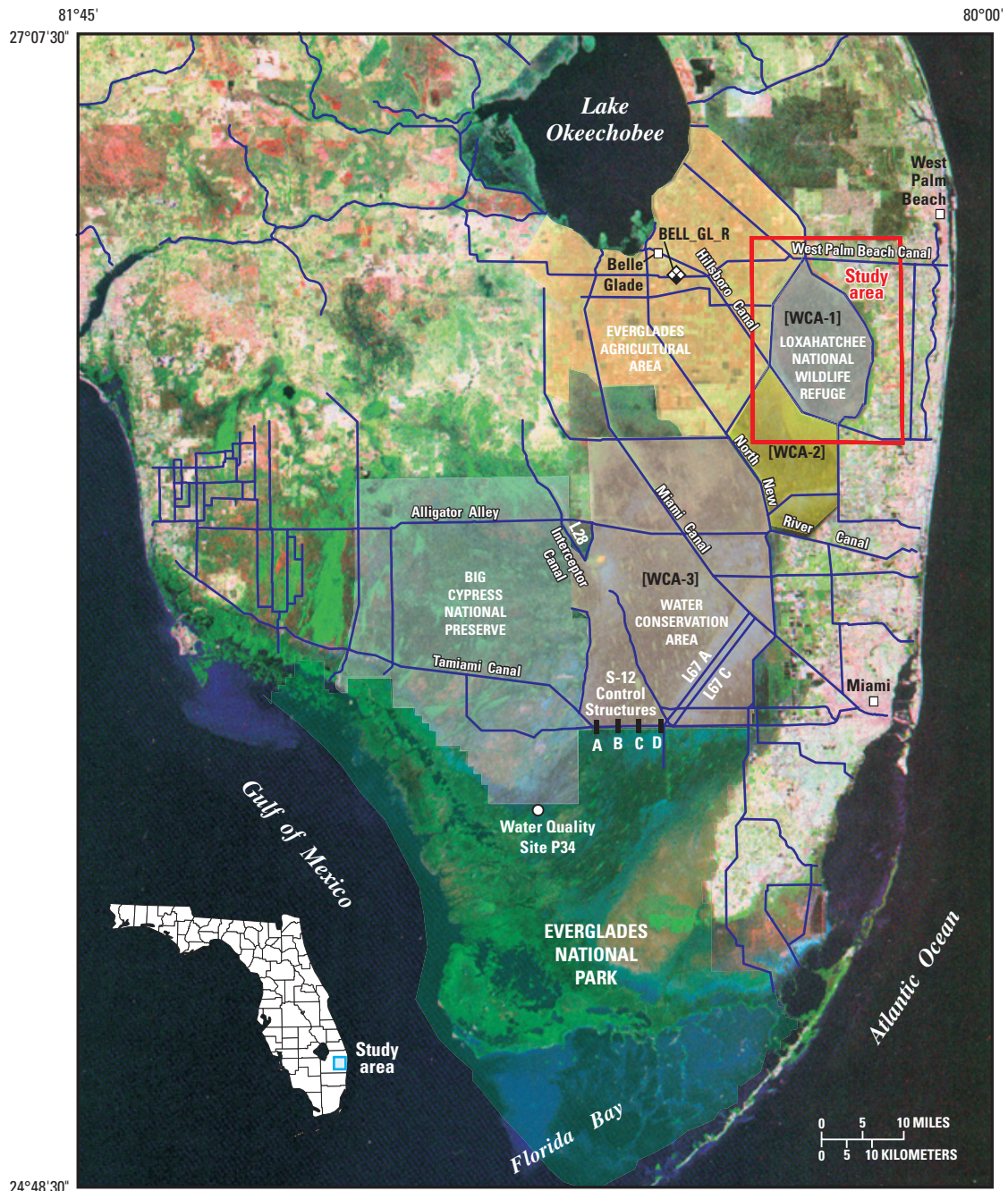
The Arthur R. Marshall Loxahatchee National Wildlife Refuge (“Refuge”) consists of about 140,000 acres of northern Everglades wetlands in southern Florida (fig. 1). The Refuge is a complex mosaic of wetland communities that grow on a bed of peat that is several feet thick, and serves as habitat for wading birds, deer, alligators, and other wildlife. The wetland now within the Refuge was once part of an uninterrupted expanse of wetlands that extended from Lake Okeechobee to Florida Bay. The Refuge is presently one of three water conservation areas (WCAs) in southern Florida (fig. 1) that receive runoff in the wet season and provide water during the dry season.

Initial drainage of the northern Everglades began in the early 1900s with the dredging of the Hillsboro and West Palm Beach Canals. In 1951, the U.S. Fish and Wildlife Service secured a license agreement from the Central and Southern Florida Flood Control District and created the Refuge. The eastern boundary of the Refuge was constructed during the early 1950s and consisted of the L-40 levee and canal. During the mid- to late 1950s, the L-7 levee and canal and pumps at S-5A and S-6 were constructed along the western boundary. The Refuge was enclosed in 1961 with the completion of the L-39 levee along the southern boundary and designated WCA-1. Control structures S-10A, S-10C, and S-10D were installed along the L-39 levee to regulate discharge from WCA-1 into WCA-2 to the south (Light and Dineen, 1994). By the early 1960s, the Refuge was bordered by drained land of the Everglades Agricultural Area (EAA) to the west and rapidly growing agricultural and urban development to the east. In addition to the area enclosed by the canals, the Refuge also includes three small adjacent land areas to the east that contains the Refuge Headquarters and one to the west (fig. 2, compartments A-D).

The northern Everglades historically was a soft-water, peat ecosystem characterized by “noncalcareous” periphyton and dominated by diatoms and desmids that formed thin brown coatings on plant stems (Gleason and Spackman, 1974). Canals and pumps have introduced hard water with high levels of dissolved solids into parts of the northern Everglades. Micronutrients that enter the marsh, such as phosphorus and inorganic forms of nitrogen, usually are removed rapidly by biological processes, but dissolved solids are less affected by these processes. Sulfur, a macronutrient, appears to be partially removed by biological processes. In marsh areas that are still nutrient limited but now have increased specific conductance and altered ionic concentrations, periphyton composition has changed from noncalcareous forms to calcium carbonate mats dominated by filamentous cyanobacteria (Gleason and Spackman, 1974; McCormick and others, 2004). There is concern that water-management strategies associated with Everglades restoration may increase the extent of canal-water intrusion into the Refuge, and that the consequent effects on water chemistry will alter the periphyton communities and the overall ecosystem (McCormick and others, 2004; South Florida Water Management District, 2005b,c).

Currently, the two primary sources of water to the Refuge are rainfall and canal water from pump stations that drain agricultural lands (EAA) to the west and urban areas to the east. In recent years, much of the water pumped into the Refuge passes through large STAs before being released into the perimeter canals that surround the Refuge. Rainfall accounts for 56 percent of the water entering the Refuge, and canal water pumped from EAA lands accounts for about 40 percent. Two pump stations (ACME 1 and 2) along the northeast Refuge boundary drain developing land (Village of Wellington) and account for the remaining 4 percent of the water entering the Refuge (U.S. Fish and Wildlife Service, 2002). Station S-5A pumps water from the West Palm Beach Canal, whereas stations G-251 and G-310 pump water from STA-1W (fig. 2). Prior to 2001, station S-6 pumped water from the Hillsboro Canal into the Refuge and accounted for about 30 percent of the total water entering the Refuge through the structures. Station S-6 began diverting water into STA-2 (not shown) in 2001; to compensate for the decreased inflow to the Refuge, S-5A inflows were increased through STA-1W (STA-1E was to be added later). Outflows from the Refuge are decreased when necessary to hold more water in the Refuge (U.S. Fish and Wildlife Service, 2002).

Discharge and phosphorus loads in water flowing from STA-1W into the Refuge increased sharply during water years 2002 and 2003 (water years begin on October 1 of the previous year and end on September 30 of the given year). Discharge for water year 2003 was about 600,000 acre-feet, compared with about 100,000 acre-feet during most water years prior to 2002. Loads of phosphorus for water year 2003 from STA-1 increased to more than 100,000 kg, compared with less than 20,000 kg during most prior water years, such as 1995-2001 (South Florida Water Management District, 2005c, App 4-12, fig. 1).



Base from U.S. Geological Survey Satellite Image of South Florida, 1992-1993
Universal Transverse Mercator Projection
Zone 17

Figure 1. Location of the study area and Federal and State lands in southern Florida.

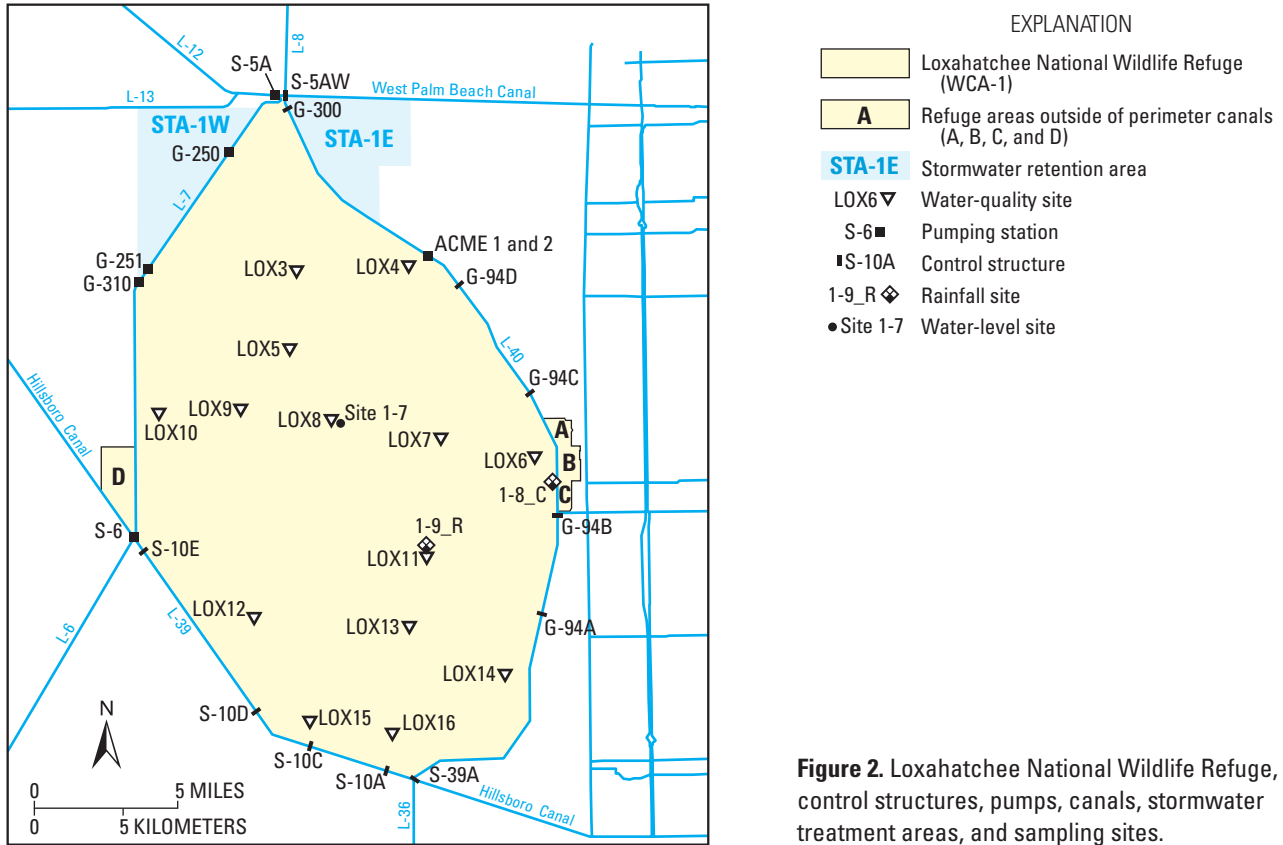


Figure 2. Loxahatchee National Wildlife Refuge, control structures, pumps, canals, stormwater treatment areas, and sampling sites.

Base from U.S. Geological Survey digital data, 1:2,000,000, 1972
 Albers Equal-Area Conic Projection
 Standard Parallels 29°30' and 45°30', Central Meridian -83°00'

The Lake Okeechobee regulation schedule and operational plans for water management in WCA-2, WCA-3, and Everglades National Park partly determine Refuge inflows and outflows. The creation of the two STAs at the northern end of the Refuge and the rerouting of water away from the Refuge at station S-6 were implemented to provide cleaner water to the Refuge than that previously coming directly from S-6 without the benefit of treatment in the two new STAs, but these changes will alter the location, timing, and volume of inflows to the Refuge.

Collectively, these changes may affect the ecology of the Refuge if they increase canal-water intrusion into the Refuge marshes. Previous research indicates that changes in major ion concentrations can cause changes in plant and animal communities (Brandt and others, 2004; Gleason and Spackman, 1974; McCormick and others, 2004). More information, however, is needed to determine: (1) when canal water enters the marsh; (2) how far canal water moves into the marsh; (3) which management operations affect water movement into the marsh; and (4) how movement of canal water into the marsh affects the ecology (Brandt, and others, 2004; Gleason and Spackman, 1974; McCormick and others, 2004).

The U.S. Geological Survey (USGS) initiated a study in 2004 to evaluate and summarize water-quality conditions in the Loxahatchee National Wildlife Refuge for the period of record, 1974-2004. The study was funded by the USGS South Florida Greater Everglades Ecosystem Sciences Program. The study

supports the U.S. Department of the Interior’s “Science Plan in Support of Ecosystem Restoration, Preservation, and Protection in South Florida” in that it provides baseline information on water-quality patterns and trends that are needed to support Everglades Restoration. The study also supports the goal of the U.S. Fish and Wildlife Service to conserve and, if needed, restore fish, wildlife, and plant life for present and future generations.

Purpose and Scope

This report describes and summarizes the results of analyses of surface water-quality data collected in the Refuge at marsh sites between 1978 and 2003 and at selected major inflow locations between 1974 and 2004. The analyses include an evaluation of seasonal and long-term trends as well as the possible effects of hydrologic, climatic, and human-induced perturbations at selected sites. The report presents: (1) an analysis of long-term trends for five selected constituents, namely, specific conductance, chloride, sulfate, total phosphorus, and total nitrogen at sites S-5A, S-6, LOX8, LOX13, and LOX15; (2) an evaluation of baseline water-quality conditions in the Refuge; and (3) a spatial comparison of selected water-quality constituents at sites S-6, S-5A, and LOX3 to LOX16. The database developed for this report is available at the South Florida Information Access (SOFIA) web site at <http://sofia.usgs.gov/exchange/mcpherson/loxdata.html>

Methods

Considerable effort was expended to select valid water-quality data sets with accompanying water-level data. Statistical methods cannot produce valid trends without valid and sufficient data as input. Computer programs were developed to screen large amounts of data and direct data reviewers to possible errors. A robust, non-parametric statistical program, S-ESTREND, was used for data sets that met its input requirements.

Data Sources

The data used to analyze water quality in the Refuge were from several sources. The most extensive water-quality database for southern Florida (DBHYDRO), which also contains water-level and meteorological data, is maintained by the South Florida Water Management District (SFWMD). Therefore, most of the data used in this study were from the SFWMD DBHYDRO database. Hydrologic data, such as water level and flow (discharge), are useful for interpreting water-quality data and were compiled and stored with each analysis, if available. Data collected at selected canal sites near the Refuge also were included in the study. Only data from grab samples from DBHYDRO were used in this study; time-composited samples were excluded. Additional water-quality data, including depth-integrated samples collected at several intervals across the canal as part of the USGS National Water-Quality Assessment (NAWQA) Program since 1996 at S-6, were reviewed and integrated into the analysis. The data set compiled and used in this study is available online (U.S. Geological Survey, 2006).

Water-quality studies and sample collection have been conducted in the Refuge since the early 1970s (McPherson and others, 1976b; Richardson and others, 1990) and have increased in number and scope since 1994 (Walker, 1999a, b). The SFWMD has collected water-quality data at water control structures S-5A and S-6 since June 1974. Within the Refuge, water-quality data were collected at sites CA1-1 to CA1-16 beginning in June 1978 and ending between December 1982 and July 1983. These data were summarized by Richardson and others (1990). Sites CA1-3 through CA1-16 were later renamed LOX3 through LOX16 and sampling resumed on a monthly basis beginning in 1993-94. Both sets of site names are stored in DBHYDRO, distinguished from each other by 1-second differences in latitude and longitude, although the locations are identical. Data collected at both sets of site names were combined to create a long-term record for each of the sites.

Water-quality data collected within the Refuge have been archived by the SFWMD, and, since 2000, published in annual summaries (South Florida Water Management District 2000; 2005c). The summaries include baseline conditions for each water year (October 1 to September 30) and yearly excursions from Class III criteria in the Refuge. Class III criteria for water quality were established to ensure safe recreational

use of water and the propagation and maintenance of a healthy, well-balanced population of fish and wildlife (Florida Department of Environmental Protection, 1996). The SFWMD also has monitored pesticide residues in water and sediment in canals near the Refuge for more than 10 years and releases quarterly summaries of these data online (South Florida Water Management District, 2005d).

Data Selection and Screening

Specific conductance, chloride, sulfate, total phosphorus, and total nitrogen data were selected for evaluation of long-term trends. These data were used for statistical analyses at sites S-6 and S-5A from 1974 to 2004 and at sites LOX8, LOX13, and LOX15 from 1978 to 2003.

Chloride concentration and specific conductance (Hem, 1992, p. 118 and 67, respectively) are the most chemically and biologically conservative water-quality indicators and tracers of the commonly determined constituents, and they typically have long and reliable analytical records. Background sulfate concentrations are low in remote freshwater wetlands of southern Florida; sulfate concentrations that are elevated above natural background concentrations are good indicators of human activities (Miller and others, 1999, p. 8). Increased sulfate is associated with increased mercury methylation, a major environmental concern in southern Florida, and also may contribute to declines in native plant populations by altering chemical conditions in sediments (Bates, and others, 2002; Orem, 2004). For example, in the absence of oxygen, bacteria can convert sulfate into hydrogen sulfate, a toxic sulfur compound. Background total phosphorus concentrations are low in freshwater wetlands that have not been affected by agricultural and urban development, and total phosphorus is considered to be the primary growth-limiting nutrient for plants and a primary factor in controlling the ecological balance of the Everglades (South Florida Water Management District, 2005a,c). Nitrogen is an important micronutrient that also can affect the ecological balance, and high total nitrogen concentrations are an ecological concern, especially in tidal and estuarine waters (Brandt and others, 2002).

Water-level measurements at site 1-7 in the center of the Refuge (fig. 2) were stored in the USGS National Water Information System (NWIS) database with each of the Refuge water-quality analyses to provide a consistent, long-term water-level record that reflects seasonal rainfall and evapotranspiration more accurately than do the highly variable, manipulated water levels in the surrounding canals. For sites S-5A and S-6, site-specific water-level data were compiled and stored in NWIS with the corresponding water-quality data.

Multiple data screening techniques were used to remove erroneous data from this study's data sets to improve the interpretations. Chemical logic (relations between different chemical species or physical properties) and statistical or graphical checks were used to assess the validity of water-quality constituents. For example, because the contribution of each major ion to the specific conductance of water can be computed (Miller and others, 1988), computer programs were used to screen the data for large discrepancies between major ions and specific

conductance; such discrepancies were used to direct the data reviewer to analyses that contain errors. Dissolved phosphorus and orthophosphate concentrations were checked to verify they were not greater (beyond normal analytical errors) than total phosphorus concentrations in the same samples.

Data Analysis

Data used for this study were collected between 1978 and 2004. As previously mentioned, the water-quality constituents selected for analysis were specific conductance, chloride, sulfate, total nitrogen and total phosphorus. Additional factors that could influence long-term trends also were considered. In some cases, the statistical methods used for this study decreased the effects of seasons and long-term wet or dry periods on trend analyses. A timeline of events related to hydrology and stormwater treatment in the Refuge is presented in table 1. A timeline of major storms and fire events in the Refuge is presented in table 2.

Rainfall, Water Level, and Flows in the Refuge

Water quality in the Refuge is affected by seasonal and long-term changes in rainfall (fig. 3), water level, and flows. For the period in which water-quality data are available, annual water conditions in the Everglades have been described as dry during 1974-76 and 1985 and very dry during 1989-91 (Frederick and Ogden, 2001). For the period of record at site 1-7, the slope of a simple linear regression fit to the water-level data yielded an increase in water level of about 0.91 ft for the 50-year period from 1954 to 2004, with an average increase of 0.018 ft/yr (fig. 4).

Low water level in the marsh and sloughs generally results in ponding and increased major ion and nutrient concentrations because of evapotranspiration, the enhanced breakdown of organic material, and the buildup of waste from aquatic and terrestrial wildlife that concentrate in and near the remaining surface water. Conversely, rainfall, high water level, and flowing water may: (1) decrease concentrations by dilution or flushing major ions and nutrients out of the marsh; or (2) increase concentrations by introducing water enriched in major ions and nutrients from agricultural or urban sources.

Table 1. Timeline of events related to hydrology and stormwater treatment in the Loxahatchee National Wildlife Refuge.

[Information provided by M. Waldon, U.S. Fish and Wildlife Service, written commun., 2005]

Date	Description	Information source
1915	Palm Beach (C-51) Canal completed	Silveira (1996)
1915	Hillsboro Canal completed	Silveira (1996)
1951-06-08	Loxahatchee NWR established	Richardson and others (1990)
1952 to 1954	L-40 Levee & Canal constructed	Light and Dineen (1994)
1954 to 1959	L-7 Levee & Canal constructed	Light and Dineen (1994)
1955	S-5A pump station begins operations	Anonymous (1955); South Florida Water Management District (2005b)
1957-04-01	S-39 gate flow starts	DBHYDRO flow record
1957-04-30	S-6 begins operations	South Florida Water Management District (2005b)
1960-11-01	S-5AS discharge to Refuge begins	DBHYDRO stage record
1961	L-39 Levee completed	Light and Dineen (1994)
1961	S-10A, C, and D completed	Light and Dineen (1994)
1975	S.N. Knight pump installed	Lin and Greg (1988)
1980-08	ACME 1 pump begins operation	DBHYDRO flow record
1980-08	ACME 2 (G-94D) begins operation	DBHYDRO flow record
1983	S-10E operational	Lin and Greg (1988)
1988	S.N. Knight pump ends operation	Lin and Greg (1988)
1988b	G-94C (Ross Structure) operational	Lin and Greg (1988)
1988a	G-94B operational	Lin and Greg (1988)
1988b	G-94A operational	Lin and Greg (1988)
1994-02-10	G-251 pump station begins operation	DBHYDRO flow record
1994-05-06	G-250 pump station begins operation	DBHYDRO flow record
1994-08-24	ENR flow through started	Goforth (2005)
1999-06-07	S-5AS discharge to Refuge ends, levee and gates complete	DBHYDRO stage record
1999-08-26	G-300, 301, and S-5A distribution works completed, flow begins	DBHYDRO flow record
2000	STA-1W cell 5 flow through started	DBHYDRO flow record
2000-07	STA-1W flow through started	Goforth (2005)
2000-10	G-310 begins operations	South Florida Water Management District (2005b)
2001-05	S-6 diverted to STA-2	Goforth (2005)
2002-12-31	G-250 pump station ends operations	DBHYDRO flow record
2004-05	STA-1E flow through started	South Florida Water Management District (2005a, p. 19)

Table 2. Timeline of major storm and fire events in southern Florida.

[Information provided by M. Waldon, U.S. Fish and Wildlife Service, Boynton Beach, Fla., written commun., 2005]

Date	Description	Information source
1955	Fire, 10,000 acres	Richardson and others (1990)
1962	Fire, over 100,000 acres	Richardson and others (1990)
1979-09-03	Hurricane David	Gentry (1984)
1981	Fire, 6,500 acres on west side	Richardson and others (1990)
1981-08-16 to 18	Tropical Storm Dennis	Gentry (1984)
1989-04	Fire, 45,000 acres on west side and north end	Richardson and others (1990); Brandt and others (2002)
1999-10-15	Hurricane Irene	South Florida Water Management District (2001)
2004-09-04	Hurricane Frances	M. Waldon, written commun., U.S. Fish and Wildlife Service, 2005
2004-09-16	Hurricane Ivan (no direct impact to Refuge)	Stewart (2005)
2004-09-25	Hurricane Jeanne	M. Waldon, written commun., U.S. Fish and Wildlife Service, 2005

Factors to Consider in Long-Term Trend Analyses

Water-quality trends can be produced by changes in a number of factors, including seasonal and long-term variations in rainfall, evapotranspiration, and water flows, as well as changes in water-management practices, land use, and water treatment. The goal of trend analysis was to determine if there are trends due to changes in loading to the drainage basin rather than to dilution or concentration that is caused

merely by seasonal rainfall patterns or unusually wet or dry periods. The analysis of water-quality data to determine long-term trends, however, is complicated by three basic factors: (1) the variety and complexity of natural and human-induced hydrologic changes; (2) changes over time in the methods used to collect and analyze water samples; and (3) changes in the frequency and (or) timing of sampling. It was necessary to account for the changes in sampling and analytical techniques over time to better interpret historical water-quality data from the Refuge and place the trend results in an appropriate context.

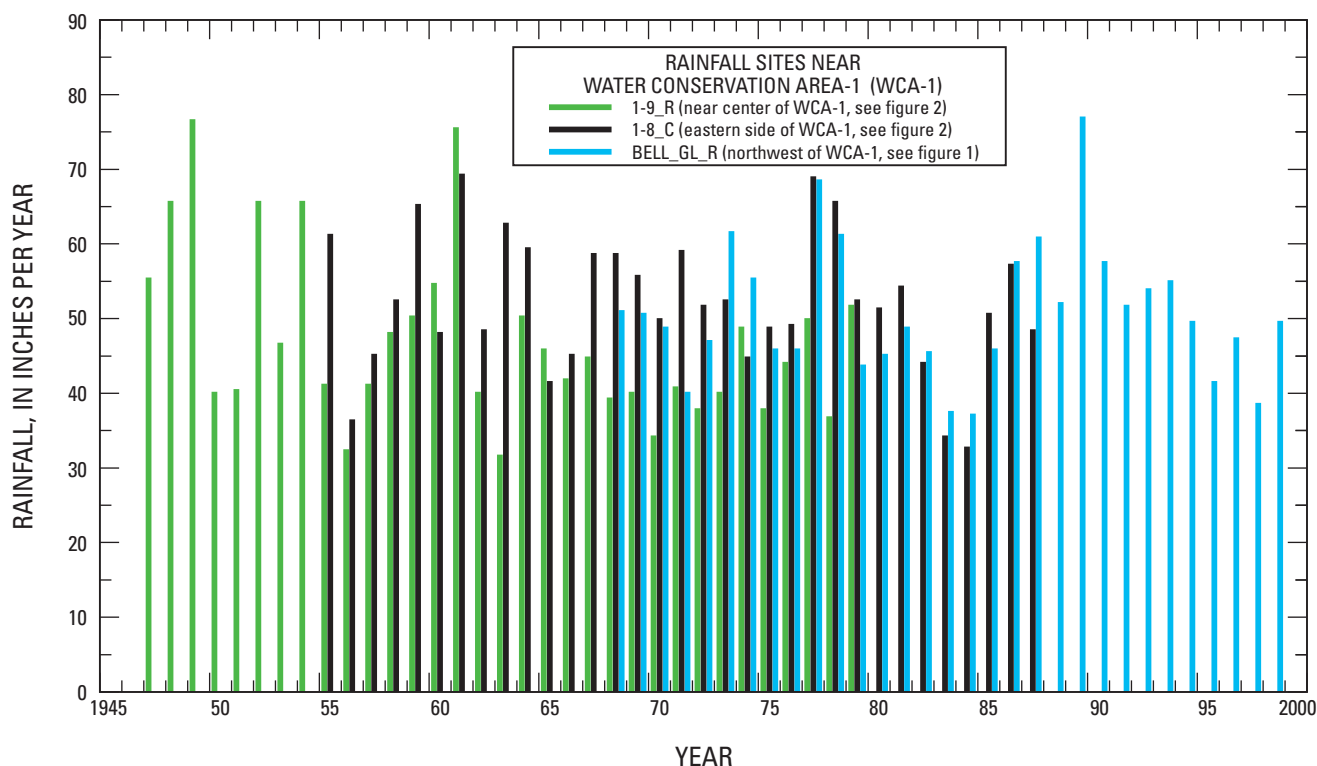


Figure 3. Total annual rainfall at three sites in the vicinity of the Loxahatchee National Wildlife Refuge, 1947-1999.

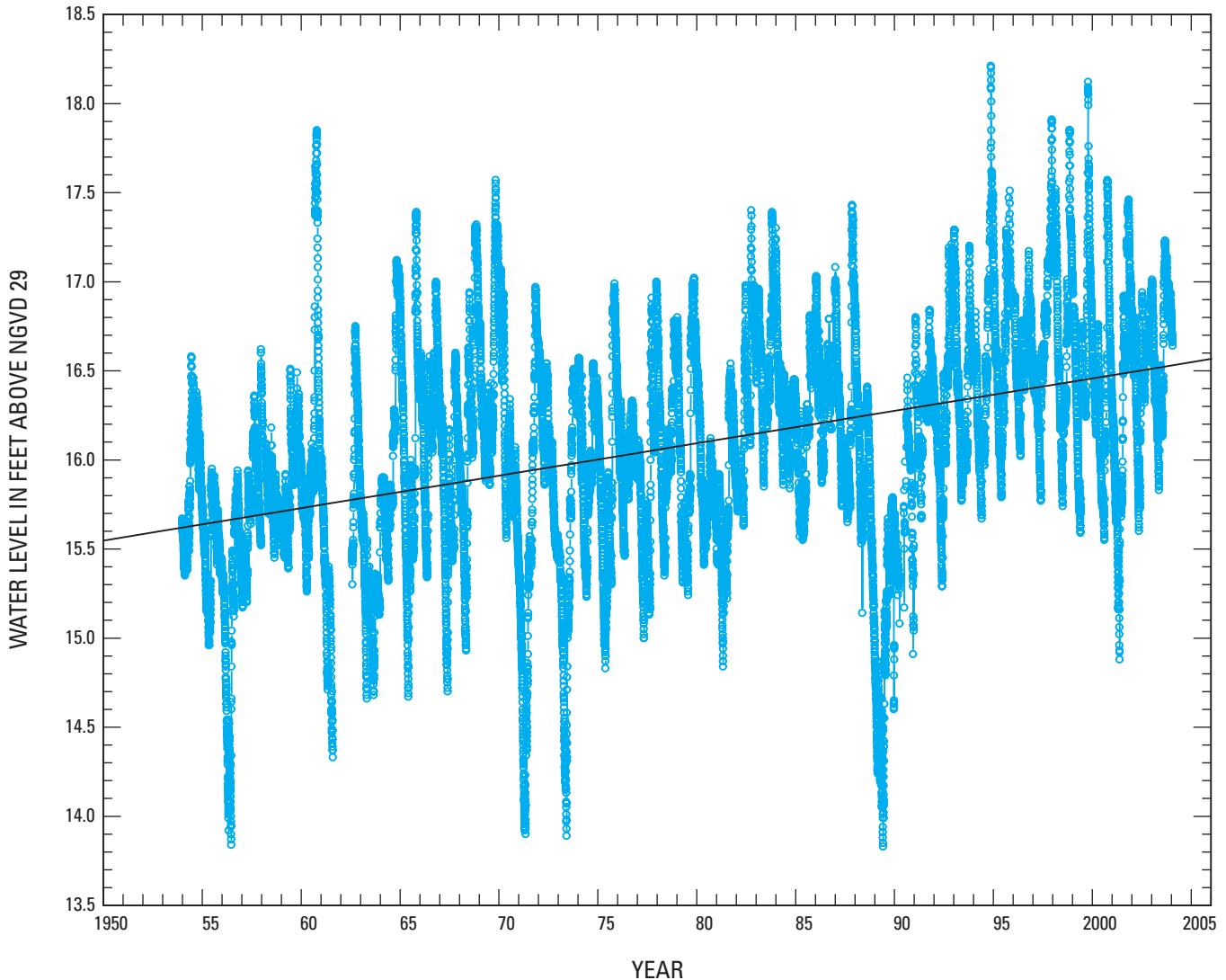


Figure 4. Long-term water levels in the Refuge at site 1-7 with a simple linear regression, 1954-2004.

In trend analysis, hydrologic change can be partially compensated for by using statistical computer programs, such as S-ESTREND (Slack and others, 2003), that fit a relation between concentration and either flow or water level, and use this relation to minimize the effects of wet and dry seasons on concentrations. By using these techniques, an apparent trend in concentration during a long drought may not be statistically valid because the water-level adjustment compensated adequately for the effects of water level on concentration. To meet the requirements for reliable statistical analysis, however, programs such as S-ESTREND require sufficient data with a suitable distribution throughout the period of interest. Consequently, a lack of suitable, long-term data sets can limit the use of such programs for trend analysis.

Sample-collection methods in the Refuge changed between sampling periods and were considered when interpreting long-term trends for this study. The earliest water-quality data for the Refuge sites were collected in 1978

and stored in DBHYDRO with site names CA1-1 through CA1-55. Prior to 1993, all CA1 samples were collected using a polyethylene sampler lowered from a hovering helicopter (Millar, 1981; M. Waldon, U.S. Fish and Wildlife Service, oral commun., 2005). This technique may have affected sample concentrations due to downdrafts and (or) helicopter exhaust. Helicopter downdrafts agitate the water, which can disturb bottom sediments and increase the concentration of unfiltered constituents (total phosphorus, total nitrogen, and other unfiltered constituents that are enriched in bottom sediments) above that of a sample from undisturbed water. Unless stratification existed between shallow and deep water during helicopter sampling events, however, any mixing caused by the downdraft would probably not substantially change the specific conductance and concentrations of dissolved (filtered) constituents such as chloride, sodium, and calcium. It also is possible that sulfur oxides and nitrogen oxides, which are water-soluble gases from helicopter exhaust, may

have increased the sulfate, nitrite, nitrate, and total nitrogen concentrations during the early sampling. If constituent concentrations since 1994 are lower only because of changes in the sampling approach (helicopter as compared to wading), false trends in total phosphorus, total nitrogen, and sulfate could be produced by the statistical analyses that do not represent the true trends in undisturbed Refuge water.

By 1994, the samples were collected some distance away from a helicopter by landing and wading to collect samples, possibly resulting in a less disturbed sample (M. Waldon, U.S. Fish and Wildlife Service, oral commun., 2005). Therefore, concentrations and trends in water-quality data from 1994 to the present may be influenced less than the earlier data by the effects of sampling methods. Total phosphorus sampling resumed in June and September 1993 at the LOX sites, and other laboratory determinations resumed in June through August 1994.

Laboratory analytical methods and minimum reporting levels (MRLs) for constituents analyzed statistically in this study have changed over the years, and these changes can affect the results of some trend analyses; this is especially true if many of the concentrations are near or less than the respective MRL for the analytical methods used. The MRLs also have varied over the period of record within and between agencies. For example, the USGS reported total phosphorus concentrations as low as 0.01 mg/L during the 1970s and 1980s; during the mid-1980s, the SFWMD began reporting total phosphorus concentrations as low as 0.004 mg/L. The total phosphorus concentrations, therefore, appear to decrease after 1985 because of the lower MRL, suggesting an apparent downward trend over time, even though the concentrations may have been the same during both periods.

Additionally, trends are more difficult to determine if a large percentage of the data is reported as censored values; that is, data reported as less than the MRL (for example, less than 0.004 mg/L) for a specific method of measurement. Because all measurements have random errors and some have biases associated with them, concentrations near the MRLs can be influenced and biased by such errors even though the data are not censored. For example, if the pre-1988 MRL for sulfate is 5 mg/L and the variability is ± 3 mg/L, a “true” concentration of 3 mg/L could be reported as 6 mg/L. If the analytical method changed in 1988 and the MRL was revised to less than 2 mg/L, a “true” concentration of 3 mg/L may be reported by the laboratory as 3 mg/L. Thus, the latter method could report one half the concentration of the former, when both “true” concentrations were actually the same.

In this study, the factors discussed here were most likely to affect trend analyses at sites with low concentrations of sulfate and total phosphorus. In some cases, a large percentage of the total phosphorus and sulfate concentrations were censored, and trends may be influenced by changes in censoring levels. However, the effects of changes in MRLs were minimized in this study by using S-ESTREND to determine trends. Data for specific conductance, chloride, and total nitrogen were well above the MRLs, and therefore, were less influenced by long-term changes in analytical methods.

Changes in the frequency or timing of sampling can affect the results of water-quality trend analysis. For example, if the sampling frequency during the year increases, seasonal trends will be more obvious. If the fraction of samples collected during the dry season increases with time, water-quality constituents that are highest during the dry season also may appear to increase with time if statistical methods are used that do not distinguish between seasons. An increase in sampling frequency also will increase the probability of collecting samples during periods of extremely heavy rainfall or during droughts, which could result in a greater range in water-quality values than would be evident with fewer samples.

Tobit regressions can be influenced by a seasonal bias in sampling dates during the period of record. For example, if most samples were collected during the dry season (October-May), concentrations would appear higher than if most were collected during the rainy season (June-September). Trends other than those shown may be present but were not detected because of limitations in the data sets or statistical procedures.

Statistical Analysis for Trends

Locally weighted scatter-plot smoothing (LOESS) plots (Slack and others, 2003) were used to evaluate long-term data for trends and to show the generalized direction of change in concentration with time. LOESS plots are especially useful for visualizing the direction of concentration changes in data that are highly scattered. LOESS also was used within the S-ESTREND program to adjust for the normal seasonal changes in concentration caused by variations in water level. Without these adjustments, it is difficult to distinguish concentration changes related to seasonal water-level changes from actual long-term trends in concentration caused by other changes within the drainage basin. An advantage of using LOESS for flow- and water-level adjustment of water-quality data is that no advanced knowledge is needed about the relation between the two variables. The technique allows the user to describe a relation between two variables even when simple or commonly used equations do not describe the relation between them. LOESS is accomplished by fitting a linear regression for many small parts of the x-axis (the horizontal axis) to form a smooth line. The LOESS regression weights the closer (local) data points more heavily than the more distant ones and is similar to a moving average.

When viewing plots of data and LOESS lines, the reader may perceive a trend in concentration that is not statistically significant, especially when statistical programs adjust for severe wet and dry periods. Additionally, the uncensored seasonal Kendall test uses selected data with a preference for the center of a “season,” which refers to a part of the year selected by the S-ESTREND user. The selection of seasons is usually based on the abundance of data throughout the year and the typical annual cycle of wet and dry periods. Thus, only a subset of the available data might be used to determine trends. This selection process also minimizes serial correlations—problems that can produce misleading statistical results.

The uncensored seasonal Kendall test and Tobit regression procedures, provided with the S-ESTREND program, were used to analyze water-quality data for trends. A 95-percent confidence level ($p = 0.05$) was used for all of the statistical tests; at this level, there is a 5-percent chance of concluding that there is a trend where none exists. The uncensored seasonal Kendall test requires that: (1) at least 5 years of data are available, (2) no more than about 5 percent of the data are censored, and (3) no more than one censoring level exists. In addition, there are requirements for a minimum abundance of data in the first and last fifth of the timespan being tested. This test allows water-quality data to be flow or water-level adjusted. The uncensored seasonal Kendall test was used to identify trends in specific conductance, chloride, sulfate, total phosphorus, and total nitrogen.

The uncensored seasonal Kendall test is nonparametric and considered robust; that is, it is not sensitive to outliers in the data that can create misleading or erroneous results (Schertz and others, 1991). Because the seasonal Kendall test is nonparametric, the data set is not required to have a specific distribution, such as a normal (Gaussian) or log-normal distribution, to produce valid trends. For normally distributed data, nonparametric tests are almost (95 percent) as powerful as parametric tests; for data that are not normally distributed, the nonparametric tests used here are more powerful than parametric tests.

The uncensored seasonal Kendall test compares data for each season for a selected time period, which reduces the effect of seasonal water-quality changes, and, combined with water-level adjustment, improves the ability to determine valid long-term trends. Three seasons were used—January to May, June to September, and October to December. These seasons correspond to the late dry season, rainy season, and early dry season in southern Florida, respectively. Comparisons were made between concentrations for a given season during the first year and each following year to compute the number of increases and decreases. Concentrations for the same season were then compared between the same season in the second year and each following year, and so on.

For each season, a single value was selected for use in the seasonal Kendall test. For seasons with multiple values, the value with a water level associated with it and that is most centered in the season with respect to time was selected to represent the season (Schertz and others, 1991). Because of this selection process, some of the data visible on a graph and that influence the shape of the LOESS plots may not be used by the seasonal Kendall test procedure. Consequently, graphs showing all of the data points over time may appear to show a trend that is not statistically significant using this procedure.

To assist in interpreting the results of the uncensored seasonal Kendall tests, the change in concentration (starting with zero in the first year) in its original units was plotted against time for a period of years. The change in concentration was computed by multiplying the seasonal Kendall slope

estimator generated by the S-ESTREND program times the difference between the ending and starting years of a trend. For example, a slope of +14.369 mg/L per year was computed by the program for chloride at LOX15 for 1998-2003 ($14.368 \text{ mg/L} \times 5 \text{ years} = 71.8 \text{ mg/L}$). The slope generated by the program is the median of all possible slopes used in the seasonal comparisons for the test period. The use of the median slope reduces, or in some cases, eliminates the influence of extreme values in a data set.

The Tobit regression analysis was used to test for trends in sulfate and TP concentrations. Tobit regression was used when more than 5 percent of the data for a constituent were censored or when more than one censoring level occurred in the data (usually for sulfate and total phosphorus at interior sites). A maximum of 20-percent censored values is recommended, but the program allows the user to set the maximum to more than 20 percent; the 20-percent default was used for these analyses. The Tobit regression analysis does not adjust for water level and is more susceptible to trends that result only from long dry or wet periods or seasonality. The Tobit regression analysis is a parametric test that assumes the data are normally distributed (data fit a bell-shaped or Gaussian distribution). Because water-quality data often deviate from a normal distribution, logarithmic data transformations were used to improve the normality of the data and the effectiveness of the method.

In some cases, data requirements for using the S-ESTREND program prevented the use of the full period of record for statistical analysis. In addition, the S-ESTREND program assumes a monotonic trend (the trend is a straight line increase or decrease with time or there is no trend). S-ESTREND can only evaluate a change from an increasing to a decreasing trend (or decreasing to increasing) in concentration as a straight-line change during the entire selected period, and in this study the long-term trends were seldom monotonic. Consequently, LOESS plots were used to decide where to break the data sets into shorter periods for trend analysis, even though LOESS plots are influenced by long dry or wet periods.

Water Quality

Water quality in the Refuge marsh is characterized by: (1) low specific conductance, which was typically between 60 and 100 $\mu\text{S}/\text{cm}$; (2) a predominance of sodium and chloride ions; (3) low nutrient concentrations; and (4) high concentrations of dissolved organic matter. Water quality in nearby canals is characterized by specific conductance that often exceeds 1,000 $\mu\text{S}/\text{cm}$. The canal water has greater chloride, sodium, and magnesium ion concentrations, higher (darker) color, and higher dissolved organic matter and nutrient concentrations than the Refuge marsh (McPherson and others, 1976a,b).

Seasonal changes in water quality in the Refuge marsh are a result of natural processes, water management, and land-use activities. As water level and flows decline during the dry season (October-May), ionic concentrations increase because of evapotranspiration and geochemical and biological processes, especially in ponded water (Waller, 1982). Drought and fire can cause geochemical changes in Everglades peat that stimulate the release of constituents, such as sulfate and nutrients, to surface waters after the peat is reflooded (Krabbenhoft and Fink, 2001). A decline in water level in these wetlands can increase canal inflows and alter wetland water quality (McPherson and others, 1976b; Waller, 1982; Walker, 1997, 1999a,b). Land-use activities in the surrounding urban and agricultural areas affect water quality in canals and in wetlands that receive canal inflows. Concentrations of phosphorus at inflows to the Refuge (at structures S-5A and S-6) increased in the late 1970s and the 1980s. Walker (1997) attributed these increases in phosphorus concentration to the expansion of agricultural land use and to changes in water management that resulted in long-term nutrient enrichment in the WCAs. After about 1991, phosphorus concentrations decreased at the S-12 structures, which are down gradient from the Refuge. Walker (1997) speculated that this decrease may reflect post-1991 changes in water management and water treatment, and a shift from vegetables to other crops in the EAA. Rice and others (2002) estimated that implementation of best management practices in the EAA reduced farm phosphorus loads an average of 55 percent between the 1996 and 1998 water years.

Water-quality conditions in the Refuge are occasionally outside the prescribed range of Class III water-quality criteria established by the State of Florida. The South Florida Water Management District (2005c, Chapter 2A, p. 18-19) summarized excursions (values outside of the prescribed range) from Class III criteria in the Refuge for the 1978-2002, 2003, and 2004 water years. The highest percentages of excursions from the criteria were for dissolved oxygen, alkalinity, and specific conductance at the Refuge inflow sites. Concentrations of un-ionized ammonia were generally below the Class III criterion of 0.02 mg/L. There were only 3 excursions in 1,447 LOX marsh samples and 39 excursions in 2,019 inflow samples during the 1978-2002 period (South Florida Water Management District, 2005c, p. 2A-18). At a pH of 8.0, only about 5 percent of the ammonia plus ammonium ion is in the form of ammonia, the more toxic of the two nitrogen species. At the lower pH values typically present in the Refuge, the percentage is smaller than 5 percent because more ammonia is converted to ammonium ion as pH decreases. Based on the SFWMD water-quality data, it seems unlikely that un-ionized ammonia frequently exceeds the Class III criterion at the Refuge marsh sites.

Background Water-Quality Characterization

Efforts to restore the southern Florida environment require specific and reasonable goals to direct such efforts and measure progress. A useful approach in establishing such goals is to describe background conditions in areas that have been minimally impacted by human activities as estimates of predevelopment conditions. To help define background water quality, two Refuge sites in the northern Everglades ridge and slough area (fig. 2, LOX8 and LOX13) and one site in the southern Everglades (fig. 1, P-34) were selected. Sites LOX8 and LOX13 were selected because they are remote sites away from canals, have low median specific conductance and sulfate concentrations, and few specific conductance and sulfate values that deviated greatly from the median. This low deviation from the median probably indicates that canal water seldom reaches these sites and has minimal effects on their water quality. Sulfate is a good indicator of human influences on water quality in freshwater areas of southern Florida (Miller and others, 1999). Miller and others (2004) also have shown P-34 to be a suitable site for background water quality. All three sites also had correlations between water level and water-quality concentrations of selected constituents, indicating that concentrations respond primarily to evapotranspiration and rainfall and minimally to the inflow of canal water. The inverse relation between water level at site 1-7 and specific conductance and total phosphorus at LOX8 is shown in figure 5.

At background sites, specific conductance and sodium, calcium, magnesium, chloride, alkalinity (mainly bicarbonate ions), total nitrogen, and dissolved organic carbon concentrations increased between about 40 to 70 percent in May near the end of the dry season compared to September at the end of the wet season. Such increases are probably caused by evapotranspiration. The effects of ground water inflow on the normal seasonal variations in surface-water quality in the Refuge is probably small because perched water levels are thought to limit inputs of ground water and its solutes (M. Waldon, U.S. Fish and Wildlife Service, oral commun., 2005).

Median concentrations at the end of the dry and wet seasons for the period of record at LOX8, LOX13, and P-34 were used to characterize background water quality in the Everglades (table 3). Water samples from LOX8 and LOX13 predominantly contained sodium and chloride ions followed by calcium and bicarbonate (shown as alkalinity) ions, based on the amount of ionic charge per liter rather than mass per liter. Water samples in the southern Everglades at P-34 predominantly contained calcium and bicarbonate ions. Water at LOX8 and LOX13 had relatively lower pH and specific conductance and higher color than at P-34.

The differences between water quality at the Refuge background sites (LOX8 and LOX13) and at P-34 can largely be attributed to differences in soil and surficial geology. The Refuge sites are on thick (about 6-10 ft) peat soils that are a source of organic color and partially isolate surface water from the underlying limestone—a source of calcium and

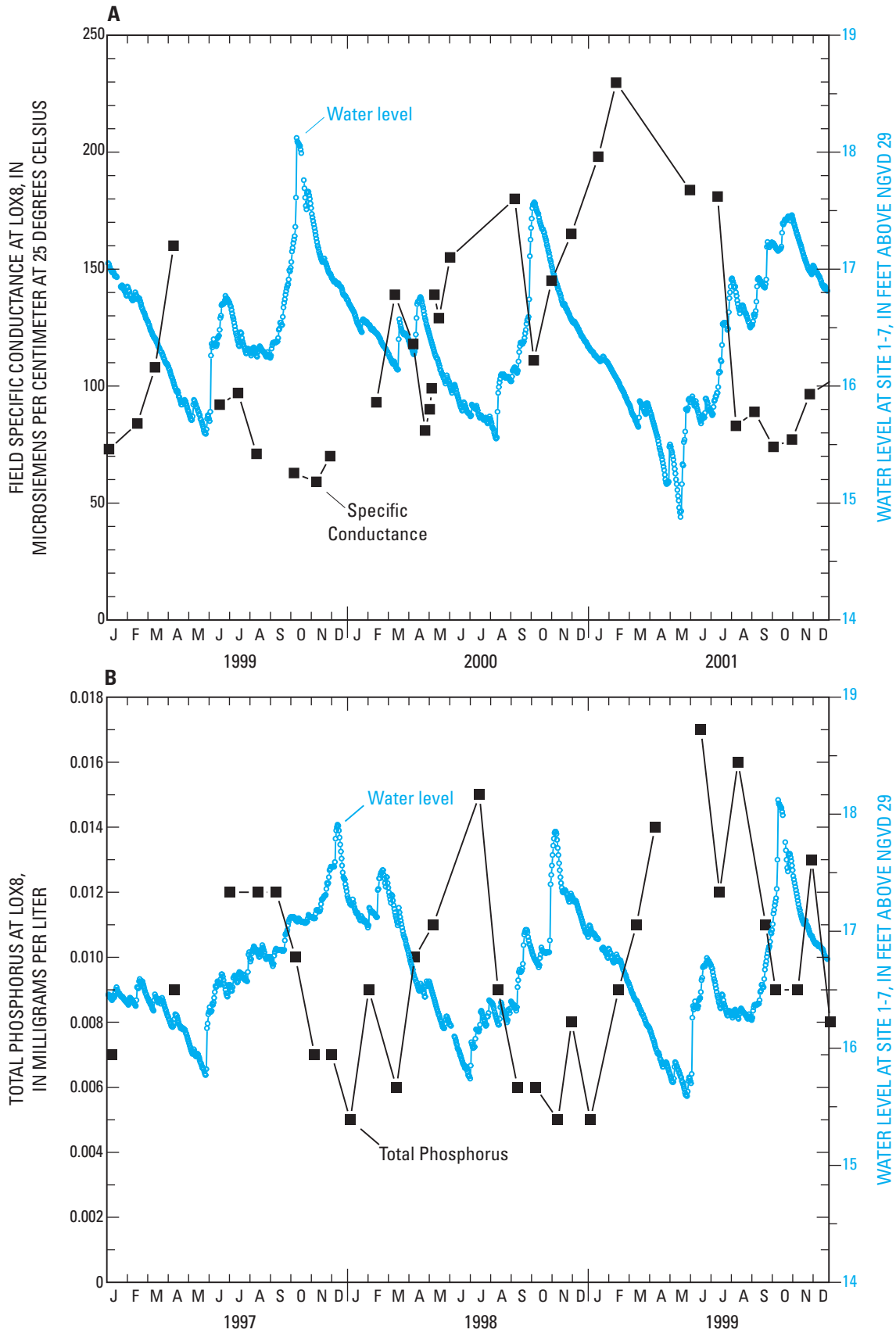


Figure 5. Water level at site 1-7 and specific conductance (A) and total phosphorus concentration (B) at site LOX8.

Table 3. Median values for water-quality constituents and other indicators at the end of the dry and wet seasons (May and September, respectively) for periods of record at selected background sites in the Arthur R. Marshall Loxahatchee National Wildlife Refuge (LOX8 and LOX13) and in Everglades National Park (P-34).

[Units in milligrams per liter, except as noted. $\mu\text{S}/\text{cm}$ at 25° C, microsiemens per centimeter at 25 degrees Celsius; meq/L, milliequivalents per liter; Pt-Co units, platinum-cobalt units; pH units, the negative of the base 10 logarithm of the hydronium ion activity that is used as a measure of the acidity or basicity of water; CaCO_3 , calcium carbonate; --, not analyzed; <, less than]

Constituent	LOX13		LOX8		P-34	
	May	September	May	September	May	September
Alkalinity, as CaCO_3 (adjusted)	18.0	11.2	14.0	9.5	175 ¹	119
Ammonia, as N	0.010	0.012	0.02	0.02	<0.01	<0.01
Anion sum, meq/L	0.985	0.603	1.056	0.683	4.283	2.864
Calcium	7.5	4.4	5.5	4.0	65.8	43.5
Calculated total dissolved solids	101	64	114	76	224	150
Cation sum, meq/L	1.002	0.603	1.021	0.669	4.244	2.809
Chloride	16.0	9.5	20.0	12.5	26.2	17.0
Color, Pt-Co units	65	67	75	60	20	18
Dissolved organic carbon	24.9	16.2	31.8	20.8	--	--
Dominant anion based on charge	Chloride	Chloride	Chloride	Chloride	Bicarbonate	Bicarbonate
Dominant cation based on charge	Sodium	Sodium	Sodium	Sodium	Calcium	Calcium
Field specific conductance, $\mu\text{S}/\text{cm}$ at 25° C	101	60 ¹	103 ¹	68 ¹	432	286
Ionic balance, percentage	0.9	0.0	-1.7	-1.0	-0.4	-1.0
Magnesium	1.4	0.9	1.8	1.3	3.0	2.3
Nitrite plus nitrate, as N	0.001	0.004	0.002	0.005	0.007	0.004
Number of values used for medians	4-11	3-7	4-9	7-10	2-9	7-20
Orthophosphate (filtered) , as P	<0.002	<0.002	<0.002	0.002	<0.004	<0.004
pH, pH units	5.9	6.2	5.9	6.4	7.7	7.7
Potassium	0.4	0.3	0.65	0.33	0.7	0.5
Silica	5.1	3.6	3.4	3.7	4.9	4.7
Sodium	11.5	6.9	13.3	8.1	16.0	10.0
Sulfate	0.6	0.3	0.3	0.3	2	<2
Suspended solids	7	1	4	1	<3	<3
Total nitrogen, as N	1.6	0.9	1.7	1.2	1.6	1.0
Total phosphorus, as P	0.01	0.01	0.011	0.010	0.009	0.004
General date range	5/79 – 5/03	5/79 – 9/02	5/79 – 5/03	9/78 – 9/03	5/61 – 5/95	9/62 – 9/99

¹A computed value was substituted for the median to be consistent with the rest of the analysis. The synthesis of the major ion analyses from medians produced reasonable results; however, adjustments were needed for some analyses to produce better self-consistency. For example, specific conductance computed from major ions was substituted for the median field specific conductance if there was a disagreement of more than a few percent. One alkalinity computed to produce an agreement between the cation sum and the anion sum was substituted for the median alkalinity. Specific conductance was computed using a specialized data review program written by the senior author (Miller and others, 1988). All other values are medians.

bicarbonate ions. Near site P-34, however, little or no bottom sediment separates surface water from the underlying limestone. The dissolution of limestone tends to make water basic, and consequently, raise the pH of the water.

Median nutrient concentrations (as nitrogen or phosphorus) were low at all three background sites, where dilution by rainfall during the wet season and concentration by evapotranspiration during the dry season are the dominant controls. At LOX8, median ammonium ion concentrations were 0.02 mg/L in both May and September, and nitrite plus nitrate increased from 0.002 in May to 0.005 mg/L in September, perhaps because of rainfall inputs. Median orthophosphate concentrations were less than 0.002 (LOX13 and LOX8) or less than 0.004 mg/L (P-34), except for a wet-season median concentration of 0.002 mg/L at LOX8. In the Refuge, background median total phosphorus

concentrations were all near 0.01 mg/L during the wet and dry seasons. Median concentrations of total nitrogen and organic carbon increased by about 40-70 percent between the wet and dry seasons, as did specific conductance and several major ions, possibly indicating similar seasonal controls on concentration. Median pH values (5.9-6.4) were all mildly acidic, as expected for colored water (60-75 Pt-Co units) overlying peat deposits. At LOX8 and LOX13, sulfate concentrations were low (0.3-0.6 mg/L) during the wet and dry seasons. Median sulfate at P-34 ranged from less than 2 mg/L during wet seasons to 2 mg/L during dry seasons. Low sulfate concentrations also were observed in other remote areas of the Big Cypress National Preserve and Everglades National Park, indicating minimal human-induced effects on water quality in these areas (Miller and others, 1999).

Trends in Water Quality and Water Level over Time

Five sites (LOX8, LOX13, LOX15, S-5A, AND S-6) were analyzed for trends (figs. 6-10), and as noted earlier, the statistically significant trends were reported at the 95-percent confidence level. For LOX8, LOX13 and LOX15, the 1978-83 data were combined with the 1993-2003 data for statistical and graphical analyses (figs. 6-8). Water-level data are included in the figures to show relations between water level and concentrations of water-quality constituents. The factors associated with differing sampling approaches described earlier were considered when interpreting trends that include data before and after 1993, especially for total phosphorus and total nitrogen.

Of the five sites analyzed, LOX8 is the farthest from canals that transport contaminated water and is the most “natural” of the five sites tested. Site LOX13 also is relatively natural, and like LOX8, is considered a background water-quality site. Site LOX15 is about 1 mi from the Hillsboro Canal and occasionally is influenced by water from canals that surround the Refuge (fig. 11). Canal structures S-5A and S-6 discharge into the Refuge EAA water, which typically has constituent concentrations that exceed those at the background sites.

A number of significant long- and short-term trends were identified for specific conductance, chloride ion, sulfate ion, total phosphorus, and total nitrogen using the uncensored seasonal Kendall test (fig. 12a-e). The trend lines in figure 12 show the amount of change in the original concentration units, starting with zero in the first year of the test period. The concentration changes in figure 12 are the product of the slope multiplied by the time period in years; therefore, the longer the test period, the greater the change. Consequently, it is preferable to use the slope for comparisons between different time periods and between different constituents. For each constituent, the seasonal Kendall slope estimators are medians of all possible slopes computed for the test period. Greater emphasis was placed on the seasonal Kendall results than the Tobit regression results because the seasonal Kendall test minimizes seasonal effects and is water-level adjusted, resulting in more reliable trends.

Specific conductance—The long-term trends in specific conductance for the period of record (from about 1977 to 2003) are downward (decreasing) at S-5A and S-6 (fig. 12). Specific conductance at S-5A shows the most pronounced decline of about -340 $\mu\text{S}/\text{cm}$, followed by S-6 with a decline of about -280 $\mu\text{S}/\text{cm}$ for that period. Interior sites LOX8 and LOX13 show significant long-term (1978-2003) changes of about +37 and -36 $\mu\text{S}/\text{cm}$, respectively. To place these changes at LOX8 and LOX13 in context, the median specific conductance for the period of record at LOX8 and LOX13 is about 100 $\mu\text{S}/\text{cm}$ for May (near the end of the dry season) and about 60 to 70 $\mu\text{S}/\text{cm}$ for September (near the end of the wet season). The water quality at LOX15 can be greatly affected by canal water inflows (McPherson and others, 1976b). During 2000-03, for example, large amounts of poor-quality water entered the Refuge and affected concentrations of some water-quality constituents at LOX15. Although the

specific conductance at LOX15 showed no long-term trend, it increased about 560 $\mu\text{S}/\text{cm}$ between 1998 and 2003 and showed a trend similar to S-6 during that period. At S-6, specific conductance increased by about +370 $\mu\text{S}/\text{cm}$ between 1999 and 2004 (fig. 12).

Specific conductance is related to the electrical conductivity of all the ions in solution and will change in response to concentration changes in major ions (Miller and others, 1988). Therefore, a relation exists between changes in specific conductance and changes in concentrations of dominant major ions such as sodium, calcium, chloride, and sulfate. At the marsh sites, sulfate concentrations typically are low and responsible for only a small fraction of the total specific conductance.

Chloride—Long-term trends in chloride concentration for the period of record (1974-2003) are downward for S-5A (-85 mg/L) and S-6 (-54 mg/L), and these trends are steeper before about 1997 (fig. 12). Chloride at LOX13 decreased by about -7 mg/L between 1978 and 2002. Chloride increased by about +72 mg/L at LOX15 between 1998 and 2003, probably because of the greater than normal canal water inflow to the Refuge from 2000 to 2003 (M. Waldon, oral commun., U.S. Fish and Wildlife Service, 2005). If the concentration of chloride ion changes by 1 mg/L, sodium ion concentration must change by an equivalent amount to maintain charge balance; consequently, specific conductance would be expected to change by about 3.2 $\mu\text{S}/\text{cm}$ using the relation between major ion concentrations and specific conductance (Miller and others, 1988). Charge balance is the chemical principle that in a solution, the sum of the positive charges must equal the sum of the negative charges and result in a net charge of zero (a charge balance or electroneutrality).

Sulfate—The only significant sulfate trend identified by the uncensored seasonal Kendall test was an increase of about +30 mg/L at LOX15 between 1998 and 2003 (fig. 12). The low sulfate concentrations at LOX8 and LOX13 for the period of record and the absence of a long-term downtrend at LOX15 suggest that sampling from a hovering helicopter did not have a detectable influence on sulfate concentrations and trends. Sulfate concentrations typically were low at LOX8 and LOX13, and the high percentages of values below MRLs at these sites (49.1 and 41.7 percent, respectively) prevented trend analyses using the seasonal Kendall test. If the concentration of sulfate ion changes by 1 mg/L and calcium ion changes by an equivalent amount to maintain charge balance, specific conductance would be expected to change by about 2.9 $\mu\text{S}/\text{cm}$.

Total phosphorus—Structures S-5A and S-6 show downward long-term trends for total phosphorus concentration between 1974 and 2003 of -0.06 and -0.05 mg/L, respectively (fig. 12). Between 1980 and 1989, total phosphorus concentrations at S-5A trended downward -0.25 mg/L. Several relatively high total phosphorus concentrations (greater than 0.30 mg/L) from 1978 to 1984 at S-5A and S-6 may have contributed to the downtrends (figs. 9 and 10). The majority of total phosphorus concentrations at S-5A and S-6 were less than 0.20 mg/L for the period of record. Site S-6 was sampled from the ground and all concentrations were above the MRLs.

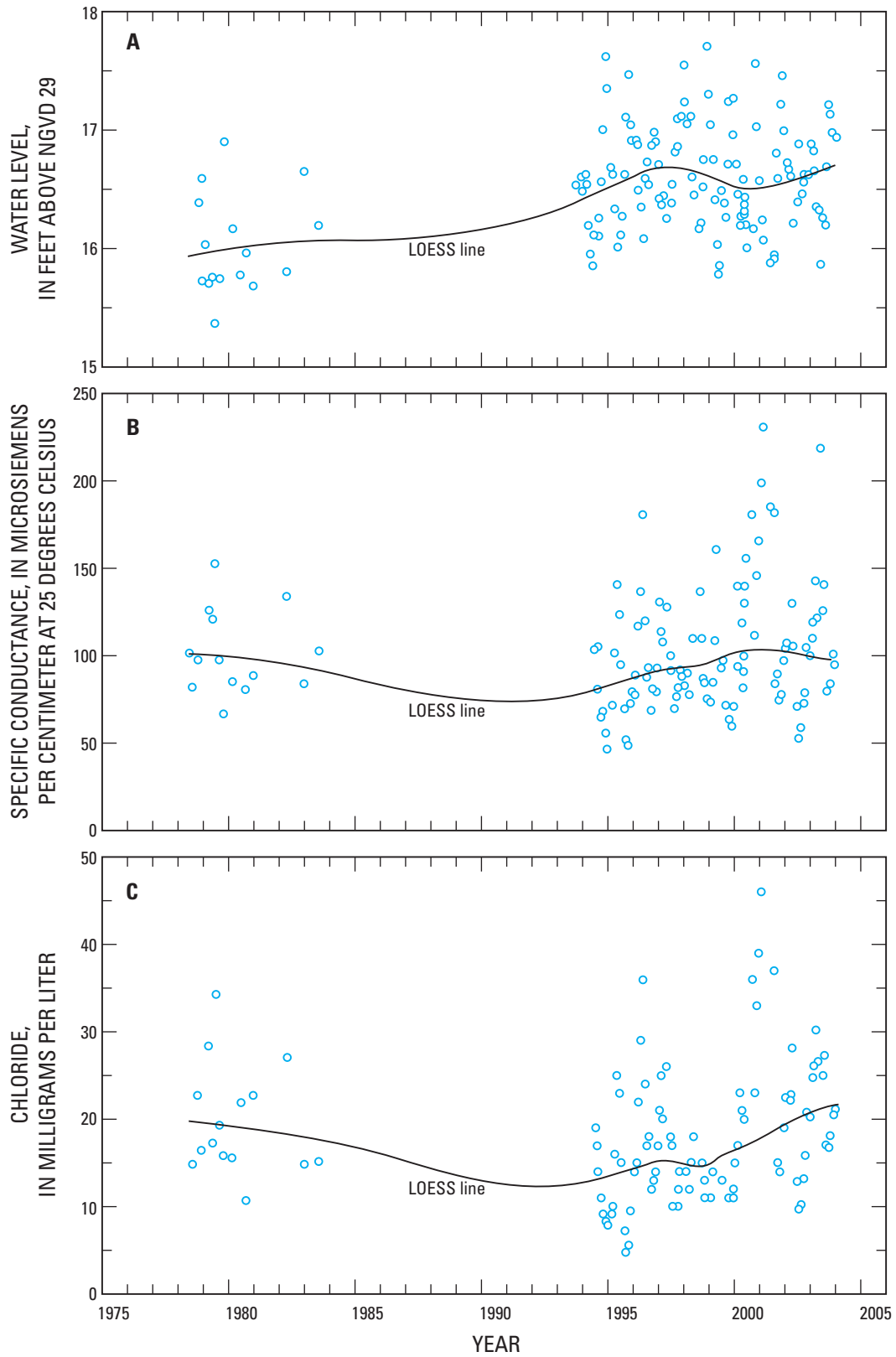


Figure 6. Water level at site 1-7 and water-quality data for the period of record at site LOX8 with LOESS lines: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

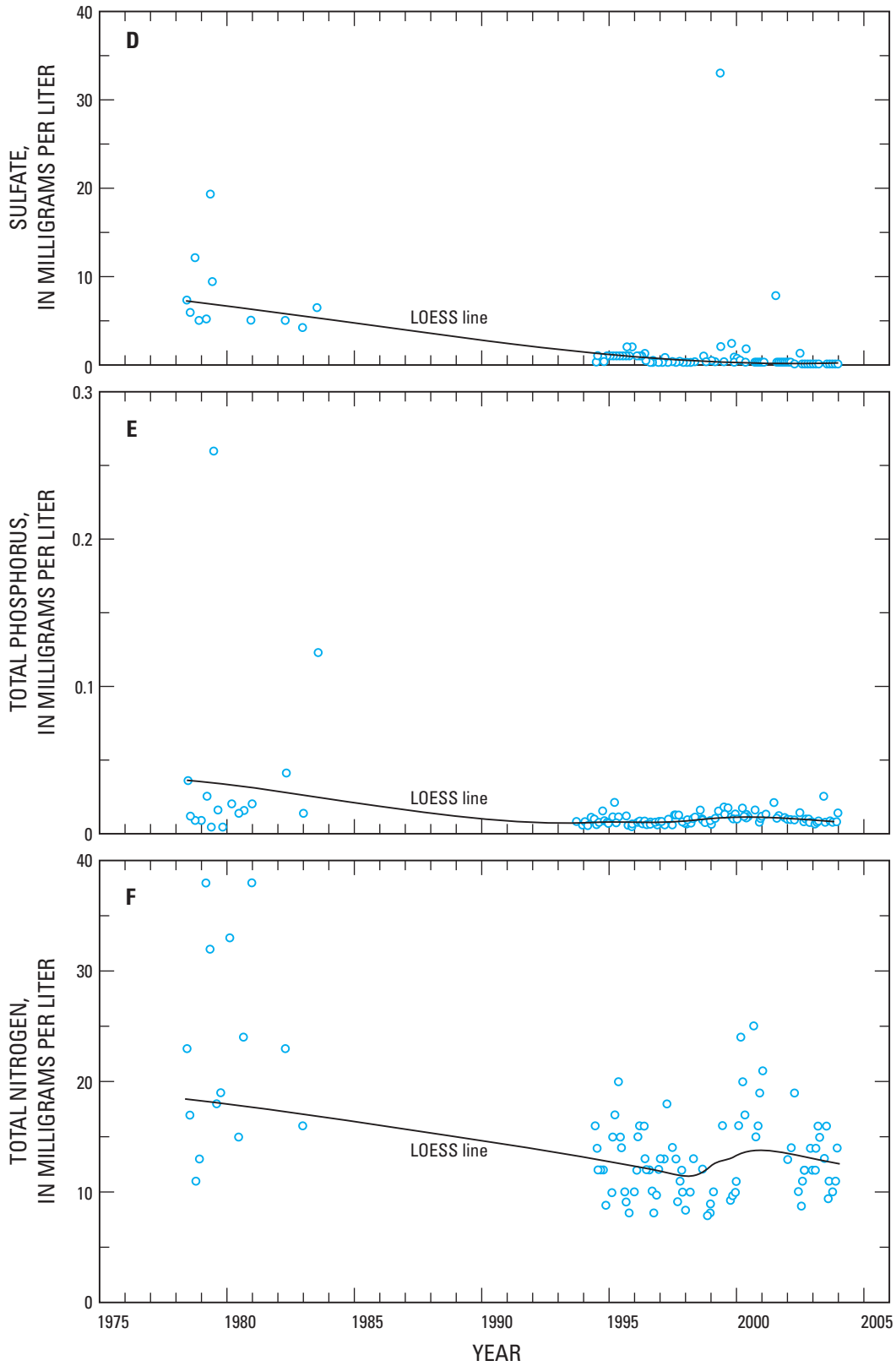


Figure 6. Water level at site 1-7 and water-quality data for the period of record at site LOX8 with LOESS lines—Continued: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

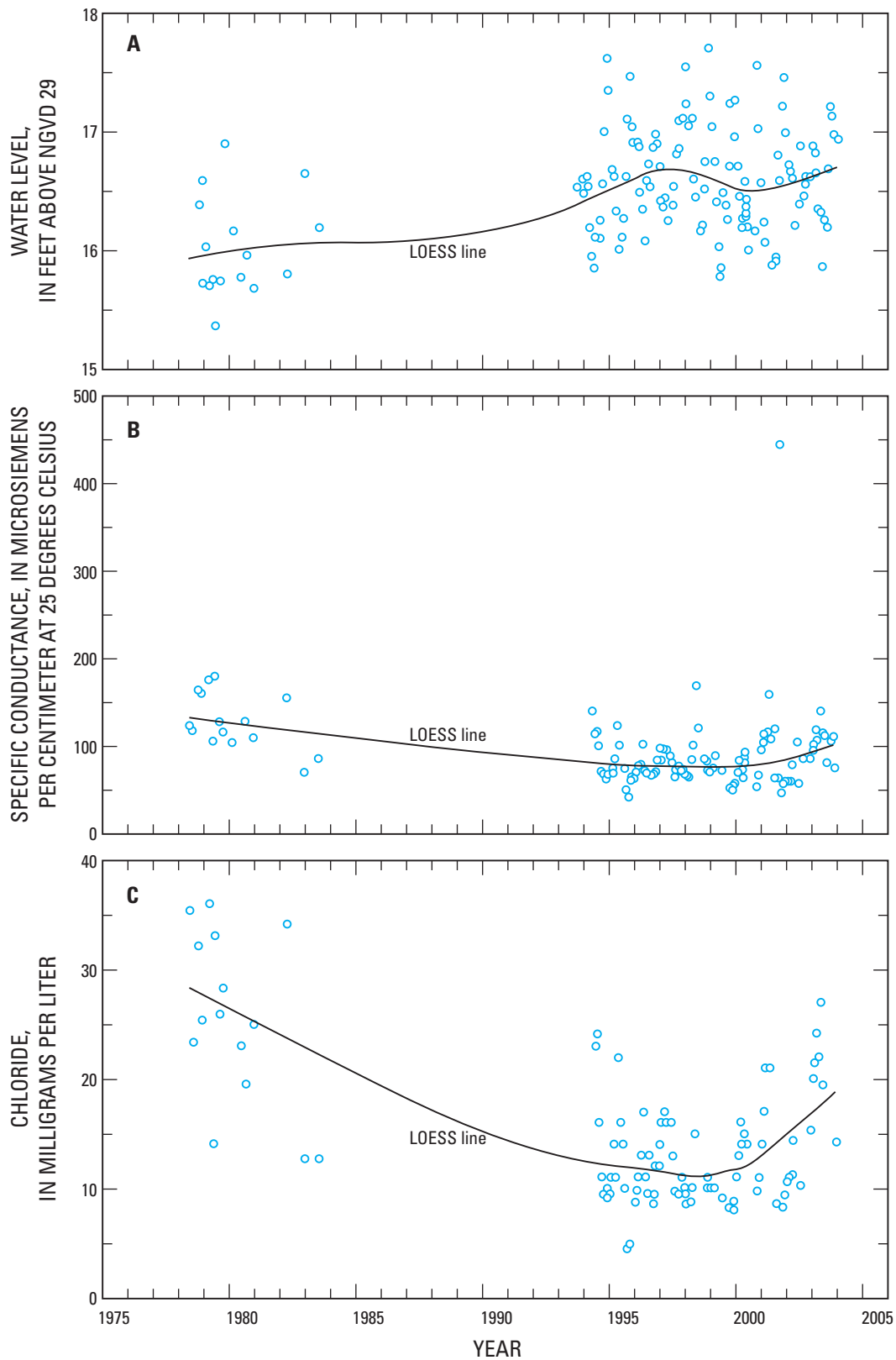


Figure 7. Water level at site 1-7 and water-quality data for the period of record at site LOX13 with LOESS lines: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

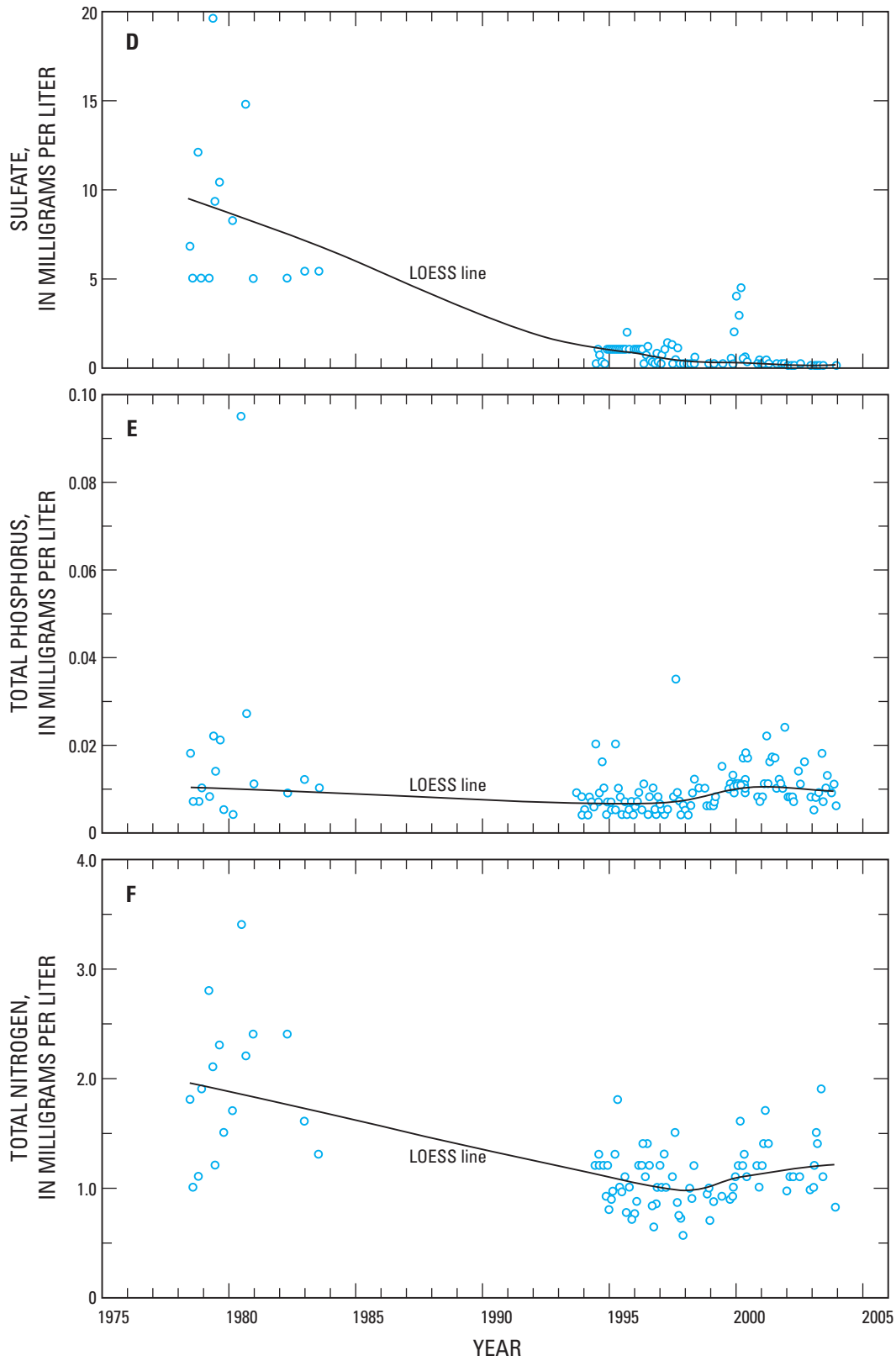


Figure 7. Water level at site 1-7 and water-quality data for the period of record at site LOX13 with LOESS lines—Continued: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

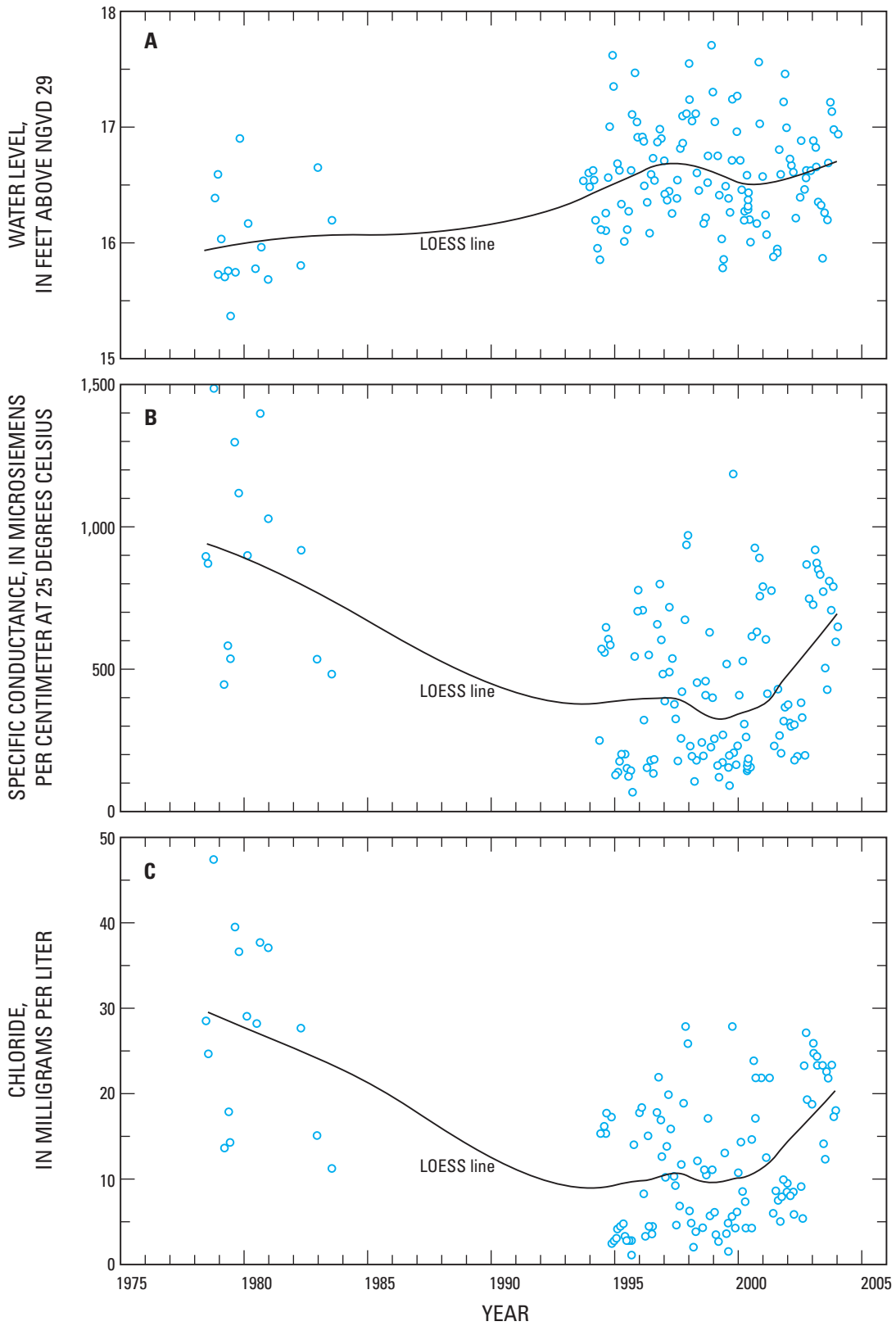


Figure 8. Water level at site 1-7 and water-quality data for the period of record at site LOX15 with LOESS lines: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

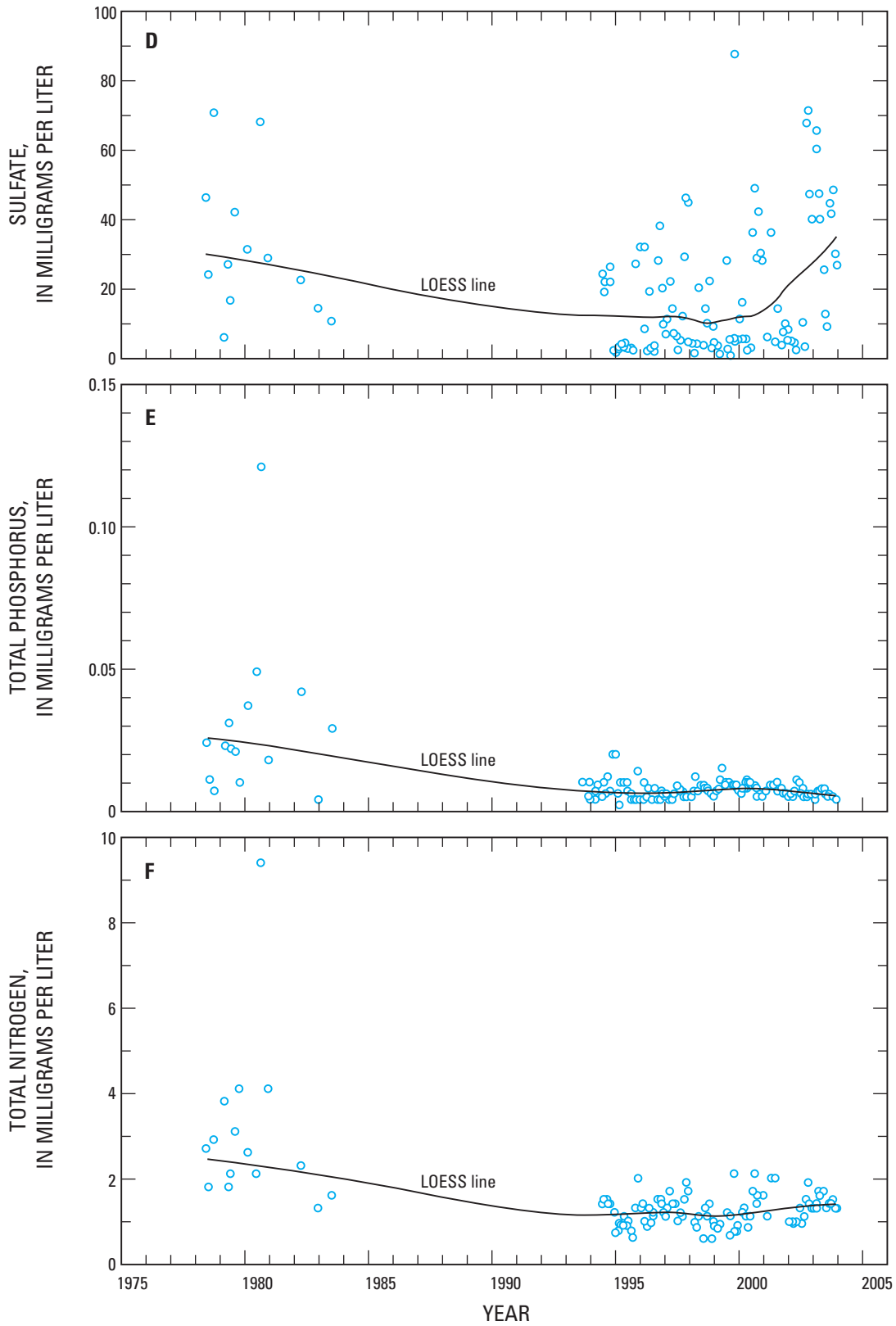


Figure 8. Water level at site 1-7 and water-quality data for the period of record at site LOX15 with LOESS lines—Continued: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

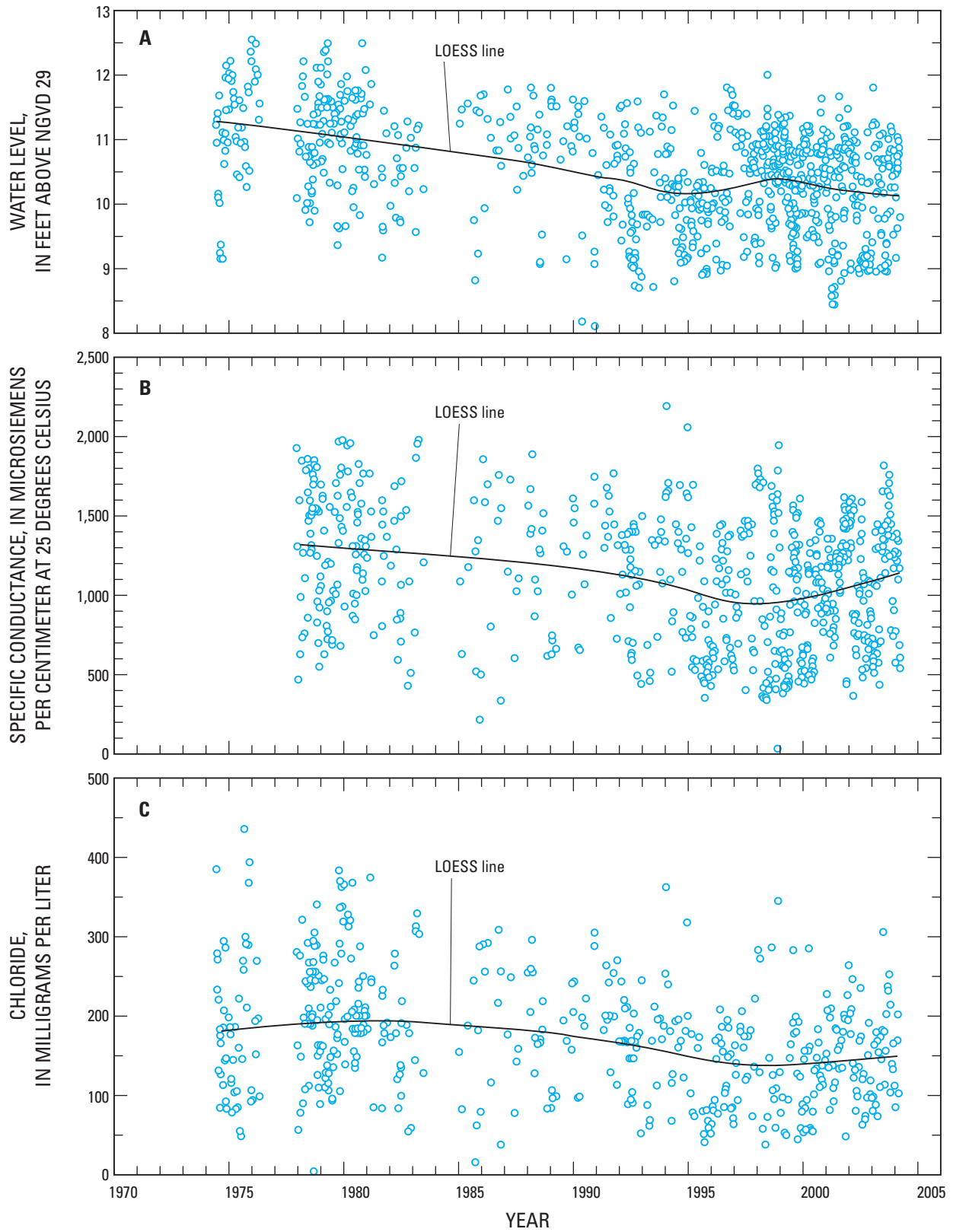


Figure 9. Water level and water-quality data for the period of record at site S-5A with LOESS lines: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

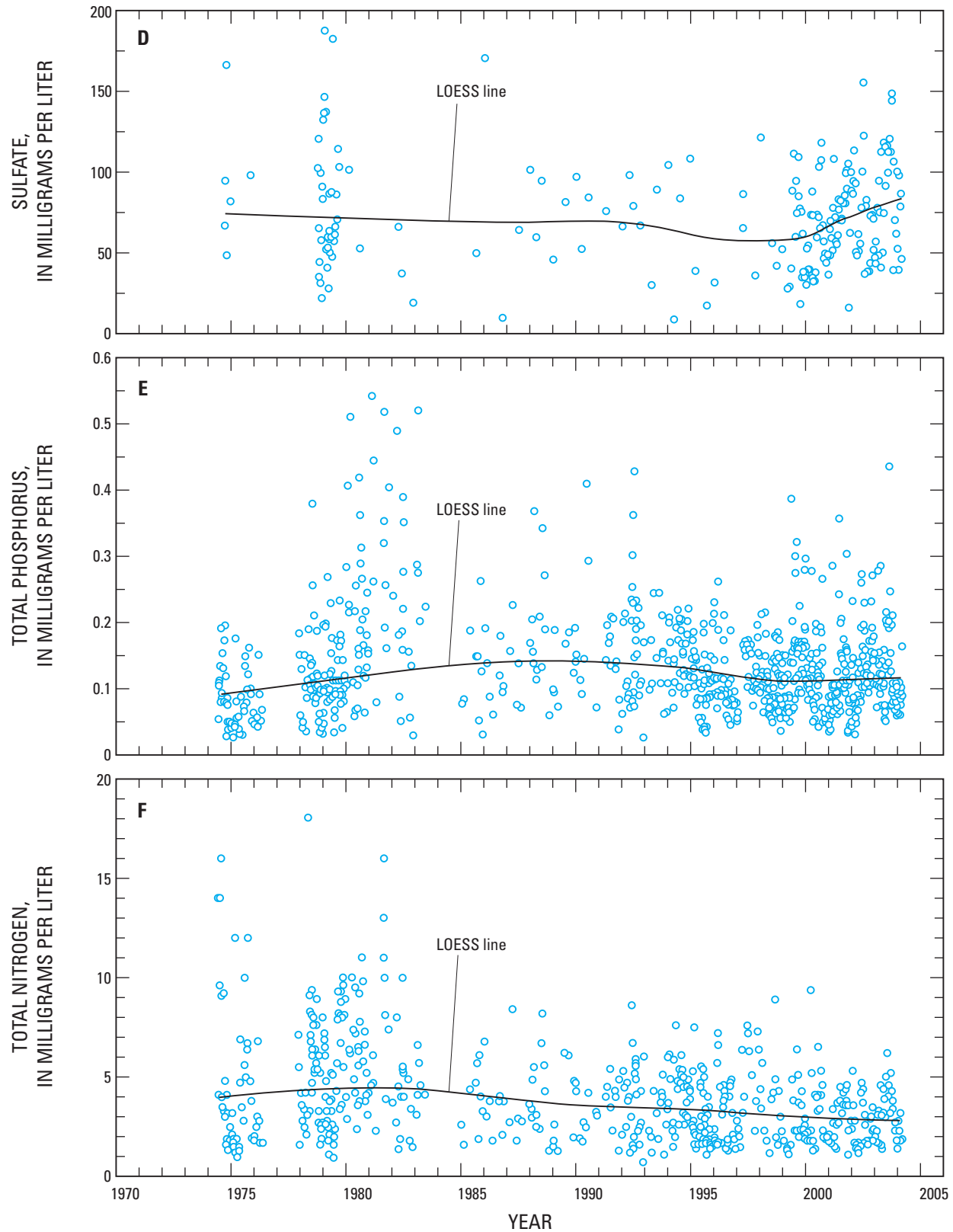


Figure 9. Water level and water-quality data for the period of record at site S-5A with LOESS lines—Continued: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

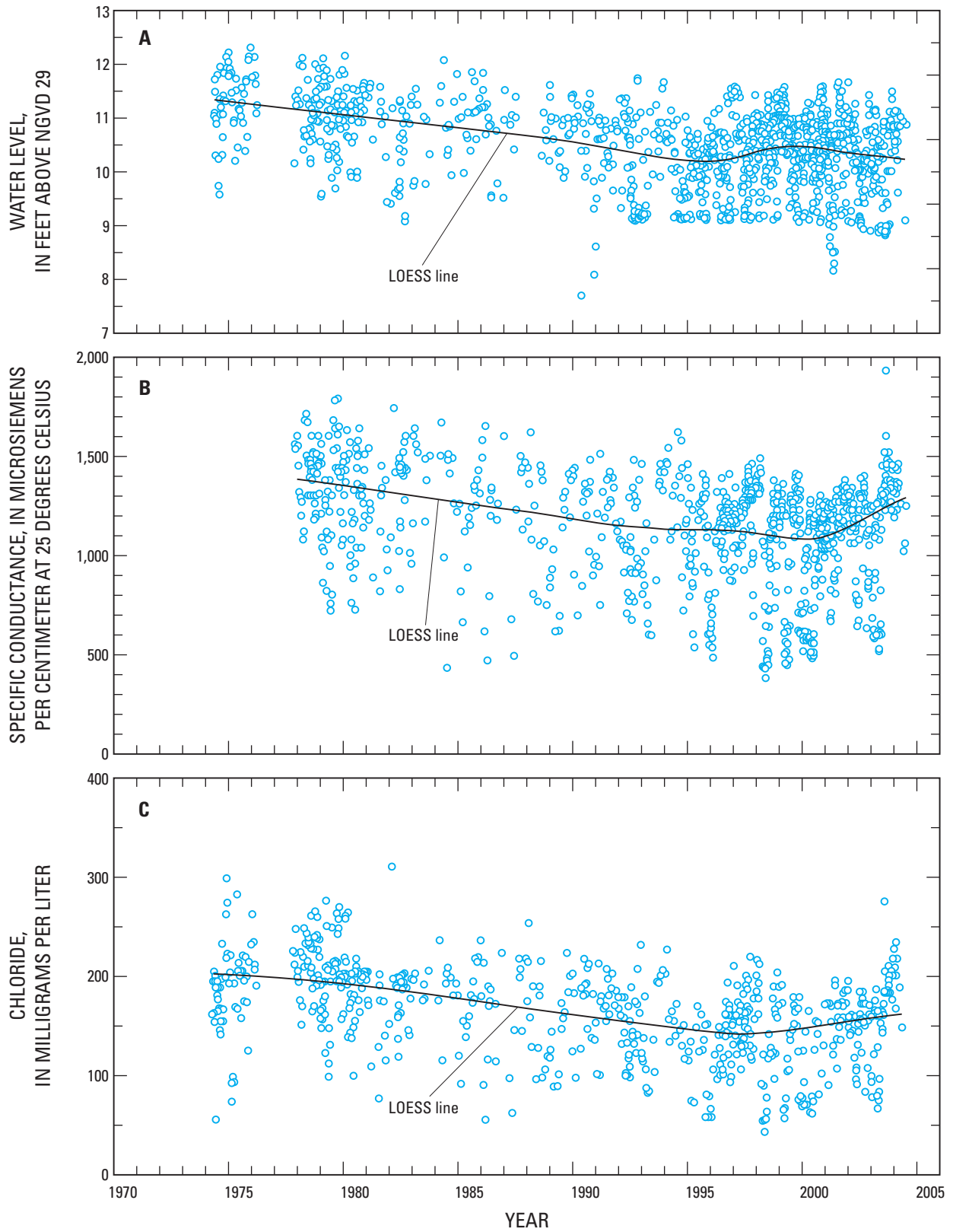


Figure 10. Water level and water-quality data for the period of record at site S-6 with LOESS lines: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

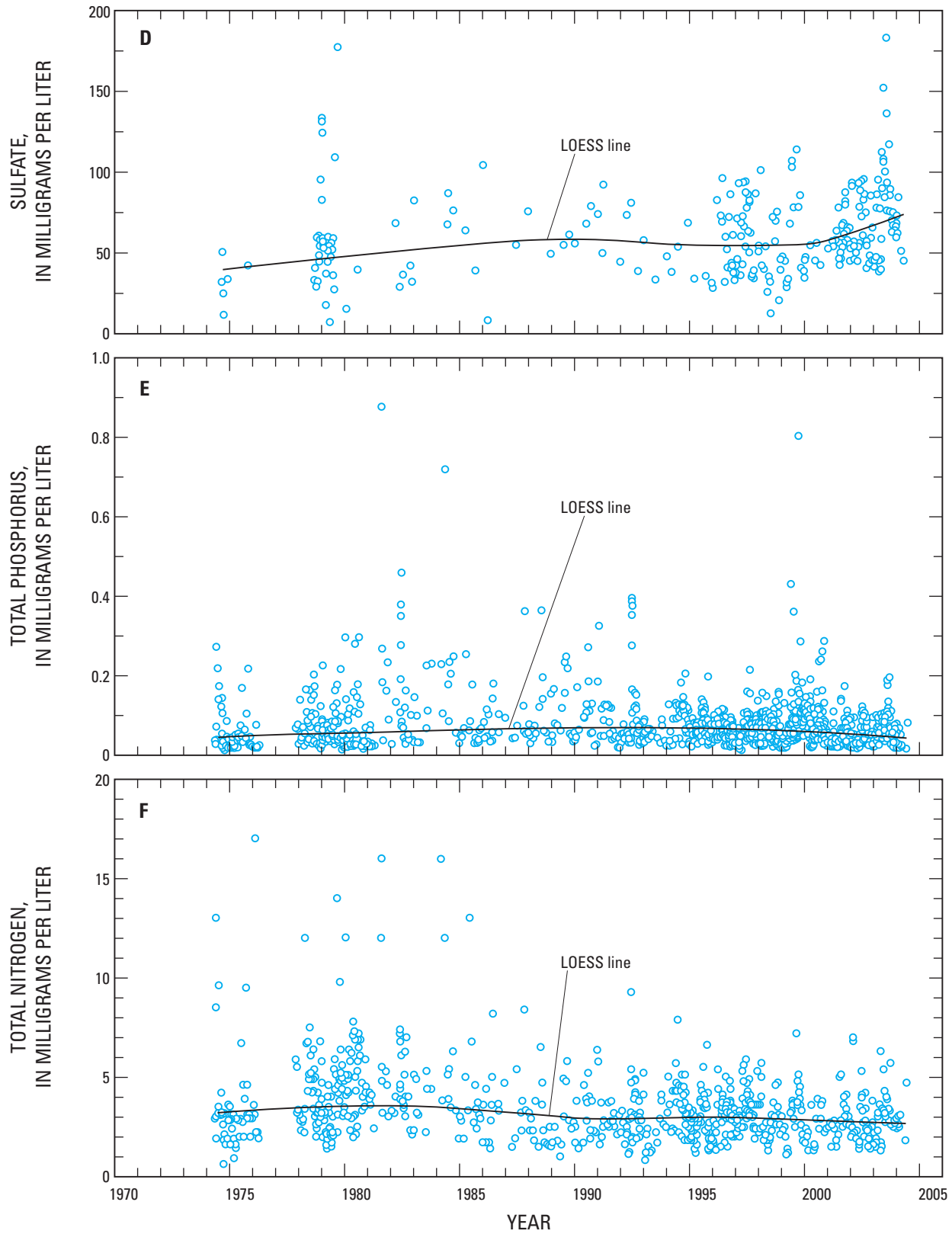


Figure 10. Water level and water-quality data for the period of record at site S-6 with LOESS lines—Continued: A. water level, B. specific conductance, C. chloride concentration, D. sulfate concentration, E. total phosphorus concentration, and F. total nitrogen concentration.

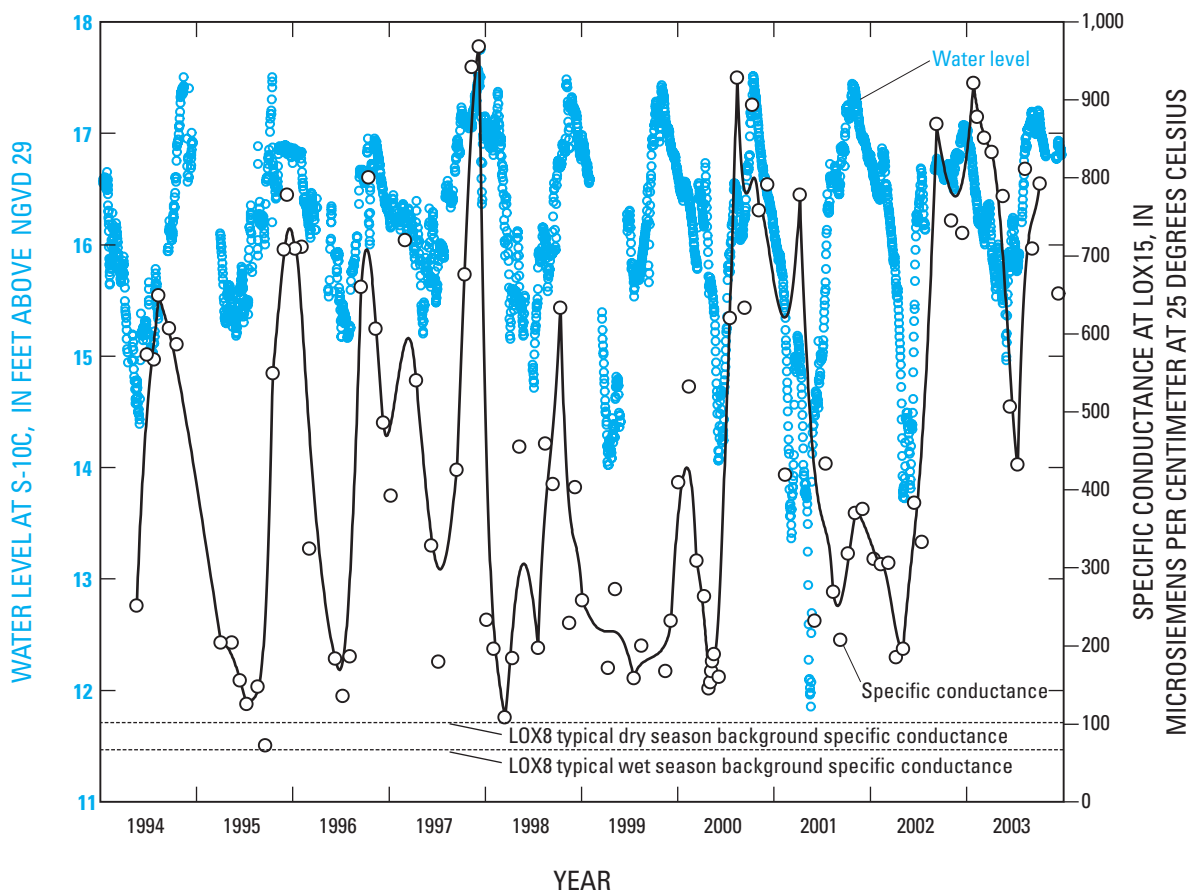


Figure 11. Water level in the Hillsboro Canal at site S-10C and specific conductance at site LOX15, 1994 – 2003. The specific conductance data were fitted with a Bezier curve to show patterns of change. The Bezier curve does not connect all points.

These trends at S-5A and S-6, therefore, are considered reliable and relatively unaffected by changes in sampling and analytical methods. Long-term total phosphorus concentration trends at LOX15 could not be tested using the uncensored seasonal Kendall test because of insufficient data prior to 1994. The total phosphorus concentrations at LOX15 were relatively stable after 1994, with minor seasonal fluctuations; no trends were detected using the uncensored seasonal Kendall test for that period. Total phosphorus concentration at LOX13 showed a slight increase of 0.006 mg/L between 1978 and 2003, and also between 1994 and 2003. It is possible that the long-term trend at LOX13 was affected by downdraft from the hovering helicopter used during sampling prior to 1994; however, such effects are not obvious graphically, and a downtrend rather than the observed uptrend is the expected result of such effects. No total phosphorus trends were detected at LOX8 using the uncensored seasonal Kendall test. At LOX8 and LOX15, total phosphorus concentrations before 1994 showed more variability than after 1994; the pre-1994 variability may have been the result of helicopter downdrafts (figs. 6 and 7).

Total nitrogen—Sites S-5A and S-6 had similar long-term downtrends in total nitrogen of -2.1 and -1.9 mg/L, respectively, between 1974 and 2003 (fig. 12). At S-6, total nitrogen concentration increased 2.7 mg/L between 1974 and 1981. At S-5A, total nitrogen concentration decreased 3.9 and 1.2 mg/L for 1980-89 and 1981-2002, respectively. Water at S-6 and S-5A was not sampled by helicopter and all concentrations were above the MRLs; therefore, the trends for S-6 and S-5A are considered reliable and relatively unaffected by changes in sampling and analytical methods. At LOX15, total nitrogen concentration decreased 0.8 mg/L between 1978 and 2003. Plots of total nitrogen concentration at LOX8, LOX13, and LOX15 all show some higher values and greater variability before 1994 than afterwards (figs. 6-8). This could be due to the effects of sampling from helicopters described earlier. Although water-quality changes in the canals and periodic intrusion of canal water into the marsh of the Refuge may increase total nitrogen concentrations at LOX15, such effects are less likely at LOX8 and LOX13.

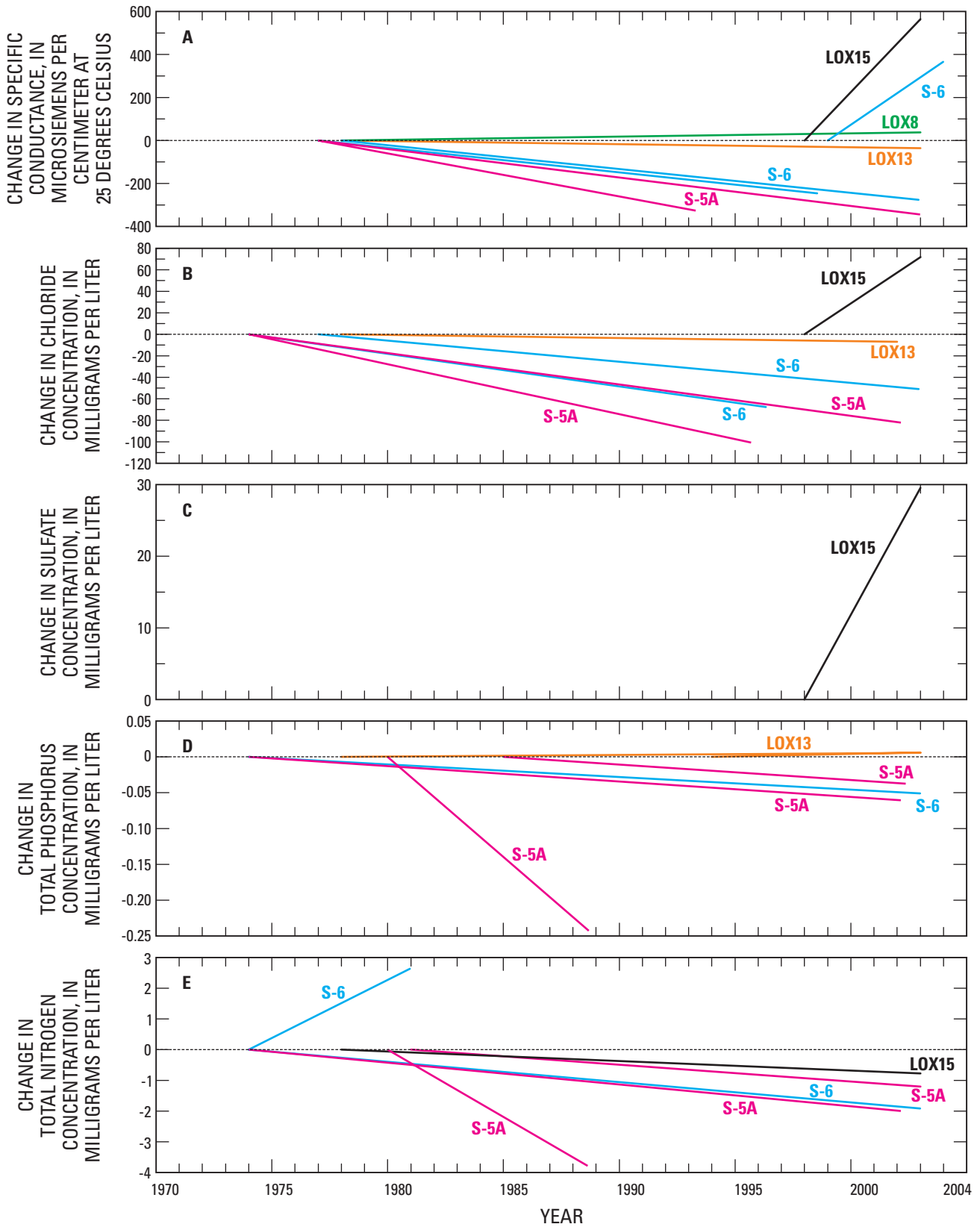


Figure 12. Significant water-quality trends based on the uncensored seasonal Kendall test. The trend lines all start at the zero line in the first year of the test period and end in the last year of the test period. The slopes are the rate of change in specific conductance or concentration per year.

Tobit regressions total phosphorus, total nitrogen, and sulfate—Tobit regressions produced uptrends in total phosphorus concentration at LOX8, LOX13, and LOX15, total nitrogen concentration at LOX8, and sulfate concentration at LOX15 from 1993-94 to 2003. The uptrends probably occurred, in part, from dilution of the Refuge surface water by relatively heavy rainfall during 1994 and 1995, followed by concentration of solutes (dissolved substances) by evapotranspiration during the subsequent period of lower rainfall through 2003. In addition, above-normal inflow of canal water into the Refuge occurred during 2000-03 (M. Waldon, U.S. Fish and Wildlife Service, oral commun., 2005). For S-5A, the Tobit regression produced an uptrend in sulfate concentration from 1998 to 2004 and downtrends in total phosphorus concentration from 1990 to 2000. Tobit regressions usually were attempted when the seasonal Kendall test could not be used because of a high percentage of censored data, or the occurrence of more than one censoring level. Trends produced by Tobit regressions, however, could be affected by seasonal effects and long wet or dry periods, rather than long-term trends in concentration caused by changes in loading in the drainage basin.

Relation between canal water levels and specific conductance—Water-level fluctuations in the canals bordering the Refuge may coincide approximately with changes in water quality at nearby marsh sites, especially near the southern and western sides of the Refuge. Site LOX15 often displays such effects (fig. 11). From 1994 to 2003, specific conductance peaks at LOX15 often occurred near the peak annual water levels at S-10C. Most peaks in specific conductance occurred near the end of the rainy season or early in the dry season, and are influenced by rainfall and water-management operations. Minimum specific conductance values at LOX15 are typically between 100 and 200 $\mu\text{S}/\text{cm}$, and are above the typical rainy season background value of about 60 $\mu\text{S}/\text{cm}$ for LOX8 and LOX13. This indicates that LOX15 usually is influenced by high-conductance water from canals. At LOX15, maximum specific conductance values typically peak between 600 and 1000 $\mu\text{S}/\text{cm}$; the maxima for the canal sites are about 1,500-2,000 $\mu\text{S}/\text{cm}$.

Spatial Patterns in Water Quality

Median concentrations of selected constituents were used to show general spatial patterns in water quality and the influence of canal water on the Refuge sampling sites (figs. 13-19). The 1994-2003 period was chosen for this analysis because it is characterized by relatively consistent and improved field sampling protocols and laboratory analyses.

Specific conductance is a useful indicator of the degree to which canal waters penetrate the marshes of the Refuge. Specific conductance is a relatively conservative¹ property of

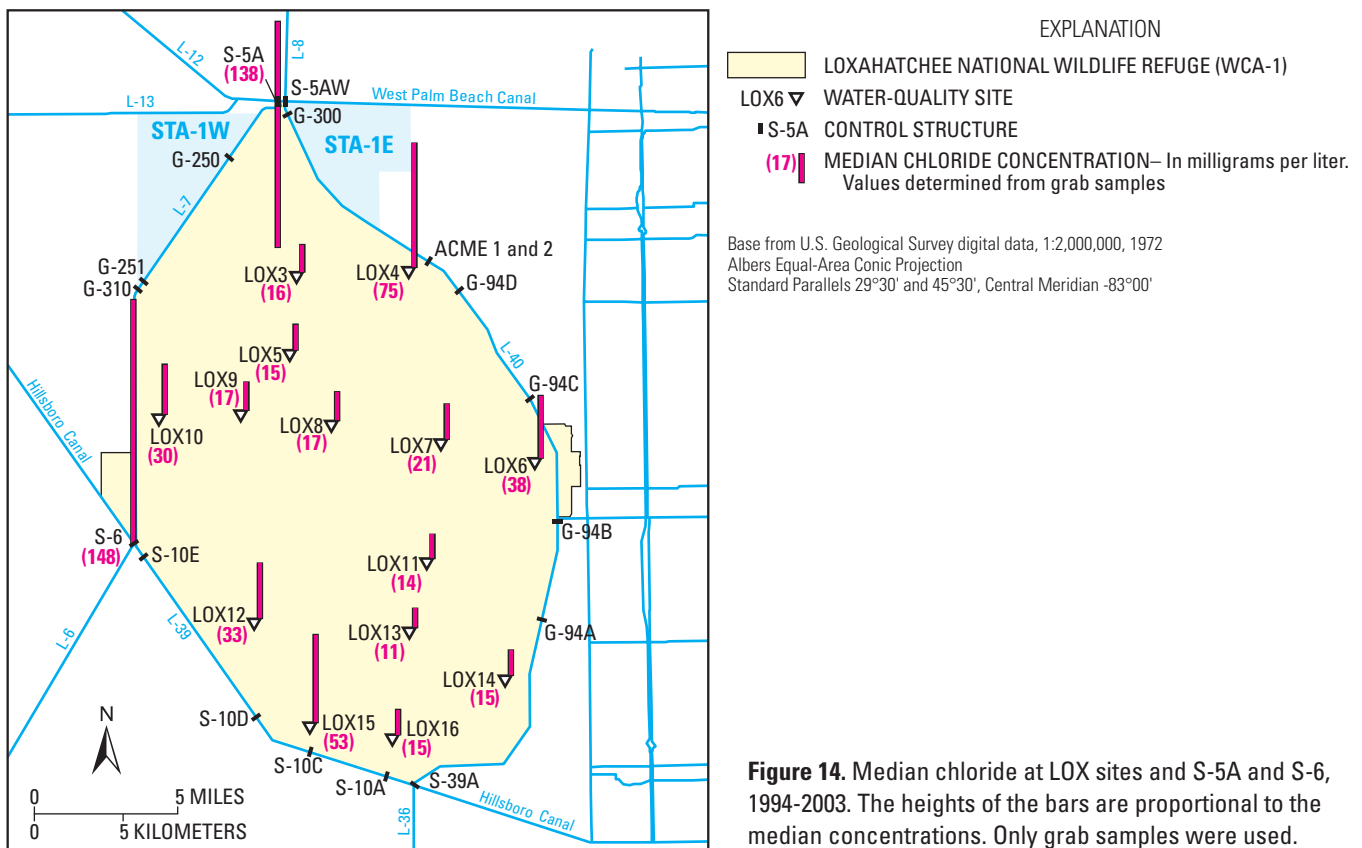
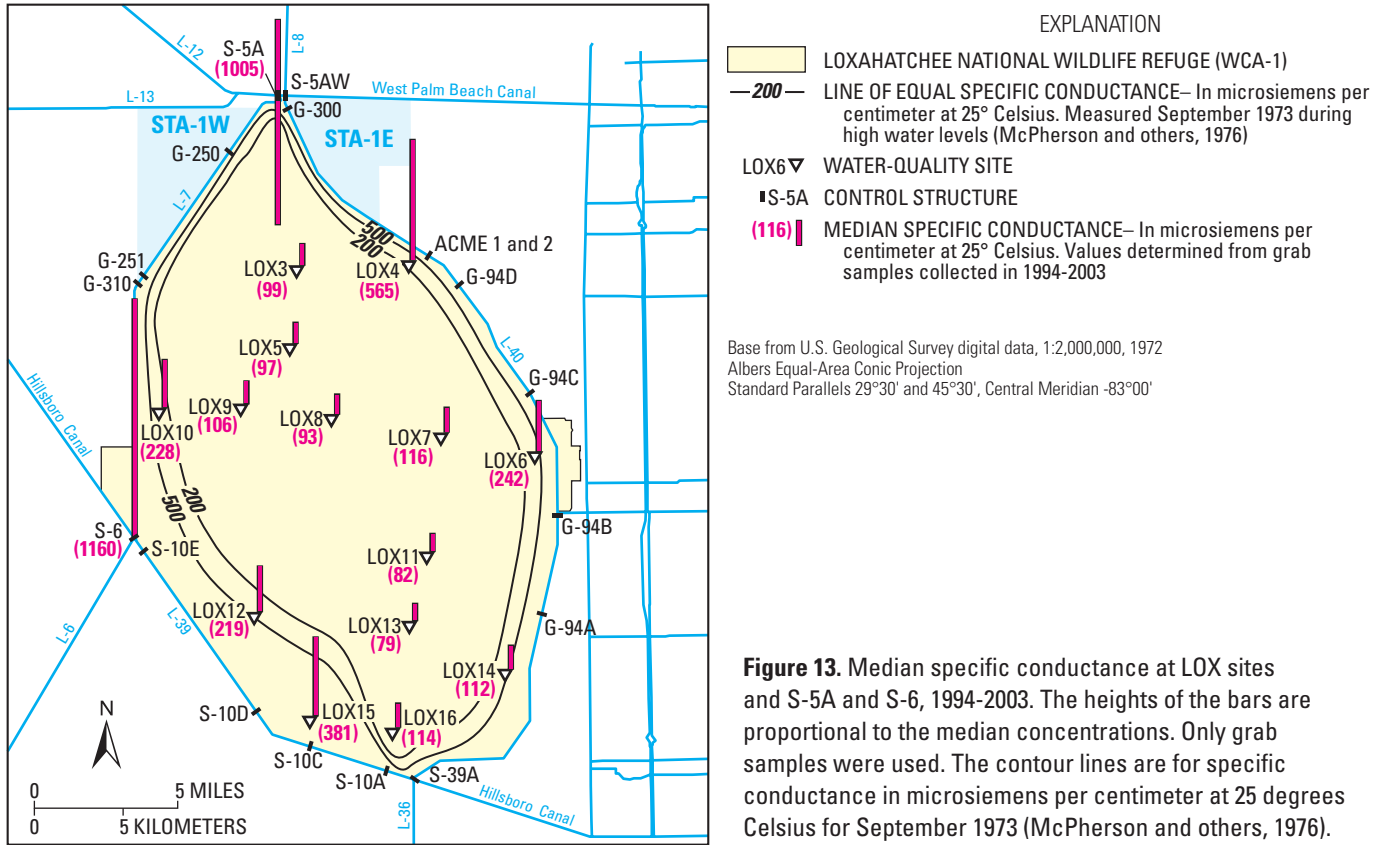
water over the ranges observed in the Refuge because little is gained or lost by chemical and biological processes in most environments. Additionally, differences between canal water and interior marsh water are quite distinct. Median specific conductance values are about an order of magnitude higher (1,005-1,160 $\mu\text{S}/\text{cm}$) in the canals than in the remote interior Refuge sites (about 100 $\mu\text{S}/\text{cm}$). Penetration of canal water into the Refuge was greatest along the southwestern side, both for the decade from 1994 to 2003 and for January 1973 (McPherson and others, 1976b; shown as contour lines on figure 13). Some of the LOX sites near the canals (LOX4, LOX6, LOX10, LOX12, and LOX15) are influenced substantially by canal water at times, and thus, both water-management actions and the natural hydrologic cycle affect these sites. Median specific conductance values at these sites are, therefore, intermediate between those of the canals and the background (natural) sites. The source of the high specific conductance as well as chloride and sulfate in the canals is primarily agricultural drainage that is enriched through the use of fertilizers (Bates and others, 2002).

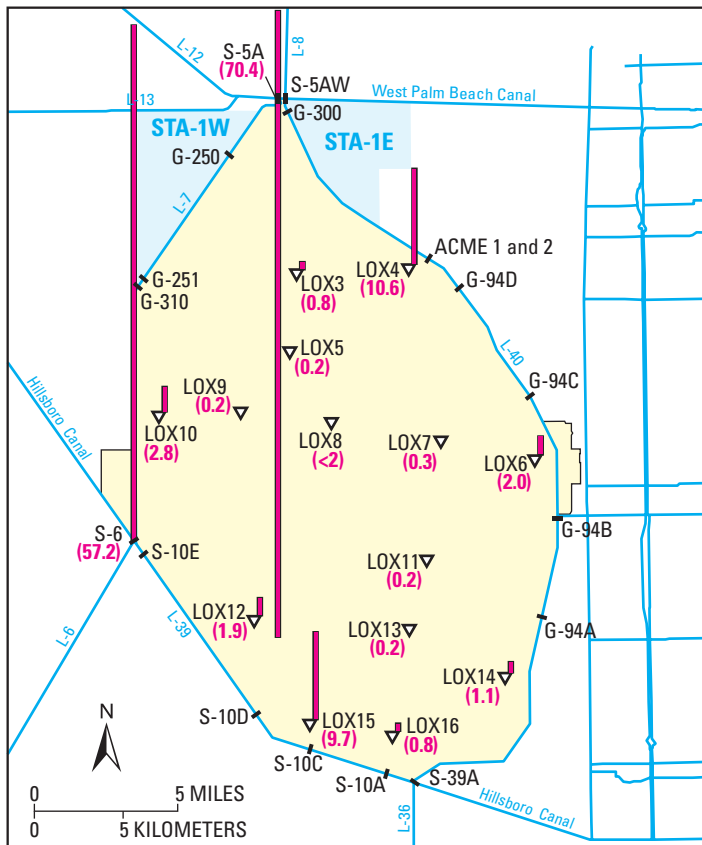
The spatial patterns of median chloride concentrations were similar to specific conductance. Chloride concentrations were about one order of magnitude higher at canal sites (138-148 mg/L) than at remote interior sites (11-21 mg/L) (fig. 14).

Median sulfate concentrations are typically low (0.2-0.8 mg/L) at interior LOX sites away from the canals (fig. 15). This is consistent with data from background sites in Big Cypress National Preserve (Miller and others, 1999), where sulfate in water was low (most were between less than 0.1 and 2.0 mg/L) at remote background sites and high values served as a good indicator of human-induced effects. Median sulfate concentrations ranged from 0.8 to 10.6 mg/L at LOX sites near canals, and from 57.2 to 70.4 mg/L at the canal sites. Agricultural drainage canals are a major source of sulfate to the northern Everglades (Bates and others, 2002).

Specific conductance and concentrations of chloride can be used to estimate the percentage of canal water mixed with marsh water at sites in the Refuge. At the interior marsh sites, median chloride concentrations ranged from 11 to 21 mg/L, and at sites close to the canals, median chloride concentrations ranged from 15 to 75 mg/L. Using the median concentration at LOX13 as the background chloride concentration and at S-5A as the canal concentration, the median chloride concentration at LOX15 suggests water at the site is generally about 31 percent canal water and 69 percent background water. Using median sulfate concentrations (as was done for chloride) to estimate the fractions of water from canals and from background water at LOX15, the result is 17 percent canal water and 83 percent background water at LOX15. This result suggests that in this low-sulfate environment, only about one half (54 percent) of the sulfate from canal water typically reaches LOX15; the rest presumably is taken up by marsh plants, algae, and bottom sediments.

¹A curvature exists in the relation between specific conductance and ionic concentrations such as calcium, sodium, chloride, sulfate, and bicarbonate ions, but this curvature should be minor over the range observed in this report. See Miller and others (1988). For example, doubling the concentrations of major ions with a predicted specific conductance of 1,091 $\mu\text{S}/\text{cm}$ gave a predicted specific conductance of 2,141 $\mu\text{S}/\text{cm}$; that is 98 percent of 2 times 1,091 $\mu\text{S}/\text{cm}$.



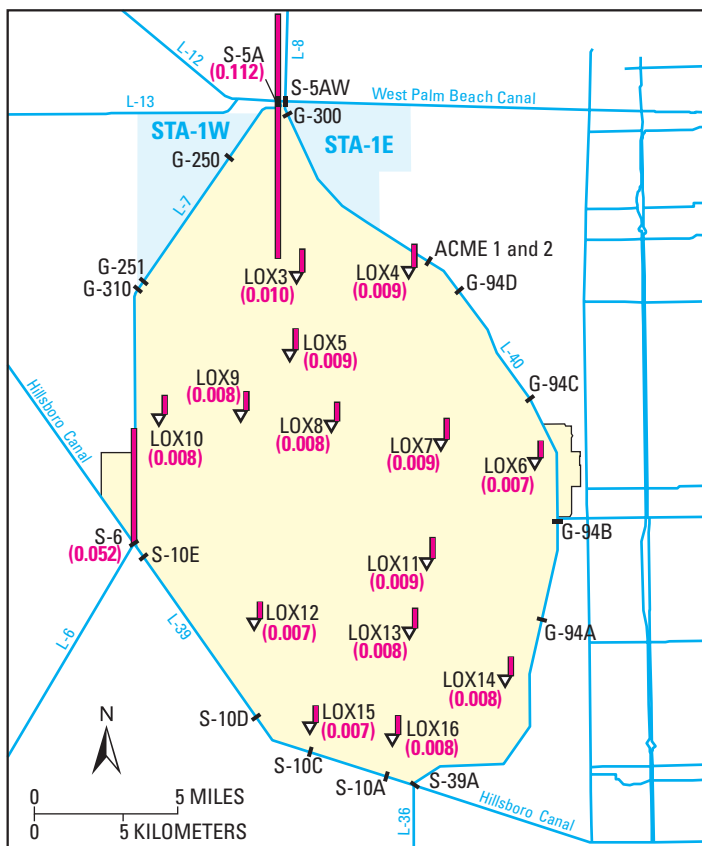


EXPLANATION

- LOXAHATCHEE NATIONAL WILDLIFE REFUGE (WCA-1)
- LOX6 ▽ WATER-QUALITY SITE
- S-5A CONTROL STRUCTURE
- MEDIAN SULFATE CONCENTRATION— In milligrams per liter. Values determined from grab samples.

Base from U.S. Geological Survey digital data, 1:2,000,000, 1972
 Albers Equal-Area Conic Projection
 Standard Parallels 29°30' and 45°30', Central Meridian -83°00'

Figure 15. Median sulfate at LOX sites and S-5A and S-6, 1994-2003. The heights of the bars are proportional to the median concentrations. Only grab were samples used.



EXPLANATION

- LOXAHATCHEE NATIONAL WILDLIFE REFUGE (WCA-1)
- LOX6 ▽ WATER-QUALITY SITE
- S-5A CONTROL STRUCTURE
- MEDIAN TOTAL PHOSPHORUS CONCENTRATION— In milligrams per liter. Values determined from grab samples.

Base from U.S. Geological Survey digital data, 1:2,000,000, 1972
 Albers Equal-Area Conic Projection
 Standard Parallels 29°30' and 45°30', Central Meridian -83°00'

Figure 16. Median total phosphorus at LOX sites and S-5A and S-6, 1994-2003. The heights of the bars are proportional to the median concentrations. Only grab samples were used.

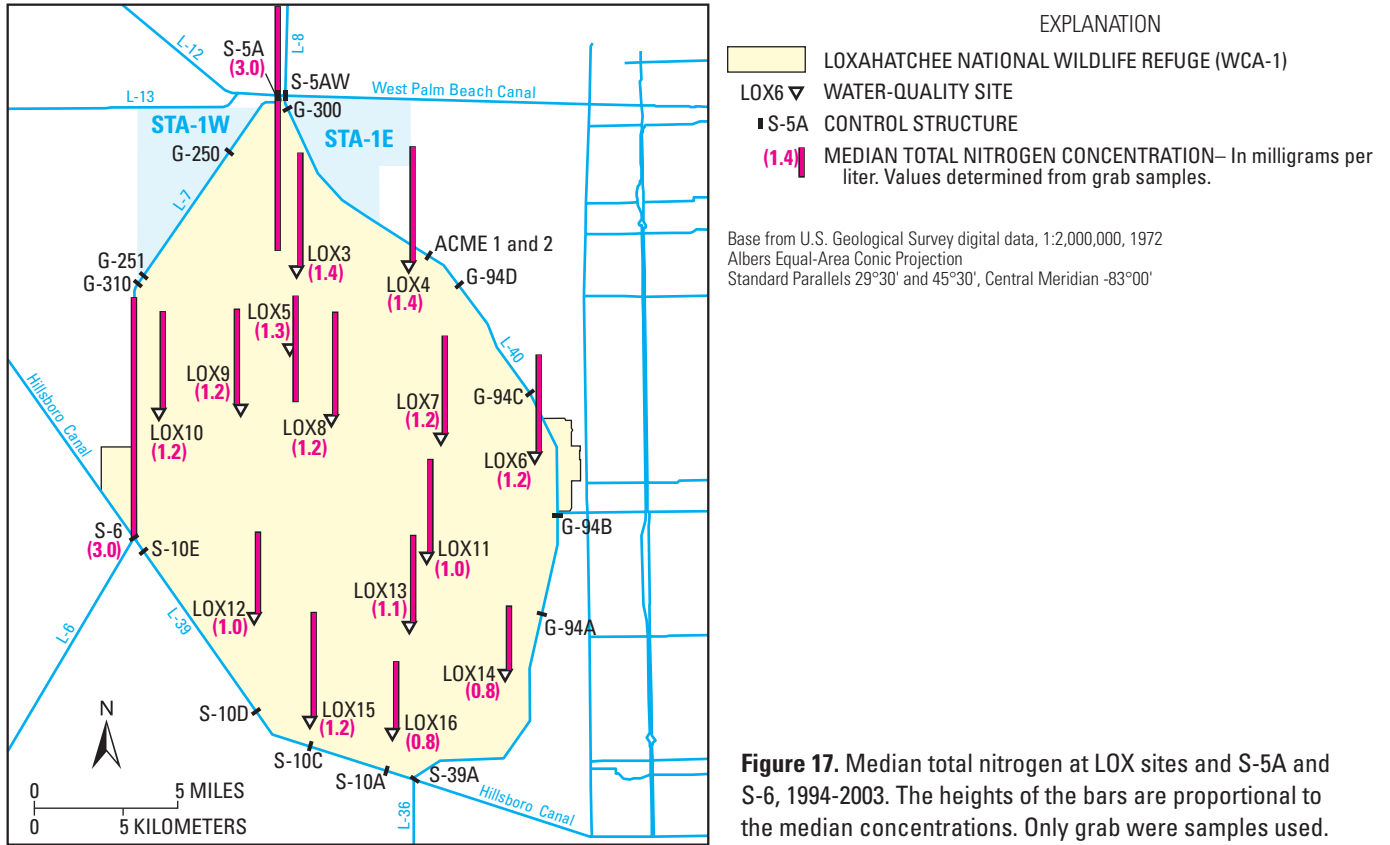


Figure 17. Median total nitrogen at LOX sites and S-5A and S-6, 1994-2003. The heights of the bars are proportional to the median concentrations. Only grab were samples used.

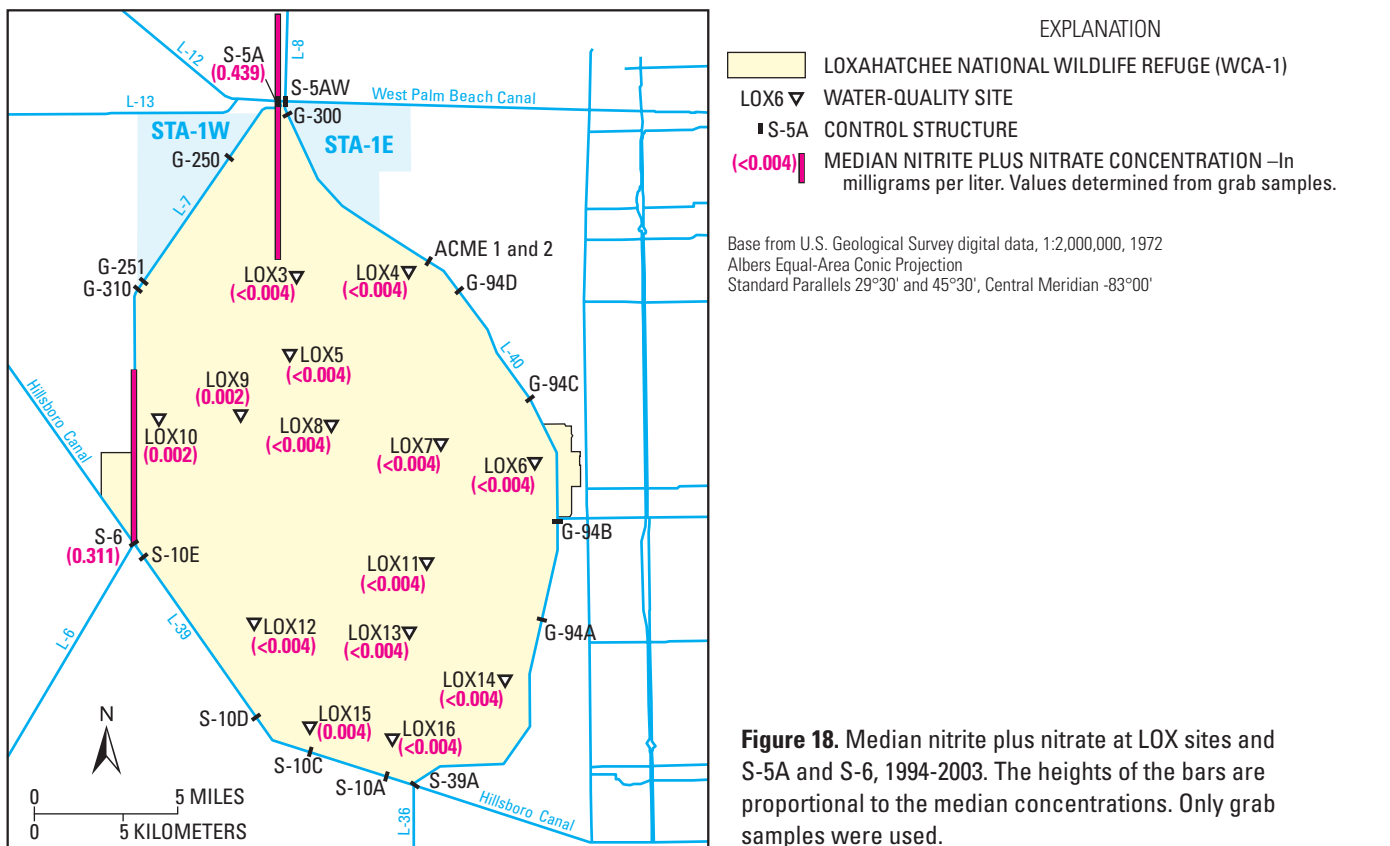
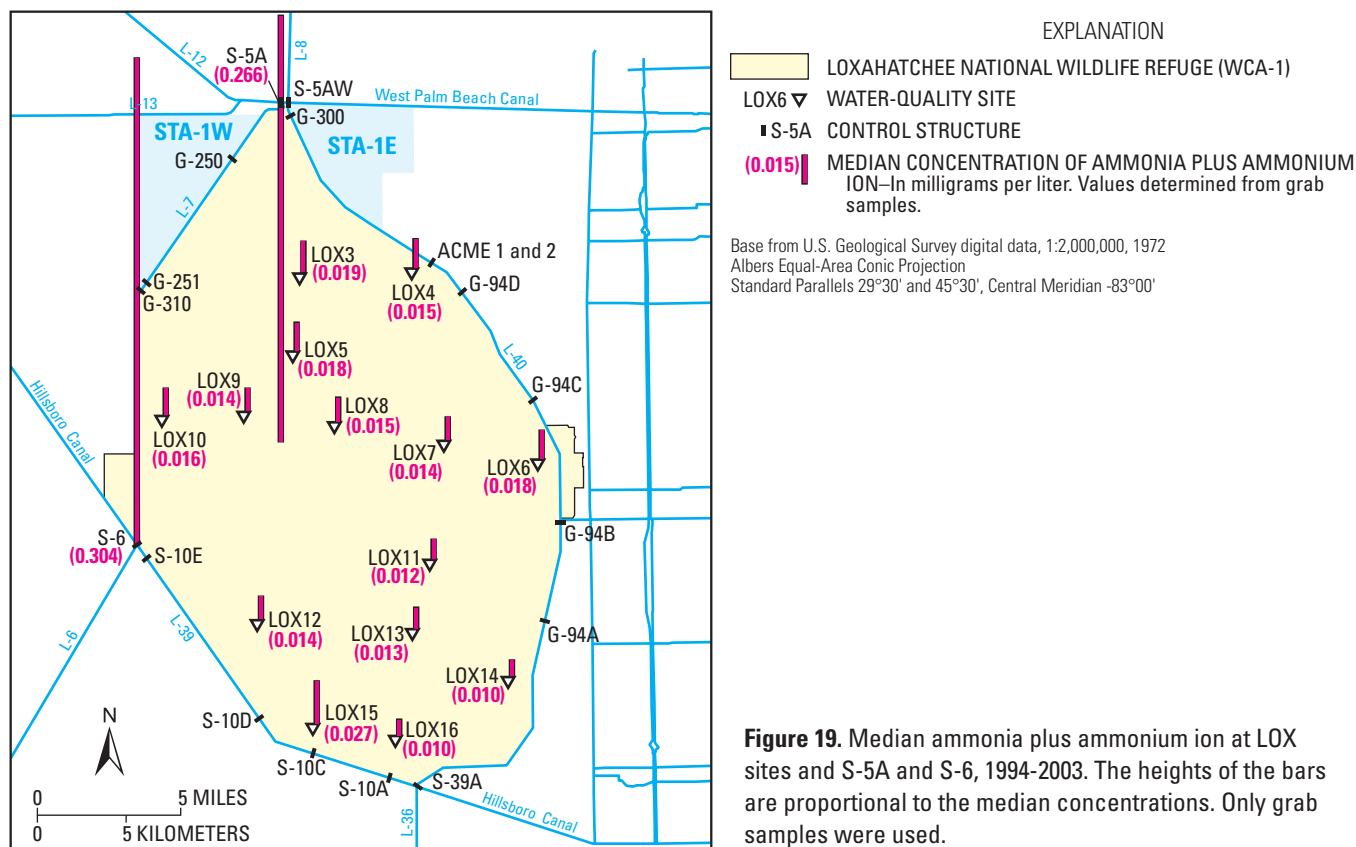


Figure 18. Median nitrite plus nitrate at LOX sites and S-5A and S-6, 1994-2003. The heights of the bars are proportional to the median concentrations. Only grab samples were used.



Median concentrations of total phosphorus were higher in canals than near the canals or in the interior marsh (fig. 16). For example, total phosphorus concentrations at S-6 and S-5A were 0.052 and 0.112 mg/L, respectively. Median concentrations at the remote LOX sites ranged from 0.008 to 0.010 mg/L. Near the canals, the median total phosphorus concentrations ranged from 0.007 to 0.010 mg/L, which is nearly identical to the more remote sites. This similarity between LOX sites away from canals and near canals confirms the rapid uptake of phosphorus by marsh vegetation reported in numerous studies (McPherson and others, 1976b; McCormick and others, 2004).

Median concentrations of total nitrogen ranged from 0.8 to 1.4 mg/L at the marsh sites, compared with 3.0 mg/L at S-6 and S-5A (fig. 17). The inorganic forms of nitrogen (nitrite plus nitrate and ammonia plus ammonium ion) also were higher in canals than in the interior marshes (figs. 18 and 19). Median concentrations of nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) ranged from less than 0.004 to 0.004 mg/L at the marsh sites, whereas median concentrations at S-6 and S-5A were 0.311 and 0.439 mg/L, respectively. Median concentrations of ammonia plus ammonium ions ($\text{NH}_3 + \text{NH}_4^+$) ranged from 0.010 to 0.027 mg/L at the marsh sites, compared with 0.304 and 0.266 mg/L at inflow sites S-6 and S-5A, respectively (fig. 19). Possible reasons for the higher concentrations of inorganic nitrogen in the canals are: (1) the substantial input of water containing soluble components of fertilizer from

nearby agricultural fields through surface- and ground-water flow, and (2) the greater depths (lower bottom-surface-area-to-volume ratios) and flow rates of canals reduce the contact time with vegetation that can consume nitrogen, especially its inorganic forms.

Pesticides and other Organic Compounds in Water and Sediment

Pesticides and other organic compounds in unfiltered water have been measured at pump stations S-6 and S-5A by the SFWMD since 1984 and 1987, respectively. The end date for the SFWMD pesticide data set used for this study is April 2002. USGS filtered pesticide data collected at S-6 from August 1996 to January 2005 also were used in this study. Most pesticide samples had few detectable concentrations, and thus, most of the data are reported as less than the MRLs. For the period of record at S-6, the most commonly detected pesticides (in filtered and unfiltered samples) in water were atrazine, metolachlor, simazine, ametryn, ethoprop, tebuthiuron, and hexazinone. Filtered atrazine was detected in 87 of 88 samples collected from 1996 to 2005, with a maximum concentration of 12.0 $\mu\text{g/L}$. At S-6, p,p'-DDE, chlorpyrifos, methomyl, aldrin, linuron, and other compounds were detected infrequently. Between April 1987 and March 2002, the most commonly detected pesticides in unfiltered water at S-5A

were atrazine, ametryn, and simazine. Unfiltered atrazine was detected in 57 of 75 samples, with a maximum concentration of 12.3 µg/L. At S-5A, metolachlor, hexazinone, bromacil, and other compounds were detected less frequently.

Only two water samples were collected from the Refuge marsh, and no detections were reported. The samples were collected at LOX8 and LOX16 on January 18, 1980, and were analyzed for 21 compounds, including the herbicides 2,4,5-T and 2,4-D as well as several organochlorine and organophosphorus pesticides. All determinations were reported as less than 0.01 µg/L, except for chlordane (less than 0.1 µg/L) and toxaphene (less than 1 µg/L).

Bottom-sediment samples for pesticide analyses were collected by SFWMD at LOX8, LOX10, S-5A, and S-6. Samples were collected annually at LOX8 and LOX10 from 1994 to 2004. Samples were collected more frequently at S-6 and S-5A, beginning in 1976 and 1987, respectively. Many pesticide compounds were measured at all of these sites, but most determinations were reported as less than the MRLs. A number of detections were reported at S-6 and S-5A, especially for p,p'-DDD, p,p'-DDE, ametryn, p,p'-DDT, and atrazine. At S-6 and S-5A, chlordane and other compounds were detected infrequently. The highest concentration for the DDT family of compounds was 390 µg/kg for p,p'-DDE at S-6 in July 1996.

Summary and Conclusions

Water quality in the interior marshes of the Arthur R. Marshall Loxahatchee National Wildlife Refuge is characterized by low concentrations of dissolved ions, predominantly sodium and chloride. Water quality in the marsh is affected primarily by natural seasonal processes such as evapotranspiration, rainfall, and biological activity. During the dry season, evapotranspiration exceeds precipitation. Specific conductance and concentrations of conservative ions at marsh background sites typically increased by 40 to 70 percent between the end of the rainy season in September and the end of the dry season in May.

Until recently, water entered the Refuge from rainfall and from perimeter canals that received water from two large pumping stations (S-5A and S-6). These stations receive water that travels through agricultural land that is intensely farmed and typically contains relatively high concentrations of dissolved ions, nutrients, and pesticides. Specific conductance and concentrations of some dissolved ions and nutrient species are an order of magnitude higher at S-5A and S-6 canal sites than at interior marsh sites. Water quality in marshes bordering the canals can be affected substantially by canal water inflows, and these effects can extend several miles or more into the marshes, depending on the location within the Refuge and water level in the canals. As canal water flows into the marsh, processes such as the uptake by periphyton, rooted vegetation, and bottom sediments, and the settling of particulate matter

reduce concentrations of nutrients to a greater degree than concentrations of conservative ions such as chloride that are decreased only by dilution from mixing with water containing lower concentrations of these ions.

Long- and short-term trends for specific conductance, chloride ion, sulfate ion, total phosphorus, and total nitrogen at five sites were evaluated, primarily using the uncensored seasonal Kendall test with a water-level adjustment to reduce the effects of long wet or dry periods. Significant long-term trends for specific conductance, chloride, total phosphorus and total nitrogen at canal sites S-5A and S-6 generally were downward from 1974 to 2003. Trends at marsh sites from 1978 to 2003 generally were minor or not evident. In recent years (between 1998 and 2003), however, one marsh site (LOX15) near the Hillsboro Canal showed an increase in specific conductance of about 560 µS/cm and an increase in sulfate of 30 mg/L. Site LOX15 is strongly influenced by intrusions of canal water; during 2001-03, increases in specific conductance and sulfate at LOX15 coincided with increased canal inflows of water with high nutrient concentrations from STA-1W.

Concentrations of pesticides and other organic compounds in water and sediment have been measured by the South Florida Water Management District at inflow pumping stations S-5A and S-6. Most pesticides have been found at concentrations near or less than the minimum reporting level (MRL) for the analytical methods used. At S-6, the most commonly detected pesticides were atrazine, metolachlor, simazine, ametryn, ethoprop, tebuthiuron, and hexazinone. Atrazine (filtered) was detected in 87 of 88 samples collected between 1996 and 2004, with a maximum concentration of 12.0 µg/L. At S-5A, the most commonly detected pesticides in water were atrazine, ametryn (unfiltered), metachlor, and simazine. Atrazine (unfiltered) was detected in 57 out of 75 samples (1987-2002), with a maximum concentration of 12.3 µg/L. Only two water samples from the Refuge marshes have been analyzed for pesticides, and neither contained detectable concentrations. Although a number of pesticides, including p,p'-DDD, p,p'-DDE, ametryn, p,p'-DDT, and atrazine, have been detected in bed sediments, most concentrations were near or less than the respective MRLs for the analytical methods used. The highest concentrations for the DDT family of compounds (390 µg/kg of p,p'-DDE) occurred in sediment from S-6.

Proposed changes in the flow of canal water into the Refuge associated with Everglades restoration could adversely affect water quality over greater expanses of marsh, especially if the changes result in increased canal-water intrusion into Refuge marshes. The inflow of water from STAs with even relatively low nutrient concentrations could adversely affect water quality of the marsh if this additional water has high concentrations of pesticides or major ions. Major ions such as chloride and calcium that are not easily removed by the STAs can create an ecological imbalance within the low ionic-strength, soft-water marsh ecosystem.

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