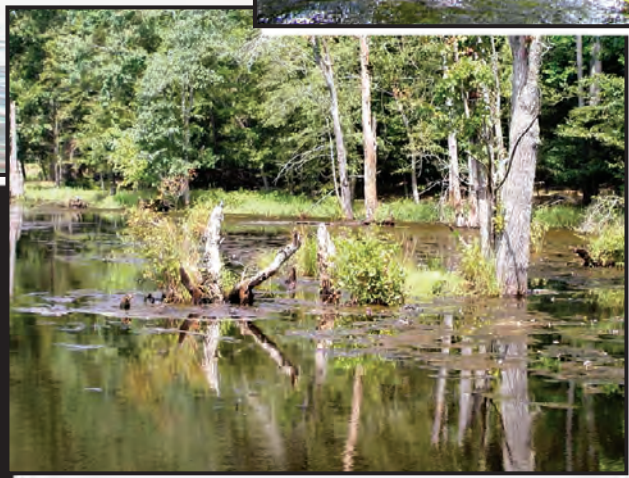


Prepared in cooperation with the City of Newport News, Virginia

# Processes Affecting Phosphorus and Copper Concentrations and Their Relation to Algal Growth in Two Supply Reservoirs in the Lower Coastal Plain of Virginia, 2002–2003, and Implications for Alternative Management Strategies



Scientific Investigations Report 2006–5277

**Cover.** Left photograph—**Lee Hall Reservoir at Route 143 near Lee Hall, Virginia** (view looking upstream). Top right photograph—**Curtis Run above Lee Hall Reservoir near Lee Hall, Virginia** (view looking downstream). Bottom right photograph—**Lee Hall Reservoir below Curtis Run near Lee Hall, Virginia** (view looking downstream). *Photographs by Gary K. Speiran, U.S. Geological Survey, August 2003.*

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By Gary K. Speiran, Nancy S. Simon, and Maria L. Mood-Brown

Prepared in cooperation with the City of Newport News

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## Conversion Factors

### Inch/Pound to SI

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
Length		
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
Area		
acre	4,047	square meter (m <sup>2</sup> )
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )
Volume		
million gallons (Mgal)	3,785	cubic meter (m <sup>3</sup> )
Flow rate		
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m <sup>3</sup> /s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)
pound per acre (lb/acre)	1,836	kilogram per square meter (kg/m <sup>2</sup> )

### SI to Inch/Pound

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
Length		
centimeter (cm)	0.3937	inch (in.)
micrometer (μm)	0.00003937	inch (in.)
Volume		
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.0002642	gallon (gal)
Flux rate		
gram per square meter per year ((g/m <sup>2</sup> )/y)	0.003279	ounce per square foot per year ((oz/ft <sup>2</sup> )/y)
milligram per liter per day ((mg/L)/d)	0.0001335	ounce per gallon per day ((oz/gal)/d)
milligram per square centimeter (mg/cm <sup>2</sup> )	0.03278	ounce per square foot (oz/ft <sup>2</sup> )

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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

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 in milligrams per liter (mg/L), micrograms per liter (μg/L), millimole per mole (mmol/mol), or parts per thousand (per mil).

Concentrations of chemical constituents in sediment are given in milligrams per gram (mg/g), micrograms per gram (μg/g), parts per million (ppm), or micromoles per gram (μmol/g).

# Processes Affecting Phosphorus and Copper Concentrations and Their Relation to Algal Growth in Two Supply Reservoirs in the Lower Coastal Plain of Virginia, 2002–2003, and Implications for Alternative Management Strategies

By Gary K. Speiran, Nancy S. Simon, and Maria L. Mood-Brown

## Abstract

Elevated phosphorus concentrations commonly promote excessive growth of algae in waters nationwide. When such waters are used for public supply, the algae can plug filters during treatment and impart tastes and odors to the finished water. This increases treatment costs and results in finished water that may not be of the quality desired for public supply. Consequently, copper sulfate is routinely applied to many reservoirs to control algal growth but only is a “temporary fix” and must be reapplied at intervals that can range from more than 30 days in the winter to less than 7 days in the summer. Because copper has a maximum allowable concentration in public drinking water and can be toxic to aquatic life, water suppliers commonly seek to develop alternative, long-term strategies for managing reservoirs. Because these are nationwide issues and part of the mission of the U.S. Geological Survey (USGS) is to define and protect the quality of the Nation’s water resources and better understand the physical, chemical, and biological processes in wetlands, lakes, reservoirs, and estuaries, investigations into these issues are important to the fulfillment of the mission of the USGS.

The City of Newport News, Virginia, provides 50 million gallons per day of treated water for public supply from Lee Hall and Harwoods Mill Reservoirs (terminal reservoirs) to communities on the lower York-James Peninsula. About 3,500 pounds of copper sulfate are applied to each reservoir at 3- to 99-day intervals to control algal growth. Consequently, the USGS, in cooperation with the City of Newport News, investigated the effects of management practices and natural processes on phosphorus (the apparent growth-limiting nutrient), copper, and algal concentrations in the terminal reservoirs to provide information that can be used to develop alternative management strategies for the terminal reservoirs.

Initial parts of the research evaluated circulation and stratification in the reservoirs because these factors affect

phosphorus availability to algae. Results indicate that (1) water flows through both reservoirs in a “plug-flow” manner; (2) little water in the lower part of Lee Hall Reservoir, into which pumped water enters, flows into the upper part of the reservoir and mixes with that water; (3) Lee Hall Reservoir generally does not stratify; and (4) Harwoods Mill Reservoir stratifies from April to June through September or October into an upper epilimnion that does not mix with water in the lower hypolimnion.

The ratio of dissolved nitrogen to phosphorus concentrations (N:P) for sites in both reservoirs generally was greater than 20:1, indicating that phosphorus likely is the growth-limiting nutrient in both reservoirs. Phosphorus was present predominantly as suspended, rather than dissolved, species except in the hypolimnion of Harwoods Mill Reservoir and the natural inflow represented by Baptist Run. Because Harwoods Mill Reservoir stratified, field-measured physical and chemical characteristics and concentrations of nitrogen and phosphorus species changed sharply over short depth intervals in this reservoir. Dissolved phosphorus concentration increased from 0.015 to 0.057 milligrams per liter between a depth of 15 feet (ft) and the bottom (depth of 18 ft), indicating the release of phosphorus by the decomposition of organic material and (or) the reduction of iron oxides in bed sediment and the lower water column. Because the mixing boundary between the epilimnion and the hypolimnion likely was between depths of 6 and 10 ft, such sources in the hypolimnion would not contribute phosphorus to the growth of algae in the epilimnion from which water is withdrawn for supply until the breakdown of stratification in the fall. Furthermore, laboratory studies of samples from both reservoirs indicated that dissolved phosphorus was released from suspended particles at rates of 0.0007 to 0.0019 milligrams per liter per day. At these rates of release, particles could produce the maximum dissolved phosphorus concentrations measured in the water column within 30 days. Because the Harwoods Mill Reservoir was

stratified for 60 to 90 days by the sampling date, more than enough time had passed to produce the elevated concentrations observed in the hypolimnion of the reservoir. This indicates that the release of phosphorus from suspended particles likely is a major source of elevated dissolved phosphorus in Lee Hall Reservoir and the hypolimnion of Harwoods Mill Reservoir.

The presence of an upward increasing gradient in phosphorus concentrations in interstitial water in the bed sediment of Lee Hall Reservoir further indicates that the bed sediment is not a major source of phosphorus to algae in the water column. Because of a strong relation between dithionite-extracted phosphorus and iron in the bed sediment, a large part of the phosphorus appears to be bound to poorly crystallized iron oxides in the bed sediment. The ratios of dissolved phosphorus to dissolved iron in samples collected from the bottom of the water column in Harwoods Mill Reservoir, however, were 20 to 290 times the ratio of dithionite-extracted concentrations in the bed sediment, strongly indicating that a source other than bed sediment is the major source of phosphorus to the water column.

Part of the need for frequent application of copper sulfate to both reservoirs appears to be the binding of copper to particles (possibly algae and other organic material) and settling of the particles to the bottom as bed sediment. This is substantiated by the presence of more than 50 percent of the total copper in the suspended form in most water-column samples and greater concentrations of copper at depth in both reservoirs even though copper sulfate is applied at the surface in a dissolved form. Settling is further substantiated by the copper concentrations in the bed sediment that ranged from 0.56 to 6.7 milligrams per gram in Lee Hall Reservoir and 1.3 to 7.5 milligrams per gram in Harwoods Mill Reservoir. Furthermore, once copper is in the bed sediment, little copper is released as indicated by copper in interstitial water of box-core samples from Lee Hall reservoir remaining less than detectable concentrations.

Concentrations of sulfate in the water column of both reservoirs ranged from 2.5 to 13.8 milligrams per liter. Such low concentration could account for phosphorus not being released from the iron oxides even when dissolved-oxygen concentrations are low in the sediment and overlying water. In the literature, such sulfate concentrations have been shown to limit phosphorus release from bed sediment although the mechanism has not been identified.

Because of the short hydraulic retention times of the reservoirs, the release of dissolved phosphorus from suspended particles, and the limited release of phosphorus from bed sediment, the natural and pumped inflows ultimately appear to be the main sources of phosphorus to algae in the terminal reservoirs. Consequently, practices that control phosphorus concentrations in the inflows, not practices such as the application of alum or nitrate that sequester phosphorus in the bed sediment, likely will control algal growth in the terminal reservoirs most successfully. Additionally, the binding of copper in the bed sediment appears to limit exposure of copper to parts of the environment other than those exposed directly

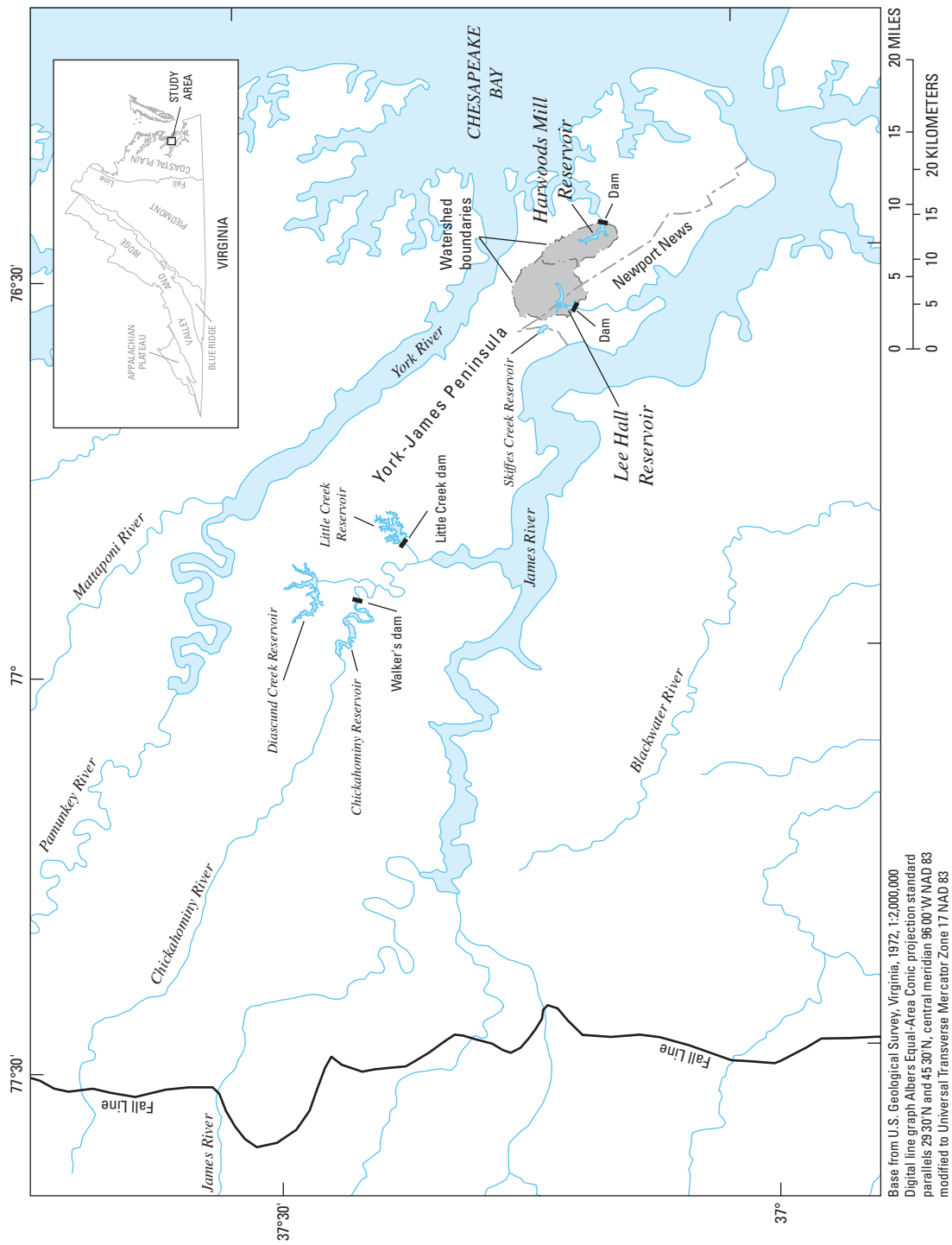
to the bed sediments. Although pumping water from outside watersheds directly to the water-treatment plants or through other reservoirs in the Newport News water-supply system, such as Little Creek Reservoir, would reduce phosphorus loads to the terminal reservoirs, these practices cannot be used to reduce phosphorus loads from the natural inflows. Phosphorus in natural inflows likely needs to be controlled near areas where the water flows into the reservoirs because much of the phosphorus likely is derived naturally from nonpoint sources within the largely forested watersheds.

## Introduction

Because phosphorus typically is the growth-limiting nutrient in freshwater systems, elevated phosphorus concentrations promote excessive algal growth, thereby degrading the water quality in water-supply reservoirs and other water bodies nationwide. Algae in water withdrawn for public supply plug filters during treatment and can impart tastes and odors to the finished water, thereby increasing treatment costs and resulting in finished water that may not be of the desired quality. Consequently, copper sulfate is routinely applied to reservoirs to control algal growth. Copper sulfate, however, only is a “temporary fix” and must be reapplied.

Treatment of water with copper sulfate can have other undesirable effects. Copper has a maximum allowable concentration in public drinking-water supplies and can be toxic to aquatic life. Accordingly, the action level for copper is 1.3 milligrams per liter (mg/L) in drinking-water supplies in Virginia (Commonwealth of Virginia, 2005). When considering aquatic life, only dissolved copper is bioavailable copper and is considered toxic to aquatic life. The dissolved copper concentration toxic to aquatic life depends on the hardness of the water. Based on hardness concentrations in reservoirs in the lower Coastal Plain Physiographic Province of Virginia, the dissolved copper concentration causing acute toxicity to aquatic life is about 8 micrograms per liter ( $\mu\text{g/L}$ ); the concentration causing chronic toxicity is about 6  $\mu\text{g/L}$ . Consequently, alternative reservoir-management strategies might be needed to reduce or eliminate copper-sulfate use where these concentrations are exceeded.

The City of Newport News provides treated water for public supply to communities of the lower York-James Peninsula, Virginia, from a combination of surface- and ground-water sources. An average 50 million gallons per day (Mgal/d) of raw water is withdrawn collectively from Lee Hall and Harwoods Mill Reservoirs (fig. 1) and treated for public supply in water-treatment plants located at the lower end of each reservoir. The water is derived from natural inflows from the reservoir watersheds and pumpage into the reservoirs from the surface-water sources outside of their watersheds. These two reservoirs commonly are referred to as terminal reservoirs because they are the last in a sequence of supply reservoirs through which water flows before treatment.



**Figure 1.** Locations of the study area, Lee Hall and Harwoods Mill Reservoirs, and other features in the Coastal Plain Physiographic Province of Virginia.

Results of monthly water-quality monitoring of the terminal reservoirs by city officials indicate that phosphorus likely is the growth-limiting nutrient for algae in these reservoirs (Ronald Harris, City of Newport News, written commun., 2003). Primary sources of phosphorus to the reservoirs likely include runoff from the watersheds and water pumped from the outside watersheds. Because of excessive algal growth, copper sulfate is applied at intervals that can range from more than 30 days in the winter to less than 7 days in the summer. Even with the application of copper sulfate to the reservoirs, chlorophyll concentrations typically are greater than would be expected for the total phosphorus concentrations observed in the water (U.S. Environmental Protection Agency, 2000). Consequently, internal cycling of phosphorus from the water column and bed sediment may be additional sources of dissolved phosphorus for promoting algal growth.

To develop a long-term strategy for managing algae in Lee Hall and Harwoods Mill Reservoirs, a better understanding of factors affecting phosphorus sources and reservoir processes is needed. Critical needs include information on (1) the relative contribution of different phosphorus sources, (2) the accumulation and release of phosphorus in bed sediment, (3) release of phosphorus from particles in the water column, and (4) the fate of copper in the reservoirs. Providing the information to assist in developing such a strategy fits the mission of the U.S. Geological Survey (USGS) because algal growth and the use of copper sulfate to control this growth in water-supply reservoirs is widespread across the Nation. Thus, information to help manage reservoir systems can be valuable in helping other water suppliers manage their reservoir systems and provide a better quality supply to their customers. A study that provides such information is a part of the USGS priority issues of defining and protecting the quality of the Nation's water resources and better understanding the physical, chemical, and biological processes in wetlands, lakes, reservoirs, and estuaries. To obtain the needed information, the USGS in cooperation with the City of Newport News conducted an investigation of processes affecting phosphorus and copper concentrations in water and bed sediment in relation to algal growth in the terminal reservoirs from April 2002 through December 2003.

## **Purpose and Scope**

The purpose of this report is to describe the effects of processes affecting phosphorus and copper concentrations in water and bed sediment in relation to algal growth in Lee Hall and Harwoods Mill Reservoirs. The report also discusses the implications of these effects on alternative strategies for managing phosphorus, copper, and algae in the reservoirs.

This report is based on results from routine water-quality monitoring conducted by City of Newport News officials from January 2000 through December 2003 and data collected by the USGS from April 2002 through December 2003. City officials collect and analyze water samples once a month

from selected sites in the two reservoirs and weekly from the raw water withdrawn for public supply. Data collected by the USGS are from periodic sampling at selected sites in the reservoirs during the summer of 2002 and target sampling during investigations of specific natural processes and management practices. Although both Lee Hall and Harwoods Mill Reservoirs were included in this investigation, greater emphasis was given in the field investigation to Lee Hall Reservoir because about 50 percent more water is withdrawn from Lee Hall Reservoir than from Harwoods Mill Reservoir under normal operating conditions.

## **Literature Review**

The general water quality or trophic condition of lakes and reservoirs often is linked to phosphorus concentrations because phosphorus typically limits the growth of algae in freshwater systems (Wetzel, 1975). Lakes and reservoirs generally are grouped into discrete trophic classes ranging from oligotrophic (limited algal growth from low phosphorus concentrations) to eutrophic (abundant algal growth from elevated phosphorus concentrations). Mesotrophic is the classification for lakes and reservoirs between oligotrophic and eutrophic. The wide range in size and other characteristics of lakes and reservoirs can make generalizations of relations among phosphorus concentrations, algal growth, and trophic condition difficult. Janus and Vollenweider (1984) concluded that with the same phosphorus input, phosphorus concentrations in lakes and reservoirs increase as the residence time decreases. Janus and Vollenweider (1984) also concluded that uptake of phosphorus by sediment was a major control on phosphorus concentrations in oligotrophic lakes but had little effect in eutrophic lakes.

Because traditional trophic classifications are discrete designations of a continuum and such designations can be biased, Carlson (1977) developed a trophic state index (TSI) to numerically classify lakes based on measured lake quality. Measurements used to calculate a TSI can include total phosphorus (TP) concentrations, Secchi depth (SD), and chlorophyll-*a* (chl) concentrations. The numeric index ranges from zero for the least eutrophic lake (better than any measured) to about 100 or 110 (a practical limit). A change in a particular index value of 10 represents a change in the respective measured value by a factor of 2. Although index values generally are similar for all types of measurements, biological index values, such as for Secchi depth and chlorophyll-*a* concentration, will diverge from values for total phosphorus during cold-weather months because temperature and sunlight, not phosphorus concentration, limit algal growth.

The Commonwealth of Virginia currently (2006) is developing nutrient criteria for lakes and reservoirs throughout Virginia based on the effects of nutrient concentrations on aquatic life (Virginia Department of Environmental Quality, 2006). Because reservoirs in Virginia generally are phosphorus limited, criteria are being considered for chlorophyll *a* and



total phosphorus for the type of reservoir and the ecoregion in which the reservoir is located. The criteria for Lee Hall and Harwoods Mill Reservoirs are based on warm-water reservoirs in ecoregion 14. These criteria are for median concentrations of 25  $\mu\text{g/L}$  for chlorophyll *a* and 0.040 mg/L for total phosphorus from April through October. Another criterion being considered for chlorophyll *a* is the 90<sup>th</sup> percentile, or 60  $\mu\text{g/L}$ . Although chlorophyll *a* is the preferred criterion because it represents the biological response of the water body, total phosphorus is thought to be a better criterion for reservoirs to which an algicide, such as copper sulfate, has been applied because biological response is altered by the algicide.

Internal phosphorus cycling from bed sediment has been identified as an important source of phosphorus in many lakes and reservoirs and has been the subject of extensive research (Stefan and Hanson, 1981; Jacoby and others, 1982; Andersen and Jensen, 1992; Welch and Cooke, 1995; Pettersson, 1998). Research commonly focuses on thermally stratified lakes and reservoirs in which hypolimnetic dissolved-oxygen concentrations become depleted and phosphorus concentrations increase, but some researchers also have studied shallow eutrophic lakes (Welch and Cooke, 1995; Golosov and Ignatieva, 1999). Mass-balance calculations commonly are used to determine the phosphorus cycling from bed sediment; bed-sediment contributions typically are not measured but are calculated as the difference between other phosphorus sources and sinks. In stratified lakes, the phosphorus contribution from bed sediment also has been calculated from the increase in phosphorus concentrations in the hypolimnion. In a study by Graber and Hartman (1985), bed sediment was calculated to have contributed 70 to 80 percent of the phosphorus to several lakes when the lakes were stratified and algal blooms were most prevalent.

Water-column conditions have been identified as being more important to the flux of phosphorus from bed sediment than are the gradients in phosphorus concentrations in bed-sediment interstitial water (Moore and others, 1998). Sufficiently oxidizing (aerobic) conditions, when dissolved-oxygen concentrations generally are greater than 2 mg/L, maintain iron in its most oxidized state (ferric iron) at the sediment surface forming poorly crystallized iron oxides (iron oxyhydroxides) that strongly bind phosphate in water. When conditions in the water column become sufficiently reducing or anaerobic (dissolved-oxygen concentrations near 0 mg/L), ferric iron in iron oxides is bacterially reduced to form more soluble ferrous iron and releases phosphate bound to this solid phase. Ferrous compounds are orders of magnitude more soluble than ferric compounds.

Sulfate concentrations in the water column also appear to affect the release of phosphate from bed sediment; the nature of the relation depends on the dissolved-oxygen concentration in the water column (Caraco and others, 1989). In freshwater systems, the phosphorus released is less than 1 millimole per mole of carbon at sulfate concentrations less than about 5.8 mg/L under anaerobic conditions. When the water is aerobic, the low rate of phosphorus release continues under

sulfate concentrations of about 9.6 to 28.8 mg/L. Although the mechanism that limits phosphorus release was not definitely identified, a likely process is that sulfide from the sulfate reduction forms ferrous sulfide and enhances phosphorus release. Thus, at sulfate concentrations above these thresholds, sulfate more readily reduces and binds ferrous iron and releases more phosphorus.

Particles (largely dead, decomposing algae) suspended in the water column also can be a source of phosphorus. More than 90 percent of the phosphorus in the water column in lakes and reservoirs typically is bound in living cells, in dead or particulate organic material, or is sorbed to inorganic and organic particles (Wetzel, 1975). Pettersson (1998) observed that the total phosphorus concentration in the water column at fixed sites decreased as the sediment settled and was deposited as bed sediment. Based on these findings, an unknown part of the increased dissolved phosphorus concentration in the hypolimnion that has been attributed to bed-sediment release can be derived from the release from settling and resuspended particles. One natural source of phosphorus is cycling that results from the sequential growth and decline in populations of particular species of algae. Typically, the predominant algal species in lakes and reservoirs change throughout the growing season (Wetzel, 1975). The effects of copper sulfate on algae can accelerate the growth and decline in algal populations, thus providing an appreciable source of dead algae in the water column. Resuspension of bed sediment also can be a source of phosphorus to the water column (Reddy and others, 1996; Hansen and others, 1997; Hupfer and others, 2000; Koski-Vähälä and others, 2000). Thus, a combination of settling water-column particles, resuspended bed sediment, and bed sediment can contribute to internal phosphorus cycling.

Several methods are used to reduce the recycling of phosphorus from bed sediment of lakes and reservoirs. These include dredging to remove the phosphorus-rich sediment (Peterson, 1982; Van der Does and others, 1992; Kleeberg and Kohl, 1999), application of alum to form a barrier to the release of phosphorus from the sediment (Cooke and Kennedy, 1978; Welch and others, 1982; Welch and others, 1986; Young and others, 1988; DeGasperi and others, 1993; Holz and Hoagland, 1999; Panuska and Robertson, 1999; Welch and Cooke, 1999; James and others, 2000), hypolimnetic aeration (Lean and others, 1986; Gächter and Wehrli, 1998), and application of calcium nitrate to limit the reduction of ferric iron to ferrous iron (Foy, 1986; DeGasperi and others, 1993; Søndergaard and others, 2000). Each method has succeeded in varying degrees and typically produces benefits lasting only several years.

## Description of Study Area

The study area is on the lower York-James Peninsula in the lower part of the Coastal Plain Physiographic Province of Virginia (fig. 1). The peninsula is bounded by the York River to the north, the James River to the south, and Chesapeake



Bay to the east. The Coastal Plain consists of layers of unconsolidated gravel, sand, silt, clay, and shell material having a total thickness greater than 1,500 feet (ft) in the study area and forming local and regional aquifer systems (Meng and Harsh, 1988). The shallow, local aquifers typically are interconnected hydrologically with the wetlands, streams, lakes, and reservoirs.

## Physiographic and Geologic Characteristics

Land-surface altitudes in the watersheds range from the reservoir levels (about 20 ft) to about 85 ft in the Lee Hall Reservoir watershed and about 55 ft in the Harwoods Mill Reservoir watershed. Land surface is characterized as level to gently sloping terraces at progressively higher altitudes separated by scarps (Johnson, 1972; Johnson and others, 1993). Stream valleys steeply incise these terraces. The terraces substantially affect the hydrology of the watersheds because of their generally low relief and direct relation to the near-surface formations that form the shallow aquifer system. Both reservoirs and surrounding parts of the drainages lie on the Huntington Flat that generally has a maximum altitude of 30 to 45 ft. It is separated from lower terraces by the Big Bethel Scarp. The foot of the scarp is about 15 ft. The remainder of the watershed lies on Grafton Plain (48 to 60 ft), Grove Plain (70 to 75 ft), and Lackey Plain (80 to 90 ft). Seasonal sinkhole ponds known as Grafton Ponds are on the Grafton Plain.

Different formations that form the shallow aquifer system directly underlie these terraces and likewise are all underlain by the Yorktown Formation. The shallow aquifer system discharges ground water directly to the terminal reservoirs and to the streams in their watersheds. The lithology, inferred depositional environments, and extents of the shallow formations in the vicinity of these reservoirs and their watersheds are described in detail in previous investigations by Johnson (1972), Brockman and Richardson (1992), Brockman and others (1997), and Speiran and Hughes (2001). Three formations are described here because of the direct effects of the formations on the hydrology and water quality of the reservoirs.

Holocene alluvial and marsh deposits are present at land surface primarily in the river valleys and beneath the reservoirs, and consist of clay, silt, and sand. Deposition continues in stream channels, flood plains, and reservoirs. The Shirley Formation is at land surface or underlies Holocene deposits beneath the Huntington Flat. The Shirley Formation consists of gravel, sand, silt, clay, and peat deposited in riverine and estuarine environments. The Moore House Member of the Yorktown Formation immediately underlies the surface formations in the study area and consists of fine-grained sand, shell hash, and bioclastic sand deposited during a

marine-regressive period in a progressively shallowing sea. In the upper part of the Moore House Member, much of the shell has weathered from the sediment, leaving fine-grained sand, silt, and clay. Based on the altitudes, sediments of the Shirley Formation and Holocene deposits directly underlie parts of the Lee Hall and Harwoods Mill Reservoirs.

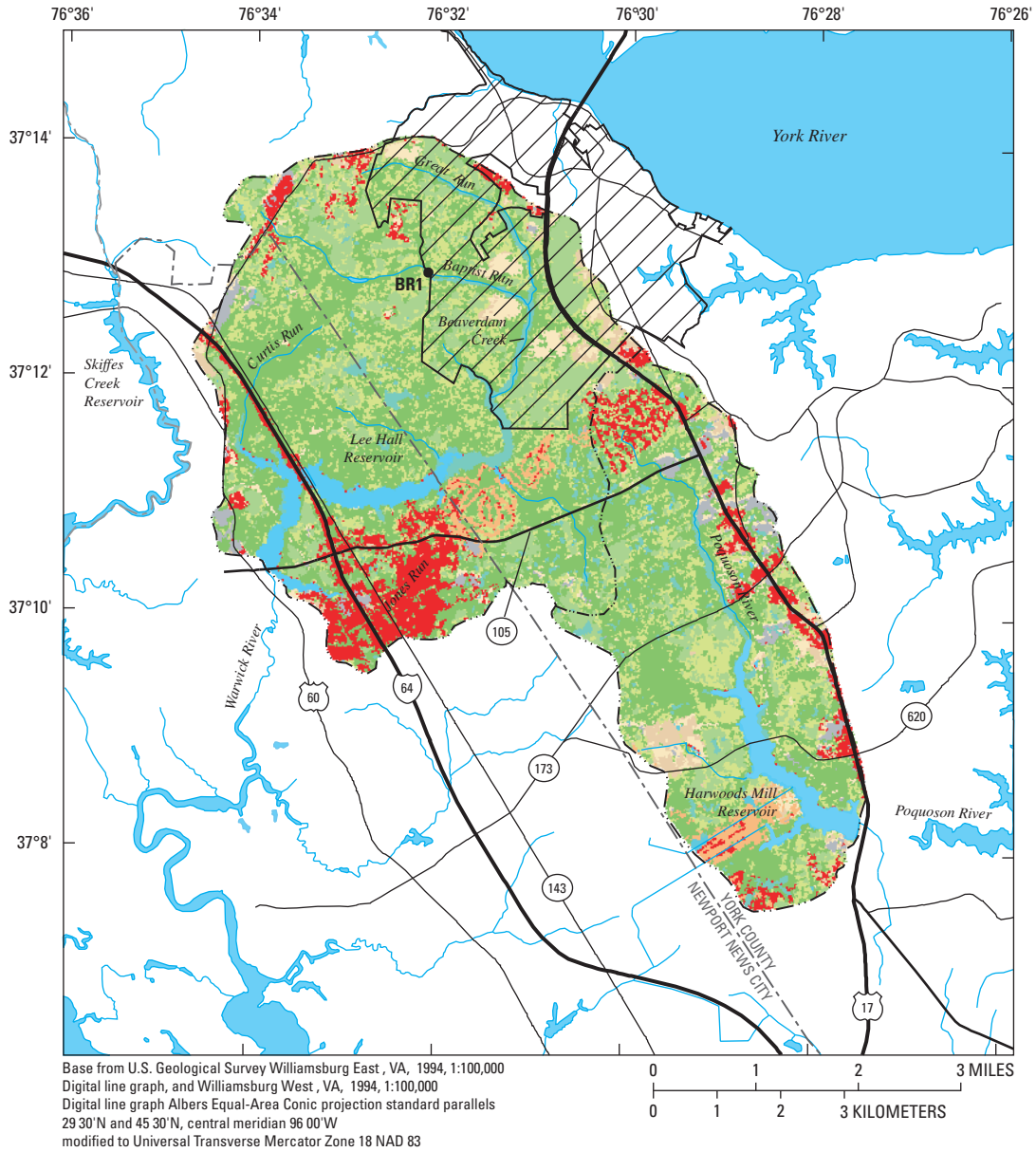
## Land Use

As forested land use in a watershed decreases and agricultural and urban uses increase, the loads of nitrogen and phosphorus to surface waters increase (Winter and others, 1998). Although the lower York-James Peninsula is urbanizing rapidly, the reservoir watersheds are largely forested (table 1; fig. 2; U.S. Geological Survey, 1999). Forests cover approximately 7,752 acres (75 percent) of the 10,336-acre Lee Hall Reservoir watershed. This large percentage of forested area includes two parks: one owned and maintained by the City of Newport News to protect the water supply and the other, the Yorktown Battlefield Unit of Colonial National Historical Park, maintained by the National Park Service. Approximately 992 acres (9.6 percent) scattered across the watershed are classified as developed/urban land use. Remaining land use includes 524 acres (5.1 percent) of agriculture (pasture and row crops), 399 acres (3.9 percent) of wetlands, 338 acres (3.3 percent) of open water, and 331 acres (3.2 percent) of urban/recreational grass and barren land.

Approximately 3,909 acres (67 percent) of the 5,838-acre Harwoods Mill Reservoir watershed is forested (fig. 2; table 1). This large area remains forested largely because the City of Newport News owns much of the watershed to help protect the water supply. The Virginia Division of Natural Heritage manages 394 acres to protect ecologically important seasonal sinkhole ponds, locally known as Grafton Ponds (Clark, 1998). Approximately 506 acres (8.7 percent) are developed/urban use. These developed areas are located primarily along the U.S. Highway 17 corridor and form the eastern boundary and northern end of the watershed. Another

**Table 1.** Land use in the watersheds of Lee Hall and Harwoods Mill Reservoirs, Virginia, in 1992 (U.S. Geological Survey, 1999).

Use	Lee Hall Reservoir		Harwoods Mill Reservoir	
	Acres	Percent of watershed	Acres	Percent of watershed
Agriculture	524	5.1	494	8.5
Barren	143	1.4	218	3.7
Developed/urban	992	9.6	506	8.7
Forest	7,752	75.0	3,909	67.0
Open water	338	3.3	292	5.0
Urban/recreational grass	188	1.8	169	2.9
Wetlands	399	3.9	250	4.3
Total	10,336	100.1	5,838	100.1



LAND USE		EXPLANATION	
<span style="color: red;">■</span>	Urban	<span style="border: 1px dashed black; padding: 2px;"> </span>	COLONIAL NATIONAL HISTORICAL PARK
<span style="background-color: gray; width: 10px; height: 10px; display: inline-block;"></span>	Transitional	<span style="border-bottom: 1px dashed black; width: 20px; display: inline-block;"></span>	WATERSHED BOUNDARY
<span style="background-color: #90EE90; width: 10px; height: 10px; display: inline-block;"></span>	Deciduous forest	<b>BR1</b> ●	WATER-SAMPLE COLLECTION SITE
<span style="background-color: #90EE90; width: 10px; height: 10px; display: inline-block;"></span>	Evergreen forest		
<span style="background-color: #90EE90; width: 10px; height: 10px; display: inline-block;"></span>	Mixed forest		
<span style="background-color: #FFDAB9; width: 10px; height: 10px; display: inline-block;"></span>	Pasture/hay		
<span style="background-color: #FFDAB9; width: 10px; height: 10px; display: inline-block;"></span>	Row crops		
<span style="background-color: #FFA07A; width: 10px; height: 10px; display: inline-block;"></span>	Urban/recreational grasses		
<span style="background-color: #4682B4; width: 10px; height: 10px; display: inline-block;"></span>	Wetlands		
<span style="background-color: #ADD8E6; width: 10px; height: 10px; display: inline-block;"></span>	Open water		

**Figure 2.** Land use and other features of the Lee Hall and Harwoods Mill Reservoir watersheds, Virginia.

major development is an international airport near the western edge of the lower part of the reservoir. Remaining land use includes 494 acres (8.5 percent) of agriculture, 250 acres (4.3 percent) of wetlands, 292 acres (5.0 percent) of open water, and 387 acres (6.6 percent) of urban/recreational grass and barren land.

### Reservoir Characteristics

Characteristics of Lee Hall and Harwoods Mill Reservoirs and their watersheds affect hydrology and phosphorus sources and cycling in the reservoirs. A 2,400-ft long dam constructed on the Warwick River in 1893 forms Lee Hall Reservoir (fig. 3). Beaverdam Creek is the main tributary that flows into the reservoir (fig. 2); the Warwick River is the tidal stream below the dam spillway that drains the watershed (fig. 3). The Warwick River is a tributary to the lower, estuarine part of the James River. Other named tributaries include Curtis Run and Jones Run. Because of the heavy development density and high phosphorus contributions identified by Hoehn (1985), Jones Run is dammed above Lee Hall Reservoir, and water is diverted around the reservoir into the Warwick River below Lee Hall Dam. Water pumped from outside watersheds enters an arm of Lee Hall Reservoir as flow from Curtis Run. Interstate 64 (I-64) and State Road 143 cross the reservoir over causeways and bridges immediately upstream from this arm of the reservoir and divide the reservoir into two parts (fig. 3). Both parts of the reservoir have similar volumes. Constriction of the reservoir by this crossing likely limits circulation between the two parts

of the reservoir. A railroad also crosses the reservoir over a causeway about halfway between I-64 and the dam. This crossing restricts flow more than the I-64 crossing because flow through a culvert under the causeway is controlled by sluice gates. Water is withdrawn from the reservoir through an intake at the water-treatment plant. The intake is downstream from the dam where runoff from Jones Run is diverted around the reservoir. A constriction on the Jones Run arm formed by another causeway likely is from an old road crossing and limits the circulation of water between the main part of the reservoir and the water-treatment plant.

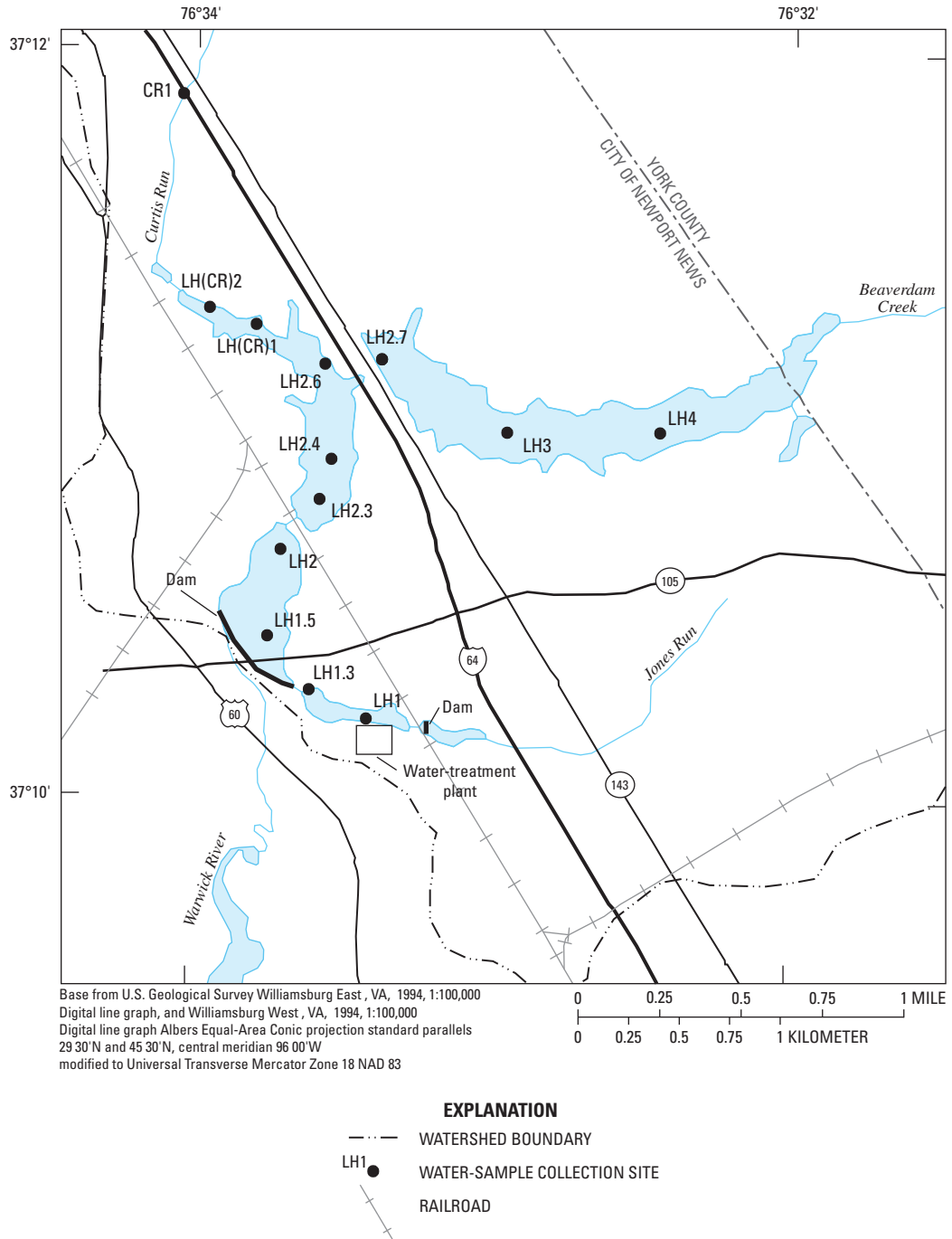


Figure 3. Sampling sites and other features near Lee Hall Reservoir, Virginia.

An 800-ft long dam that was constructed on the Poquoson River in 1919 forms Harwoods Mill Reservoir; the Poquoson River is free flowing above the reservoir and tidal below it (fig. 4). No named tributaries flow into the reservoir. Water pumped from outside watersheds enters the western side of the reservoir through an unnamed tributary located more than three quarters of the distance up the reservoir from the dam. State Road 620 crosses the reservoir over a causeway through which a pipe connects the two parts of the reservoir upstream from the midpoint of the reservoir. This pipe is near the western end of the causeway and cannot readily be seen, even from a boat. Because of the small size of the pipe, circulation between the two parts of the reservoirs likely is limited. Water

is withdrawn from the reservoir through an intake at the water-treatment plant located at the lower end of the reservoir.

Other physical characteristics of Lee Hall and Harwoods Mill Reservoirs are similar in many respects but are different in others. Full-pool altitude of Lee Hall Reservoir is 17.5 ft below the sluice gates and 20.3 ft above the sluice gates (table 2). Full-pool altitude of Harwoods Mill Reservoir is 20 ft. The reservoirs are shallow; depths are as great as 15.6 and 22.0 ft but average 5.5 and 9.8 ft in Lee Hall and Harwoods Mill Reservoirs, respectively. Lee Hall Reservoir covers 493 acres; the part above the I-64 crossing covers approximately 336 acres, and the part below the crossing covers approximately 157 acres. Harwoods Mill Reservoir covers

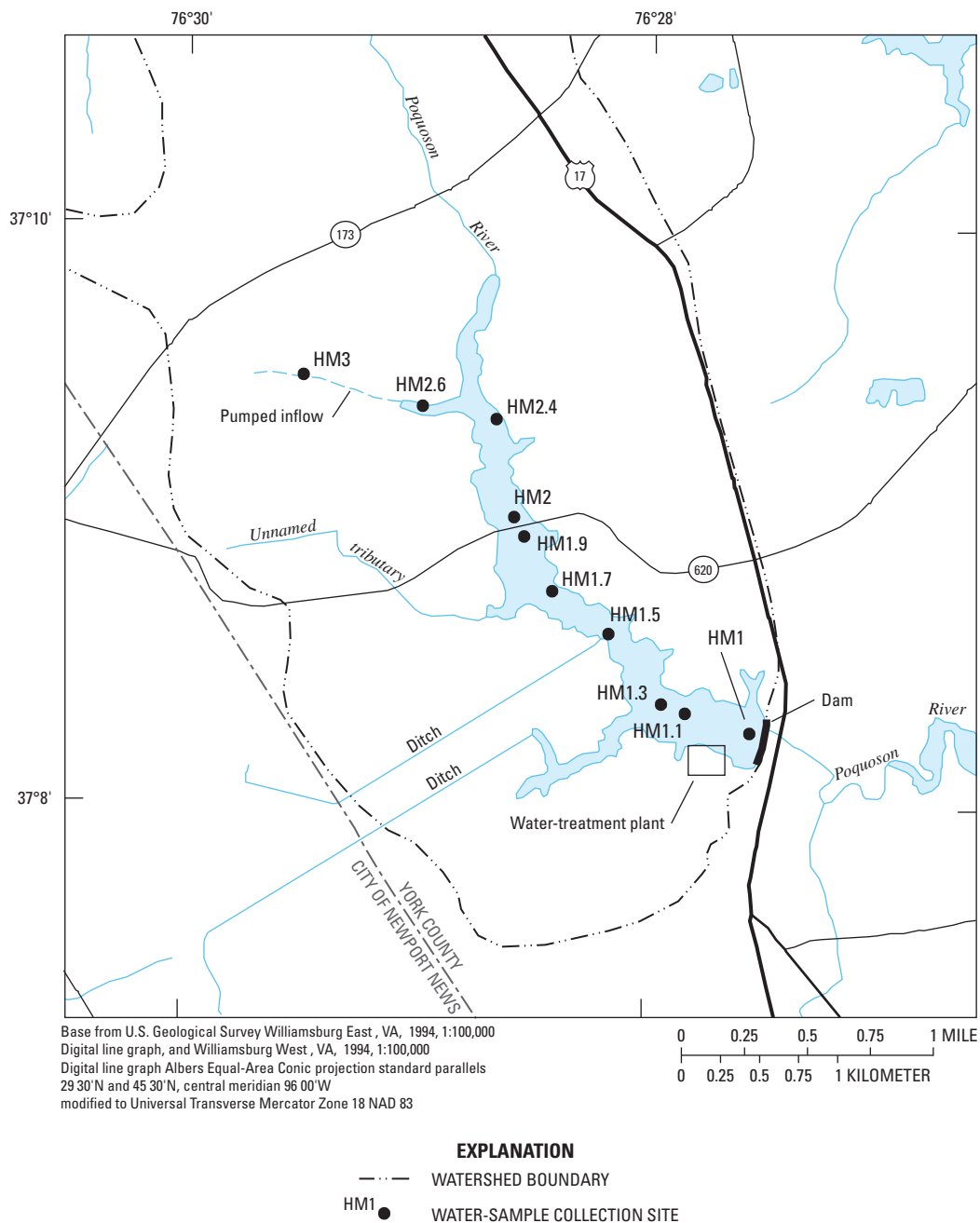


Figure 4. Sampling sites and other features near Harwoods Mill Reservoir, Virginia.

**Table 2.** Physical characteristics of Lee Hall and Harwoods Mill Reservoirs, Virginia (Ronald Harris, City of Newport News, written commun., 2002, unless noted).

Physical characteristic	Reservoir	
	Lee Hall	Harwoods Mill
Construction completion, year	1893	1919
Drainage area, square miles	14.1	8.0
Full pool elevation, feet above North American Vertical Datum of 1988	20.3/17.5 <sup>a</sup>	20
Maximum depth, feet	15.6	22
Average depth, feet	5.5	9.8
Surface area, acres	493	265
Reservoir volume, million gallons	876	846
Average natural inflow, assuming 15.2 inches of runoff, million gallons per day (Richardson, 1994)	10.3	5.8
Long-term average inflow of ground-water discharge from the watershed, assuming 7.9 inches of ground-water discharge, million gallons per day (Richardson, 1994)	5.3	3.0
Long-term average direct ground-water discharge to the reservoir, million gallons per day (Calculated)	1.3	1.9
Average water-treatment plant pumpage, million gallons per day	30	20
Average volume pumped, 2000–2003, million gallons per day	24.8	24.6
Peak volume pumped, 2000–2003, million gallons per day	42	55.5
Hydraulic retention time based on average natural inflow only, days (Calculated)	85	146
Hydraulic retention time based on average withdrawals, days (Calculated)	29/15 <sup>b</sup>	42
Hydraulic retention time based on average daily withdrawals for 2000–2003, days (Calculated)	35/18 <sup>b</sup>	34
Hydraulic retention time based on peak daily withdrawals for 2000–2003, days (Calculated)	21/11 <sup>b</sup>	15

<sup>a</sup>Upper reservoir/lower reservoir.<sup>b</sup>Whole reservoir/lower reservoir only.

approximately 265 acres. The reservoir drainage areas are 14.1 and 8.0 mi<sup>2</sup>, respectively. The volumes of the reservoirs are similar—876 million gallons (Mgal) for Lee Hall Reservoir and 846 Mgal for Harwoods Mill Reservoir. About half of the volume (440 Mgal) of Lee Hall Reservoir is above I–64.

## Hydrology

Flow into the reservoirs consists of natural inflows from their watersheds and water pumped from outside watersheds. Water pumped from outside watersheds provides the water needed for supply not provided by natural inflows. The outside watersheds include the Chickahominy River (Chickahominy Reservoir), Diascund Creek Reservoir, Little Creek Reservoir, and Skiffes Creek Reservoir (fig. 1). The Chickahominy River is the predominant source of water from outside watersheds.

The Chickahominy River is a tributary to the James River with headwaters in the lower part of the Piedmont Physiographic Province (fig. 1). The Chickahominy River flows into the James River about at the midpoint of the James River between Chesapeake Bay and the Fall Line (the lower

limit of the Piedmont Physiographic Province). Water is withdrawn from the Chickahominy River just above Walkers Dam where a small in-stream reservoir is formed. Upstream from this reservoir, the flood plain of the Chickahominy River forms broad, bottomland-hardwood wetlands that are common in the Coastal Plain. These wetlands attenuate peak flows from stormwater runoff, remove sediment from runoff, and impart a substantial amount of dissolved organic carbon to the water (Speiran, 2000). Below the dam, the river is tidal. During certain combinations of low freshwater flow, high tides, and certain wind directions and strengths, salty water can enter Chickahominy Reservoir and be pumped into the terminal reservoirs (Lynch, 1992).

Diascund Creek Reservoir is formed by a dam on a tributary to the Chickahominy River below Walkers Dam. This reservoir has numerous tributary creeks that typically drain through wetland flood plains. Little Creek Reservoir is formed by a dam on a tributary to the Chickahominy River even farther below Walkers Dam. Unlike Diascund Creek Reservoir, all of the free-flowing streams upstream from the Little Creek Dam are inundated by the reservoir. Skiffes Creek Reservoir is formed by a dam on the tributary to the James

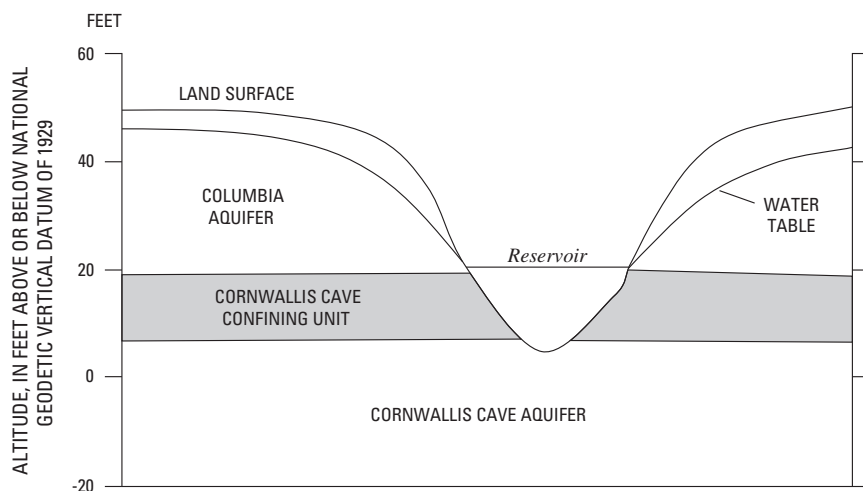


River that drains the watershed immediately west of the Lee Hall Reservoir watershed. Stream valleys above the dam contain wetlands.

Natural inflows consist of a combination of direct discharge to the reservoirs and flow through tributaries from both surface runoff and ground-water discharge. Surface runoff results from precipitation in the watershed that does not infiltrate the soils. Ground-water discharge also contributes to streamflow during periods of surface runoff. When surface runoff ends and streams return to base-flow conditions, streamflow is entirely ground-water discharge. Surface runoff typically is greatest in the late winter and early spring when evapotranspiration rates are low, ground-water levels are high, and soils readily become saturated. Ground-water discharge rates also are high at these times.

The flood plains of some of the streams that flow into the terminal reservoirs contain bottomland-hardwood wetlands, which attenuate peak stormwater flows and substantially affect water quality. Beaverdam Creek, the main natural inflow into Lee Hall Reservoir (fig. 3), contains the most extensive wetlands of all the natural inflows.

Ground-water discharge is derived from the shallow aquifer system. The vertical extent of this system can be defined in several ways (Brockman and Richardson, 1992; Brockman and others, 1997; Speiran and Hughes, 2001). The shallowest part, however, includes the Columbia aquifer, the Cornwallis Cave confining unit, and the Cornwallis Cave aquifer (fig. 5). The Columbia aquifer generally is an unconfined or water-table aquifer consisting of Holocene sediment, sediment of the Shirley Formation, and sediment of other formations that directly underlie the terraces. The Columbia aquifer also can contain sediment of upper parts of the Moore House Member of the Yorktown Formation. The Cornwallis Cave confining unit consists of lower parts of Holocene sediments, lower parts of the Shirley Formation and other formations that directly underlie the terraces, and upper parts of the Moore House Member of the Yorktown Formation. The Cornwallis Cave aquifer likely is a confined or semiconfined



**Figure 5.** Generalized geohydrologic section showing relation of the shallow aquifer system to Lee Hall and Harwoods Mill Reservoirs, Virginia.

aquifer consisting primarily of the Moore House Member of the Yorktown Formation but possibly includes overlying and underlying sediments.

Ground-water discharge is an important source of water to the reservoirs. Ground water discharges to the streams in the reservoir watersheds and directly to the reservoirs. Richardson (1994) determined that ground-water discharge provides 47 to 79 percent (median of 74 percent) of the annual flow in streams in the Coastal Plain of Virginia. Thus, ground-water discharge usually contributes more to streamflow than does surface runoff. Direct discharge typically is to shallow, near-shore waters of reservoirs rather than to deeper waters. In the terminal reservoirs, ground water also may discharge to the deep parts of the reservoirs where the channels of the original streams may have incised through clayey sediment that forms much of the reservoir bottoms and into more permeable aquifer material. Ground water also may discharge through springs that originally may have been present in the stream channels and valleys. Such springs are common in stream channels and at the base of valley walls in the Beaverdam Creek watershed (Focazio, 1997; Speiran and Hughes, 2001). Much of the ground-water discharge to streams throughout the reservoir watersheds likely is through spring discharge.

## Historic Water Quality

Chickahominy, Diascund Creek, and Little Creek Reservoirs are the primary sources of surface water pumped into Lee Hall and Harwoods Mill Reservoirs (fig. 1). Mean concentrations of total phosphorus from these sources in the mid-1980s were 0.049, 0.028, and 0.014 mg/L, respectively (Lynch, 1992). The total phosphorus concentration of Little Creek Reservoir without pumpage from other sources, however, likely would have averaged 0.005 mg/L (Lynch, 1992). In a limnological study of the terminal reservoirs conducted during this same period, total phosphorus concentrations in natural inflows from eight sites on tributaries to Lee Hall Reservoir ranged from 0.03 to 0.07 mg/L; concentrations did not exceed 0.04 mg/L in Lee Hall Reservoir below the I-64 causeway (Hoehn and others, 1986). Total phosphorus concentrations in single grab samples collected at these tributary sites during each of two stormwater-runoff periods in May 1985 ranged from 0.02 to 0.46 mg/L. Since this study, inflows having high phosphorus concentrations either have been diverted to avoid discharge into the reservoir or are being treated to remove phosphorus.

Hoehn (1985) concluded that the shallow depth of Lee Hall Reservoir inhibits thermal stratification because sharp thermal gradients were not present at any study sites in the reservoir. At some sites, however, gradients in dissolved-oxygen concentrations were sharp near the bottom of the reservoir.

These gradients indicate a substantial effect of the decomposition of organic material in bed sediment or in the lower part of the water column. This decomposition may be a source of phosphorus to the reservoir.

Total phosphorus concentrations near the water surface of Harwoods Mill Reservoir ranged from 0.02 to 0.12 mg/L and generally decreased from the arm where water was pumped into the reservoir from outside watersheds to the water-treatment plant (Hoehn, 1985). Thus, phosphorus concentrations indicate that the pumpage likely is an important source of phosphorus to Harwoods Mill Reservoir.

Hoehn (1985) further concluded that Harwoods Mill Reservoir is of sufficient depth to stratify thermally and chemically for only short periods at the lower end near the water-treatment plant. In most of the reservoir, however, stratification did not clearly develop; at all except the sampling site closest to the water-treatment plant, the vertical thermal gradient was small and gradual, showing no sharp change typical of thermal stratification. At some sites, dissolved-oxygen concentrations declined sharply near the bottom of the reservoir, whereas concentrations decreased uniformly with depth at other sites. Near the water-treatment plant, however, phosphorus concentrations in August 1984 showed the effects of stratification and possible bed-sediment and water-column cycling of phosphorus. Near the reservoir surface, total phosphorus concentration was 0.02 mg/L, total soluble phosphorus concentration was 0.01 mg/L, and orthophosphorus concentration was less than the reporting level. Near the bottom of the reservoir, however, total phosphorus concentration was 0.27 mg/L, total soluble phosphorus 0.09 mg/L, and orthophosphorus concentration was 0.08 mg/L. Hoehn (1985) also reported that throughout the reservoir during July and August 1984, total phosphorus concentrations were greater near the bottom than near the surface of the reservoir, although only a small part of the reservoir was thermally stratified.

## Nutrient Chemistry

Nutrients are present in aquatic systems in particulate and dissolved forms or species (Mitsch and Gosselink, 1993). Particulate species can be present in the water column and bed sediment; dissolved species can be present in the water column and in interstitial water of the bed sediment. The particular nutrient species and its location in the aquatic system affect the availability of the nutrient to stimulate algal growth; only certain dissolved species stimulate algal growth (table 3). Consequently, knowledge of the chemistry affecting nutrient speciation is essential in controlling nutrient cycling and algal growth.

In aquatic systems, all phosphorus species are present as phosphate. Particulate forms of phosphate can be bound to inorganic minerals or present in organic compounds. In aerobic environments, iron oxides are the most common inorganic minerals containing phosphate and likely are not available to algae. When dissolved-oxygen concentrations

are sufficiently low, iron oxides are chemically reduced and release phosphate as dissolved orthophosphate ( $\text{PO}_4^{-3}$ ) or as organic phosphate, depending on the form(s) bound to the iron. When water is oxygenated, iron oxides form and remove phosphate from solution.

The decomposition of particulate organic material that contains phosphate produces dissolved organic compounds (commonly measured as dissolved organic carbon (DOC)) that also contain phosphate. Most phosphate in DOC likely is not available to most algae. As bacteria further decompose the dissolved organic compounds, phosphate is released from the organic compounds into solution as orthophosphate. Inorganic forms of dissolved phosphorus typically are thought to be bioavailable. The dissolved-oxygen concentration in water controls this decomposition; organic compounds typically decompose more rapidly when dissolved-oxygen concentrations are abundant than when they are limited.

Polyphosphates are used to prevent scaling in boilers and were used as a builder in detergents. The use of polyphosphates in detergents was banned in Virginia after the State signed the 1983 Chesapeake Bay Agreement. Polyphosphates hydrolyze to form orthophosphate. Orthophosphate likely is the primary source of phosphorus available to algae for photosynthesis. Because orthophosphate is synthesized readily by algae, orthophosphate concentrations seldom occur much above reporting levels in natural aquatic systems.

Commonly used analytical determinations include total or whole-water phosphate, a measure of all of the phosphate in the sample; dissolved phosphate, a measure of all of the dissolved species; and dissolved orthophosphate (actually dissolved reactive phosphate). Concentrations of all species typically are expressed either as phosphorus (P) or orthophosphate ( $\text{PO}_4^{-3}$ ). The concentration of suspended particles can be calculated by subtracting the dissolved from the total phosphorus concentrations.

Particulate forms of nitrogen can be bound to inorganic minerals and organic compounds. Ammonium ( $\text{NH}_4^+$ ) is the primary nitrogen species bound to inorganic material because the ionized species bind to silt and clay minerals by cation exchange. Nitrogen also can be chemically bound to organic material which also can be bound to inorganic minerals, such as iron oxides. As particulate organic material decomposes, it can form dissolved organic compounds that contain dissolved organic nitrogen. When bacteria decompose the dissolved organic material, nitrogen is released or mineralized to form ammonia ( $\text{NH}_3$ ). Ammonia is a gas that can escape to the atmosphere but readily hydrolyzes in water to form ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). In the normal pH range for aquatic systems (5.5 to 8.5), ammonium hydroxide readily ionizes to form ammonium and hydroxyl ions ( $\text{NH}_4^+$  and  $\text{OH}^-$ ). The ammonium ion can be immobilized by binding onto the silt and clay minerals. Where the dissolved-oxygen concentration is near 0 mg/L, ammonium typically remains unchanged. Where the dissolved-oxygen concentration is sufficiently greater than 0 mg/L, ammonium oxidizes (nitrifies) through a series of reactions mediated by bacteria to ultimately form



**Table 3.** Characteristics and environmental significance of nitrogen and phosphorus species, and typical analytical methods of determination.

Nutrient	Species	Characteristics	Environmental significance	Typical U.S. Geological Survey analytical method
Nitrogen	Organic	In organic particles derived from plant and animal tissue; in soluble organic compounds dissolved in water.	Limited as a factor contributing to eutrophication but can contribute when mineralized to ammonia as organic compounds decompose.	Analyzed with ammonia as filtered or whole-water Kjeldahl nitrogen. Determined by the difference between the Kjeldahl and ammonia analyses.
Nitrogen	Ammonia	Cation ( $\text{NH}_4^+$ ) formed by decomposition of organic compounds; commonly exchanges onto silt and clay particles; also present as a dissolved cation and gas ( $\text{NH}_3$ ).	Of the oxidation state most readily used to synthesize cell material; hence, contributes to eutrophication. Elevated concentrations typically indicate recent contamination and(or) low dissolved-oxygen concentrations. Can be toxic to fish.	Analyzed as filtered or whole-water ammonia. Whole-water analysis typically includes ammonia bound to sediment.
Nitrogen	Nitrite	Soluble anion ( $\text{NO}_2^-$ ) derived from intermediate step in the bacterially mediated oxidation of ammonia; not commonly elevated in concentration.	In elevated concentrations indicates a significant recent source of contamination. Contributes to eutrophication.	Analyzed with nitrate ( $\text{NO}_2^-$ plus $\text{NO}_3^-$ ) and also independently.
Nitrogen	Nitrate	Soluble anion ( $\text{NO}_3^-$ ) derived from final step in the bacterially mediated oxidation of ammonia.	Elevated concentrations typically are derived from the application of inorganic commercial fertilizers or the bacterially mediated oxidation of ammonia (nitrification) in point and nonpoint sources of contamination. Contributes to eutrophication.	Analyzed with nitrite. Determined by the difference between the nitrite plus nitrate and nitrite analyses.
Nitrogen	Elemental	Gaseous form of nitrogen ( $\text{N}_2$ ) dissolved in water; major gas present in the atmosphere.	Can be used as a nutrient only by nitrogen-fixing organisms. Commonly does not contribute to eutrophication.	Analyzed as a gas.
Phosphorus	Organic	Phosphate in organic particles derived from plant and animal tissue; in soluble organic compounds dissolved in water.	Limited contributing factor to eutrophication but can be released to form orthophosphate and contribute to eutrophication when organic compounds decompose.	Part of the total and dissolved phosphorus analyses along with polyphosphates and orthophosphorus. Not determined independently. Can be inferred through an extraction sequence not commonly performed.
Phosphorus	Polyphosphates	Dehydrated phosphate ions dissolved in water. Hydrates to form orthophosphate.	Commonly used in detergents before the practice was discontinued and to prevent scaling in boilers.	Part of the dissolved phosphorus analysis along with organic phosphorus and orthophosphorus. Not determined independently with commonly used techniques.
Phosphorus	Orthophosphorus	Anion ( $\text{PO}_4^{-3}$ ) derived from decomposition of organic compounds, release from minerals, and hydrolysis of polyphosphates.	Growth-limiting nutrient for algae in most freshwater aquatic systems. Likely the primary form used by algae.	Analyzed independently and as part of the dissolved phosphorus analysis.

nitrate ( $\text{NO}_3^-$ ). Nitrite ( $\text{NO}_2^-$ ) is one of the intermediate species formed by these reactions. Consequently, ammonia concentrations increase only to a limited extent in oxygenated environments. Additionally, nitrite concentrations typically are near the minimum reporting level where dissolved oxygen is abundant because the transformation of nitrite to nitrate is rapid. Nitrate is extremely soluble and, therefore, is readily transported through aquatic systems including ground-water systems. Where dissolved-oxygen concentrations are sufficiently depleted and nitrate is present, the nitrate can be reduced (denitrified) by bacteria to form nitrogen gas ( $\text{N}_2$ ). Nitrogen gas is the main gas present in the atmosphere and can be used only by certain algae in photosynthesis.

Ammonium, nitrite, and nitrate are readily used by algae for photosynthesis. Because ammonium is of the same oxidation state as the organic compounds that algae synthesize from inorganic nitrogen, and nitrite and nitrate are of different oxidation states, ammonia is more readily used by algae in photosynthesis.

Commonly used analytical determinations include whole water and dissolved Kjeldahl nitrogen (organic plus ammonia nitrogen), dissolved ammonia nitrogen, dissolved nitrite plus nitrate nitrogen, and dissolved nitrite nitrogen. Ammonia bound to clays cannot be analyzed as ammonia with commonly used analytical techniques and is measured only as part of the Kjeldahl analysis. Concentrations of nitrogen species not determined by specific analytical determinations (organic nitrogen and nitrate nitrogen) can be determined by the difference between values of the appropriate determinations.

## Study Methods

Officials with the City of Newport News have collected and analyzed water samples from selected sites in Lee Hall and Harwoods Mill Reservoirs once a month since about 1990 and weekly from the raw-water withdrawals for public supply. USGS personnel collected samples periodically at selected sites in the reservoirs during the summer of 2002 and during targeted investigations of specific processes. Summer months were targeted for data collection because algal populations are the greatest during the summer.

### Data-Collection Sites

The primary USGS data-collection sites were those also used by the City of Newport News; the nomenclature used in this report for these sites is similar to that used by the City. The primary data-collection sites in Lee Hall Reservoir included site LH1 at the lower end of the reservoir near the water-treatment plant, site LH2 immediately downstream from the railroad crossing, and site LH3 above I-64 and in the part of the reservoir affected minimally by pumpage from outside sources (fig. 3; table 4). The USGS also collected samples

at site CR1 on Curtis Run (fig. 3), which represents pumped inflow, site BR1 on Baptist Run (a tributary to Beaverdam Creek) (fig. 2), which represents natural inflow, and at supplemental sites in the reservoir. Although a stream site located on Beaverdam Creek would have represented natural inflow better than site BR1, backwater from beaver dams and stream access limited site selection. Because the stream channel in lower Beaverdam Creek has a lower gradient and broader channel than the stream channel at Baptist Run, water probably flows more slowly and the water quality likely is different at Beaverdam Creek.

The primary data-collection sites in Harwoods Mill Reservoir used by the City of Newport News were site HM1 at the lower end of the reservoir near the water-treatment plant, site HM2 immediately upstream from where State Road 620 crosses the reservoir, and site HM3 on an unnamed tributary used for pumping inflow into Harwoods Mill Reservoir. The City of Newport News uses the HM3 site to represent pumped inflows into both reservoirs. Because the emphasis of this study was on Lee Hall Reservoir, the USGS used only one site, HM1, as the primary data-collection site in Harwoods Mill Reservoir. Supplemental sites in Harwoods Mill Reservoir also were used for collecting samples (fig. 4; table 4).

The project nomenclature of the supplemental sites in both reservoirs is based on the nomenclature of the primary sites. This nomenclature adds a decimal number to the downstream primary site number and represents the approximate fraction of the distance of the secondary site between the downstream and upstream primary sites. For example, the supplemental site in Lee Hall Reservoir located about halfway between sites LH1 and LH2 is designated as site LH1.5. For supplemental sites located upstream from the last primary site, the whole-number designations are continued. For example, the supplemental site located upstream from site LH3 is designated as site LH4. In Lee Hall Reservoir, all primary sampling sites are located along the path of natural inflow from Beaverdam Creek to the water-treatment plant; no primary sampling sites are located in the Curtis Run arm of the reservoir into which the water from outside watersheds is pumped. To clearly identify supplemental sites in the Curtis Run arm of the reservoir, the designation “(CR)” was added to the LH designation (fig. 3; table 4). These designations are followed by an upstream sequence number similar to the primary sites. Thus, the two sites in the Curtis Run arm are designated LH(CR)1 and LH(CR)2.

**Table 4.** Descriptions of water-quality and bed-sediment sampling sites in or near Lee Hall and Harwoods Mill Reservoirs, Virginia, 2002–2003.

[USGS, U.S. Geological Survey; WTP, water-treatment plant; U.S., United States]

Project site number	USGS station number	Location description
<b>Lee Hall Reservoir</b>		
LH1	0204279240	Lee Hall Reservoir at WTP near Lee Hall, VA
LH1.5	0204279232	Lee Hall Reservoir at Route 105 near Lee Hall, VA
LH2	0204279230	Lee Hall Reservoir above Route 105 near Lee Hall, VA
LH2.3	0204279228	Lee Hall Reservoir above railroad bridge near Lee Hall, VA
LH2.6	0204279225	Lee Hall Reservoir at Interstate 64 near Lee Hall, VA
LH2.7	0204279213	Lee Hall Reservoir at Route 143 near Lee Hall, VA
LH3	0204279210	Lee Hall Reservoir above Interstate 64 near Lee Hall, VA
LH4	0204279200	Lee Hall Reservoir below aqueduct near Lee Hall, VA
BR1	0204278995	Baptist Run at Route 637 near Yorktown, VA
LH(CR)1	0204279224	Lee Hall Reservoir above power lines near Lee Hall, VA
LH(CR)2	0204279223	Lee Hall Reservoir below Curtis Run near Lee Hall, VA
CR1	0204279220	Curtis Run above Lee Hall Reservoir near Lee Hall, VA
<b>Harwoods Mill Reservoir</b>		
HM1	01677850	Harwoods Mill Reservoir above U.S. Highway 17 at Tabb, VA
HM1.1	0167784610	Harwoods Mill Reservoir below submerged dam near Tabb, VA
HM1.3	01677846	Harwoods Mill Reservoir above submerged dam near Tabb, VA
HM1.5	01677835	Harwoods Mill Reservoir at airport near Tabb, VA
HM1.7	01677832	Harwoods Mill Reservoir above airport near Tabb, VA
HM1.9	0167783010	Harwoods Mill Reservoir below Route 620 near Tabb, VA
HM2	01677830	Harwoods Mill Reservoir at Route 620 near Tabb, VA
HM2.4	01677825	Harwoods Mill Reservoir at Tributary 1 near Tabb, VA
HM2.6	01677823	Harwoods Mill Reservoir in Tributary 1 near Tabb, VA
HM3	01677820	Harwoods Mill Reservoir in Tributary 1 near Tabb, VA

## Sample Collection and Analysis

Water samples were collected from the reservoirs by the USGS and City of Newport News personnel in a similar manner, using a peristaltic pump with a weighted silicon tube that was graduated in 1-ft intervals and attached to a small-diameter, steel cable to minimize stretching of the tubing and assure accurate depth determinations. Surface samples identified in this report with an “S” suffix, such as LH1S, were collected from about 1 ft below the water surface. Bottom samples designated with a “B” suffix, such as LH1B, were collected about 1 ft from the bottom of the reservoir to avoid pumping bed sediment.

Some of the sample-collection and processing methods used by USGS personnel differed from those used by City of Newport News personnel. USGS personnel dedicated a separate set of weighted tubing and cable for each sample collected, whereas City of Newport News personnel used the same tubing at each site after rinsing it with native water

before collecting a sample. USGS personnel soaked the inside of the tubing with hydrochloric acid, rinsed it with a de-ionized water and detergent solution, and rinsed it again with de-ionized water before each use. Once the tubing was lowered to the sampling depth, native water was pumped through the tubing for about 5 minutes to establish equilibrium between the water and the tubing.

Water samples also were collected periodically during base flow and at different times during selected runoff periods on Baptist Run. During base flow, samples were collected from the midpoint of the stream by using a peristaltic pump with a weighted silicon tube. During runoff periods, samples were collected at the midpoint of the stream by using a depth-integrating sediment sampler.

Water temperature, pH, specific conductance, and dissolved-oxygen concentrations were measured on site by USGS personnel using a YSI 6600 multiparameter sonde in accordance with methods described by Wilde (variously dated) and the instrument manufacturer (YSI Incorporated, undated).

These measurements were made by City of Newport News personnel using a Hydrolab multiparameter sonde. USGS personnel measured chlorophyll concentrations (considered to be total chlorophyll) with an optical probe on the sonde according to manufacturer specifications (YSI Incorporated, undated). At least one sample was collected during most sample-collection periods, processed on site using methods described by Wilde (variously dated), and then shipped overnight on dry ice to the USGS National Water Quality Laboratory (NWQL) in Arvada, CO, for analysis of chlorophyll *a* using methods described by Arar and Collins (1997). Selected physical and chemical characteristics were measured in the field at 1-ft-depth intervals from the surface to the bottom of the reservoirs and at 1 ft below the surface in the streams during each sample-collection period.

Samples requiring filtration that were collected by USGS personnel were filtered on site whereas such samples collected by City of Newport News personnel were filtered after they arrived at the City of Newport News laboratory. Samples collected and analyzed by the USGS for dissolved nutrients, cations, and anions were filtered through 0.45-micrometer ( $\mu\text{m}$ ) pore-size capsule filters. Although these samples are designated as dissolved, colloidal particles also can be present in the samples because of the filter pore size. Samples analyzed for concentrations of nutrients, anions, cations, and organic carbon were processed and preserved according to USGS methods documented in Wilde and others (1999). Samples were chilled and shipped overnight to the NWQL. The NWQL analyzed the samples for nutrients using methods described by Fishman and Friedman (1989), Patton and Truitt (1992; 2000), and Fishman (1993); for major ions using methods described by Fishman and Friedman (1989), Fishman (1993), and American Public Health Association (1998); for dissolved organic carbon using methods described by Brenton and Arnett (1993); for copper using methods described by Faires (1993); and for total iron using methods described by Garbarino and Struzeski (1998). Analytical data from the NWQL were published in USGS annual data reports (White and others, 2003; 2004). In some instances, analytical results reported by the NWQL contained estimated concentrations for values less than the minimum reporting level (MRL). Estimated values are identified in tables but are not discussed in this report.

A minimum of 10 percent of the samples collected by both USGS and City of Newport News personnel were collected for quality-assurance (QA) purposes. The QA samples consisted of replicate samples collected at selected sites during sampling or equipment blanks. QA data from the USGS analyses were published with the other analytical data in USGS annual data reports (White and others, 2003; 2004). Equipment blanks indicated an absence of contamination by the equipment and methods used. Analyses of replicate samples indicated good agreement among the replicate samples.

Samples collected by City of Newport News personnel were analyzed by the City of Newport News Waterworks

Laboratory. As a laboratory for a water-treatment facility, the laboratory analyzes samples using analytical methods of the U.S. Environmental Protection Agency. Because the samples are collected and analyzed as part of a long-term waterworks program and not specifically for this project, the laboratory did not go through USGS certification but is certified by the Virginia Department of Consolidated Laboratory Services (DCLS). DCLS is certified by the NWQL for nutrient analyses. The data collected by City of Newport News personnel are identified in this report as “Newport News data” and are included in appendixes that only are available online at <http://pubs.water.usgs.gov/sir2006-5277>.

Selected samples were analyzed for the abundance of oxygen-18 ( $^{18}\text{O}$ ) and deuterium (D), the heavy, stable isotopes of oxygen and hydrogen in reservoir water, stream water, and the pumped inflow to help determine the effects of mixing and stratification in the reservoirs. Oxygen-18 and deuterium occur in the natural environment, including in water molecules, where the more abundant lighter isotopes (oxygen-16 ( $^{16}\text{O}$ ) and hydrogen (H), respectively) are present (Gat and Gonfiantini, 1981; Coplen, 1993). The abundance of oxygen-18 and deuterium in water varies on global and local scales; therefore, measurement of the abundance of oxygen-18 and deuterium in water can be an important tool in evaluating hydrologic processes and pathways. Variability occurs because the heavy isotopes react chemically and physically in a different manner from the light isotopes. These differences in reactions result in fractionation that depletes or enriches the abundance of oxygen-18 and deuterium in the source water. Evaporation and condensation are among the processes that fractionate oxygen-18 and deuterium. When water evaporates, a proportionally larger number of atoms of the lighter isotopes ( $^{16}\text{O}$  and H) evaporate, leaving the heavier isotopes in the water that remains.

Because of the limited abundance of oxygen-18 and deuterium, the ratios of oxygen-18 to oxygen-16 ( $^{18}\text{O}/^{16}\text{O}$ ) and deuterium to hydrogen (D/H) can be measured to an order of magnitude greater accuracy than actual concentrations (Coplen, 1993). To provide a common reference, ratios of the isotopic composition of samples typically are compared to those of a standard solution. Comparisons are expressed as delta ( $\delta$ ) values in units of parts per thousand (per mil) as indicated by the following equation for  $^{18}\text{O}$ :

$$\delta^{18}\text{O} = \left[ \frac{{}^{18}\text{O}/{}^{16}\text{O}_{\text{Sample}}}{{}^{18}\text{O}/{}^{16}\text{O}_{\text{Standard}}} - 1 \right] * 1,000. \quad (1)$$

The equation for deuterium is similar to the equation for oxygen-18. Values from oxygen and hydrogen isotope samples are reported relative to those of the Vienna Standard Mean Ocean Water (VSMOW). A negative value indicates that the sample is isotopically depleted in the heavy isotope relative to



the standard and is referred to as isotopically “light.” This is typical of waters in the Virginia Coastal Plain.

The relation of  $\delta^{18}O$  and  $\delta D$  in precipitation is defined by the equation:

$$\delta D = m\delta^{18}O - d, \quad (2)$$

where  $m$  is the slope of the relation, and  $d$  is the deuterium excess.

Globally, the mean deuterium excess in precipitation is +10 per mil (Craig, 1961). The line formed by this relation applied globally is called the “global meteoric water line” and has a slope of 8. Because the deuterium excess differs by location, a different equation can be derived for local precipitation. The resulting relation generally will be parallel to the global meteoric water line. If isotopes in precipitation that contributes to streamflow are not fractionated, the isotopic composition of stream water will coincide with that of the local meteoric water line. If a substantial part of the water evaporates, the fractionated isotopes will form a relation having a slope less than 8 and typically ranging from 3 to 6 (Coplen, 1993). In moderate climates, such as areas near the terminal reservoirs, evaporation typically is not a factor in fractionating isotopes in water except where large lakes or reservoirs provide a large surface area for evaporation (Gat and Gofiantini, 1981). Speiran (2000) determined that the local meteoric water line for the Chickahominy River basin had a slope of 8 and a deuterium excess of 13.8. Because of the broad and shallow wetland characteristics of the river, evaporation appreciably fractionated the water. The slope of the evaporation line was 5.1, and the deuterium excess was -4.0.

## Targeted Investigations

Targeted investigations were conducted to evaluate selected physical, chemical, and biological processes in the reservoirs. Because many of the processes that affect water quality are biologically mediated, including dissolution and formation of minerals, they commonly are termed “biogeochemical” processes. The targeted investigations included evaluations of (1) circulation and hydraulic retention time, (2) the vertical distribution of nutrient concentrations in the water column, (3) the release of phosphorus from particles suspended in the water column, (4) effects of copper-sulfate applications, (5) the settling of phosphorus as bed sediment, and (6) distributions of phosphorus, copper, and other constituents in bed sediment and interstitial water.

## Circulation and Hydraulic Retention Time

Thermal and chemical stratification can substantially affect circulation, biogeochemical processes and, consequently, the spatial and temporal distribution of nutrients and other water-quality characteristics. The high rates of pumpage into and out of Lee Hall and Harwoods Mill Reservoirs

combined with flow restrictions by the causeway crossings can alter flow and possibly cause water to flow through just a part of reservoir cross sections (short circuit) rather than flow uniformly through entire cross sections (plug flow) along the length of the reservoirs and thereby affect water quality. Such effects on flow in the reservoirs can affect how well water quality in a cross section is represented by water quality at a sampling site and whether water-quality differences among sites represent changes in the quality of water flowing through the reservoirs or represent other circulation patterns. Consequently, knowledge of stratification and circulation in the reservoirs was essential in the final selection of data-collection sites and interpretation of data from these sites. A study, therefore, was conducted August 8–13, 2003, to evaluate stratification and circulation in the reservoirs during a period when extremes in such conditions were expected to occur. Results of this study are supported further by isotope analyses and results of other studies.

The study was conducted by measuring water-quality characteristics on site at 1-ft-depth intervals in multiple cross-section vertical profiles at all reservoir sites shown in figures 3 and 4, from the upper to the lower ends of the reservoirs. One to five profiles were measured in each cross section, depending on the reservoir width and depth at the site. In cross sections having five vertical profiles, the profiles were located at the midpoint in the cross section, at the right and left quarter points, and within 5 to 20 ft of the right and left banks. Surface and bottom water samples were collected from selected midpoints and analyzed for concentrations of nutrients, major ions, and stable isotopes. Effects of stratification, pumpage, and flow restriction were evaluated by comparing water quality vertically and laterally in the cross sections and along the length of the reservoirs.

## Vertical Distribution of Nutrients in the Water Column

Nutrient concentrations in samples collected during a previous study (Hoehn, 1985), by the City of Newport News personnel, and during this study commonly differed between samples collected near the surface and bottom of the reservoirs, particularly in Harwoods Mill Reservoir when it was stratified. The vertical distribution in concentrations from the surface to the bottom in all three studies, however, was not certain, and such distributions can help in the evaluation of phosphorus sources. Samples were collected and physical and chemical characteristics were measured at 1- to 2-ft-depth intervals from the surface to the bottom at site LH1 on August 12, 2003, and at site HM1 on August 11, 2003 (figs. 3, 4), to provide a single “snapshot” of the distribution at each site, because nutrient concentrations typically differ the most at these sites between the surface and bottom during the mid to late summer. Samples were analyzed for dissolved and whole-water concentrations of nitrogen and phosphorus species.

## Release of Phosphorus from Suspended Particles

Although bed sediment commonly is cited as a source of dissolved phosphorus to the water column, release of phosphorus from particles suspended in the water column also can be a major phosphorus source (Pettersson, 1998). Consequently, release of dissolved phosphorus from particles in samples collected from the water column was investigated in a laboratory study. Samples were collected from sites LH1S, HM1S, and HM1B at the same time that samples were collected for investigating the vertical distribution of nutrients in the water column. Twelve polyethylene 500-milliliter (mL) bottles were filled with sample water from each site, wrapped in aluminum foil, and incubated in the dark at 25 degrees Celsius (°C) in the Virginia Water Science Center laboratory. Incubation of samples began the morning of August 13, 2003. Sets of three bottles for each site were removed from the incubator and processed at the same time of morning on August 14, August 18, and August 22, 2003, for triplicate analyses of total and dissolved phosphorus by the NWQL.

## Effects of Copper-Sulfate Application

Copper-sulfate application can affect biogeochemical processes that release and take up nutrients in the reservoirs because of the toxic effects of copper on algae, bacteria, and other aquatic organisms. Knowledge of such effects can help to better understand processes controlling nutrient concentrations and the variability in nutrient concentrations during routine sampling. Consequently, water samples were collected and analyzed periodically from before one application to before the next application.

Copper sulfate was applied to Lee Hall Reservoir on September 20 and October 9–10, 2002, and to Harwoods Mill Reservoir on September 19 and October 8, 2002. Samples were collected at sites LH1, LH2, and LH3 (fig. 3) on September 18, 23, and 27 and October 8, 2002 (2 days before and 3, 7, and 18 days after the first copper-sulfate application). Samples were collected at site HM1 (fig. 4) on September 17, 23, and 27 and October 7, 2002 (2 days before and 4, 8, and 18 days after the first copper-sulfate application). The first and last sets of samples were collected at the same time as the City of Newport News monthly sampling. Physical and chemical characteristics were measured on site at 1-ft-depth intervals. Water samples were analyzed for concentrations of nutrients, major ions, dissolved and total copper, dissolved and total iron, dissolved organic carbon, chlorophyll, and stable isotopes.

## Settling of Phosphorus as Bed Sediment

Settling of particles containing phosphorus as bed sediment can be a large part of the phosphorus budget. A study of the rate of phosphorus settling was conducted by collecting

settling particles for analysis of phosphorus concentrations during the study of copper-sulfate application. A single collector was deployed on the reservoir bottom at sites LH1, LH3, and HM1 (figs. 3, 4) during the first sample-collection period of the copper-sulfate application study (September 17–18, 2002). Three collectors were deployed on the reservoir bottom at site LH2 to collect replicate samples. Each collector was retrieved and replaced with a clean collector during each subsequent sampling period (September 23 and 27 and October 7–8, 2002); no new collectors were deployed during the last sample-collection period.

Collectors consisted of plastic containers (15.75 inch (in.) long by 10.6 in. wide by 10 in. high) wedged into weighted wire baskets. Each basket was suspended from four ropes (one connected to the midpoint of each side of the basket and one to the midpoint of each end of the basket). The other ends of the ropes were connected to a float to permit retrieval of the collector. To deploy the collectors, each collector was lowered to the bottom of the reservoir after it was filled with native water from the sampling site to reduce buoyancy and allow the collector to settle to the reservoir bottom. A moderately tight-fitting, weighted lid covered the plastic container during deployment and retrieval to prevent bed sediment disturbed during deployment from settling into the collector and to prevent collected particles from washing out of the collector during collector retrieval. The lid had a metal eye attached to the midpoint of each side and a rope attached to its center. This rope was used to remove the lid after collector deployment and to cover the collector during retrieval. The ropes at the sides of the basket were threaded through the metal eyes to guide the lid directly onto the collector for retrieval.

Collectors were deployed and retrieved from a boat that was anchored at the bow and stern to minimize swaying of the boat. If movement of the boat appeared to cause the collector to drag across the reservoir bottom during deployment, the collector was retrieved, cleaned, and redeployed. If movement of the boat disturbed the collector before the lid covered the collector during retrieval, the sample was discarded. Care was taken to minimize spillage and resuspension of settled particles during retrieval. Bed sediment that had settled in the collector during deployment or retrieval appeared distinctly different from particles that settled from the water column. This facilitated identification of contaminated samples which were then discarded.

After the collector was retrieved, the lid was removed, water and particles were poured into a 2-liter (L) graduated cylinder. The sample volume was recorded prior to being poured from the graduated cylinder into a churn splitter. The graduated cylinder was placed in a clean collector before the sample was poured into it to collect spillage. Spillage was subsequently measured and combined with the rest of the sample. The collector was rinsed with de-ionized water, which also was poured into the graduated cylinder with the sample until all particles were removed from the collector. Volume was recorded and the contents of the cylinder were then poured into the churn splitter with the rest of the

sample. Samples of the suspension were collected from the churn splitter, processed, and analyzed for total phosphorus concentrations.

Rates of settling were calculated in units of milligrams per liter per day ((mg/L)/d) based on the total volume of sample and wash water, the phosphorus concentration, and the volume of water above the collector according to the following equation:

$$\Delta C = \frac{[[TP] - [DP]] * V_s}{V_c * D}, \quad (3)$$

where

$\Delta C$  is the change in phosphorus concentration in the water column ((mg/L)/d),

$[TP]$  is the measured total phosphorus concentration (mg/L),

$[DP]$  is the measured dissolved phosphorus concentration (mg/L),

$V_s$  is the total volume of the combined collected sample and rinse water (L),

$V_c$  is the volume of the water column over the collector (L), and

$D$  is the days of deployment of the individual collector.

## Bed Sediment and Interstitial Water

Bed-sediment samples were collected from both reservoirs to determine concentrations of phosphorus, copper, and other constituents in the sediment and interstitial water to help determine the amount of phosphorus contributed from the bed sediment to the water column. Grab samples of the upper several centimeters of sediment were collected at 9 sites in Lee Hall Reservoir on August 20, 2003, (fig. 3; table 5) and at 8 sites in Harwoods Mill Reservoir on October 29, 2003, (fig. 4; table 6) by using a standard-sized ponar grab sampler. Bed-sediment cores also were collected from Lee Hall Reservoir at sites LH1 and LH3 by use of a box corer on the day the grab samples were collected. A 3.25-in. diameter by 2-ft long split-spoon core barrel also was hand driven to refusal at most sites to determine the thickness of sediment deposited over the sediment present when the reservoirs were constructed. The depth of refusal was recorded.

Sediment samples from the grab, box-core, and core-barrel samplers were visually inspected for color, texture, and the presence of benthic organisms. These characteristics were compared among different types of samples collected at the same sites. During the collection of samples from Lee Hall Reservoir, samples of floating and “rooted” aquatic plants and

**Table 5.** Physical description of bed sediment collected from Lee Hall Reservoir, Virginia, August 20, 2003.

[—, no data]

Station number	Site number (fig. 3)	Sample number in appendixes	Sample type, location, and physical description	Moisture content, in percent
0204279200	LH4	5	Grab sample from center, sandy	29.9
0204279210	LH3	1	Second split-spoon core from center, clay	62.5
0204279210	LH3	2	Split-spoon core from center, contact between clay bottom and overlying soft material	—
0204279210	LH3	3	Split-spoon core, clay bottom, no soft sediment on top	44.7
0204279210	LH3	4	Grab sample from cove near docks near south shore	75.9
0204279210	LH3	6	Grab sample from north shore, sandy (also collected macrophytes and algae)	80.1
0204279210	LH3	7	Grab sample from shallows near north shore, clay	73.8
0204279210	LH3	8	Split-spoon core from north shore, core bottom	21.7
0204279210	LH3	9	Split-spoon core from north shore, core top	75.0
0204279213	LH2.7	13	Grab sample from center, no organics?	82.4
0204279213	LH2.7	14	Grab sample from center, oily film	82.1
0204279223	LH(CR)2	11	Grab sample from center	—
0204279224	LH(CR)1	10	Grab sample from center	—
0204279225	LH2.6	16	Grab sample from enter	68.6
0204279228	LH2.3	15	Grab sample from center	85.6
0204279232	LH1.5	18	Grab sample at spillway	72.7
0204279232	LH1.5	19	Grab sample from center near bridge, organics	38.3
0204279232	LH1.5	20	Grab sample from center near bridge, sandy	66.4
0204279232	LH1.5	21	Split-spoon core, lower core section, clay	45.5
0204279240	LH1	17	Grab sample from center	—



**Table 6.** Physical description of bed sediment collected from Harwoods Mill Reservoir, Virginia, October 29, 2003.

Station number	Site number (fig. 4)	Sample number in appendixes	Sample type, location, and physical description	Moisture content, in percent
01677823	HM2.6	17	Split-spoon core from center, bottom clay, organic	76.0
01677823	HM2.6	19	Split-spoon core form center, upper fluffy zone	84.0
01677825	HM2.4	15	Split-spoon core from center, bottom clay, organic	55.9
01677825	HM2.4	16	Split-spoon core from center, upper fluffy zone	86.2
01677823	HM2.4	18	Split-spoon core from center, middle dark gray soil with roots	38.6
01677830	HM2	12	Split-spoon core from center, upper fluffy zone (6 inches)	62.4
01677830	HM2	13	Split-spoon core from center, upper fluffy zone	79.5
01677830	HM2	14	Split-spoon core from center, upper fluffy zone (6 inches)	58.2
0167783010	HM1.9	11	Split-spoon core from center, upper fluffy zone	80.7
01677832	HM1.7	9	Split-spoon core from center, lower granular zone (4 inches)	64.0
01677832	HM1.7	10	Split-spoon core from center, upper fluffy zone	82.0
01677835	HM1.3	4	Split-spoon core from shore surface material	45.0
01677835	HM1.3	5	Split-spoon core from center, lower pasty zone (4 inches)	50.2
01677835	HM1.3	6	Split-spoon core from north shore lower sediment	15.7
01677835	HM1.3	7	Split-spoon core from center, upper sandy zone, detritus	59.5
01677835	HM1.3	8	Split-spoon core from center, lower pasty zone (4 inches)	52.4
0167784610	HM1.1	3	Split-spoon core from center, upper fluffy zone	87.3
01677850	HM1	1	Split-spoon core from center, lower pasty zone (4 inches)	71.4
01677850	HM1	2	Split-spoon core from center, upper fluffy zone	89.0

algal mats also were collected for analysis. The aquatic plants and algal mats were inspected for the presence of macroinvertebrates because the absence of macroinvertebrates as noted in the bed-sediment samples might result from the application of copper sulfate. Shorelines in several areas were inspected for the presence of rooted aquatic plants and algal mats.

Each box-core sample was sealed in the core liner onboard the boat to minimize exposure to the atmosphere. Cores then were processed in a research laboratory in Reston, VA, within several hours of collection in a nitrogen-gas-filled glove bag by sectioning each core, transferring the sediment into centrifuge tubes, and sealing the tubes before removing them from the glove bag to prevent exposure to the atmosphere. Sediment cores were sectioned at 1-centimeter (cm) intervals from the interval closest to the sediment and water-column interface to a depth of 10 cm and, thereafter, at 2-cm intervals to the bottom of the core. Interstitial water was removed from the sediment solids of all intervals by centrifuging the whole-sediment samples in a nitrogen atmosphere. The centrifuge tubes then were returned to a nitrogen-filled glove bag. Approximately 2 mL of centrifuged, unfiltered, interstitial water was set aside for analysis. Up to 10 mL of centrifuged water was filtered through 0.4- $\mu$ m polycarbonate filter membranes. Because of the abundance of fine-grained sediment in the centrifuged water, the filters plugged quickly. The plugging precluded using the standard procedure of wasting the water, which initially passed through each filter, and retaining only the subsequent part of the water. One milliliter of filtrate was added to 9 mL of eluent to preserve the samples for ion

chromatographic analysis. The remaining filtrate was acidified with ultrapure nitric acid. The wet sediment in the centrifuge tubes was frozen and then freeze-dried. Dry samples were broken apart in an agate mortar and sieved to separate the particles less than 125  $\mu$ m from those larger than 125  $\mu$ m. The fraction of particles larger than 125  $\mu$ m was ground to less than 125  $\mu$ m in preparation for chemical analysis.

Bed-sediment and interstitial water were further processed and analyzed for phosphorus, copper, and other constituents using methods described by Simon and others (1999). Processing included methods for sequentially extracting different forms of phosphorus from bed sediment as described by Ruttenberg (1992). The first extraction was a magnesium chloride extraction that removed the loosely and unbound phosphorus. The next step was a dithionite extraction that removed the phosphorus that was bound to poorly crystallized iron oxides, which includes inorganic and organic forms of phosphorus that are bound to iron oxides.

## Reservoir Management Practices

Natural processes combined with management practices affect the water quality of the two terminal reservoirs by directly and/or indirectly altering the hydraulic characteristics and the physical and biogeochemical processes of the reservoirs. Pumping of water from outside sources, withdrawal of water for public supply, and application of copper sulfate

to control algal growth are the major management practices that affect the terminal reservoirs. These practices appreciably affect both reservoirs similarly in many respects but differently in others.

### Reservoir Pumpage

Pumpage into the reservoirs is controlled so that the combination of natural and pumped inflows generally meets but does not exceed the average needs for public supply, loss by evapotranspiration, and leakage through the dam. Thus, the amount of pumped inflows into the terminal reservoirs is influenced heavily by the rates of natural flows into the reservoirs. When natural flow into either reservoir exceeds withdrawal, water usually is not pumped into that reservoir. Consequently, water only flows over the dam of either reservoir when high natural inflows persist long enough to raise the reservoir level above the spillway.

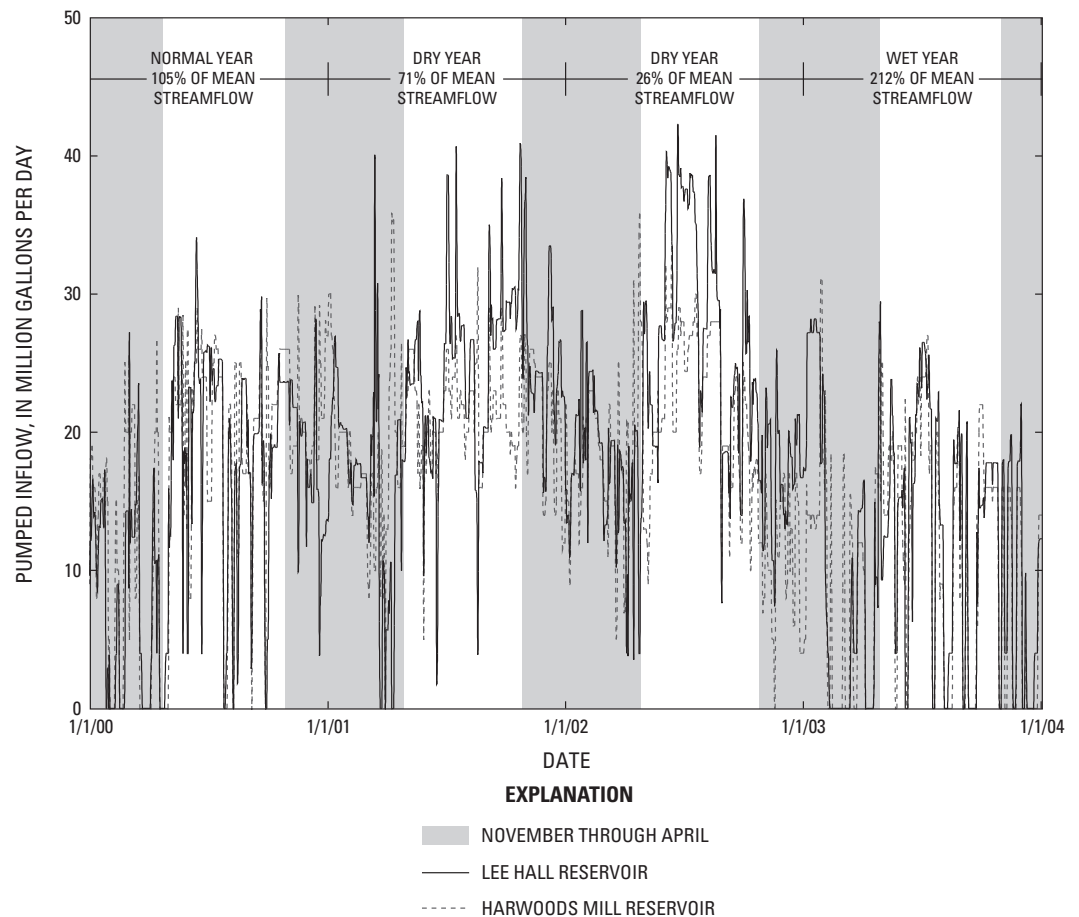
The water-treatment plant at Lee Hall Reservoir is the older of the two treatment plants and has the largest design capacity for treating water. Raw water historically was withdrawn from Lee Hall and Harwoods Mill Reservoirs at rates proportional to their design capacities; withdrawal

rates typically averaged 30 and 20 Mgal/d, respectively. Withdrawals from the reservoirs from 2000 to 2003, however, were not consistent with this practice, because failure of parts of the Lee Hall water-treatment plant and reconstruction of the entire plant temporarily reduced the capacity of the plant. This resulted in temporary alternative operation strategies that affected pumpage into the reservoirs as well as withdrawals.

Natural hydrologic conditions during the study period provided some of the most extreme conditions likely to be encountered in the reservoirs; the study began during severe drought conditions and ended during extremely wet conditions. Based on streamflow records at the gage on the Chickahominy River at Providence Forge (station 02042500), annual streamflow in 2002 was the lowest on record (26 percent of normal) and the highest on record in 2003 (212 percent of normal) based on continuous record since January 1942 (White and others, 2003, 2004). Such extreme conditions were prevalent throughout the area.

Pumpage from outside watersheds into Lee Hall Reservoir averaged 11.4 to 22.4 Mgal/d annually from 2000 through 2003 and 17.7 Mgal/d for the entire 4-year period (fig. 6; table 7). About 57 percent of the pumpage was from the Chickahominy River. Peak daily pumpage

**Figure 6.** Daily rate of pumped inflow from outside surface-water sources into Lee Hall and Harwoods Mill Reservoirs, Virginia, January 2000–December 2003. (Streamflow in a normal year is 75 to 125 percent of the mean annual streamflow at Chickahominy River at Providence Forge (02042500); streamflow in a wet year is greater than 125 percent of the mean annual streamflow at station 02042500; streamflow in a dry year is less than 75 percent of the mean annual streamflow at station 02042500.)





into Lee Hall Reservoir was 42.3 Mgal/d. Daily pumpage into Harwoods Mill Reservoir averaged 10.2 to 20.3 Mgal/d annually from 2000 through 2003 and 16.4 Mgal/d for the entire period. About 73 percent of that pumpage was from the Chickahominy River. Peak daily pumpage into Harwoods Mill Reservoir was 35.8 Mgal/d. Pumpage rates into both reservoirs were greatest in 2001 and 2002, two extremely dry years, and least in 2003.

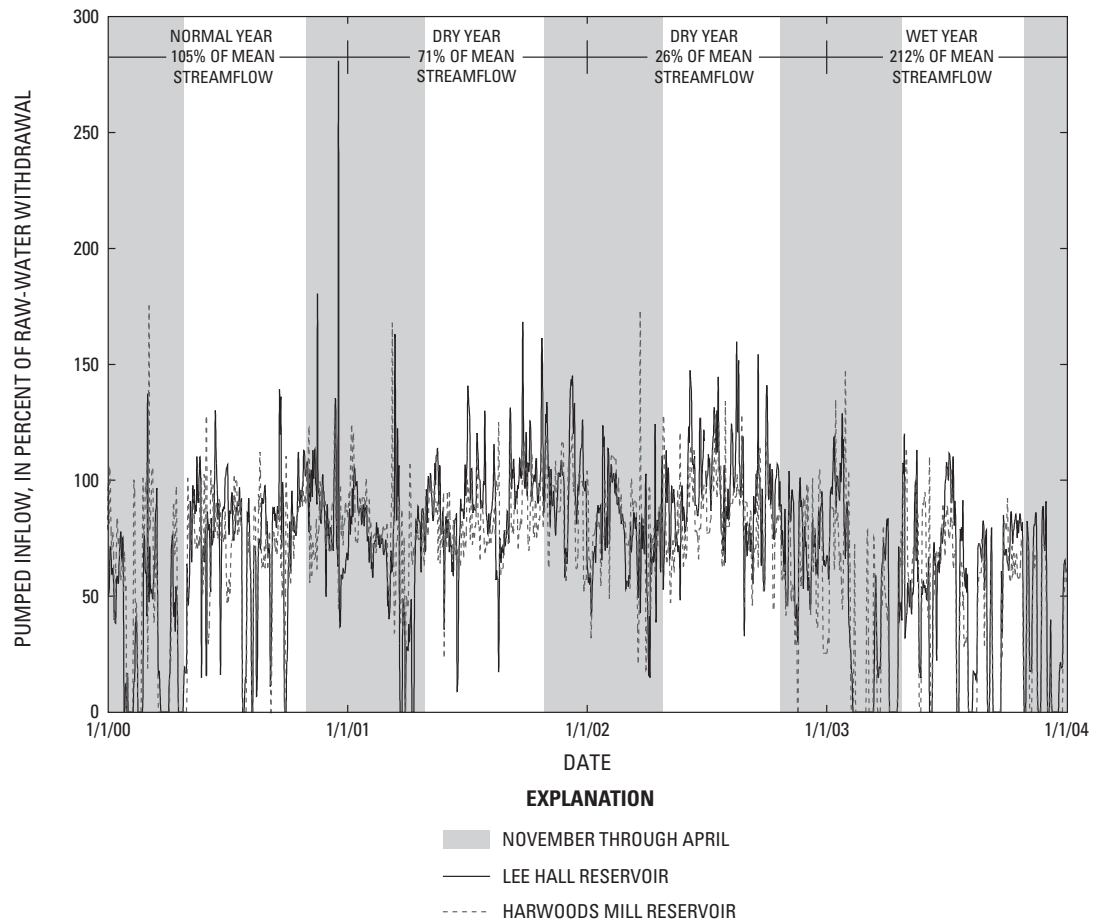
Raw-water withdrawals from Lee Hall Reservoir averaged 23.9 to 26.2 Mgal/d annually from 2000 through 2003 and 24.8 Mgal/d for the entire period. Peak daily withdrawal from Lee Hall Reservoir for the 4-year period was 42.0 Mgal/d. Raw-water withdrawals from Harwoods Mill Reservoir averaged 23.3 to 25.7 Mgal/d annually from 2000 through 2003 and 24.6 Mgal/d for the entire period (table 7). Peak daily withdrawal for the 4-year period was 55.5 Mgal/d.

Thus, pumpage into and from both reservoirs was similar during this period.

Daily pumpage from outside watersheds into Lee Hall Reservoir averaged 48 to 87 percent of the raw-water withdrawals annually from 2000 through 2003 and averaged 71 percent for the entire period (fig. 7; table 7). Daily pumpage from outside watersheds into Harwoods Mill Reservoir averaged 42 to 82 percent of the raw-water withdrawals annually from 2000 through 2003 and 67 percent for the entire period.

Although the average raw-water withdrawals from Lee Hall Reservoir exceeded those from Harwoods Mill Reservoir by only 0.2 Mgal/d for the entire period, average pumpage into Lee Hall Reservoir exceeded pumpage into Harwoods Mill Reservoir by 1.3 Mgal/d. This greater difference in volume of pumped flow into Lee Hall Reservoir could result

**Figure 7.** Pumped inflow from outside surface-water sources as a percent of the raw-water withdrawal for public supply, January 2000–December 2003, Lee Hall and Harwoods Mill Reservoirs, Virginia. (Streamflow in a normal year is 75 to 125 percent of the mean annual streamflow at Chickahominy River at Providence Forge (02042500); streamflow in a wet year is greater than 125 percent of the mean annual streamflow at station 02042500; streamflow in a dry year is less than 75 percent of the mean annual streamflow at station 02042500.)



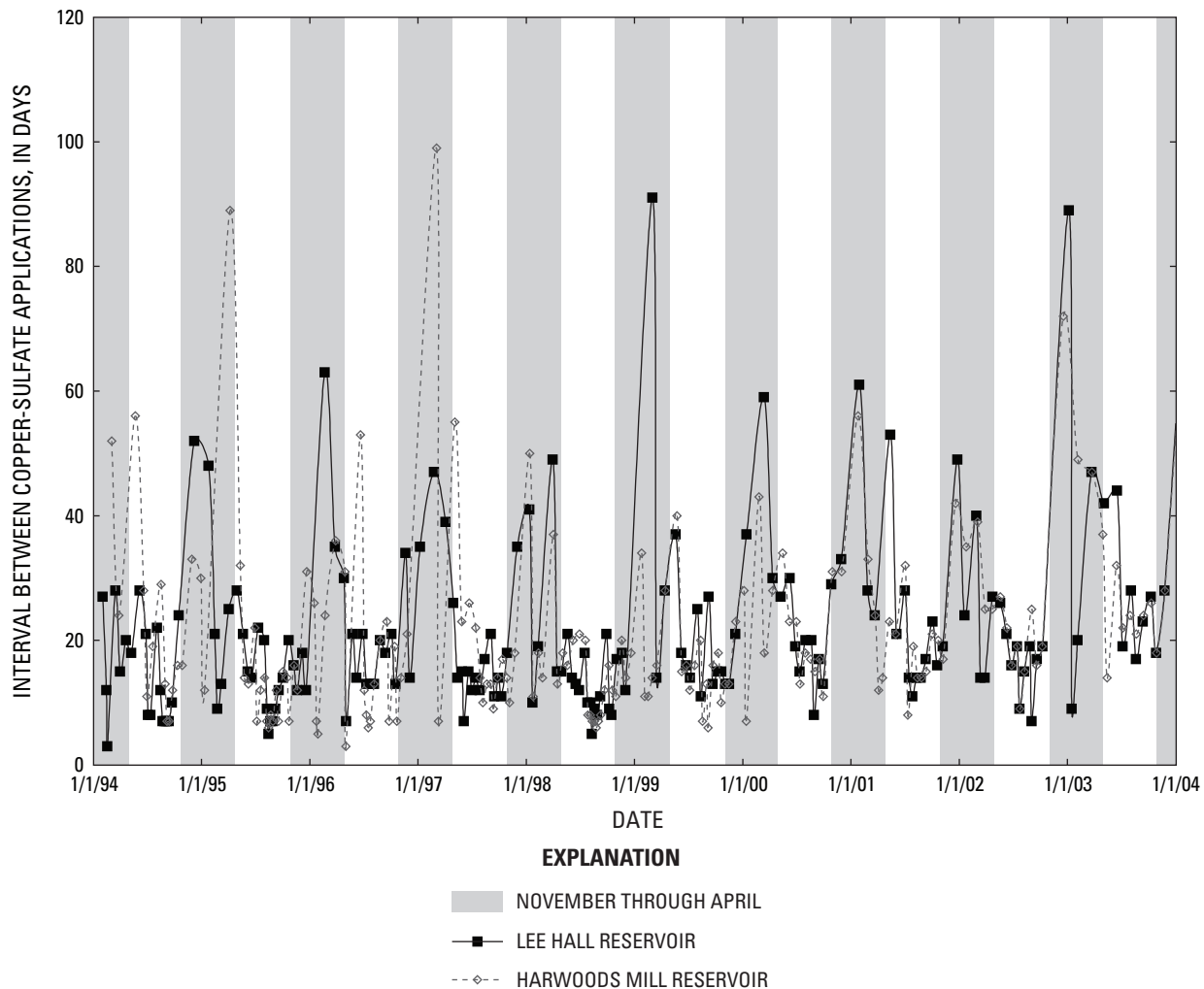
from a combination of greater natural flow into Harwoods Mill Reservoir, greater evaporation from Lee Hall Reservoir, or greater leakage beneath the Lee Hall dam. Greater flow into Harwoods Mill Reservoir is not likely because the Lee Hall Reservoir watershed is about 75 percent larger than the Harwoods Mill Reservoir watershed. Greater evaporation from Lee Hall Reservoir is likely because the surface area of Lee Hall Reservoir is about 86 percent larger than the surface area of Harwoods Mill Reservoir. The effects of leakage beneath the dam are uncertain, but the dam forming Lee Hall Reservoir is about three times the length of the dam forming Harwoods Mill Reservoir.

### Copper-Sulfate Application

Copper sulfate typically has been applied to both reservoirs throughout the year at intervals that depended on the rate of algal fouling of the filters of the water-treatment plants. Copper sulfate was applied to each reservoir in recent years

by mixing the chemical with water and spraying the solution onto the reservoir surface with a line of spray heads attached to a pipe that extended across the stern of a boat. The boat traversed across the width of each reservoir from one end to the other. The chemical solution was not applied in the shallowest parts of the reservoirs. Although only one reservoir was treated at times, both reservoirs typically were treated during most periods with copper sulfate applied to one reservoir and then to the other. Application to both reservoirs typically can be completed in 2 days. From 1994 through 2003, intervals between copper-sulfate applications ranged from 3 to 99 days; the shortest intervals typically occurred during the summer and early fall (fig. 8).

Although application amounts varied, 3,600 pounds (lb) of copper sulfate typically were applied to Lee Hall Reservoir (7.3 pounds per acre (lb/acre)) and 3,500 lb to Harwoods Mill Reservoir (13.2 lb/acre) during each application. Although application rates differed by reservoir area, rates by reservoir volume were 4.1 lb per million gallons for both reservoirs.

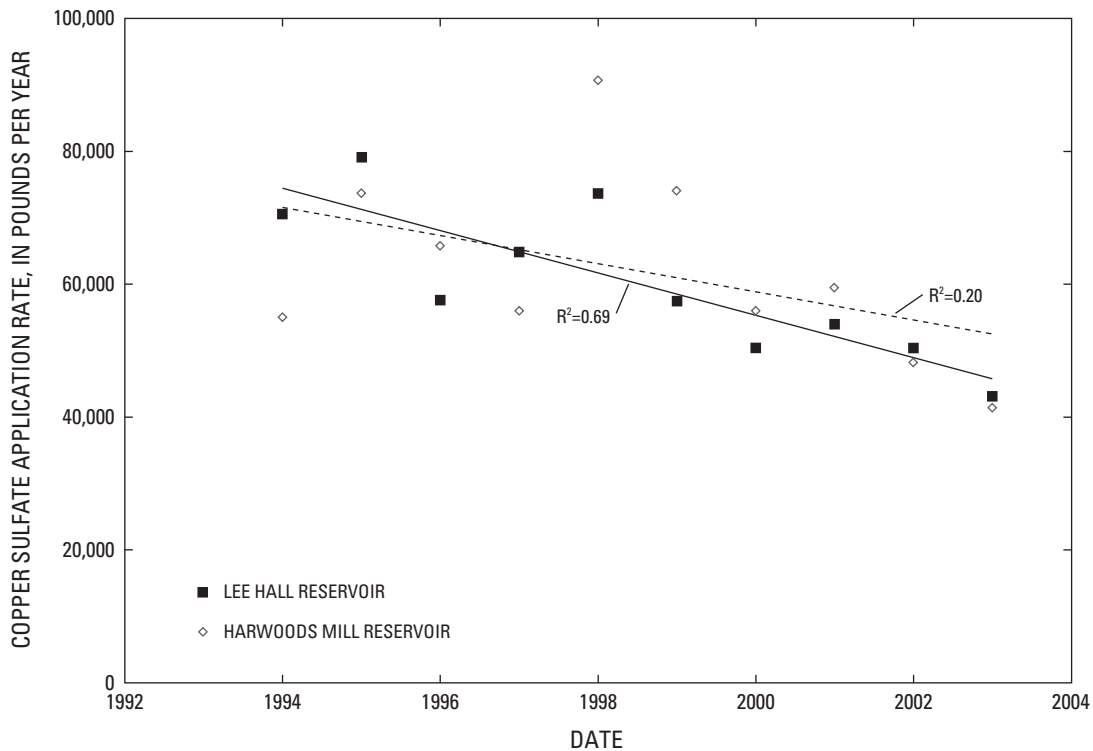


**Figure 8.** Intervals between copper-sulfate applications, January 1994–December 2003, Lee Hall and Harwoods Mill Reservoirs, Virginia.

Because copper sulfate is hydrated, copper is only 25.2 percent of the weight of the chemical, which resulted in a typical application being 907 and 882 lb (1.84 and 3.33 lb/acre) of copper to Lee Hall and Harwoods Mill Reservoirs, respectively. Because of the varied application intervals and amounts, annual application amounts of copper sulfate during 1994–2003 ranged from 43,100 to 79,150 lb (10,861 to 19,946 lb of copper) for Lee Hall Reservoir and from 41,400 to 90,700 lb (10,433 to 22,856 lb of copper) for Harwoods Mill Reservoir (fig. 9). Annual rates of application reflect a general decrease from 1994 through 2003. This trend is stronger for Lee Hall Reservoir ( $R^2 = 0.69$ ) than for Harwoods Mill Reservoir ( $R^2 = 0.20$ ).

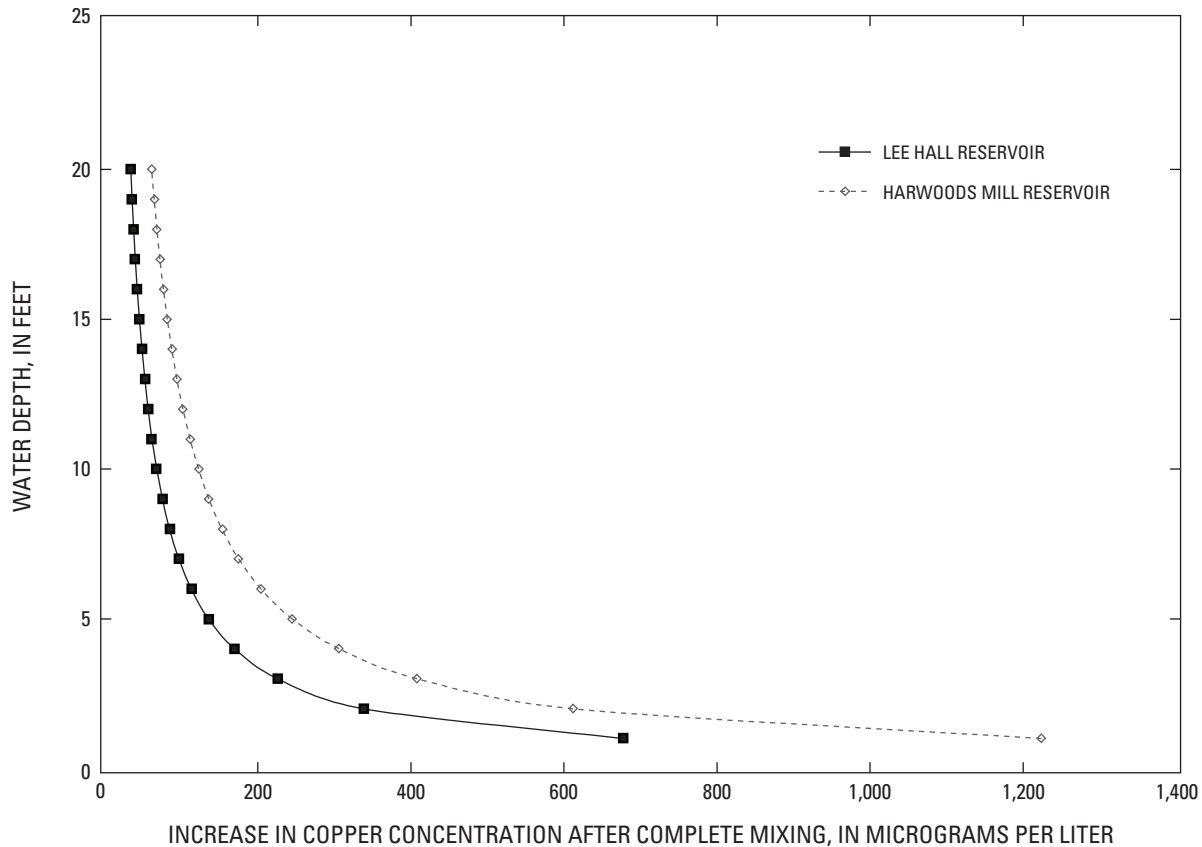
If copper sulfate were applied evenly across the reservoirs, the concentration after complete vertical mixing at a given location would depend on the reservoir depth at that location (fig. 10) and the copper concentration prior to application. The concentration for a given depth differs between the reservoirs because of the differences in

application rates and surface areas of the two reservoirs. The resulting copper concentration is less in deep parts of the reservoir because the chemical is diluted more by the greater water volume, which results from greater depth. If a reservoir becomes stratified, mixing is limited to the epilimnion, which decreases the volume for mixing and increases the resulting concentration. Lee Hall Reservoir, however, generally does not stratify. After a 3,600-lb application in Lee Hall Reservoir, the initial concentrations at sites LH1, LH2, and LH3 (fig. 3) after complete mixing would increase 62, 56, and 75  $\mu\text{g/L}$ , respectively, because depths typically average 11, 12, and 9 ft, respectively, at these sites. After a 3,500-lb application in Harwoods Mill Reservoir, the concentration after complete mixing would increase 62  $\mu\text{g/L}$  without stratification at site HM1 (fig. 4) where the depth typically is 18 ft. When Harwoods Mill Reservoir stratifies during the summer to a typical thermocline depth of 10 ft, the resulting concentration after complete vertical mixing in the epilimnion would increase 112  $\mu\text{g/L}$ .



**Figure 9.** Annual copper-sulfate application rates and least-squares regression of application rates, 1994–2003, for Lee Hall and Harwoods Mill Reservoirs, Virginia.





**Figure 10.** Increase in concentrations of copper at areas of varying depths after complete vertical mixing of 3,600 pounds of copper sulfate applied to Lee Hall Reservoir and 3,500 pounds of copper sulfate applied to Harwoods Mill Reservoir, Virginia.

## Effects of Processes on Water Quality

Thermal and chemical stratification, flow constrictions, and the locations and amounts of natural flows and pumpage into and out of the reservoirs combine to affect reservoir circulation and hydraulic retention times. Circulation and hydraulic retention time are critical factors that control biogeochemical processes, nutrient speciation, the distribution of nutrients, and the effects of nutrients on the growth of phytoplankton. Such effects must be accounted for in selection of sampling sites and interpretation of data. Circulation through the reservoirs affects hydraulic retention times and how phosphorus circulates through different parts of the reservoirs. Hydraulic retention time is important because it affects the rate of flushing of water and constituents from the reservoir. Stratification affects the release of dissolved nutrients from settling suspended particles and bed sediment and the subsequent circulation of dissolved nutrients into the photic zone (shallow part of the reservoir where algae photosynthesize).

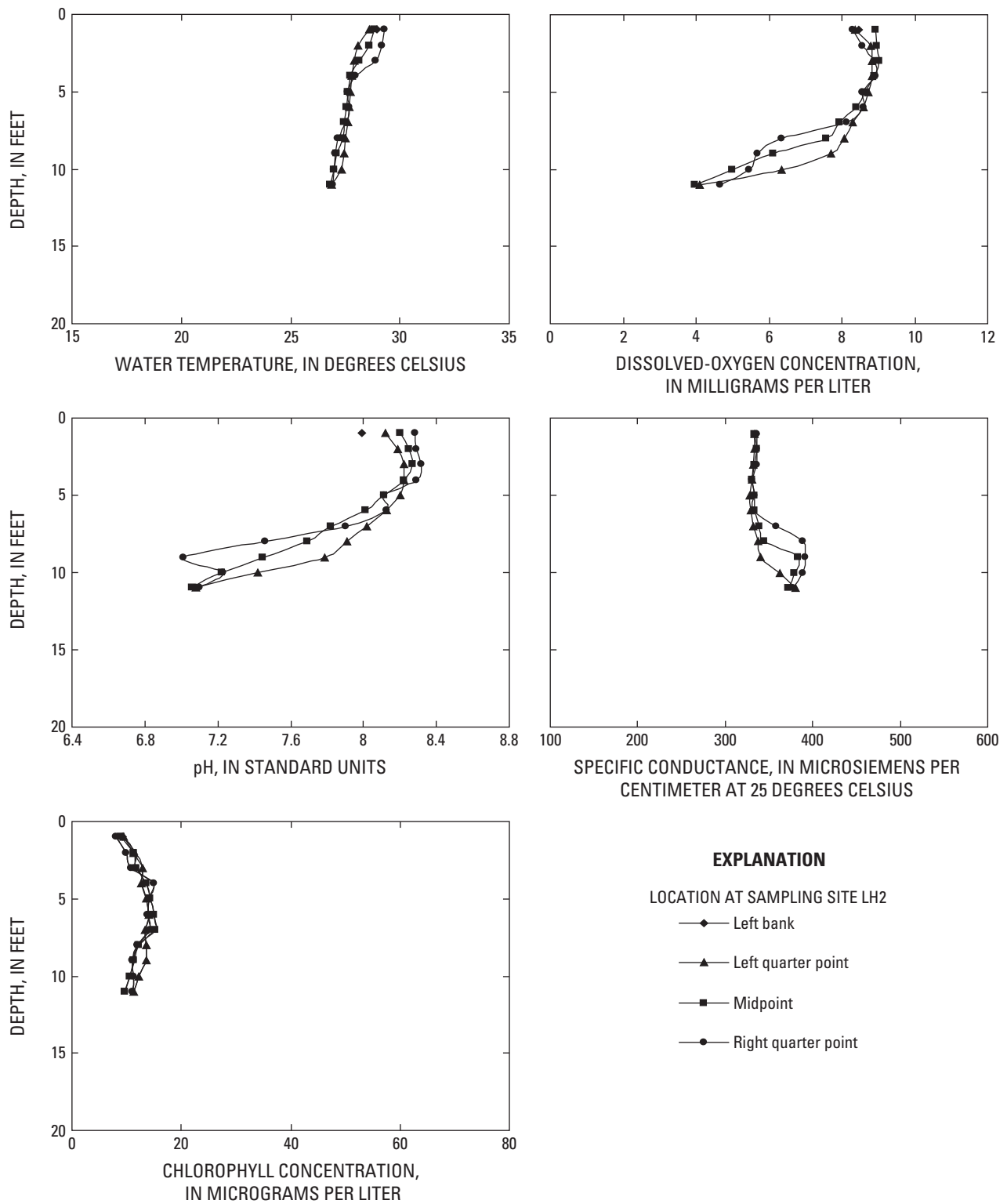
## Circulation and Hydraulic Retention Time

Because of the extreme drought conditions that persisted in 2002, the salinity and specific conductance of water pumped from the Chickahominy River increased during the summer and fortuitously provided a tracer for flow through the reservoirs. This along with water temperature, pH, and dissolved-oxygen and chlorophyll concentrations provided a unique opportunity that greatly assisted in evaluating stratification and circulation in each reservoir during the August 8–13, 2002, targeted investigation.

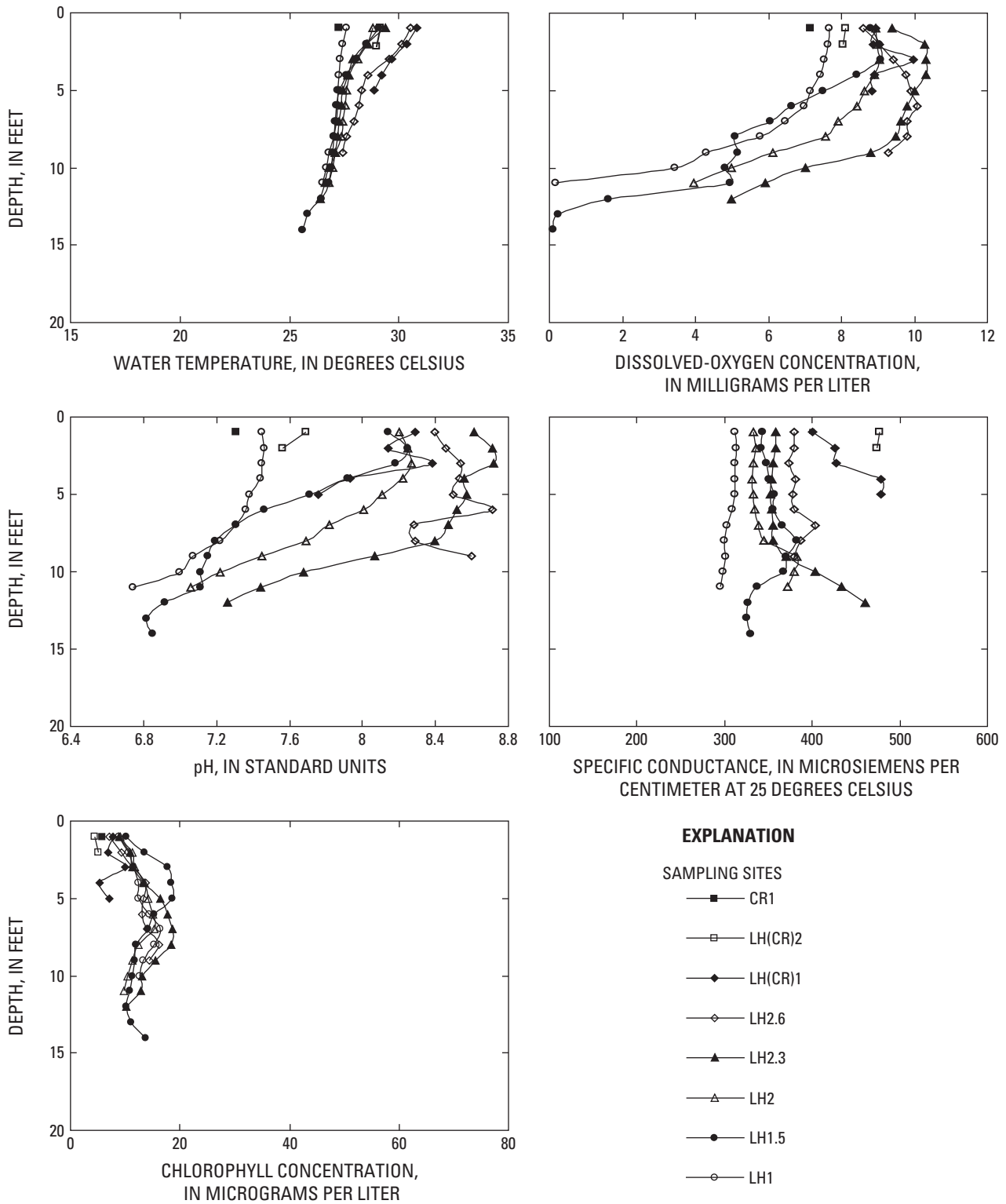
### Lee Hall Reservoir

Reservoir depth and causeway crossings are key factors that affect circulation and stratification in Lee Hall Reservoir. Similarities in water-quality characteristics among vertical profiles at site LH2 (figs. 3, 11) are typical of those observed in other cross sections. Two illustrations depict the differences between pumped and natural inflow effects among the mid-points in the cross sections. Figure 12 depicts the water quality along the flow path between the pumped inflow at site CR1





**Figure 11.** Physical characteristics and constituent concentrations with depth at the left bank, left quarter point, midpoint, and right quarter point of the cross section at site LH2, Lee Hall Reservoir, Virginia, August 13, 2002.



**Figure 12.** Physical characteristics and constituent concentrations with depth at the midpoints of cross sections along the main path of pumped inflow (site CR1) to the water-treatment plant (site LH1), Lee Hall Reservoir, Virginia, August 12–13, 2002.

and the water-treatment plant at site LH1 (fig. 3). Figure 13 depicts the water quality along the main path of natural inflow between the upper part of the reservoir (site LH4) and the water-treatment plant (site LH1, fig. 3).

Vertical temperature profiles throughout Lee Hall Reservoir in August 2002 indicate a gradual thermal gradient but no sharp thermocline typical of a thermally stratified reservoir (figs. 11–13). Water temperature throughout the reservoir generally ranged from 25 to 31 °C. Vertical differences ranged from less than 1.0 °C to about 3.5 °C. The greatest differences typically were in the upper 2 or 3 ft and likely resulted from daily heating and cooling. The lack of a sharp thermocline likely resulted from the shallow depth of the reservoir (average depth 5.5 ft, table 2), allowing vertical mixing that minimizes development of a thermal-density gradient. Vertical thermal profiles were very similar among all vertical profiles in each cross section. Vertical gradients at the midpoints of the sections affected by the pumped inflow have increased temperature and greater gradients toward the pumped inflow where the depth of the reservoir decreases (fig. 12). The warmer temperatures likely resulted from a combination of warmer water being pumped into the reservoir, greater warming of the shallow waters in the upper part of the reservoir, and measurement of temperatures at the end of the day when temperatures were warmer. Vertical thermal gradients and measured temperatures among the midpoints affected by natural inflow were similar throughout the reservoir (fig. 13), likely because drought conditions resulted in little water flowing naturally into the reservoir and all measurements were made early in the day.

Vertical gradients in dissolved-oxygen concentrations and pH were small near the surface but were sharp at depth in contrast to the gradual temperature gradients (figs. 11–13). Dissolved-oxygen concentrations ranged from about 7.5 to 10.5 mg/L near the surface to near 0 mg/L in deeper parts of the reservoir. Peak dissolved-oxygen concentrations were at depths of 2 to 4 ft rather than at the surface in some vertical profiles, probably because concentrations were supersaturated (as much as 132 percent of saturation) as a result of photosynthesis so that dissolved oxygen degassed at the water surface, particularly during windy parts of the day. The sharp decrease in dissolved-oxygen concentrations typically began below depths of 5 to 10 ft. The pH of the water had similar patterns as the dissolved oxygen, ranging from nearly 8.8 near the surface to about 6.7 near the bottom. The low dissolved-oxygen concentration near the reservoir bottom likely resulted from respiration and decomposition of algae settling into deeper parts of the reservoir, the decomposition of other settling organic particles, and the decomposition of organic material in bed sediment. These processes consume dissolved oxygen and produce carbon dioxide that forms carbonic acid and lowers the pH. Dissolved-oxygen concentrations and pH generally differed little among vertical profiles at all points in a cross section (fig. 11) compared to the midpoints along the length of the reservoir (figs. 12, 13). These differences partly resulted from diurnal changes because of the differences in

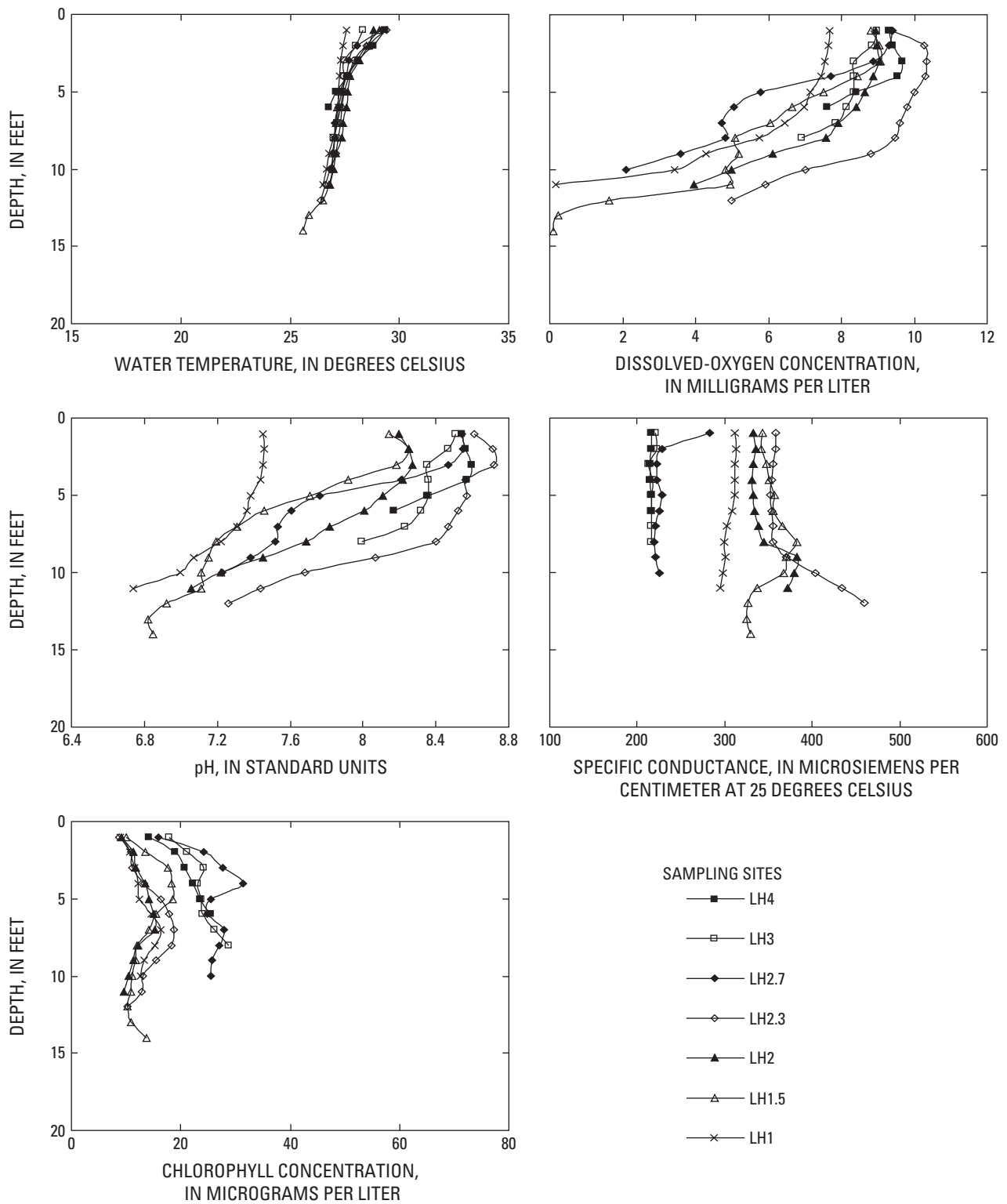
sampling times but primarily resulted from spatial differences within the reservoir. Diurnal effects on dissolved-oxygen concentrations and pH are greatest in the photic zone and least near the bottom.

Although exact conditions differ from year to year, water-temperature and dissolved-oxygen data for 2003 (Ronald Harris, City of Newport News, written commun., 2003) show seasonal changes typical of Lee Hall Reservoir and other shallow reservoirs in temperate climates. In January and February 2003, the water temperature was relatively uniform vertically (fig. 14). Increased vertical gradients in water temperatures first appeared in March or April as the water began to warm and continued through September. The vertical temperature gradient was small from October through December.

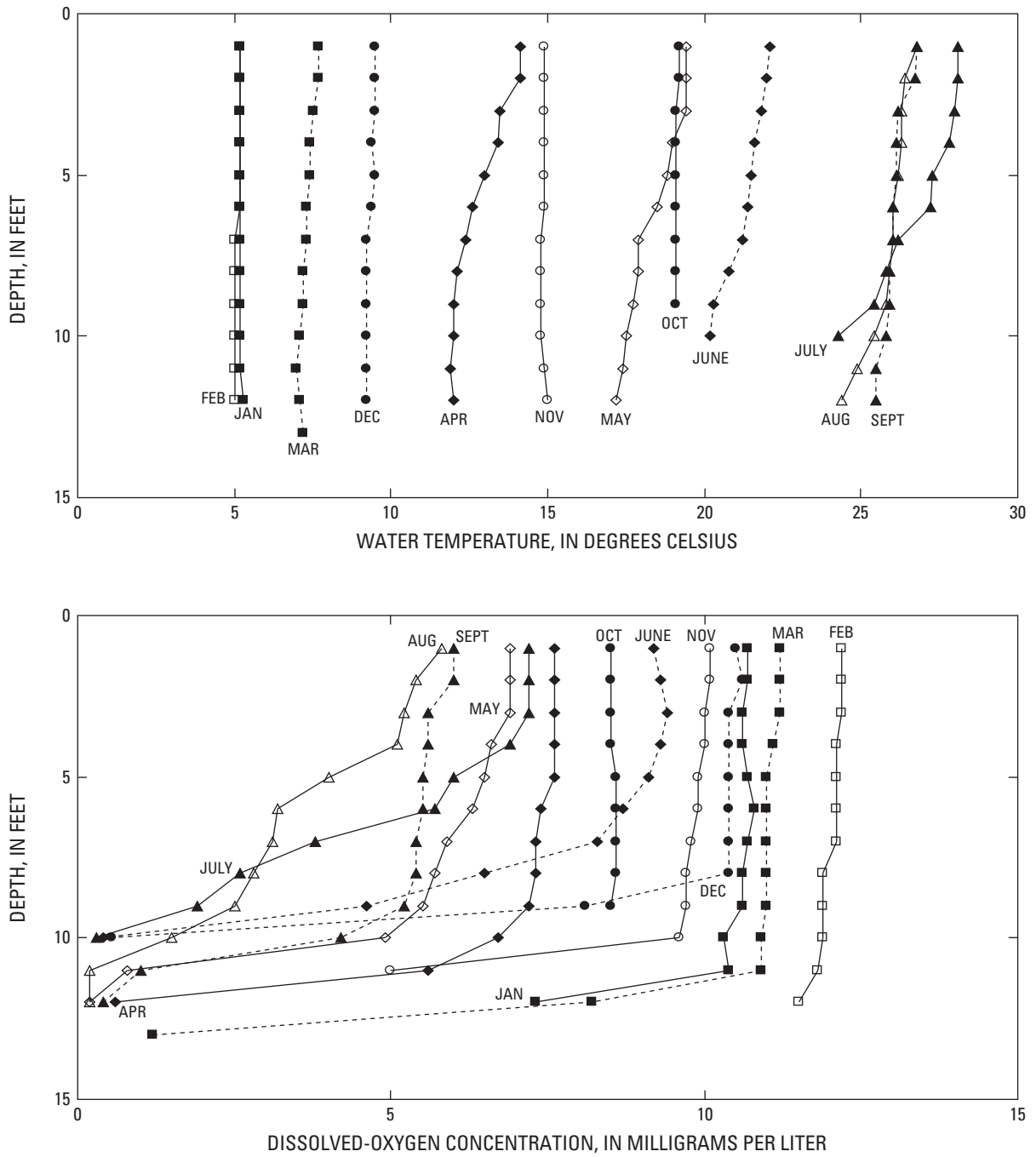
Dissolved-oxygen concentrations also changed seasonally, but unlike water temperature, a sharp decline in the dissolved-oxygen concentration to near 0 mg/L was present near the bottom of the reservoir during most of the year. During summer months, dissolved-oxygen concentrations decreased as saturation decreased, and the depth of the sharp decline decreased.

Specific conductance provides a good indicator of circulation in Lee Hall Reservoir. Patterns in specific conductance generally were similar among the vertical profiles in each cross section (fig. 11). At midpoints affected by the pumped inflow, lateral differences and, in some instances, vertical differences in specific conductance among the midpoints were appreciable (fig. 12). Specific conductance decreased from about 475 microsiemens per centimeter at 25 °C ( $\mu\text{S}/\text{cm}$ ) at site LH(CR)2 to about 300  $\mu\text{S}/\text{cm}$  at site LH1 because specific conductance in the pumped inflow from the Chickahominy River increased through time. Specific conductance at the midpoints affected only by natural inflows (sites LH2.7, LH3, and LH4), however, was consistently near 215  $\mu\text{S}/\text{cm}$  vertically and laterally, showing little mixing with the pumped inflow (fig. 13). The higher specific conductance near the surface at site LH2.7 (the site adjacent to the I-64 causeway) likely resulted from wind-driven circulation of water having higher specific conductance through the causeway. The narrow width of the causeway opening likely limited circulation.

The higher specific conductance near the bottom at many of the sites affected by the pumped inflow (fig. 12) could result from dissolution of bed sediment but also could indicate that denser, higher conductance water flowed beneath less dense, lower conductance water. Flow of the denser water near the bottom is more likely because the higher specific conductance was not evident at the sites above the I-64 causeway (pumpage did not flow into this part of the reservoir) or at site LH1; bed sediment at these sites likely would contribute dissolved constituents in similar amounts as sediment at the other sites. The absence of the higher conductance water at depth at site LH1 may result from the shallower depth at site LH1, the causeway constriction that separates site LH1 from the rest of the reservoir, or the rate of flow of water through the reservoir. The effects of density likely would not extend above the I-64 causeway because little water flowed from the



**Figure 13.** Physical characteristics and constituent concentrations with depth at the midpoints of cross sections along the main path of natural flow from the upper reservoir (site LH4) to the water-treatment plant (site LH1), Lee Hall Reservoir, Virginia, August 12–13, 2002.



**Figure 14.** Distribution of water temperature and dissolved-oxygen concentration with depth from January through December 2003 at site LH1, Lee Hall Reservoir, Virginia. (Data provided by the City of Newport News.)

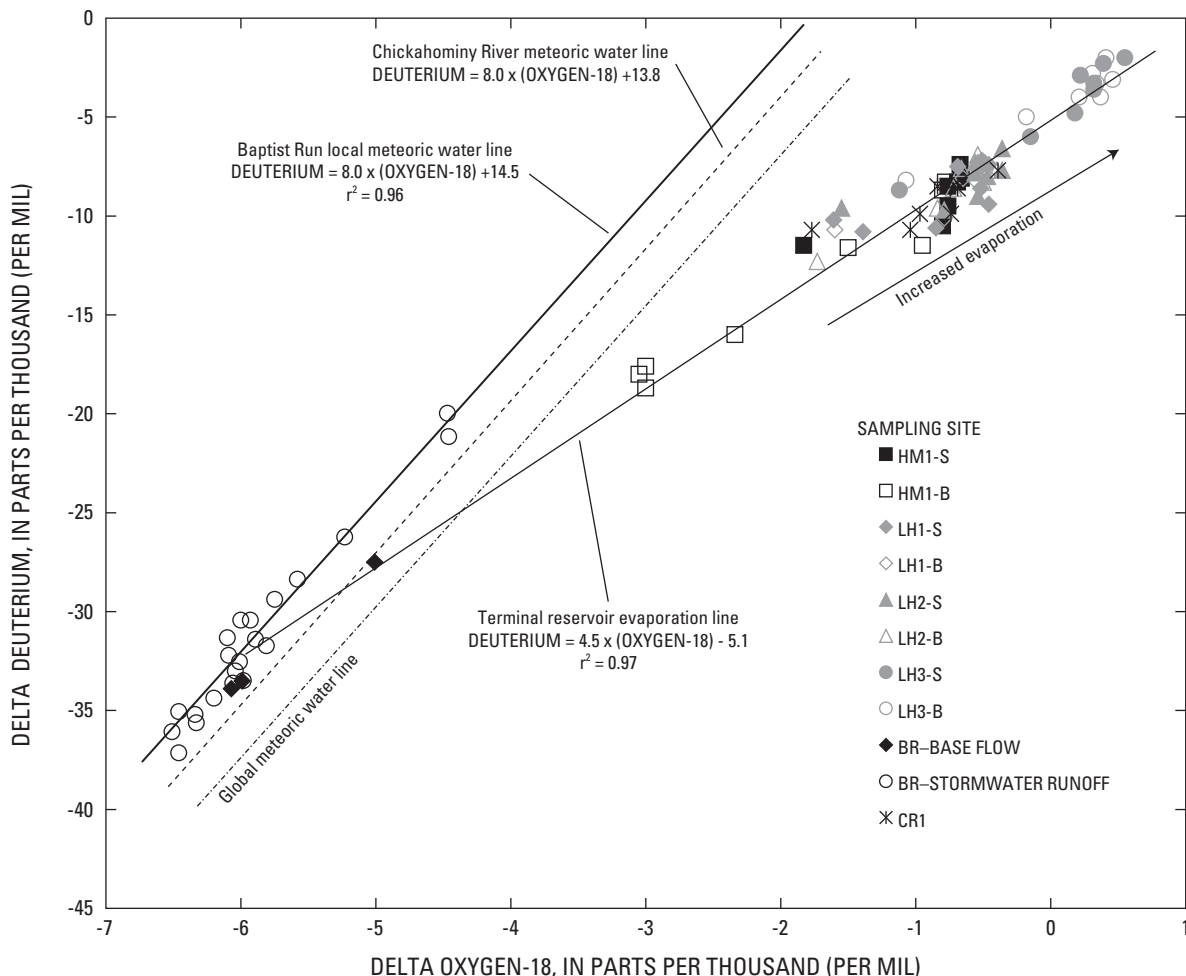


pumped inflow into that part of the reservoir. The presence of higher specific conductance at depth indicates incomplete vertical mixing of the water. The depth of increased specific conductance generally coincides with the depth of sharply decreasing dissolved-oxygen concentrations. Thus, decreased dissolved-oxygen concentration likely indicates incomplete vertical mixing.

Chlorophyll concentrations were similar among vertical profiles in each cross section; at site LH2, chlorophyll concentrations increased from 8.0 to 9.3  $\mu\text{g/L}$  near the surface to 14.0 to 15.3  $\mu\text{g/L}$  at a depth of 5 to 7 ft then decreased to 9.7 to 11.0  $\mu\text{g/L}$  near the bottom (fig. 11). Chlorophyll concentrations varied among midpoints along the flow of the pumped inflow but showed similar relative vertical distributions (fig. 12). Chlorophyll concentrations ranged from 4.4 to 8.8  $\mu\text{g/L}$  near the surface to 9.9 to 18.7  $\mu\text{g/L}$  at maximum concentration. Chlorophyll concentrations at midpoints in the part of the reservoir affected only by natural inflows were similar to each other and greater than those of sites affected by the pumped inflow (fig. 13). Chlorophyll concentrations from 14.1 to 17.8  $\mu\text{g/L}$  near the surface to 28.7 to 31.3  $\mu\text{g/L}$  at maximum concentration in the part of the reservoir affected only by natural inflow.

Overall, patterns in all field-measured water-quality characteristics indicate that pumped water flows relatively uniformly down the reservoir without the short circuiting of flow across the reservoir and having little effect on the reservoir above the constriction formed by the I-64 causeway. Thus, the water quality above the causeway is primarily influenced by the natural and not the pumped inflow. Water quality below the causeway was influenced by both natural and pumped inflows; the degree of effect of each depends on the hydrologic conditions. The railroad causeway likely restricts flow more than the I-64 causeway because water passes through the sluice gate to enter the lower part of the reservoir and would not readily flow back up the reservoir, even when wind driven. Flow through the constriction on the Jones Run arm of the reservoir likely is heavily affected by pumpage into the water-treatment plant.

Effects of evaporation on concentrations of oxygen-18 and deuterium confirm the stratification and circulation patterns indicated by the vertical profiles of the field-measured water-quality characteristics (fig. 15). The effects of evaporation on the isotopic composition of Baptist Run were small; concentrations of both base-flow and stormflow periods form a local meteoric water line that is parallel to both the global meteoric water line and the local meteoric water for the



**Figure 15.** Deuterium and oxygen-18 concentrations in Lee Hall and Harwoods Mill Reservoirs, Baptist Run, and the pumped inflow from Curtis Run, Virginia, 2002–2003.

Chickahominy River basin (Speiran, 2000). The local meteoric water line for Baptist Run has a deuterium excess of 14.5 per mil rather than the 13.8 per mil for the Chickahominy River. The isotopic composition at the intersection of the meteoric water line and the evaporation line is about that of the ground water (Speiran, 2000) that discharges to streams in the area to provide base flow. Evaporation of water from Baptist Run generally was limited because of the narrow stream channel, which is in contrast to the wide and shallow channel of the Chickahominy River.

Because of the dry conditions that prevailed during 2002, effects of evaporation on the pumped inflow and reservoir water were appreciable. The isotopic composition at sites LH1 and LH2 were similar to each other, similar near the surface and the bottom, and similar to the composition of the pumped inflow during each sampling period. Although the isotopic composition tended to be similar during each sampling period, the effects of evaporation increased from mid June to early October. Evaporation affected the isotopic composition at site LH3 substantially more than that of any other site, which confirms the apparent circulation patterns within Lee Hall Reservoir. Because site LH3 is not influenced by pumped inflow and conditions were extremely dry, little new water entered this part of the reservoir during the summer. Thus, most of the water in this part of the reservoir likely entered earlier in the year and remained there for extended periods, resulting in increased evaporation effects. This is reflected in the similar isotopic compositions of both the surface and bottom samples at site LH3 and demonstrates the greater effects of evaporation at this site than at any other sites (fig. 15).

The hydraulic retention time of Lee Hall Reservoir depends on the rate of pumped withdrawal and the relative contribution of natural and pumped inflows. When natural inflows are sufficient to supply all of the needed water, water flows through most of the reservoir. During extreme drought when natural inflows are minimal and pumped inflow is the principal source of water, water flows primarily through the lower part of the reservoir. Thus, hydraulic retention times are discussed for both the entire reservoir and the lower part of the reservoir.

If Lee Hall Reservoir were not used for public supply, the hydraulic retention would average 85 days based on calculated average natural inflows and median runoff from watersheds in the Coastal Plain of Virginia (15.2 inches per year, table 2, Richardson (1994)). Because rates of pumped inflow plus natural inflows into the reservoir typically do not exceed withdrawals unless natural inflows alone exceed withdrawals, withdrawal rates are used to calculate the hydraulic retention times. When natural inflows exceed withdrawal rates and water flows over the spillway, hydraulic retention times are less than identified here. Using the 30 Mgal/d withdrawal average based on the water-treatment plant capacity, hydraulic retention time decreases from 85 to 29 days for the entire reservoir and to 15 days for the lower part. Because average withdrawal from 2000 through 2003 was less than the average based on treatment-plant capacity, hydraulic retention time

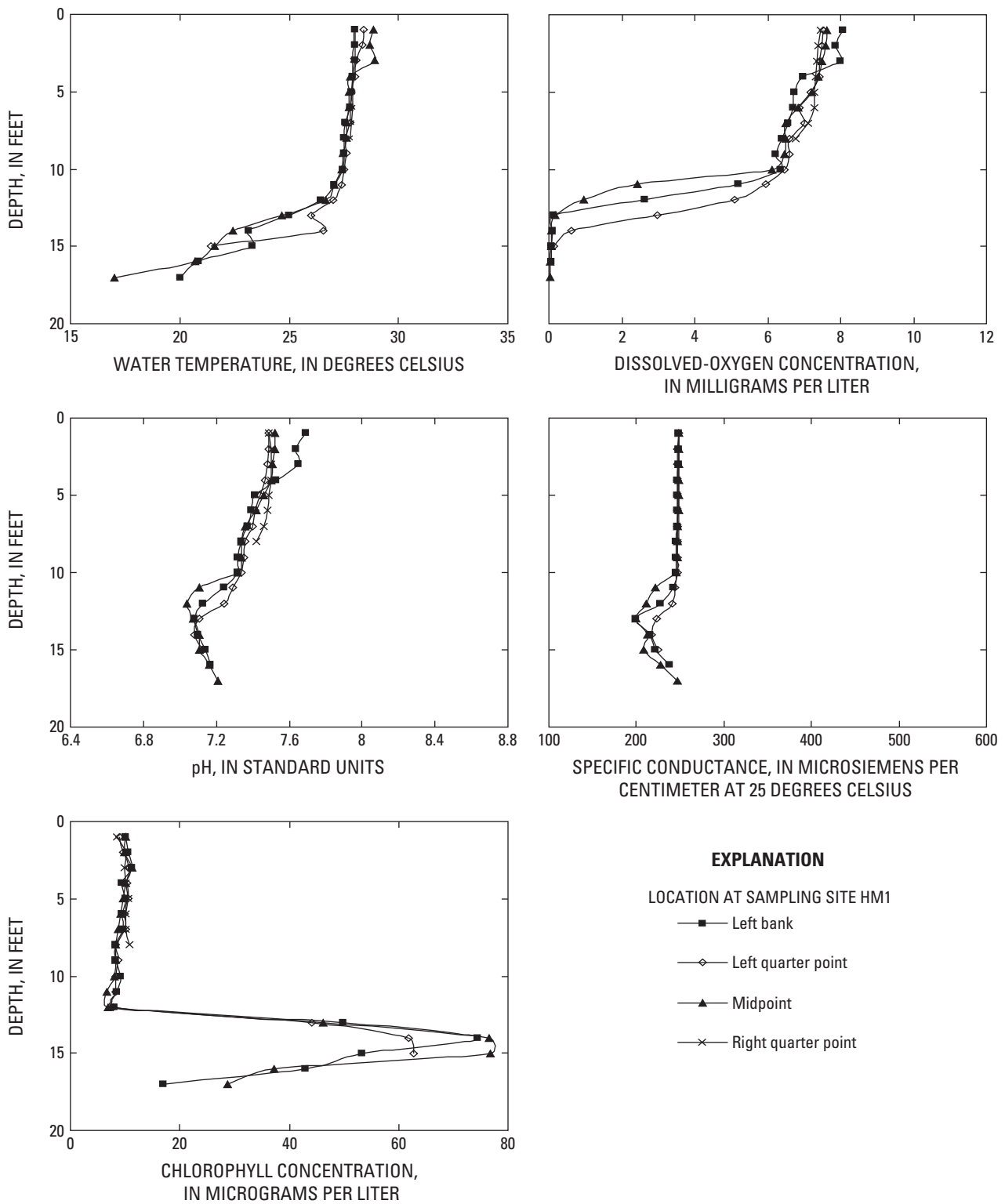
averaged 35 days for the entire reservoir and 18 days for the lower part of the reservoir for that period. Hydraulic retention time decreased to 21 days for the entire reservoir and 11 days for the lower reservoir based on peak withdrawals for the period 2000 through 2003. Peak withdrawal rates typically occur during dry summer conditions.

## Harwoods Mill Reservoir

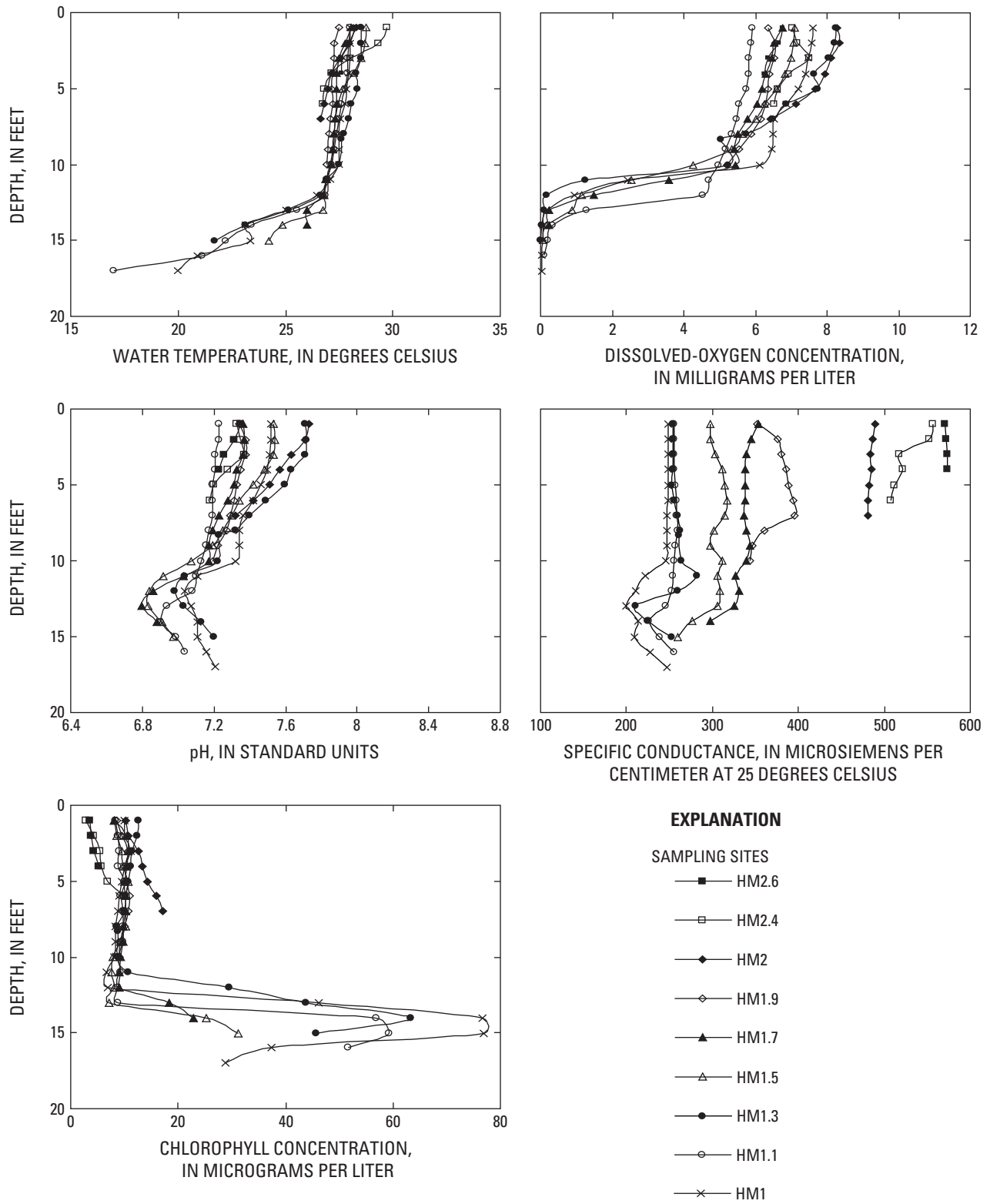
The depth of Harwoods Mill Reservoir affects the stratification and circulation of the reservoir. Vertical profiles of field-measured physical and chemical characteristics in August 2002 indicate that Harwoods Mill Reservoir thermally and chemically stratified at similar depths throughout the reservoir (figs. 16, 17). Like Lee Hall Reservoir, differences in water-quality characteristics generally are small among vertical profiles in each cross section similar to those at site HM1 (fig. 16). Differences in vertical profiles among the midpoints along the length of the reservoir (fig. 17) are greater than among vertical profiles in the cross sections (fig. 16). Near and below the thermocline, differences were not as great in water temperature and dissolved-oxygen concentration.

Vertical temperature profiles indicate a gradual thermal gradient to a depth of about 12 ft followed by a sharp thermocline from that depth to the bottom of the reservoir where the depth is greater than 12 ft; the water temperature decreased as much as 10 °C from 12 ft to the bottom. The thermocline indicates the presence of thermal stratification and associated thermal-density gradient. The uniformity of the thermocline throughout the reservoir beginning at a depth of 12 ft means that the thermocline extends more than halfway from the water-treatment plant to the pumped inflow. This is in contrast to data presented by Hoehn (1985) that indicated the presence of stratification only at site HM1. This difference in the apparent extent likely is a result of Hoehn's sampling locations in the lower reservoir; most of Hoehn's sites were located near the shore or in arms of the reservoir where the depth was shallower than in the center. Stratification prevents vertical mixing of water across the thermocline, forming an upper well-mixed zone or epilimnion and a lower poorly mixed zone or hypolimnion. Data collected by the City of Newport News from 1999 through 2003 (Ronald Harris, City of Newport News, written commun., 2003) indicate that Harwoods Mill Reservoir first stratifies between April and June and remains stratified through September or October, as indicated by profiles in 2003 that generally reflect typical annual patterns (fig. 18). The depth of the top of the thermocline varied seasonally, ranging from 3 to 15 ft during the summer months of 1999 through 2003.

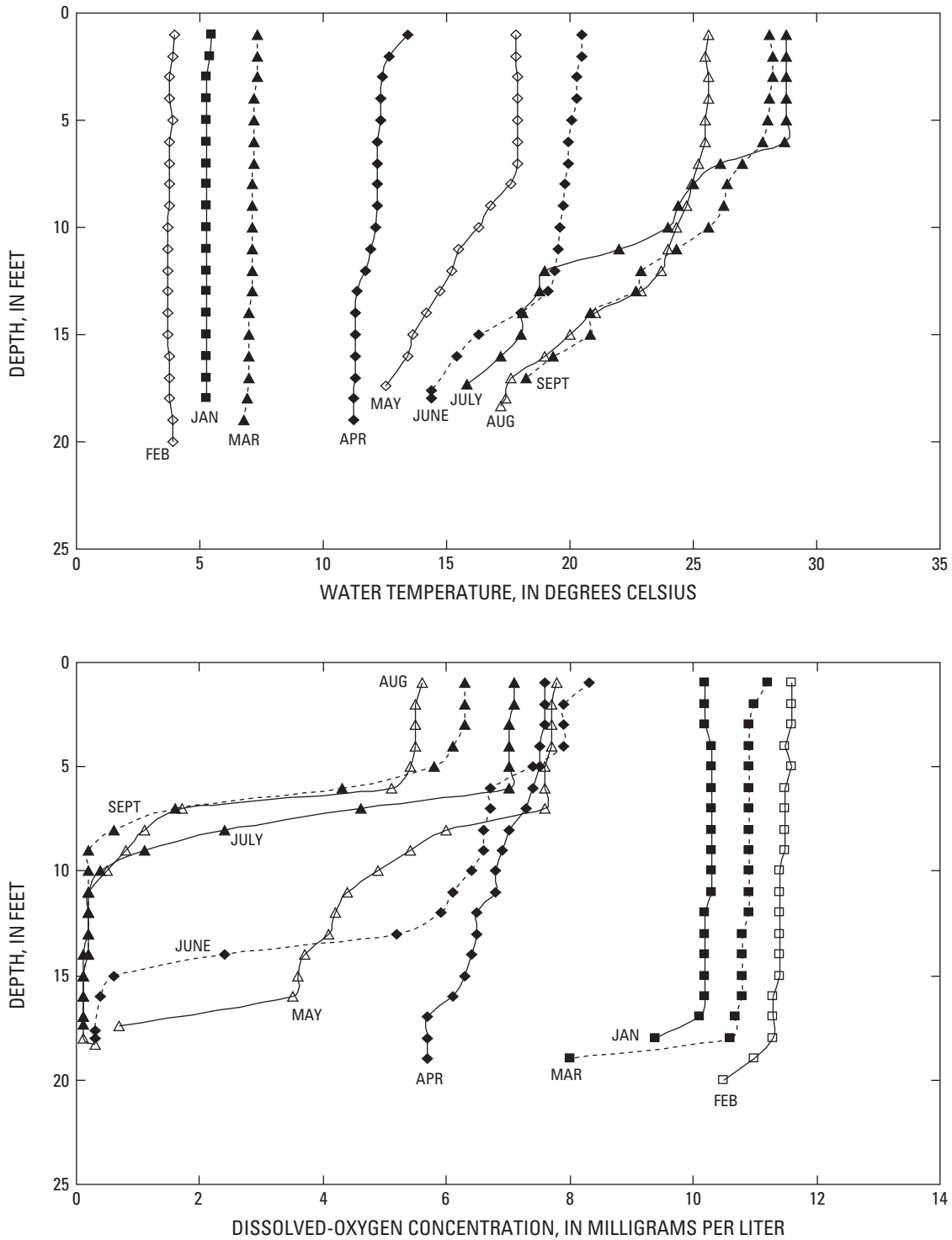
Vertical dissolved-oxygen profiles from August 2002 indicate a gradual decrease in dissolved-oxygen concentrations from the surface to a depth of 10 ft followed by a much sharper decrease below that depth until concentrations approach 0 mg/L (figs. 16, 17). Concentrations near the surface ranged from about 77 to 107 percent of saturation and appear to be above saturation as a result of photosynthesis



**Figure 16.** Physical characteristics and constituent concentrations with depth at the left bank, left quarter point, midpoint, and right quarter point of the cross section at site HM1, Harwoods Mill Reservoir, Virginia, August 8, 2002.



**Figure 17.** Physical characteristics and constituent concentrations with depth at the midpoints of cross sections along the length of Harwoods Mill Reservoir, Virginia, August 8–9, 2002.



**Figure 18.** Distribution of water temperature and dissolved-oxygen concentration with depth from January through September 2003 at site HM1, Harwoods Mill Reservoir, Virginia. (Data provided by the City of Newport News.)



by algae only in profiles measured in the afternoon. Actual concentrations decreased from about 6 to 8 mg/L near the surface to about 5 to 7 mg/L at a depth of about 10 ft then decreased to near 0 mg/L at depths of 12 to 14 ft. A dissolved-oxygen gradient or chemocline generally formed between April and June then dissipated in September or October during 1999 through 2003, as represented by City of Newport News data for 2003, which are similar to data for the other years during this period (fig. 18). The depth of the top of the dissolved-oxygen chemocline typically was near the reservoir bottom when it formed and decreased to as shallow as about 5 ft in some years during July or August before deepening and dissipating. The top of near-0-mg/L concentration of dissolved oxygen ranged in depth from about 8 ft to near the reservoir bottom. Unlike Lee Hall Reservoir, dissolved-oxygen concentrations near 0 mg/L did not persist throughout the year in Harwoods Mill Reservoir.

The presence of the dissolved-oxygen chemocline reflects the effects of thermal stratification on mixing. The epilimnion remained oxygenated because of photosynthesis by algae and aeration at the water surface. The depletion of dissolved oxygen in the hypolimnion resulted from the barrier to mixing between the hypolimnion and epilimnion, the respiration and decomposition of algae, the decomposition of other organic material in the water column and bed sediment, and the reduction of minerals such as those containing iron oxides in the bed sediment. Because of stratification, algae and other suspended materials can remain suspended as long as they remain in the epilimnion but begin to settle once they enter the hypolimnion.

Vertical pH profiles from August 2002 likely reflect a combination of effects. The pH, in general, was quite similar among vertical profiles in each cross section (fig. 16) and varied more among midpoints along the length of the reservoir (fig. 17). The pH ranged from 7.2 to 7.7 near the surface, decreased gradually to 7.1 to 7.3 at a depth of 10 ft, decreased more sharply to lows of 6.8 to 7.1 at a depth of 12 to 14 ft, and increased to 7.0 to 7.2 toward the bottom. The pH was greatest near the surface because of photosynthetic uptake of carbon dioxide by algae near the surface because carbon dioxide forms carbonic acid. The pH decreased with depth because of decreased photosynthesis, the respiration of algae that settled from the photic zone, and decomposition of dead algae and other organic material that produce carbon dioxide and organic acids. The increase in pH near the bottom may have resulted from the dissolution of carbonates, reduction of iron oxides, or other processes in the bed sediment that cannot be determined from the available data.

Vertical profiles of specific conductance from August 2002 reflect the effects of higher specific conductance in the source water from the Chickahominy River and stratification of Harwoods Mill Reservoir. Specific conductance was similar among vertical profiles in each cross section (fig. 16). At the midpoints, however, specific conductance in the epilimnion decreased from about 575  $\mu\text{S}/\text{cm}$  at site HM2.6 to about 250  $\mu\text{S}/\text{cm}$  at sites HM1, HM1.1, and HM1.3 (fig. 17). At

most sites where reservoir depth was greater than about 10 ft, specific conductance was relatively uniform above 10 ft but tended to decrease and vary below 10 ft. Specific conductance was lowest at site HM1, decreasing to 200  $\mu\text{S}/\text{cm}$ . This lower specific conductance likely reflects the conductance of the inflows in the spring when the reservoir first stratified and circulation between the epilimnion and the hypolimnion became limited. This specific conductance is similar to the specific conductance of 215  $\mu\text{S}/\text{cm}$  at site LH3 in Lee Hall Reservoir (fig. 13), which also appeared to reflect the effects of natural inflows in the early part of the year. The depth at which the specific conductance changed is generally the depth of the top of the dissolved-oxygen chemocline and not the top of the thermocline, indicating that the dissolved-oxygen concentration might be a better indicator of the base of the epilimnion and mixing zone than the water temperature.

Changes in chlorophyll concentrations at site HM1 were similar at different points in the cross section, increasing slightly from near the surface to a small peak at a depth of about 3 ft then gradually decreasing to a depth of 12 ft (fig. 16). Concentrations then increased sharply from 7 or 8  $\mu\text{g}/\text{L}$  at 12 ft to as much as 77  $\mu\text{g}/\text{L}$  at depths of 14 to 15 ft before decreasing toward the bottom. Except where the reservoir was shallower than about 8 ft, chlorophyll concentrations showed a similar pattern at the midpoints with little change at shallow depths and the sharp increase beginning below depths of 11 to 13 ft (fig. 17). The high chlorophyll concentrations likely result from a combination of two factors: the settling of algae from the epilimnion into the hypolimnion and the presence of green sulfur bacteria. Bacteria and settling algae in the hypolimnion remain there and could accumulate before settling as bed sediment because of the thermal density barrier to mixing. The green sulfur bacteria photosynthesize in low light by using sulfur in hydrogen sulfide as an electron donor in the reduction of carbon dioxide as part of photosynthesis (Wetzel, 1975, p. 274). These bacteria contain bacteriochlorophylls that would be partly detected by the chlorophyll probe. The role of these bacteria might be limited because a sulfide odor generally was not detected in water of the hypolimnion of Harwoods Mill Reservoir. The activity of these bacteria, however, could reduce the sulfide concentration below detectable concentrations.

Oxygen-18 and deuterium concentrations confirm the stratification and circulation patterns indicated by the vertical profiles of the water-quality characteristics measured onsite (fig. 15). In Harwoods Mill Reservoir during the early summer, the isotopic composition near the surface (site HM1S) reflected greater evaporation than the composition near the bottom (site HM1B). The isotopic composition of site HM1S was similar to that of the pumped inflow (represented by CR1 in figure 15) throughout the period. Harwoods Mill Reservoir first stratified in May or June, prior to the August sampling; consequently, less evaporation would have occurred in the pumped and natural inflows and the water in the reservoir at the time of stratification than during the summer. After stratification, water in the hypolimnion would remain there, mixing

little with water subsequently pumped into the reservoir, and would not evaporate like water in the epilimnion. Water in the hypolimnion, therefore, would maintain its isotopic signature from the time stratification was established. Water near the surface, however, would be replaced by recently pumped inflow, largely from the Chickahominy River, that increasingly had undergone evaporation during the summer, as indicated by the isotopic signature of CR1 (fig. 15) and would undergo additional evaporation as it flowed through the reservoir. In late September, as stratification began to break down and allow vertical mixing, the isotopic composition of sites HM1S and HM1B converged to an isotopic composition between the two.

In combining the interpretations of the physical and chemical characteristics and stable isotopes, Harwoods Mill Reservoir typically begins to stratify between April and June and remains stratified until September or October. The depth of the bottom of the epilimnion varies after the onset of stratification and may extend to depths of only 5 or 6 ft by August or September. When the reservoir is stratified, water in the reservoir primarily flows through the epilimnion to the water intake where the water is withdrawn for treatment. The similarity of all physical and chemical characteristics in the vertical profiles at different points in the cross sections combined with differences in the physical and chemical characteristics at the midpoints along the length of the reservoir indicate that water flows through the reservoir (epilimnion when stratified) as plug flow and does not short circuit through the reservoir.

Water essentially flows through the entire length of Harwoods Mill Reservoir regardless of whether pumped or natural inflows are the primary source of water. Thus, the hydraulic retention time of the reservoir depends on the rate of pumped withdrawal and the amount of inflows but not on the sources of inflows as is the case in Lee Hall Reservoir. Hydraulic retention time also is affected by stratification. The effects of stratification depend on the part of the reservoir volume that forms the epilimnion through which the water flows. If two thirds of the volume is in the epilimnion, the hydraulic retention time is two thirds of that of the unstratified reservoir. Based on information provided by the City of Newport News (Ronald Harris, City of Newport News, written commun., 2002), when the epilimnion extends to a depth of 14 ft, 90 percent of the volume of Harwoods Mill Reservoir is in the epilimnion; when the epilimnion extends to only 10 ft, 75 percent of the reservoir volume is in the epilimnion. When the epilimnion extends to only 5 ft, as sometimes is observed during July and August, about 45 percent of the total reservoir volume is in the epilimnion.

If Harwoods Mill Reservoir were not used for public supply, the hydraulic retention time of the unstratified reservoir would average 146 days based on calculated average natural inflows and median runoff from watersheds in the Coastal Plain of Virginia (15.5 inches per year, table 2, Richardson, 1994). Because rates of pumped inflow plus natural inflows into the reservoir typically do not exceed withdrawals unless

natural inflows alone exceed withdrawals, the following hydraulic retention times were calculated by using withdrawal rates. When natural inflows exceed withdrawal rates and water flows over the spillway, hydraulic retention times will be less than identified here. Using the 20 Mgal/d withdrawal average based on the water-treatment-plant capacity, hydraulic retention time decreases from 146 to 42 days for the entire reservoir. Because average withdrawal was more than the capacity-based average withdrawal from 2000 through 2003, hydraulic-retention time averaged 34 days for the reservoir for that period. Hydraulic retention time decreased to 15 days for the reservoir based on the peak withdrawals for the period 2000 through 2003. The hydraulic retention time further decreases to less than 7 days based on peak withdrawal rates when the reservoir is stratified to a depth of 5 ft, as is sometimes observed in July and August.

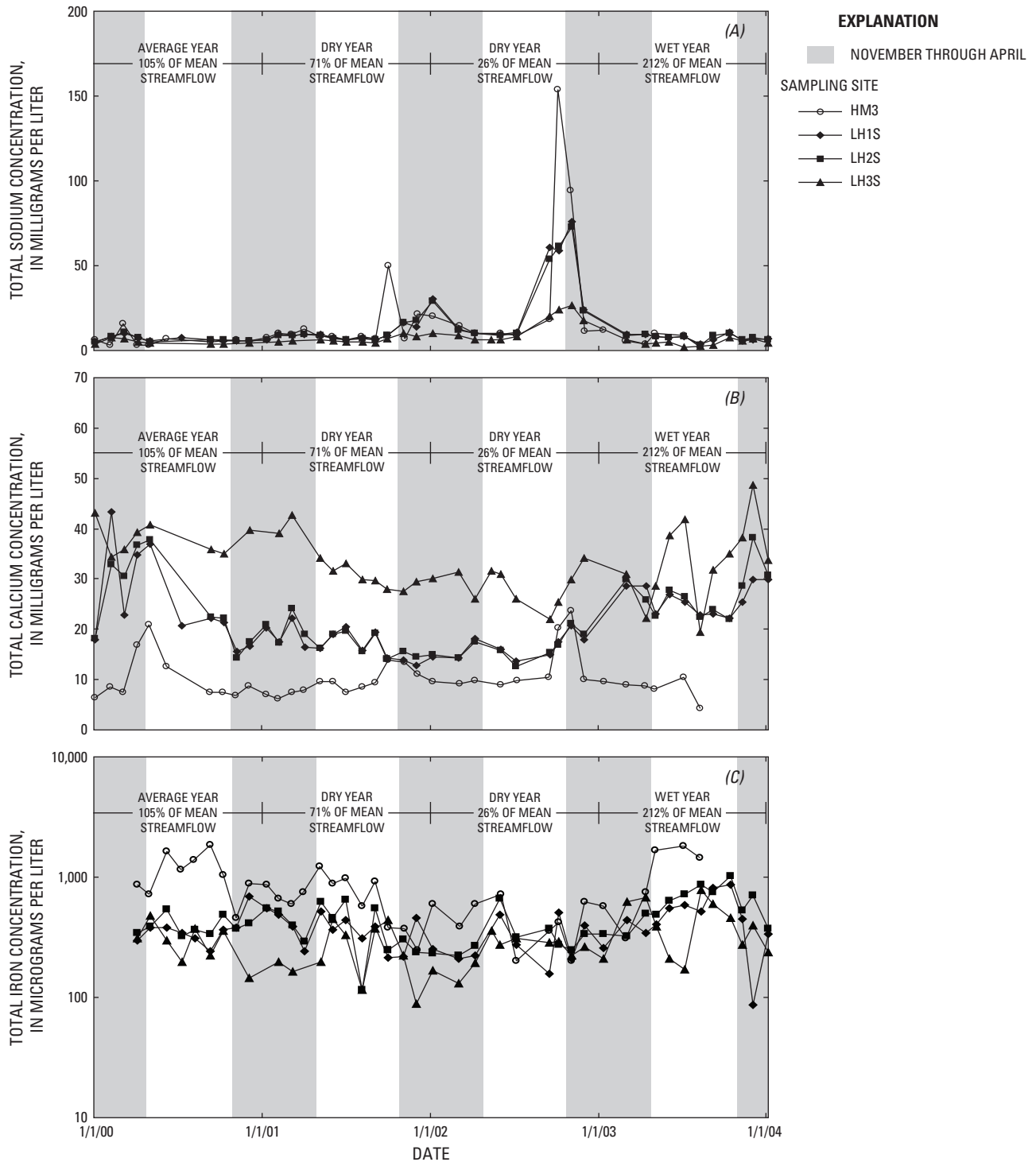
## Water Quality

Water-quality data from long-term monitoring by the City of Newport News combined with the USGS data collected during this investigation provide additional insight into the effects of natural and pumped sources, reservoir circulation, patterns in nutrient species as they may affect algal growth, and nutrient chemistry. No long-term water-quality data are available on natural flows into the reservoirs. Although reservoir processes can alter the quality of water after it enters the reservoir, inferences about source waters can be made by comparing the water quality of surface samples at sites LH1 and LH2 with that of site LH3 (an indicator of the quality of the natural inflow). The water quality of site HM3 is assumed to be the quality of the pumped inflow for both reservoirs. Additionally, water-quality data are available from other studies and from data collected at site BR1.

## Selected Ions

Data presented on selected ions are important for different reasons. Sodium and calcium are major cations that indicate the effects of large changes in water sources and water chemistry. Iron concentrations are important because iron oxides can form, bind with phosphorus, and precipitate as bed sediment. Sulfate is important because low concentrations appear to limit release of phosphorus from bed sediment (Caraco and others, 1989).

Total sodium concentrations were similarly low at sites LH1S, LH2S, and HM3 (pumped inflow) but differed slightly from concentrations at site LH3 (Newport News data for all sites). Median and maximum total sodium concentrations were higher at sites LH1S, LH2S, and HM3 (median concentrations of 8.0, 8.5, and 8.4 mg/L, respectively, and maximum concentrations of 76, 73, and 154 mg/L, respectively) than at site LH3 (median concentration of 5.5 mg/L and maximum concentration of 27 mg/L, fig. 19; table 8). Concentrations at site LH3 were on the high side of the 2.4- to 5.9-mg/L



**Figure 19.** Concentrations of (A) total sodium, (B) total calcium, and (C) total iron in samples from the pumped inflow (site HM3) and from the surface at sites LH1, LH2, and LH3, Lee Hall Reservoir, Virginia. (Streamflow in a normal year is 75 to 125 percent of the mean annual streamflow at Chickahominy River at Providence Forge (02042500); streamflow in a wet year is greater than 125 percent of the mean annual streamflow at station 02042500; streamflow in a dry year is less than 75 percent of the mean annual streamflow at station 02042500.) (Data provided by the City of Newport News, Virginia.)

**Table 8.** Summary of selected water-quality characteristics of surface samples from Lee Hall and Harwoods Mill Reservoirs, Virginia, collected and analyzed by the City of Newport News, January 2000–August 2003.

Site number (figs. 3, 4)	Determination	Chlorophyll <i>a</i> , µg/L	Specific conductance, µS/cm	Dissolved oxygen, mg/L	pH, field, standard units	Total Kjeldahl nitrogen, mg/L	Ammonia nitrogen, mg/L	Nitrate nitrogen, mg/L	Nitrite nitrogen, mg/L	Phosphorus, ortho, dissolved, mg/L	Phosphorus, total, mg/L
LH1S	Median	—	190	7.3	7.2	0.4	0.02	0.02	0.002	0.010	0.023
LH1S	Maximum	—	610	13.4	8.3	2.5	.29	.60	.009	.041	.045
LH1S	Minimum	—	97	.1	6.4	.2	.2	.02	0	.01	.010
LH1S	Number of samples	—	72	73	72	65	67	69	64	71	70
LH2S	Median	5.0	170	6.9	7.4	.4	.02	.02	.002	.01	.028
LH2S	Maximum	14.	59	13.7	8	1.5	.10	.61	.050	.027	.059
LH2S	Minimum	1.1	107	.04	6.7	.2	.02	.02	.001	.01	.010
LH2S	Number of samples	28	49	49	49	43	45	47	45	49	47
LH3S	Median	5.9	206	8.3	7.7	.4	.02	.02	.001	.01	.028
LH3S	Maximum	23.	305	12.7	8.7	3.1	.13	.30	.020	.025	.061
LH3S	Minimum	1.0	89	.2	6.6	.1	.02	.02	.001	.01	.010
LH3S	Number of samples	31	49	49	49	42	44	47	44	49	44
HM1S	Median	4.6	150	8.4	7.3	.4	.02	.02	.001	.01	.026
HM1S	Maximum	16.	.65	12.4	8.8	2.2	.15	.81	.028	.043	.068
HM1S	Minimum	1.2	70	6.0	6.4	.2	.02	.02	.001	.001	.012
HM1S	Number of samples	53	56	56	56	50	56	53	53	54	53
HM2S	Median	5.0	140	9.0	7.2	.4	.02	.02	.002	.010	.034
HM2S	Maximum	13	880	13.2	8.4	1.8	.21	.31	.008	.043	.010
HM2S	Minimum	1.6	83	6.1	6.5	.1	.02	.02	.001	.001	.010
HM2S	Number of samples	53	56	56	56	50	56	54	54	54	54
HM3	Median	2.5	100	7.9	6.8	.5	.02	.02	.002	.016	.037
HM3	Maximum	7.8	1,300	12.5	8.0	1.7	.86	.78	.010	1	.082
HM3	Minimum	0	31	.3	5.1	.2	.02	.02	.001	.003	.010
HM3	Number of samples	51	54	53	54	50	54	53	53	52	51

[µg/L, microgram per liter; µS/cm, microsiemen per centimeter at 25 degrees Celsius; mg/L, milligram per liter; —, no data]

**Table 8.** Summary of selected water-quality characteristics of surface samples from Lee Hall and Harwoods Mill Reservoirs, Virginia, collected and analyzed by the City of Newport News, January 2000–August 2003. — Continued

Site number (figs. 3, 4)	Determination	Nitrogen to phosphorus ratio	Total organic carbon, mg/L	Calcium, total, mg/L	Magnesium, total, mg/L	Potassium, total, mg/L	Sodium, total, mg/L	Iron, total, µg/L	Manganese, total, µg/L
LH1S	Median	19	6.8	21	—	—	8.0	400	150
LH1S	Maximum	120	11.	37	9.0	—	76	2,400	1,70
LH1S	Minimum	—	4.7	13	1.0	—	3.8	87	23
LH1S	Number of samples	70	47	65	65	—	65	65	67
LH2S	Median	—	7.1	22	1.8	1.9	8.5	500	12
LH2S	Maximum	—	15.	38	8.8	4.8	73	1,300	500
LH2S	Minimum	—	4.4	13	.9	1.2	2.8	220	24
LH2S	Number of samples	—	24	43	43	43	43	44	44
LH3S	Median	13	6.8	32	1.5	1.5	5.5	290	56
LH3S	Maximum	140	18.	49	4.8	3.8	27	1,700	200
LH3S	Minimum	—	4.0	19	.8	1.0	2.0	89	11
LH3S	Number of samples	44	26	45	45	45	45	46	46
HM1S	Median	18	6.6	16	2.0	2.2	7.8	390	110
HM1S	Maximum	160	11.	63	8.2	3.1	30	1,900	400
HM1S	Minimum	6.6	4.3	12	1.2	1.2	4.1	130	40
HM1S	Number of samples	43	53	39	39	26	26	50	53
HM2S	Median	11	7.6	15	1.8	2.1	9.1	590	71
HM2S	Maximum	66	16.	32	16	6.0	110	1,500	410
HM2S	Minimum	.38	4.5	1.1	.9	1.1	2.7	150	10
HM2S	Number of samples	54	53	39	39	39	38	50	52
HM3	Median	15	8.4	9.1	1.8	2.3	8.4	750	89
HM3	Maximum	110	30.	24	19.	9.2	154	5,200	2,000
HM3	Minimum	.35	2.0	4.2	.7	.6	1.8	200	21
HM3	Number of samples	51	50	37	37	37	37	48	51

[µg/L, microgram per liter; µS/cm, microsiemen per centimeter at 25 degrees Celsius; mg/L, milligram per liter; — no data]



concentration in five springs discharging from the Cornwallis Cave aquifer in the Lee Hall Reservoir watershed at Colonial National Historical Park (Speiran and Hughes, 2001). These data indicate that although differences are small, total sodium concentrations are higher in the pumped inflow than in the natural inflows during 22 of 30 sampling periods. Increased concentrations of total sodium at sites LH1S, LH2S, and HM3 periodically can result from movement of salty water up the Chickahominy River during periods of low freshwater flow and from the use of salt on roads to melt ice and snow, particularly in the Chickahominy River watershed (Lynch, 1992). The peak in concentrations at these sites in the late summer and early fall of 2003 (fig. 19) was from the salty water in the lower Chickahominy River caused by the drought conditions.

Data obtained from the City of Newport News indicate that total calcium concentrations at sites LH1S and LH2S were similar to each other, concentrations at site LH3 typically were higher than at sites LH1S and LH2S, and concentrations at sites LH1S and LH2S typically were higher than those at site HM3 (fig. 19; table 8), indicating that concentrations were greater in natural inflows than in the pumped inflow. Median concentrations at sites LH1S, LH2S, LH3S, and HM3 were 21, 22, 32, and 9.1 mg/L, respectively. Concentrations at sites LH1S and LH2S were closer to those of the pumped inflow at site HM3 during dry years when pumpage contributed a greater part of the water and closer to those at site LH3S during wet years when natural inflows contributed a larger part of the flow. Concentrations in water from five springs discharging from the Cornwallis Cave aquifer in the James River basin at Colonial National Historical Park (Speiran and Hughes, 2001) were higher (45 to 88 mg/L) than the median concentration at site LH3S (table 8). Calcium in the natural inflows likely is derived largely from the effects of shell material in the Cornwallis Cave aquifer on ground-water discharge.

Iron data obtained from the City of Newport News indicate that total iron concentrations typically were greatest in the pumped inflow (site HM3) and least at site LH3S with median concentrations of 750 and 290  $\mu\text{g/L}$ , respectively (fig. 19; table 8). Total iron concentrations in the pumped inflow were greater than those at sites LH1S and LH2S in 30 of 36 sampling periods in which samples were collected from all three sites from 2000 through 2003; total iron concentrations were less at site LH3S than at sites LH1S and LH2S during 28 of 39 sampling periods. Concentrations were higher at site LH2S (median 500  $\mu\text{g/L}$ ) than at site LH1S (median 400  $\mu\text{g/L}$ ) during 28 of 39 sampling periods and less during 9 sampling periods from 2000 through 2003 (fig. 19; table 8). Total iron concentrations at sites LH1S and LH2S were between those in the pumped inflow and at site LH3S much of the time, probably as a result of mixing water from the two sources. The decrease in total iron concentrations from sites LH2S and LH1S and part of the decrease from the pumped inflow to site LH2S may be a result of precipitation of iron oxides as water flows through the reservoir. These iron oxides

can bind dissolved phosphorus in the form of orthophosphate or organic species in the water column.

Sulfate concentrations in August 2002 were less than 15 mg/L at all Lee Hall Reservoir sites (table 9). Sulfate concentrations at the surface and bottom in Lee Hall Reservoir were 3.0 and 2.5 mg/L at site LH3, 8.6 and 9.6 mg/L at site LH2, and 13.8 and 8.1 mg/L at site LH1. The sulfate concentration was 10.9 mg/L at site LH(CR)1. Concentrations at site LH3 were slightly less than concentrations in discharge from five springs in the Beaverdam Creek watershed, which ranged from 4 to 13 mg/L (median 5.1 mg/L; Speiran and Hughes, 2001). Sulfate concentrations in the pumped inflow and at sites LH1 and LH2 were consistent with concentrations in the Chickahominy River from August 1983 through October 1986, which ranged from 2.7 to 25 mg/L (median 9.1 mg/L; Lynch, 1992). Sulfate concentrations in the Chickahominy River typically were less than 5 mg/L during warm-weather months (April–September) and less than 10 mg/L during cold-weather months. These sulfate concentrations are in the range identified by Caraco and others (1989) as limiting the release of phosphorus from bed sediment where the water column is aerobic (sulfate concentrations less than 9.6 to 28.8 mg/L) and at times are in the range limiting the release when the water column is anoxic (sulfate concentrations less than 5.8 mg/L). Although data are limited, sulfate concentrations likely can inhibit the release of phosphorus from bed sediment to the water column in Lee Hall Reservoir when the water column contains abundant dissolved-oxygen concentrations and can limit phosphorus release at least part of the time when water near the bottom of the reservoir is anoxic.

In Harwoods Mill Reservoir, concentrations of total sodium at sites HM1S, HM2S, and HM3 (pumped inflow) tended to be similar during most sampling periods (fig. 20). Median total sodium concentrations were 7.8, 9.1, and 8.4 mg/L at sites HM1S, HM2S, and HM3, respectively (table 8). Higher sodium concentrations periodically can result from movement of salty water up the Chickahominy River during periods of low freshwater flow and from the use of salt on roads to melt ice and snow particularly in the Chickahominy River watershed. Peak concentrations were 30, 110, and 154 mg/L at sites HM1S, HM2S, and HM3, respectively (fig. 20; table 8). The highest concentrations were in the late summer and early fall of 2003 and resulted from salty water in the lower Chickahominy River because of the drought conditions.

Total calcium concentrations at sites HM1S and HM2S typically were higher than those at site HM3 (fig. 20; table 8), indicating that, as in Lee Hall Reservoir, concentrations in natural inflows generally are greater than in the pumped inflow. Median total calcium concentrations at sites HM1S, HM2S, and HM3 were 16, 15, and 9.1 mg/L, respectively. Total calcium concentrations at site HM1S were greater than those at site HM2S in 27 of 38 samples collected from 2000 through 2003, which indicates a greater calcium source within the Harwoods Mill watershed than in water pumped from outside watersheds. The greater total calcium concentration

**Table 9.** Summary of selected water-quality characteristics of samples from Lee Hall and Harwoods Mill Reservoirs and pumped and natural inflows, Virginia, collected and analyzed by the U.S. Geological Survey, June 2002–October 2003.

Project site number (figs. 2–4)	Determination	Total Kjeldahl nitrogen, mg/L		Ammonia nitrogen, filtered, mg/L	Nitrite plus nitrate nitrogen, mg/L	Nitrite nitrogen, mg/L	Particulate nitrogen, mg/L	Phosphorus, total, mg/L	Phosphorus, dissolved, mg/L	Phosphorus, ortho, dissolved, mg/L	Carbon, total, mg/L
		whole water, mg/L	Kjeldahl nitrogen, filtered, mg/L								
LH1	Median	0.69	0.44	0.079	<0.013	0.002	0.28	0.031	0.006	<0.007	1.7
LH1	Maximum	.97	.91	.37	.033	.003	1.1	.069	.012	<.007	4.3
LH1	Minimum	.48	.32	<.015	<.013	.002	.20	.023	<.004	<.007	1.2
LH1	Number of samples	23	23	23	23	23	10	23	23	23	10
LH2	Median	.61	.41	.048	<.013	.002	.29	.036	.007	<.007	1.7
LH2	Maximum	.77	.71	.31	.021	.003	.65	.053	.014	<.007	2.7
LH2	Minimum	<.10	<.10	<.015	<.013	.002	.14	.031	<.004	<.007	.8
LH2	Number of samples	17	17	17	17	17	10	17	17	17	10
LH3	Median	.88	.41	<.015	<.013	.002	.47	.057	.008	<.007	3.1
LH3	Maximum	1.3	.58	.14	.022	.002	.79	.075	.011	<.007	4.4
LH3	Minimum	.62	.38	<.015	<.013	.002	.34	.041	.006	<.007	2.0
LH3	Number of samples	16	16	16	16	16	8	16	16	16	8
CR1	Median	.55	.38	.022	.086	.003	.13	.032	.007	<.007	1.3
CR1	Maximum	.70	.51	.035	.16	.003	.45	.051	.022	.010	2.9
CR1	Minimum	.47	.32	.016	.037	.002	.11	.027	.005	<.007	.9
CR1	Number of samples	7	7	7	7	7	3	7	7	7	3
BR1	Median	.36	.20	<.015	.12	.002	.087	.073	.023	.016	.6
BR1	Maximum	1.1	.31	.054	.22	.009	.087	.21	.060	.051	.6
BR1	Minimum	.085	.061	<.015	.036	.002	.087	.024	.012	.008	.6
BR1	Number of samples	23	23	23	23	23	1	23	23	23	1
HM1	Median	.78	.62	0.21	<.013	.002	.26	.042	.014	<.007	1.7
HM1	Maximum	6.0	5.5	4.8	.027	.006	1.2	.094	.13	.118	4.7
HM1	Minimum	<.10	<.10	<.015	<.013	<.002	.21	.023	.005	<.007	1.1
HM1	Number of samples	31	31	31	31	31	9	30	30	31	9

[mg/L, milligram per liter; &lt;, less than; µg/L, microgram per liter; —, no data; ROE, residue on evaporation]

**Table 9.** Summary of selected water-quality characteristics of samples from Lee Hall and Harwoods Mill Reservoirs and pumped and natural inflows, Virginia, collected and analyzed by the U.S. Geological Survey, June 2002–October 2003. — Continued

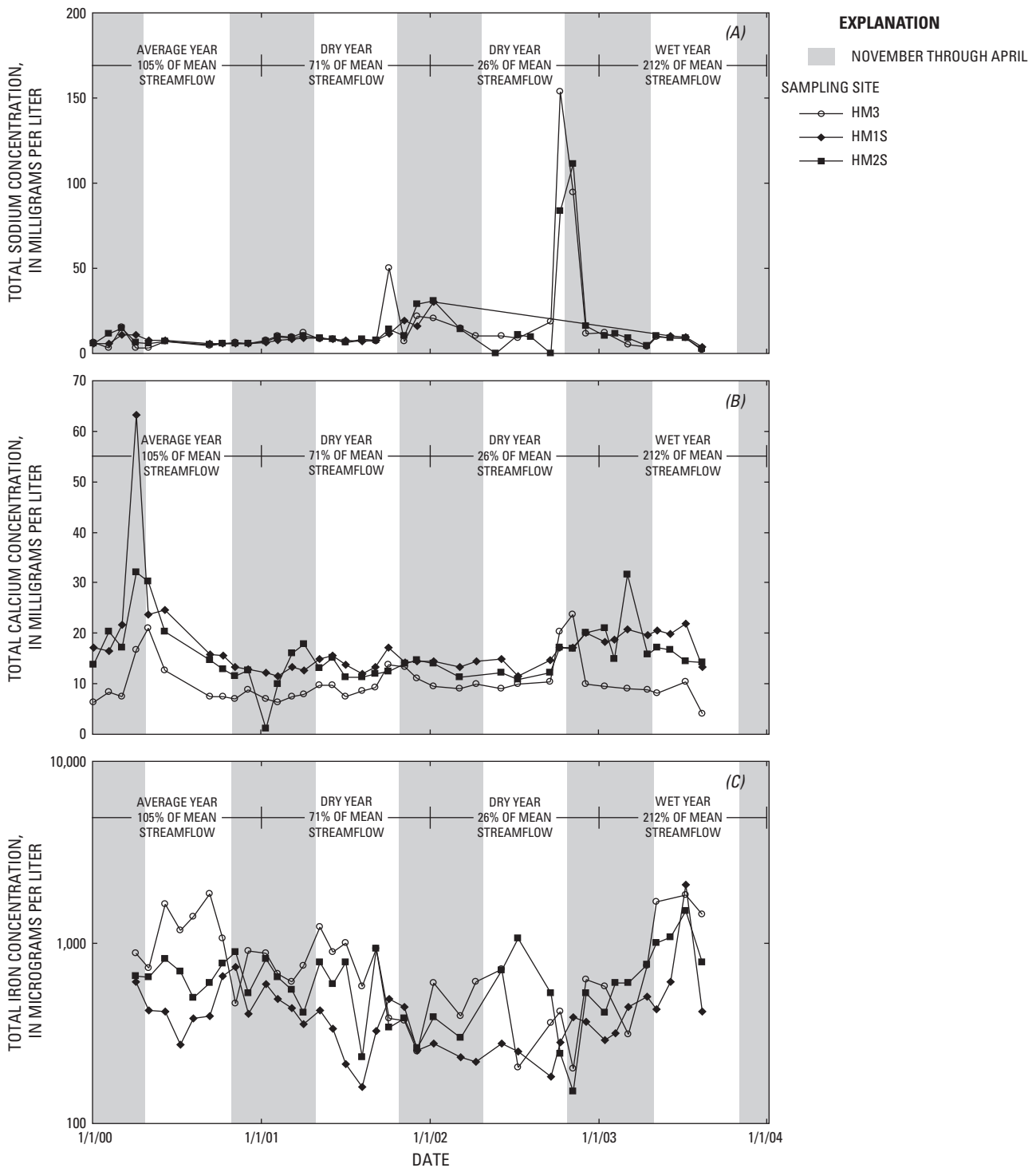
[mg/L, milligram per liter; <, less than; µg/L, microgram per liter; —, no data; ROE, residue on evaporation]

Project site number (figs. 2-4)	Determination	Carbon, inorganic, mg/L	Organic carbon, dissolved, mg/L	Organic carbon, total, mg/L	Pheophytin a, µg/L	Chloro-phyll a, µg/L	Copper, dissolved, µg/L	Copper, total, µg/L	Calcium, dissolved, mg/L	Mag-nesium, dissolved, mg/L	Sodium, dissolved, mg/L
LH1	Median	0.12	1.3	5.8	1.3	9.7	14.	26.	17	4.1	32
LH1	Maximum	.12	1.3	6.7	14.	16.	49.	120.	17	4.3	34
LH1	Minimum	.12	1.2	5.6	10	—	5.3	1.3	17	4.0	31
LH1	Number of samples	2	2	10	4	21	8	8	2	2	2
LH2	Median	.12	1.2	6.1	1.6	9.1	14.	28.	17	5.0	41
LH2	Maximum	.12	1.6	6.9	17.	16.	57.	95.	17	5.3	44
LH2	Minimum	.12	0.7	5.7	9.4	4.9	5.9	9.5	17	4.7	38
LH2	Number of samples	2	2	10	4	21	8	8	2	2	2
LH3	Median	.12	2.8	7.0	24	24.	1.8	36.	28	2.2	13
LH3	Maximum	.12	3.0	7.2	3.0	45.	42.	93.	28	2.3	14
LH3	Minimum	.12	2.7	7.0	13.	3.1	6.1	13.	28	2.1	12
LH3	Number of samples	2	2	10	3	16	8	8	2	2	2
CR1	Median	.12	1.1	6.1	17.	5.8	.40	—	16	5.6	45
CR1	Maximum	.12	1.3	6.1	17.	18.	.44	—	16	5.7	46
CR1	Minimum	.12	.9	6.1	17.	3.6	.22	—	16	5.5	43
CR1	Number of samples	2	2	3	1	4	3	—	2	2	2
BR1	Median	--	--	3.8	1.8	4.8	.59	.83	—	—	—
BR1	Maximum	--	--	3.8	1.8	7.4	.59	.83	—	—	—
BR1	Minimum	--	--	3.8	1.8	.5	.59	.83	—	—	—
BR1	Number of samples	2	2	1	1	11	1	1	—	—	—
HM1	Median	.12	1.2	6.4	12.	18.	7.8	32.	17	3.4	23
HM1	Maximum	.12	1.3	13.	31.	57.	5.9	97.	21	4.1	30
HM1	Minimum	.12	1.1	.2	8.4	5.0	.20	<0.60	15	2.7	13
HM1	Number of samples	2	2	10	9	29	10	10	4	4	4

**Table 9.** Summary of selected water-quality characteristics of samples from Lee Hall and Harwoods Mill Reservoirs and pumped and natural inflows, Virginia, collected and analyzed by the U.S. Geological Survey, June 2002–October 2003. — Continued

Project site number (figs. 2-4)	Determination	Potassium, dissolved, mg/L	Alkalinity,				Sulfate, dissolved, mg/L	Fluoride, dissolved, mg/L	Bromide, dissolved, mg/L	Silica, dissolved, mg/L	ROE at 180 degrees Celsius, dissolved, mg/L
			whole water, field, titration, mg/L	Bicarbonate, mg/L	Carbonate, mg/L	Chloride, dissolved, mg/L					
LH1	Median	3.0	38	46	0	58	10.9	0.10	0.04	4.4	174
LH1	Maximum	3.1	41	50	0	61	13.8	0.11	0.05	4.4	179
LH1	Minimum	2.9	34	42	0	55	8.1	0.10	0.04	4.4	169
LH1	Number of samples	2	2	2	2	2	2	2	2	2	2
LH2	Median	3.1	41	50	0	73	9.1	0.10	0.07	4.5	201
LH2	Maximum	3.2	41	50	0	79	9.6	0.10	0.09	4.7	211
LH2	Minimum	3.0	41	50	0	67	8.6	0.10	0.06	4.4	191
LH2	Number of samples	2.0	2	2	2	2	2.0	2.00	2.00	2	2
LH3	Median	2.1	73	82	3.5	19	2.8	0.08	0.03	5.0	137
LH3	Maximum	2.1	74	88	7	21	3.1	0.09	0.03	5.1	137
LH3	Minimum	2.1	72	76	0	17	2.6	0.08	0.03	5.0	137
LH3	Number of samples	2	2	2	2	2	2	2	2	2	2
CRI	Median	3.4	36	44	0	83	11.4	0.10	0.11	3.8	226
CRI	Maximum	3.4	36	44	0	83	11.4	0.10	0.11	3.9	229
CRI	Minimum	3.3	36	44	0	83	11.4	0.10	0.11	3.7	223
CRI	Number of samples	2	2	2	2	2	2	2	2	2	2
BR1	Median	—	—	—	—	—	—	—	—	—	—
BR1	Maximum	—	—	—	—	—	—	—	—	—	—
BR1	Minimum	—	—	—	—	—	—	—	—	—	—
BR1	Number of samples	—	—	—	—	—	—	—	—	—	—
HM1	Median	2.8	51	62.5	0	33.265	5.4	0.12	0.12	6.4	155
HM1	Maximum	3.0	80	98	0	52.86	9.0	0.14	0.22	8.2	169
HM1	Minimum	2.6	35	43	0	17.72	0.1	0.11	0.02	4.2	142
HM1	Number of samples	4	4	4	4	4	4	4	4	4	4

[mg/L, milligram per liter; <, less than; µg/L, microgram per liter; —, no data; ROE, residue on evaporation]



**Figure 20.** Concentrations of (A) total sodium, (B) total calcium, and (C) total iron in samples from the pumped inflow (site HM3) and sites HM1S and HM2S, Harwoods Mill Reservoir, Virginia. (Streamflow in a normal year is 75 to 125 percent of the mean annual streamflow at Chickahominy River at Providence Forge (02042500); streamflow in a wet year is greater than 125 percent of the mean annual streamflow at station 02042500; streamflow in a dry year is less than 75 percent of the mean annual streamflow at station 02042500.) (Data provided by the City of Newport News, Virginia.)



at site HM1S than at site HM2S could result from tributary inflows or direct spring and diffuse ground-water discharge through the reservoir bottom between these two sites.

Total iron concentrations in Harwoods Mill Reservoir tended to be higher in the summer than in the winter in the pumped inflow (site HM3) and were higher in the pumped inflow than at sites HM1S and HM2S during 25 of 35 sampling periods (fig. 20). Total iron concentrations were less at site HM1S than at site HM2S during 32 of 35 sampling periods. The decreased concentrations from site HM3 to site HM2S and from site HM2S to site HM1S (table 8) likely result from precipitation of iron oxides that can bind with phosphorus as water flows through the reservoir.

Sulfate concentrations in August 2002 were 9.0 and 1.9 mg/L at sites HM1S and HM1B, respectively (table 9). The concentration at site HM1B was less than the maximum concentration of 5.8 mg/L identified by Caraco and others (1989) as the maximum concentration below which phosphorus release is limited in an anoxic water column. Thus, low sulfate concentrations likely limit the release of phosphorus from the bed sediment to the water column in Harwoods Mill Reservoir, when the reservoir is stratified and the hypolimnion has become anoxic.

## Nutrients and Chlorophyll

Concentrations of nutrient species reflect common relations among most sample-collection sites. Phosphorus was present predominantly as suspended rather than dissolved species except in some samples from the hypolimnion of Harwoods Mill Reservoir (HM1) and the natural inflow (site BR1), primarily during base flow (fig. 21). Orthophosphorus concentrations generally were less than the 0.007-mg/L MRL in all samples except those from site BR1 (table 9). Suspended phosphorus concentrations were less than 0.67 mg/L, and dissolved phosphorus concentrations were 0.015 mg/L or less, except in some samples from sites HM1 and BR1. Both suspended and dissolved phosphorus concentrations generally were greater in the natural inflow than in the pumped inflow.

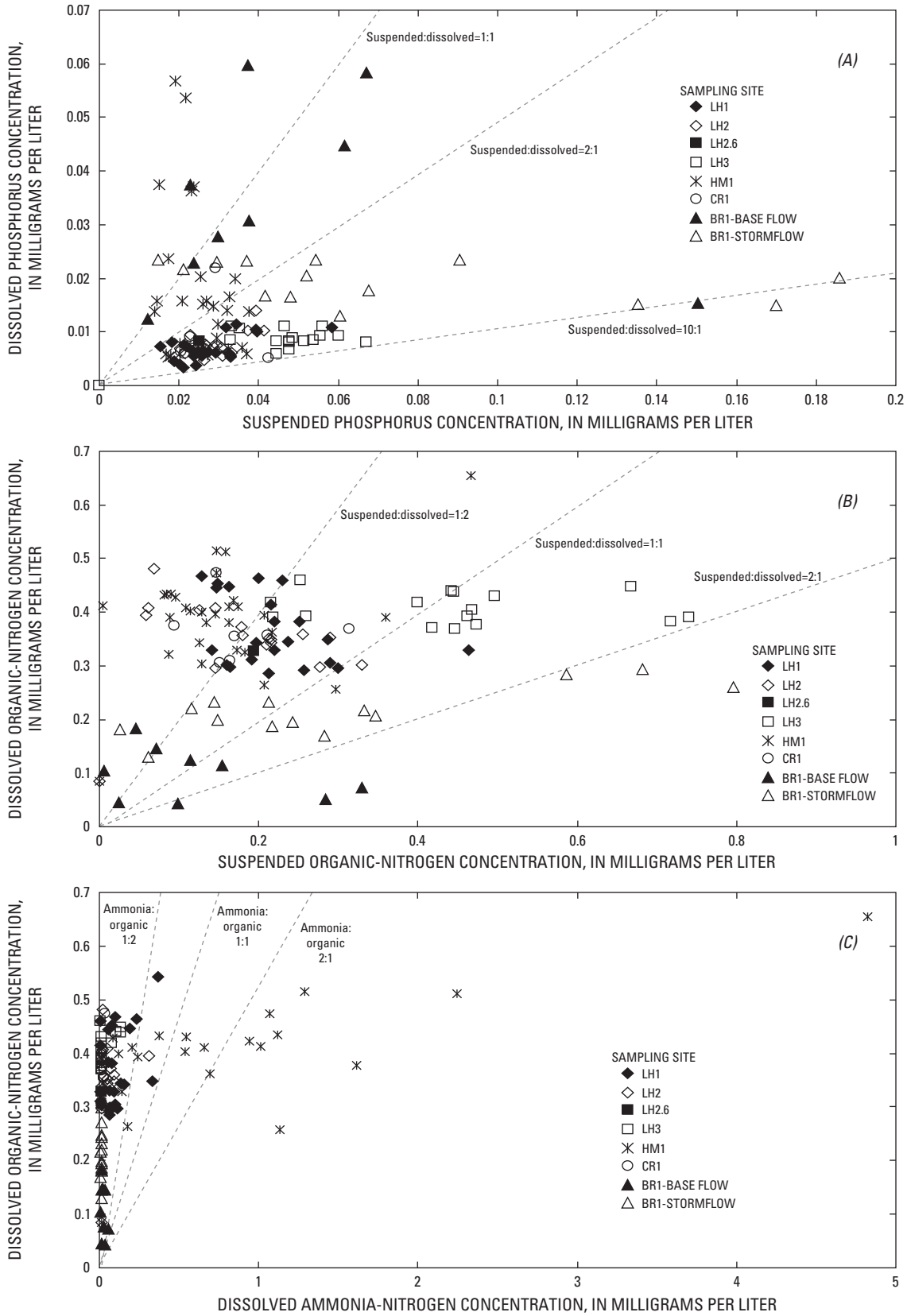
Dissolved phosphorus concentrations in the natural inflow ranged from 0.012 to 0.060 mg/L (median of 0.023 mg/L) and in the pumped inflow (site CR1) from 0.005 to 0.022 mg/L (median of 0.007 mg/L). The median dissolved phosphorus concentration in the natural inflow was half the 0.046-mg/L median of samples from the discharge from five springs in the Lee Hall Reservoir watershed (concentrations ranged from 0.029 to 0.052 mg/L) (Speiran and Hughes, 2001). Thus, discharge from springs throughout the watersheds appears to be a major source of phosphorus to the reservoirs.

Suspended phosphorus concentrations in the natural inflow ranged from 0.012 to 0.19 mg/L (median of 0.048 mg/L), and those of the pumped inflow ranged from 0.020 to 0.043 mg/L (median of 0.024 mg/L). Suspended phosphorus concentrations at site LH3 (0.033 to 0.067 mg/L) generally were higher than those at the other Lee Hall

Reservoir sites (0.015 to 0.041 mg/L) (fig. 21), apparently as a result of the higher phosphorus concentrations in the natural inflow than in the pumped inflow. The ratio of suspended to dissolved phosphorus generally ranged from 2:1 to 10:1 except for samples from sites HM1 and BR1. The higher dissolved phosphorus concentrations at sites HM1 were in the hypolimnion and likely resulted from the decomposition of organic material in the water column and/or bed sediment and possibly from the release of phosphorus from iron oxides in the bed sediment under the reducing conditions although release from iron oxides likely is limited by the low sulfate concentrations. Stratification of Harwoods Mill Reservoir precluded water in the hypolimnion from mixing with that of the epilimnion where algae photosynthesize and use dissolved phosphorus, resulting in an accumulation of dissolved phosphorus in the hypolimnion.

Organic nitrogen was the dominant nitrogen species except in the hypolimnion of Harwoods Mill Reservoir where ammonia from the decomposition of organic nitrogen was the dominant species, as is common in eutrophic reservoirs (fig. 21). Nitrite plus nitrate concentrations typically were near the 0.013- to 0.022-mg/L MRL at the reservoir sites. Dissolved organic nitrogen concentrations typically were similar to or greater than suspended organic nitrogen concentrations except in some samples from sites BR1 and LH3 in which suspended concentrations were greater than dissolved concentrations. Dissolved and suspended organic nitrogen concentrations, in the pumped inflow (site CR1) were similar to those at sites LH1 and LH2 because of the effects of the pumped inflow on these sites (fig. 21). Dissolved organic nitrogen concentrations in the natural inflow (site BR1), however, were less than those at sites LH1 and LH2; suspended concentrations at these sites were similar in most samples but greater in some storm samples (fig. 21). Although dissolved organic nitrogen concentrations at site LH3 were similar to the concentrations at sites LH1 and LH2, suspended organic nitrogen concentrations at site LH3 commonly were greater than those at sites LH1 and LH2 (fig. 21).

Although phosphorus commonly is the nutrient that limits the growth of algae in freshwater systems, nitrogen can limit algal growth in some lakes and reservoirs at certain times. The ratio of the nitrogen to phosphorus concentrations (N:P) commonly is determined to identify which nutrient likely limits algal growth. Generally, if the N:P is greater than 7:1, phosphorus is considered the growth-limiting nutrient (Wetzel, 1975). The species of nitrogen and phosphorus to consider, however, often varies. Use of total species includes all species in the aquatic system, such as species readily available for use by the algae, species incorporated in the algal biomass, and species bound in other forms that are not initially available but ultimately may become available to the algae. Comparison of total species often is used to evaluate phosphorus availability over the growing season in lakes and reservoirs having extended hydraulic retention times (several months to years) where high springtime inflows are a primary source of nutrients. Comparison of suspended species includes



**Figure 21.** The dominant nutrient species, (A) suspended and dissolved phosphorus, (B) suspended and dissolved organic nitrogen, and (C) dissolved ammonia and organic nitrogen in samples from the natural inflow site (BR1), the pumped inflow site (CR1), and sites in Lee Hall Reservoir (LH1, LH2, LH2.6, and LH3) and Harwoods Mill Reservoir (HM1), Virginia, June 2002–July 2003.

species incorporated in the algal biomass and species bound in other forms that are not initially available but ultimately may become available to the algae. Comparison of dissolved species likely is closest to including species available to algae for photosynthesis at the time the sample was collected and likely is a good indicator for the terminal reservoirs because of the short hydraulic retention times.

In both reservoirs and the pumped inflow (CR1), the N:P for total species concentrations was greater than 10:1, which indicates that phosphorus likely is the growth-limiting nutrient (fig. 22). During stormflow periods in the natural inflow (site BR1), the total N:P was consistently between 7:1 and 10:1, which also indicates that phosphorus likely is the growth-limiting nutrient. During some base-flow periods, the total N:P generally was less than 7:1 in the natural inflow, which indicates that nitrogen possibly is the growth-limiting nutrient in the inflow.

Suspended nitrogen and phosphorus provide a slightly different perspective. The suspended N:P was less than 7:1 in the natural inflow during both stormflow and base-flow periods and commonly in the reservoirs when suspended nitrogen concentrations were less than about 0.2 mg/L (fig. 22). A similar number of samples from the pumped inflow (site CR1) and sites LH1, LH2, and HM1 had N:P above and below 7:1. Site LH3 most consistently had an N:P greater than 7:1. Because this site receives water almost entirely from natural inflows and phosphorus concentrations at this site were similar to the high concentrations in the natural inflow, nitrogen concentrations appear to be partly derived from another source, possibly cycling within the reservoir or nitrogen fixation by blue-green algae. Because this relation is of suspended nutrient species, the relation represents the nutrient ratio in the algae plus other suspended particles. If healthy algae have a N:P of 7:1, the nitrogen concentration of the other suspended particles at site LH3 would be greater than that of the samples as a whole.

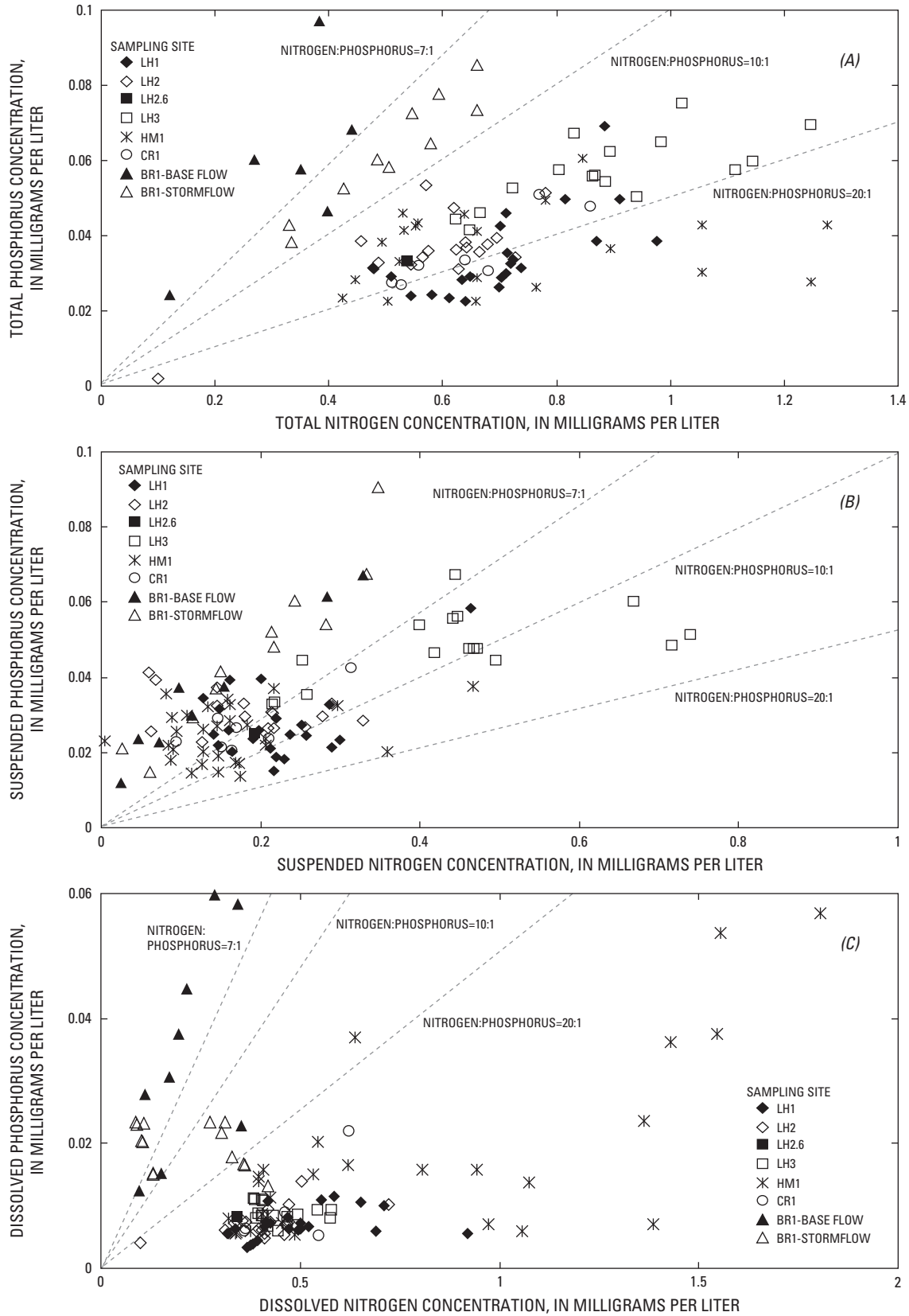
Dissolved nitrogen and phosphorus provide a perspective similar to that of the total species. The N:P at the reservoir sites and in the pumped inflow generally was greater than 20:1, but the N:P of a large number of the samples from site BR1 (particularly during base flow) was less than 7:1 (fig. 22). The low nitrogen to phosphorus ratio of the natural inflow results from a combination of low dissolved nitrogen concentrations and high dissolved phosphorus concentrations compared with other samples. Much of the dissolved phosphorus in the natural inflow appears to be used by algae in the reservoir and converted to particulate phosphorus, because the total phosphorus concentrations at site LH3 were similar to those in the natural inflow but the dissolved phosphorus concentrations were less. Although the N:P indicates that nitrogen could be the growth-limiting nutrient in the natural inflow, phosphorus appears to be the growth-limiting nutrient in the reservoirs when either suspended or dissolved nutrient species are considered.

## Vertical Distribution of Nutrients in the Water Column

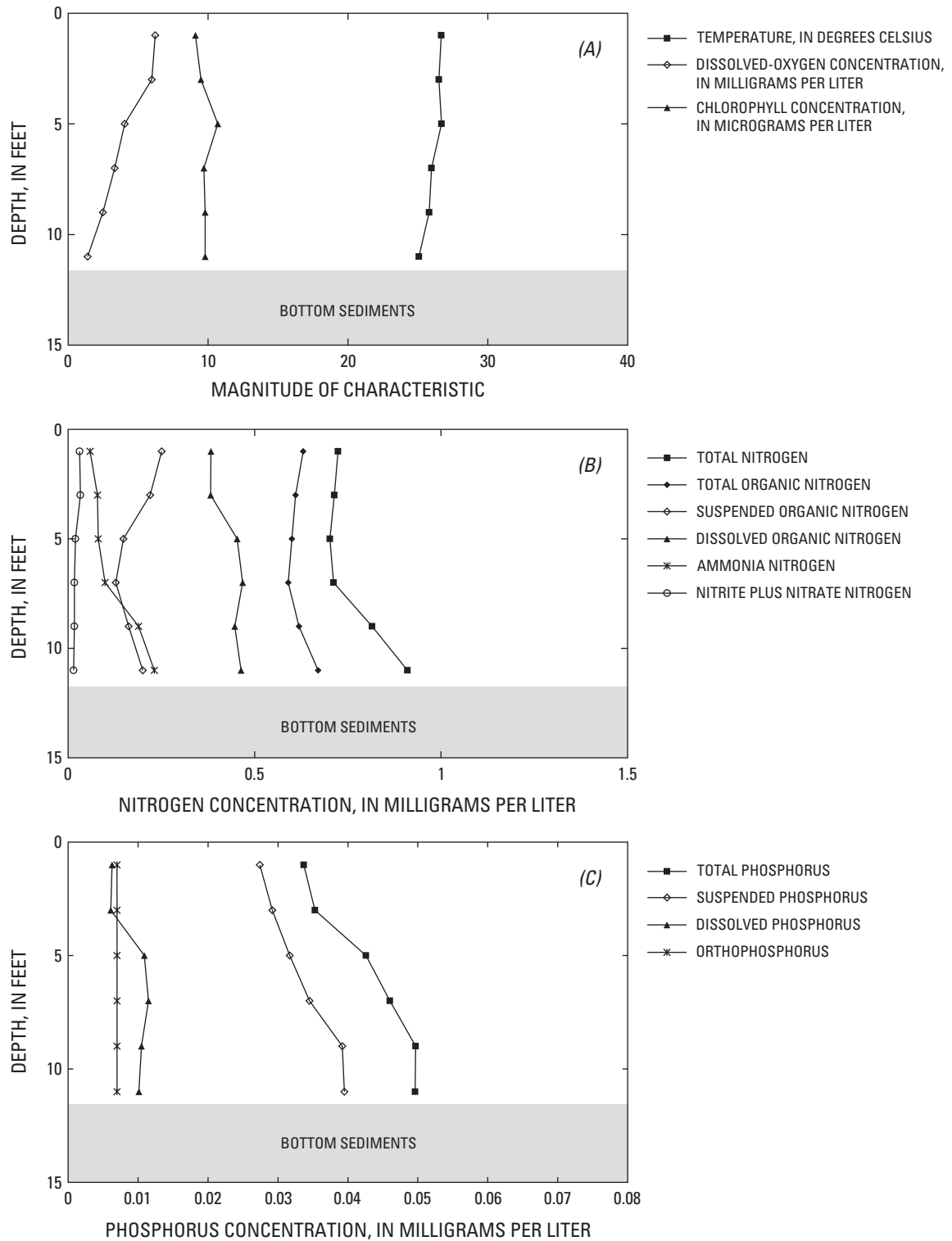
Concentrations of many nutrient species in reservoir bottom samples often were greater than those in surface samples. The vertical distribution of nutrient concentrations can provide useful information for evaluating whether bed sediment is a source of nutrients. Consequently, samples were collected at 1- to 2-ft depth intervals on August 12, 2003, at site LH1 and August 11, 2003, at site HM1 because the greatest vertical differences in nutrient concentrations occur during the summer.

On August 12, 2003, the vertical temperature difference at site LH1 was 1.6 °C and the gradient was rather uniform. Dissolved-oxygen concentrations were similar at depths from 1 to 3 ft (6.2 and 6.0 mg/L, respectively), and then they decreased uniformly to 1.4 mg/L at a depth of 11 ft (the bottom sample, fig. 23). Chlorophyll concentrations increased slightly from the surface to a peak at 5 ft and then decreased to a similar concentration (10 µg/L) below that depth.

The vertical distributions in nitrogen concentrations varied by species. Total nitrogen concentrations were rather uniform (0.71 to 0.72 mg/L) from the surface to a depth of 7 ft and then increased to 0.91 mg/L at a depth of 11 ft (fig. 23). The uniform total nitrogen concentrations to a depth of 7 ft indicate that changes in concentrations of individual species likely result from transformation among species. Dissolved organic nitrogen was the most abundant nitrogen species; concentrations increased from about 0.38 mg/L at depths of 1 and 3 ft to between 0.45 and 0.48 at depths between 5 and 11 ft. Because of the analytical uncertainty (indicated by the significant figures), this distribution could be viewed as either a general increase in concentration from the surface to the bottom or as a small increase in concentration between depths of 3 and 5 ft with uniform concentrations above and below these depths. Suspended organic nitrogen decreased from 0.25 to 0.13 mg/L between depths of 1 and 7 ft and then increased to 0.20 mg/L near the bottom. Because the increase in dissolved organic nitrogen concentrations mirrors the decrease in the suspended organic nitrogen concentrations, much of the decrease in suspended organic nitrogen is offset by the increase in dissolved organic nitrogen; thus, total organic nitrogen concentrations decrease only slightly from the surface to a depth of 7 ft (likely close to the analytical uncertainty) and then increase to the bottom. Ammonia concentrations increased gradually from 0.059 mg/L near the surface to 0.099 mg/L at a depth of 7 ft and then increased more sharply to 0.23 mg/L near the bottom. Nitrite plus nitrate concentrations were about 0.030 mg/L at depths of 1 and 3 ft and decreased from 0.020 mg/L at 5 ft to less than the 0.015-mg/L MRL at 11 ft. The increase in ammonia concentrations, suspended organic nitrogen, total organic nitrogen, and total nitrogen below a depth of 7 ft indicates possible settling and subsequent decomposition of algae and other particles from the photic zone (for all nitrogen species), resuspension of bed



**Figure 22.** Concentrations of (A) total nitrogen and total phosphorus, (B) suspended nitrogen and suspended phosphorus, and (C) dissolved nitrogen and dissolved phosphorus in samples from the natural inflow site (BR1), the pumped inflow site (CR1), and sites in Lee Hall Reservoir (LH1, LH2, LH2.6, and LH3) and Harwoods Mill Reservoir (HM1), Virginia, June 2002–July 2003.



**Figure 23.** Vertical distributions in (A) physical characteristics, (B) concentrations of nitrogen species, and (C) concentrations of phosphorus species at site LH1, Lee Hall Reservoir, Virginia, August 12, 2003.



sediment (for all nitrogen species), and(or) contribution by decomposition in bed sediment (for dissolved species only).

As commonly observed in Lee Hall Reservoir, orthophosphorus concentrations were less than the 0.007-mg/L MRL, and the total phosphorus was dominated by suspended phosphorus (fig. 23). Suspended phosphorus concentrations increased from 0.027 mg/L at a depth of 1 ft to 0.039 mg/L at a depth of 9 ft and changed little from 9 to 11 ft. Changes in dissolved phosphorus concentrations were small, and except for a shift between depths of 3 and 5 ft, vertical differences likely are close to the analytical uncertainty. Concentrations increased from 0.006 mg/L at depths of 1 and 3 ft to 0.011 and 0.012 mg/L at depths of 5 and 7 ft, respectively, and then decreased to 0.010 mg/L at 11 ft. The absence of an upward gradient of decreasing dissolved phosphorus concentrations in the deeper part of the reservoir indicates that the bed sediment may not be an appreciable source of dissolved phosphorus in Lee Hall Reservoir. The increase in suspended phosphorus to a depth of 9 ft likely indicates the importance of the settling of algae and other suspended particles and(or) the resuspension of bed sediment. Because of the short and narrow shape of the arm of the reservoir where site LH1 is located (fig. 3), the constriction by the causeway, and the forest along the north shore, resuspension at this site is less likely to be a factor.

At sites HM1, a thermocline was evident below a depth of 14 ft (fig. 24). In contrast, dissolved-oxygen concentrations were relatively uniform from the surface to a depth of 6 ft and then decreased sharply to near 0 mg/L at a depth of about 10 ft, which indicates that minimal vertical mixing began below depths of 6–10 ft, rather than below 14 ft as indicated by the water temperature. Chlorophyll concentrations were similar at depths of 1–6 ft, decreased at depths from 6 to 10 ft, and then increased sharply to a depth of 16 ft before decreasing toward the bottom. This pattern in chlorophyll concentration is consistent with patterns observed at other times and likely reflects the accumulation of algae, which settle into the hypolimnion, or the presence of green sulfur bacteria.

Dissolved organic nitrogen was the dominant nitrogen species from the surface to a depth of 13 ft below which ammonia nitrogen was the dominant species. Dissolved organic nitrogen concentrations showed a small, gradual increase with depth from 0.38 mg/L near the surface to 0.52 mg/L near the bottom; about two-thirds of the increase was below a depth of 16 ft. Suspended organic nitrogen had no distinct vertical pattern and ranged from 0.090 mg/L at a depth of 8–13 ft to 0.17 mg/L at a depth of 15 ft. Ammonia concentrations were uniformly less than the 0.015-mg/L MRL from the surface to a depth of 6 ft; concentrations then increased uniformly to a depth of 10 ft, and increased more sharply to 1.29 mg/L near the bottom. Nitrate concentrations were less than the 0.022-mg/L MRL at all depths except 8 ft where the concentration was 0.027 mg/L. The pattern in ammonia concentrations appears to reflect the controls of dissolved-oxygen concentrations. The interval from the surface to a depth of 6 ft where ammonia concentration is less than the MRL also is where the dissolved-oxygen concentrations

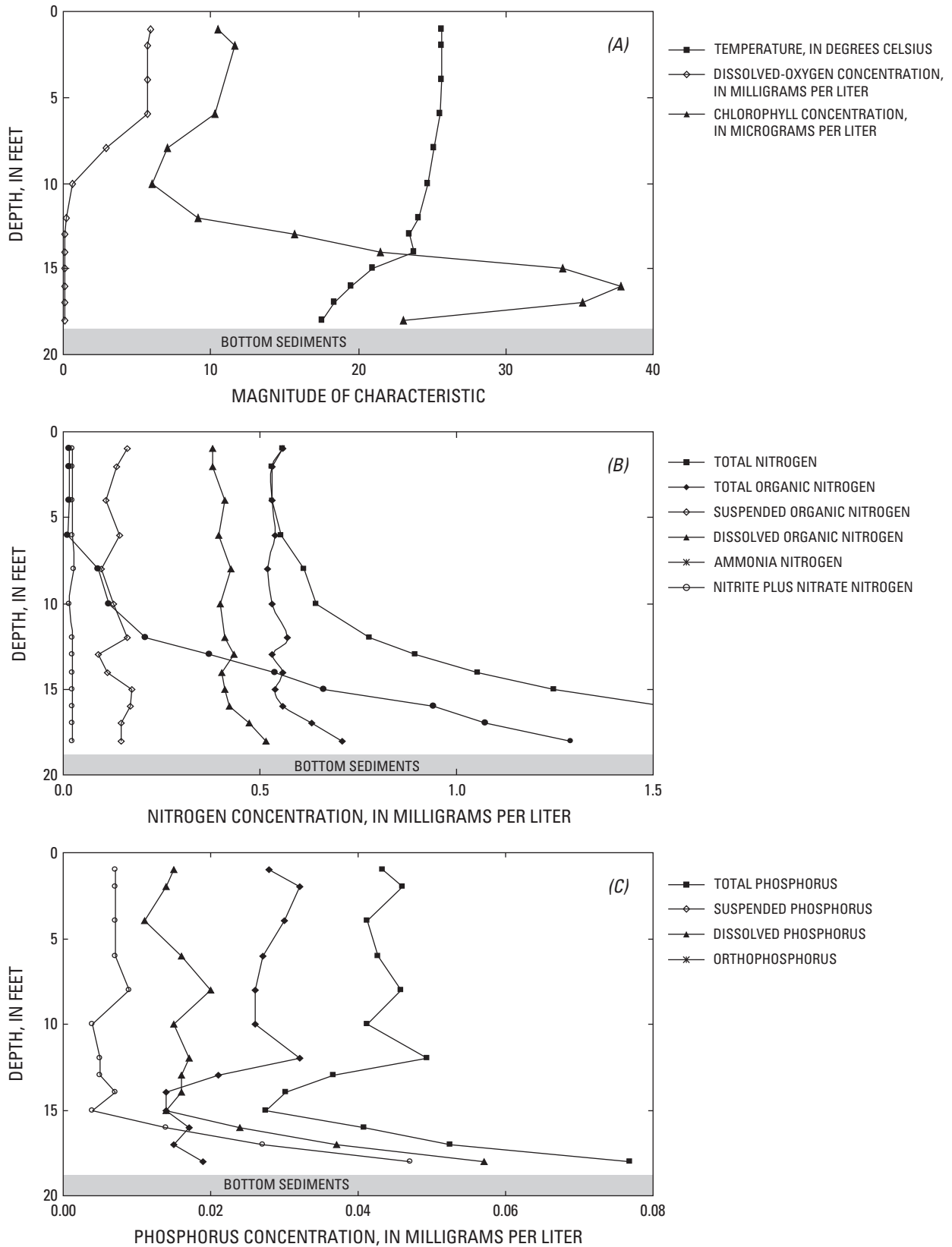
remained uniformly the highest within the water column. The interval from 6 to 10 ft where dissolved-oxygen concentrations decreased to near 0 mg/L also is the interval where ammonia concentrations gradually increased. The deeper part of the reservoir is where dissolved-oxygen concentrations were near 0 mg/L and ammonia concentrations increased most sharply with depth. Ammonia typically accumulates where dissolved-oxygen concentrations are low and ammonia that mineralizes from organic material cannot nitrify to nitrate. The distribution in ammonia concentrations supports the concept that minimal mixing likely occurs below a depth of 6–10 ft rather than below 14 ft. Nitrate that would form by nitrification of ammonia in the upper 6 ft likely would be used by algae. The 0.27 mg/L of nitrite plus nitrate at a depth of 8 ft appears to be below the photic zone where little vertical mixing occurs yet dissolved-oxygen concentrations are sufficient to promote nitrification; dissolved-oxygen concentrations appear to be too low for nitrification at greater depths.

Suspended phosphorus was the dominant phosphorus species from the surface to a depth of 14 ft, below which dissolved phosphorus was dominant (fig. 24). Changes in suspended phosphorus concentrations were near analytical uncertainty above a depth of 12 ft, decreasing from a peak of 0.032 mg/L at a depth of 2 ft to 0.026 mg/L at a depth of 8 ft and then increasing to 0.032 mg/L at a depth of 12 ft. Concentrations then decreased sharply to 0.014 mg/L at a depth of 14 ft and changed little to the bottom. Dissolved phosphorus concentrations decreased from 0.015 mg/L at a depth of 1 ft to 0.011 mg/L at a depth of 4 ft and then increased to 0.020 mg/L at a depth of 8 ft. Concentrations differed little between depths of 10 and 15 ft, averaging about 0.015 mg/L, and then increased sharply to 0.057 mg/L near the bottom. Except for the 0.009-mg/L orthophosphorus concentration at a depth of 8 ft, orthophosphorus concentrations were less than the 0.007-mg/L MRL from the surface to a depth of 15 ft; concentrations from 10 to 15 ft appear to vary slightly because values below the MRL were estimated through this interval but not above it. Because the increased dissolved phosphorus only extends from a depth of 15 ft to the bottom and dissolved-oxygen concentrations indicate that the mixing boundary between the epilimnion and hypolimnion is between 6 and 10 ft, the elevated dissolved phosphorus cannot serve as a source of phosphorus to algae in the photic zone while the reservoir is stratified whether it is derived from settling particles or bed sediment.

## Release of Phosphorus from Suspended Particles

Release of phosphorus from particles suspended in the water column is a possible source of dissolved phosphorus for use by algae; this release may be reflected in the vertical distributions of phosphorus concentrations in the water column. In samples collected August 11 and 12, 2003, from sites LH1S, HM1S, and HM1B and subsequently incubated in





**Figure 24.** Vertical distributions in (A) physical characteristics, (B) concentrations of nitrogen species, and (C) concentrations of phosphorus species at site HM1, Harwoods Mill Reservoir, Virginia, August 11, 2003.

the laboratory, dissolved phosphorus concentrations increased at rates of 0.0007, 0.0014, and 0.0019 (mg/L)/d, respectively (fig. 25). At such rates, the dissolved phosphorus concentration present in the samples for each site at the start of incubation could be derived by release from suspended particles in 8, 11, and 30 days, respectively. The dissolved phosphorus concentration in August near the bottom of site HM1 (HM1B) would represent the dissolved phosphorus derived from all sources, including that in the water at the time of stratification, releases from the bed sediment, and release from particles in the water column since Harwoods Mill Reservoir stratified and isolated the hypolimnion from the epilimnion in May 2003 (fig. 17). Because the reservoir had been stratified for nearly 90 days when the August samples were collected, release of phosphorus from particles in the water column at the rate identified for HM1B could contribute two to three times the maximum dissolved phosphorus concentration observed at site HM1 on August 11, 2003.

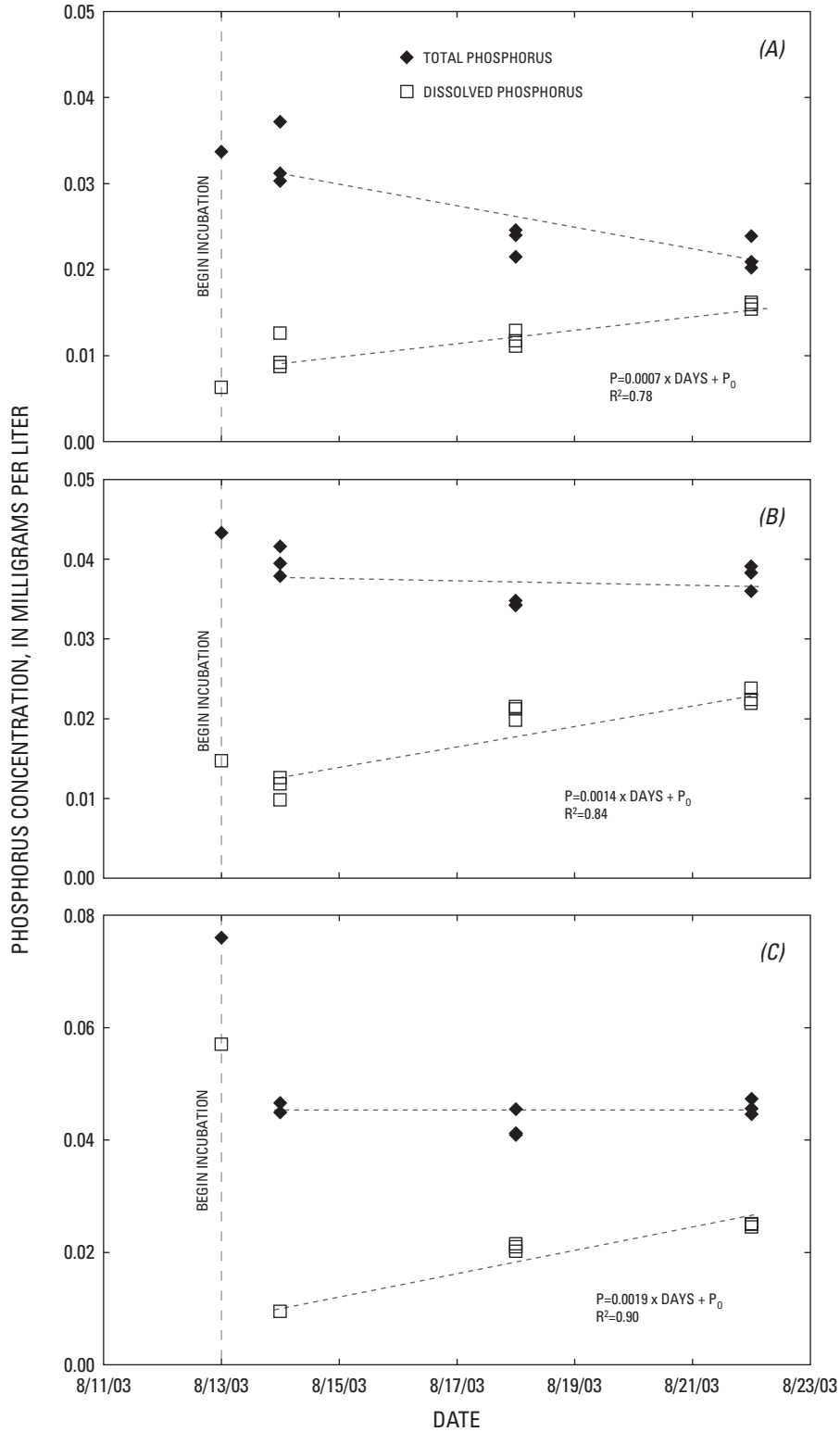
The dissolved phosphorus concentrations in the HM1B samples at the end of the first day, however, were substantially less than the concentration originally measured in the sample (fig. 25C). This likely resulted from aeration of the sample (the hypolimnion was anoxic) during sample collection, which could have oxidized dissolved iron to form poorly crystallized iron oxide particles that could have bound to the dissolved phosphorus. Particles appeared to adhere to the sides of the bottles and could not be entirely resuspended by shaking. This also would account for the lower total phosphorus after the start of incubation. Thus, it is not certain if the phosphorus that dissolved during incubation was from the precipitated iron oxide particles, the particles originally present in the sample, or both. Another perspective can be obtained by using the rate of release of dissolved phosphorus from the HM1S samples because total phosphorus concentrations at HM1S were less than those at HM1B (likely resulting in a slower release rate), and particles settle from HM1S to HM1B. The rate of production of dissolved phosphorus in the HM1S samples was 74 percent of the rate for HM1B samples, which would account for the dissolved phosphorus concentration originally in HM1B samples in 41 days, well within the nearly 90 days the reservoir had been stratified. Thus, the increase in dissolved phosphorus below 15 ft can be accounted for largely by release from suspended particles in the water column. Furthermore, such release would provide a continued phosphorus source in Lee Hall Reservoir and in the epilimnion of Harwoods Mill Reservoir while the reservoir is stratified. Consequently, although phosphorus release from bed sediment is possible, bed sediment likely is a minor source of phosphorus in the two terminal reservoirs. The possible contribution of phosphorus from bed sediment to the water column will be discussed further later in this report.

## Effects of Copper-Sulfate Application

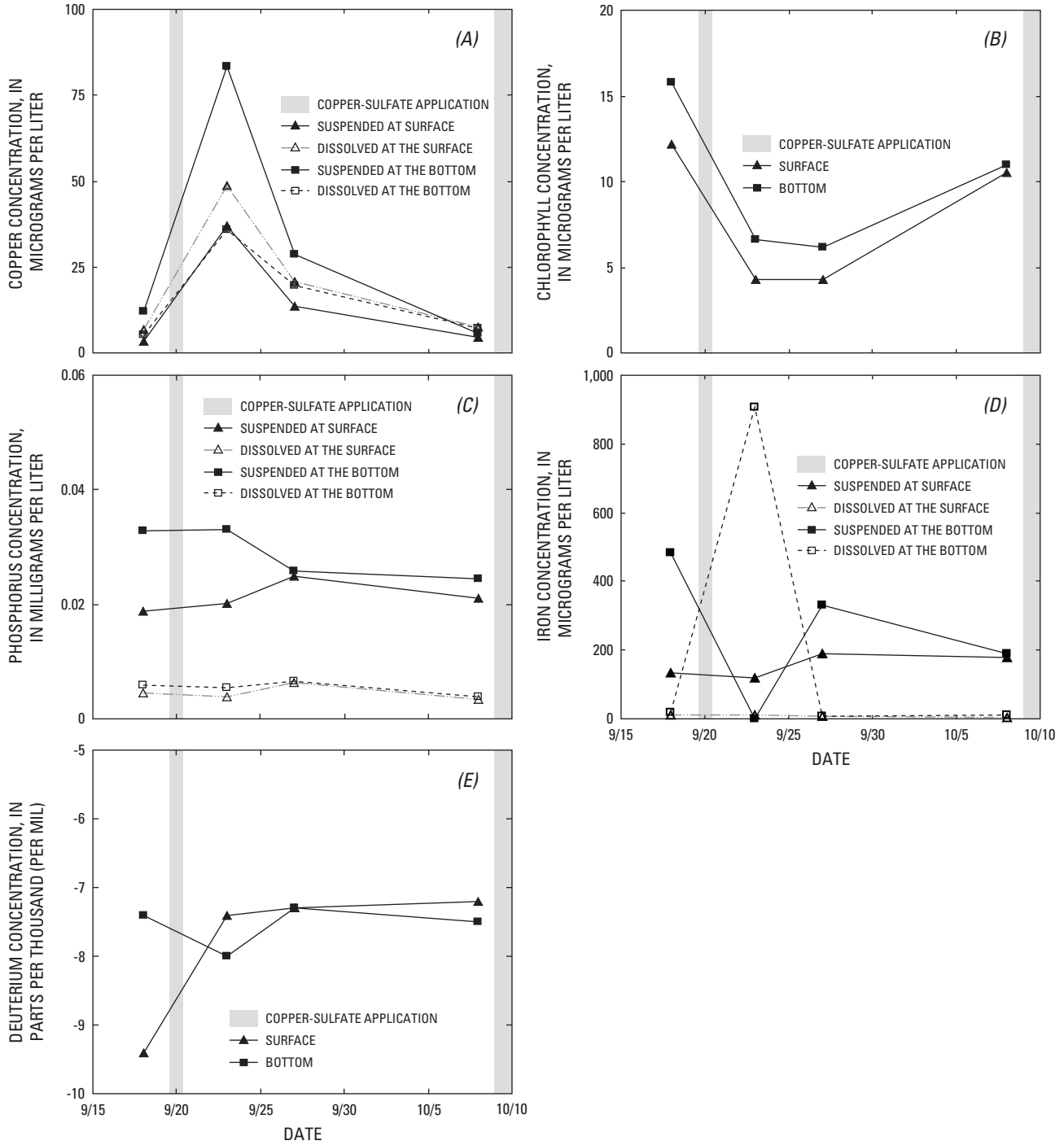
Because of the extreme drought conditions during the study of the application of copper sulfate, reservoir inflows were largely pumped from outside watersheds. Consequently, pumpage from the reservoirs largely controlled hydraulic retention times because inflow and outflow were similar when accounting for evapotranspiration. Additionally, the upper part of Lee Hall Reservoir was not part of the main circulation in that reservoir. The control of flow by pumpage, particularly through Lee Hall Reservoir, helps to evaluate the processes controlling concentrations of phosphorus, copper, and other constituents.

Thirty-six hundred pounds of copper sulfate were applied to Lee Hall Reservoir on September 20, and during October 9–10, 2002 (Horace Davis, City of Newport, oral commun., 2002). Pumped inflow rates during that period ranged from 14.0 to 36.9 Mgal/d and averaged 24.5 Mgal/d; withdrawal rates during that period ranged from 16.2 to 29.6 Mgal/d and averaged 25.8 Mgal/d (Ronald Harris, City of Newport News, written commun., 2003). Thus, pumped inflow averaged 95 percent of the withdrawal. The small difference between the pumped inflow and withdrawals likely resulted from the combined effects of natural inflows, changes in reservoir storage, and evaporation. Natural inflows, however, likely were more than 5 percent of the withdrawal because evaporation from the reservoir surface likely was substantial. Lee Hall Reservoir was not stratified during the study. Accordingly, the hydraulic retention time of the reservoir based on the withdrawal rate would have averaged 17 days.

Based on average depths of 11 ft at site LH1, 12 ft at site LH2, and 9 ft at site LH3 during the copper-sulfate application study, copper concentrations after complete vertical mixing theoretically would have increased 62, 56, and 75  $\mu\text{g/L}$ , respectively. Increases in copper concentrations observed during the first sample collection following the first application of copper sulfate likely are less than the maximum increase because samples were collected 3 days after application. At site LH1, the total copper concentration (sum of suspended and dissolved copper concentrations) actually increased 76  $\mu\text{g/L}$  near the surface from 10  $\mu\text{g/L}$  before the first application to 86  $\mu\text{g/L}$  3 days after the application (fig. 26). Near the bottom, total copper concentrations increased 101  $\mu\text{g/L}$  from 18  $\mu\text{g/L}$  before the first application to 119  $\mu\text{g/L}$  3 days after the application. These increases are greater than the 62- $\mu\text{g/L}$  increase calculated for site LH1. Approximately 42 percent of the copper near the surface was suspended, whereas about 70 percent of the copper near the bottom was suspended. The suspended copper concentration near the bottom was 83  $\mu\text{g/L}$ , substantially greater than the 36.8  $\mu\text{g/L}$  near the surface. Concentrations of both suspended and dissolved copper decreased from September 23 through October 8 to concentrations similar to those before the September 20 application (fig. 26).



**Figure 25.** Changes in total phosphorus and dissolved phosphorus concentrations in samples collected from (A) site LH1S in Lee Hall Reservoir on August 12, 2003, and (B) site HM1S and (C) site HM1B in Harwoods Mill Reservoir on August 11, 2003, then incubated in the dark at 25 degrees Celsius. ( $P_0$  is the regression line phosphorus concentration on August 13, 2003; P is phosphorus concentration on the designated day after August 13, 2003.)



**Figure 26.** Changes in concentrations of (A) copper, (B) chlorophyll, (C) phosphorus, (D) iron, and (E) deuterium during the copper-sulfate application study, September 17–October 8, 2002, at site LH1, Lee Hall Reservoir, Virginia.

At site LH2, the total copper concentration near the surface increased 85  $\mu\text{g/L}$  from 10  $\mu\text{g/L}$  before the first application to 95  $\mu\text{g/L}$  3 days after the application (fig. 27). Near the bottom, total copper concentrations only increased 35  $\mu\text{g/L}$  from 15 to 50  $\mu\text{g/L}$  during the period. These increases bracket the 56- $\mu\text{g/L}$  increase calculated for site LH2. Approximately 40 percent of the copper near the surface was suspended whereas only 17 percent of the copper near the bottom was suspended. The suspended copper concentration near the bottom appears to be somewhat anomalous compared with data for the other sites and other sampling periods at this site and, therefore, may be an erroneous value. The suspended copper concentration near the bottom was only 8.4  $\mu\text{g/L}$ , substantially less than the 38  $\mu\text{g/L}$  near the surface. Concentrations of both forms of copper (except suspended copper at site LH2B) decreased from September 23 through October 8 (fig. 27).

At site LH3, the total copper concentration near the surface increased 79  $\mu\text{g/L}$  from 13  $\mu\text{g/L}$  before the first application to 92  $\mu\text{g/L}$  3 days after the application (fig. 28). Near the bottom, total copper concentrations increased 55  $\mu\text{g/L}$  from 37  $\mu\text{g/L}$  before the first application to 92  $\mu\text{g/L}$  3 days after that application. These increases also bracketed the 75- $\mu\text{g/L}$  increase calculated for site LH3. Approximately 54 percent of the copper near the surface was suspended, and 61 percent of the copper near the bottom was suspended. Concentrations of both suspended and dissolved copper decreased for the remainder of the copper-sulfate application study.

Throughout the copper-sulfate application study, copper concentrations remained well below the action levels for public supplies. Dissolved copper concentrations at all sites, however, were near the concentrations for both chronic (6  $\mu\text{g/L}$ ) and acute (8  $\mu\text{g/L}$ ) toxicity for aquatic life immediately before the application of copper sulfate and well above these concentrations after application.

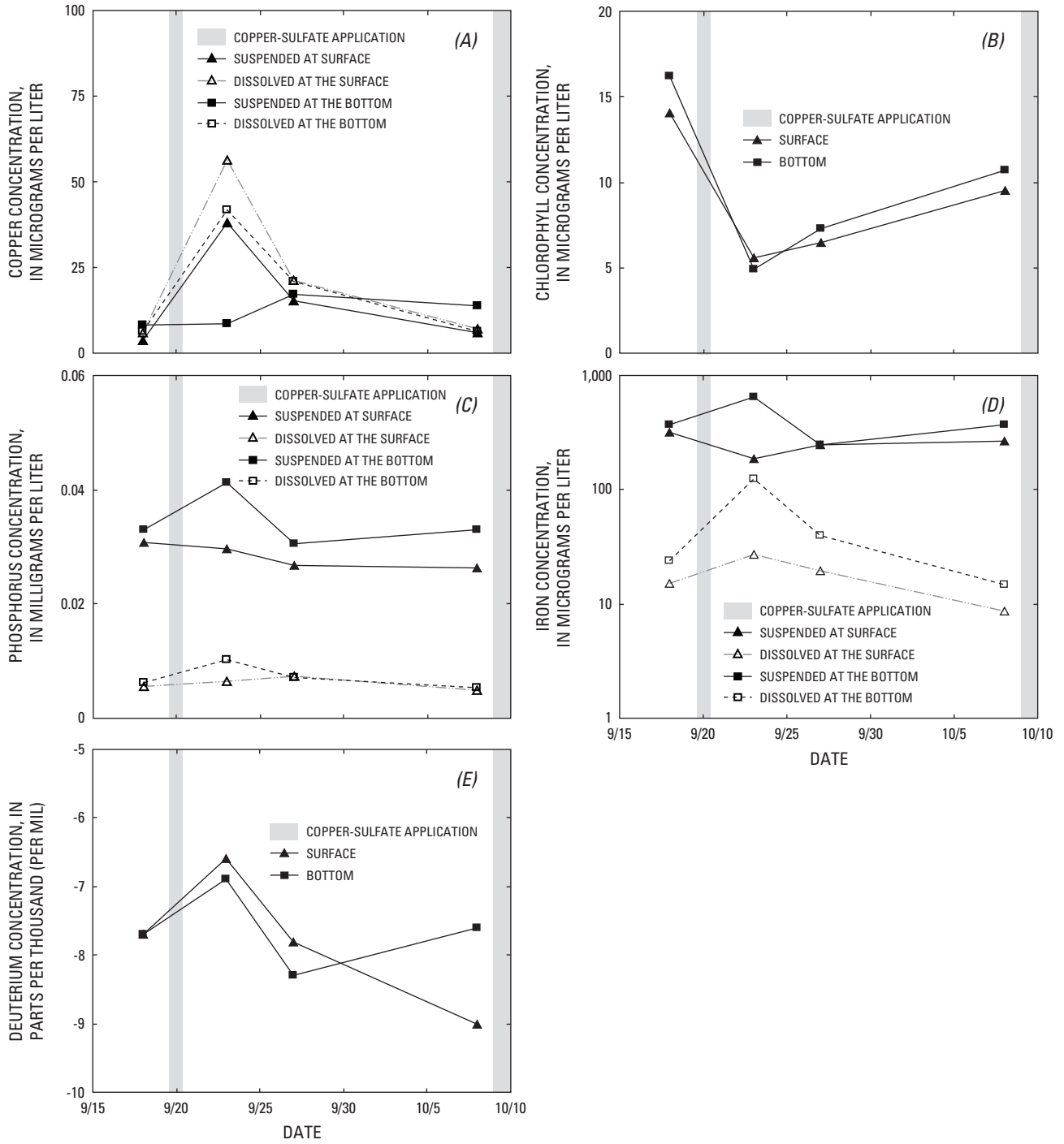
The presence of substantial amounts of suspended copper, which was applied as a dissolved solution, and higher suspended copper concentrations in bottom than in surface samples (except the first sample collected at site LH2 after copper-sulfate application) indicate that the copper readily became bound to particles, possibly algae, and then settled from suspension. The decrease in concentrations of both species of copper after the increase following application likely resulted from two processes: settling of the particles and dilution with natural and newly pumped inflow water containing little copper. The decrease in copper concentrations at site LH3 clearly indicates settling because this site was affected minimally by dilution—natural inflows were small as a result of the drought conditions, and pumped inflow minimally affects the site. The effects of settling at site LH1 also were large; dilution likely had little effect until late in the study because the 17-day hydraulic retention time means that water entering the reservoir when copper was first applied on September 20 did not reach site LH1 under plug-flow conditions until about October 7. Part of the decrease in concentration from September 27 to October 8 could have resulted

from dilution, although the observed decrease during this period was small. Although the temporal patterns in copper concentrations generally were similar, the relative effects of settling and dilution at site LH2 are not as clear. Because this site is closer to the source of pumped inflow, dilution is more likely to affect concentrations by September 27 at site LH2 than at the other sites.

Chlorophyll concentrations decreased near the surface and bottom of all three sites in Lee Hall Reservoir after the first copper-sulfate application but increased again before the second application (figs. 26–28). Such a decrease in chlorophyll concentrations is an expected and intended consequence of the application because of the toxic effects of copper on algae. Chlorophyll concentrations at site LH3 were two to four times those at sites LH2 and LH1 throughout the copper-sulfate application study; chlorophyll concentrations at site LH1 were similar to those at site LH2. Chlorophyll concentrations generally were greater near the reservoir bottom than near the surface at all sites, indicating the effects of settling of algae, even before copper-sulfate application. The chlorophyll concentrations immediately before the first application were greater than the concentrations immediately before the second application at all three sites. This could have resulted from seasonal changes in the size or chlorophyll content of the algal populations with fall approaching or from differences in factors affecting the decision to apply copper sulfate. This decision typically is based on the plugging of water filters in the water-treatment plant, which reduces the times between when the filters must be backwashed. Materials other than algae, such as organic material not derived from algae, can cause such plugging and can trigger the decision to apply copper sulfate.

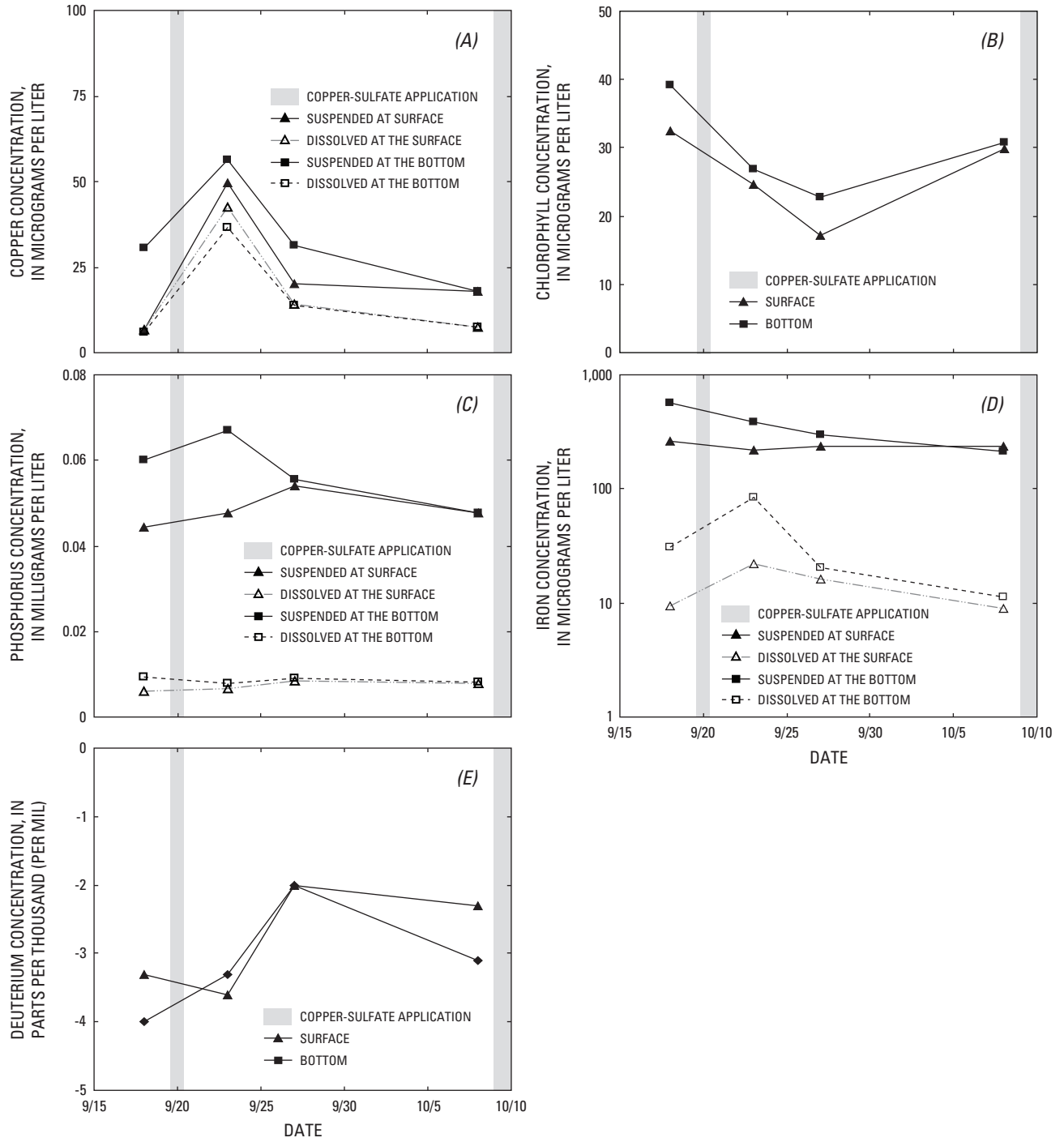
Phosphorus concentrations changed substantially less than copper and chlorophyll concentrations throughout the duration of the copper-sulfate application study (figs. 26–28). The expectation was that suspended phosphorus concentrations would decrease as algae die and dissolved phosphorus concentrations would increase as dead algae decay and release phosphorus. Such patterns, however, were not clearly evident. As during other sample-collection periods, phosphorus was present predominantly as suspended species. Dissolved phosphorus concentrations generally were less than 0.01 mg/L and generally were greater at site LH3 than site LH2 and greater at site LH2 than site LH1. Concentrations of both species generally were greater near the bottom than near the surface at all three sites during the beginning of the study and became similar at both depths (especially dissolved phosphorus) later in the copper-sulfate application study. Suspended phosphorus concentration possibly did not decrease after copper-sulfate application because a large part of the suspended particles may be incorporated in nonalgal organic material or remain bound in algal cells after they die and chlorophyll breaks down, or become resuspended from bottom sediment.

Iron consisted primarily of suspended iron in Lee Hall Reservoir except for the samples collected on September 23 at site LH1 (figs. 26–28). When iron concentrations



**Figure 27.** Changes in concentrations of (A) copper, (B) chlorophyll, (C) phosphorus, (D) iron, and (E) deuterium during the copper-sulfate application study, September 17–October 8, 2002, at site LH2, Lee Hall Reservoir, Virginia.





**Figure 28.** Changes in concentrations of (A) copper, (B) chlorophyll, (C) phosphorus, (D) iron, and (E) deuterium during the copper-sulfate application study, September 17–October 8, 2002, at site LH3, Lee Hall Reservoir, Virginia.

differed between the surface and the bottom, suspended iron concentrations were higher near the bottom, indicating the effects of settling. The dissolved iron concentrations were less than 100 µg/L in 10 of 12 samples and were higher in bottom than in surface samples. Dissolved iron concentrations increased near the bottom at all sites immediately after the copper-sulfate application. Although release of dissolved iron from the bed sediment by the reduction of poorly crystallized iron oxides would release dissolved phosphorus bound to the iron oxides, dissolved phosphorus concentrations in bottom samples increased only at site LH2 and decreased slightly at sites LH1 and LH3 (figs. 26–28). The low dissolved iron concentrations and small difference in concentrations between the bottom and the surface likely indicate little release of phosphorus bound to iron oxides from the bed sediment.

Deuterium concentrations appeared to be affected more by evaporation at site LH3 than at sites LH1 and LH2 (figs. 26–28) as also is indicated in figure 15. The differences in deuterium concentrations between surface and bottom samples were small relative to differences in concentrations between site LH3 and sites LH1 and LH2.

Thirty-five hundred pounds of copper sulfate were applied to Harwoods Mill Reservoir on September 19 and October 8, 2002 (Horace Davis, City of Newport News, oral commun., 2002). Pumped inflow rates during that period ranged from 12.0 to 25.0 Mgal/d and averaged 20.2 Mgal/d; withdrawal rates during that period ranged from 20.9 to 36.9 Mgal/d and averaged 22.8 Mgal/d (Ronald Harris, City of Newport News, written commun., 2003). Thus, pumped inflow averaged 89 percent of the withdrawal. The bottom of the epilimnion based on the dissolved-oxygen profile at site HM1 would have been between 8 and 12 ft the day before the first application. Using a depth of 12 ft, the hydraulic retention time would have averaged 31 days and the copper concentration would have increased 102 µg/L after complete vertical mixing in the epilimnion.

At site HM1, the total copper concentration near the surface increased by 74 µg/L from 23 µg/L before the first application to 97 µg/L 4 days after application (fig. 29), less than the calculated 102 µg/L increase. This smaller increase in part resulted from the settling of copper into the hypolimnion as indicated by the increase in concentration near the bottom by 14 µg/L from 19 to 33 µg/L between application and sample collection. Approximately 48 percent of the copper near the surface was suspended, whereas about 97 percent near the bottom was suspended. The distribution of copper between dissolved and suspended copper and the increase in suspended copper near the bottom indicate that although the copper was applied as a dissolved solution, copper binds to particles and settles from solution. The small change in the dissolved copper concentration near the bottom after copper-sulfate application substantiates the effectiveness of stratification in minimizing circulation between the epilimnion and hypolimnion. Because the dissolved-copper concentration near the bottom remained less than 1 µg/L after the initial application (fig. 29) in contrast to increases noted at sites in Lee Hall Reservoir (figs. 26–28),

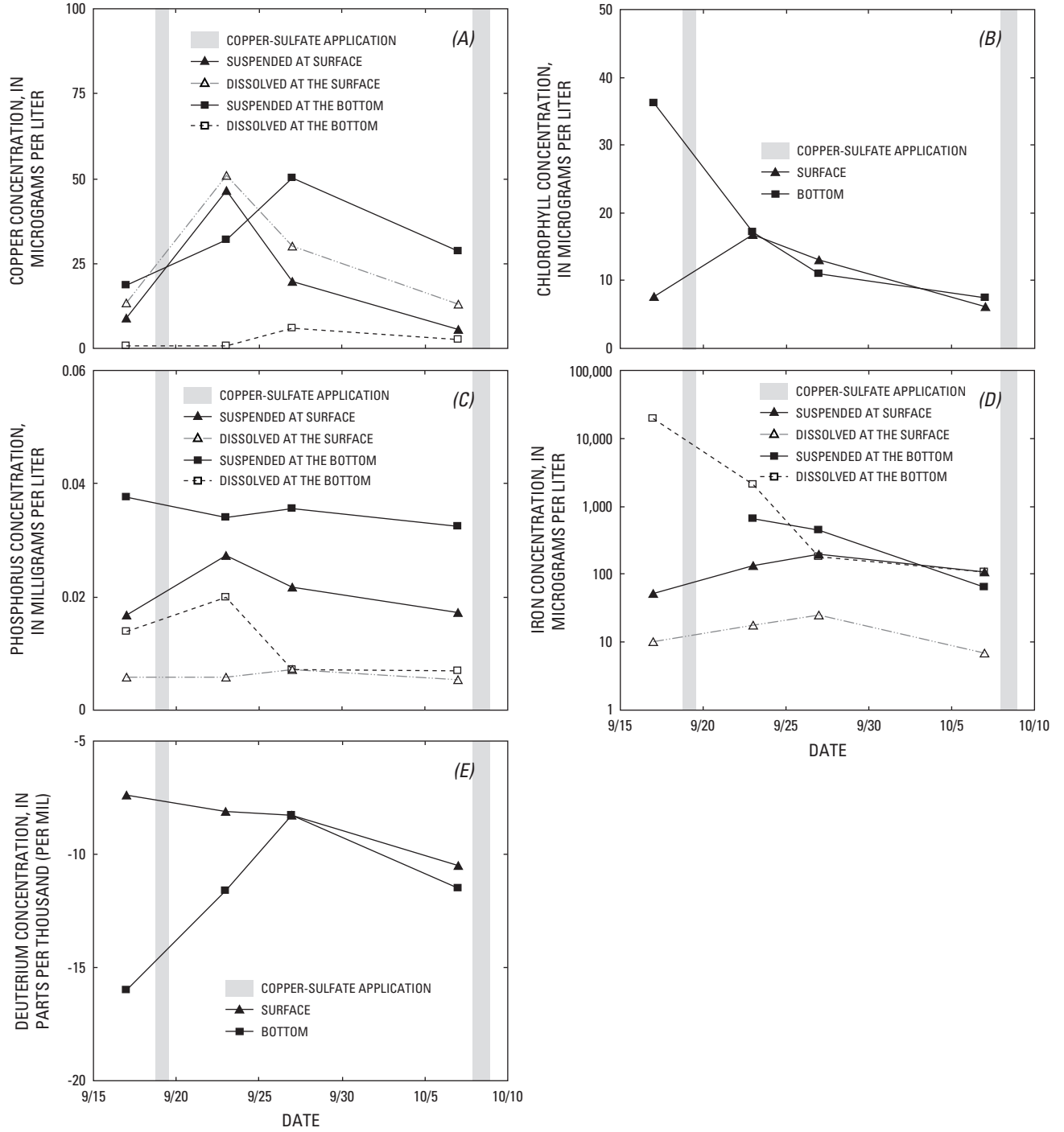
copper appears to remain bound to particles in suspension and in the bed sediment in Harwoods Mill Reservoir.

Throughout the copper-sulfate application study, copper concentrations remained well below the action levels for public supplies at both the surface and bottom at site HM1. Dissolved copper concentrations near the surface at site HM1, however, were above the concentrations for both chronic (6 µg/L) and acute (8 µg/L) toxicity for aquatic life throughout the study. Near the bottom, concentrations were less than the toxic concentrations except on September 27 when the concentration equaled the concentration for chronic toxicity.

The slight increase in the dissolved copper concentration to 6 µg/L near the bottom on September 27 appears to result partly from the breakdown of thermal stratification indicated by vertical profiles of water temperature, dissolved-oxygen concentrations, and deuterium concentrations (fig. 29). The breakdown of stratification appears to have started by September 23, based on changes in deuterium concentrations. Although the depth to which mixing extends in the epilimnion of Harwoods Mill Reservoir can be difficult to evaluate when the reservoir is stratified, the shift in deuterium from a difference of 8.6 per mil between the surface and bottom prior to application to a concentration of -8.3 per mil at both depths clearly indicates that the reservoir became mixed by September 27.

Chlorophyll concentrations at site HM1 decreased sharply near the bottom and increased near the surface from before to after the first application of copper sulfate (fig. 29B). This also appears to result from the initial breakdown of thermal stratification as the zone of high chlorophyll in the hypolimnion that began to mix with the epilimnion by September 23. Chlorophyll concentrations at both depths then decreased into October and approached the chlorophyll concentrations observed in the epilimnion when the reservoir was stratified.

Phosphorus concentrations were dominated by suspended phosphorus at both the surface and the bottom; suspended phosphorus concentrations were higher near the bottom than near the surface, even after the breakdown of stratification, indicating continued settling of suspended particles (fig. 29C). Concentrations changed little near the bottom throughout the study. The increase near the surface and small decrease near the bottom after the application could result from the onset of vertical mixing with the breakdown of stratification. The subsequent decrease near the surface with higher concentrations near the bottom than near the surface likely resulted from settling as the reservoir continued to vertically mix. Dissolved phosphorus concentrations were higher near the bottom than near the surface because dissolved phosphorus accumulated near the bottom while the reservoir was stratified; dissolved concentrations became similar at both depths when the reservoir mixed after the breakdown of stratification. Accumulation of dissolved phosphorus near the bottom could have resulted from the combined release from suspended particles and bed sediment, but most likely resulted from release from particles in the water column.



**Figure 29.** Changes in concentrations of (A) copper, (B) chlorophyll, (C) phosphorus, (D) iron, and (E) deuterium during the copper-sulfate application study, September 17–October 8, 2002, at site HM1, Harwoods Mill Reservoir, Virginia.

Suspended iron concentrations were greater than dissolved iron concentrations near the surface where the water contained abundant dissolved oxygen that would have oxidized the reduced iron and formed iron-oxide particles; suspended concentrations were substantially higher near the bottom than near the surface throughout September but were similar in October (fig. 29D). Dissolved iron concentrations (not shown) were almost 20,000  $\mu\text{g/L}$  near the bottom as a result of the reducing conditions during stratification but decreased through September 27 as stratification broke down and the water became aerobic.

## Settling of Phosphorus as Bed Sediment

Although suspended phosphorus concentrations in the water column changed little during the copper-sulfate application study, settling of suspended phosphorus as bed sediment is potentially a major process (fig. 30). During the sedimentation study, particles that settled into the collectors appeared “light weight and fluffy” and were readily resuspended during collector retrieval, although the particles were retained in the collector by the collector top. The greatest variability in the settling was at sites LH1 and LH3 where only one sample collector was deployed, and uncontaminated samples were collected during only two of the three sampling periods. At site LH2 the difference in settling rate between collection times was less than at sites LH1 and LH3, but variability among replicates was substantial. Replicate samples having the highest settling rates were greater than those having the lowest settling rate by 118 percent on September 23, 5 percent on September 27, and 86 percent on October 8. Using the range in observed settling rates of 0.0017 to 0.16 (mg/L)/d and the range in suspended phosphorus concentrations observed during the settling study, all of the suspended phosphorus in the water column would be expected to settle from the water column in 2 to 34 days. The actual magnitude of the settling, however, remains uncertain because of the small number of samples and the high variability among replicate samples and among samples collected at different times at the same site.

## Bed-Sediment and Interstitial-Water Quality

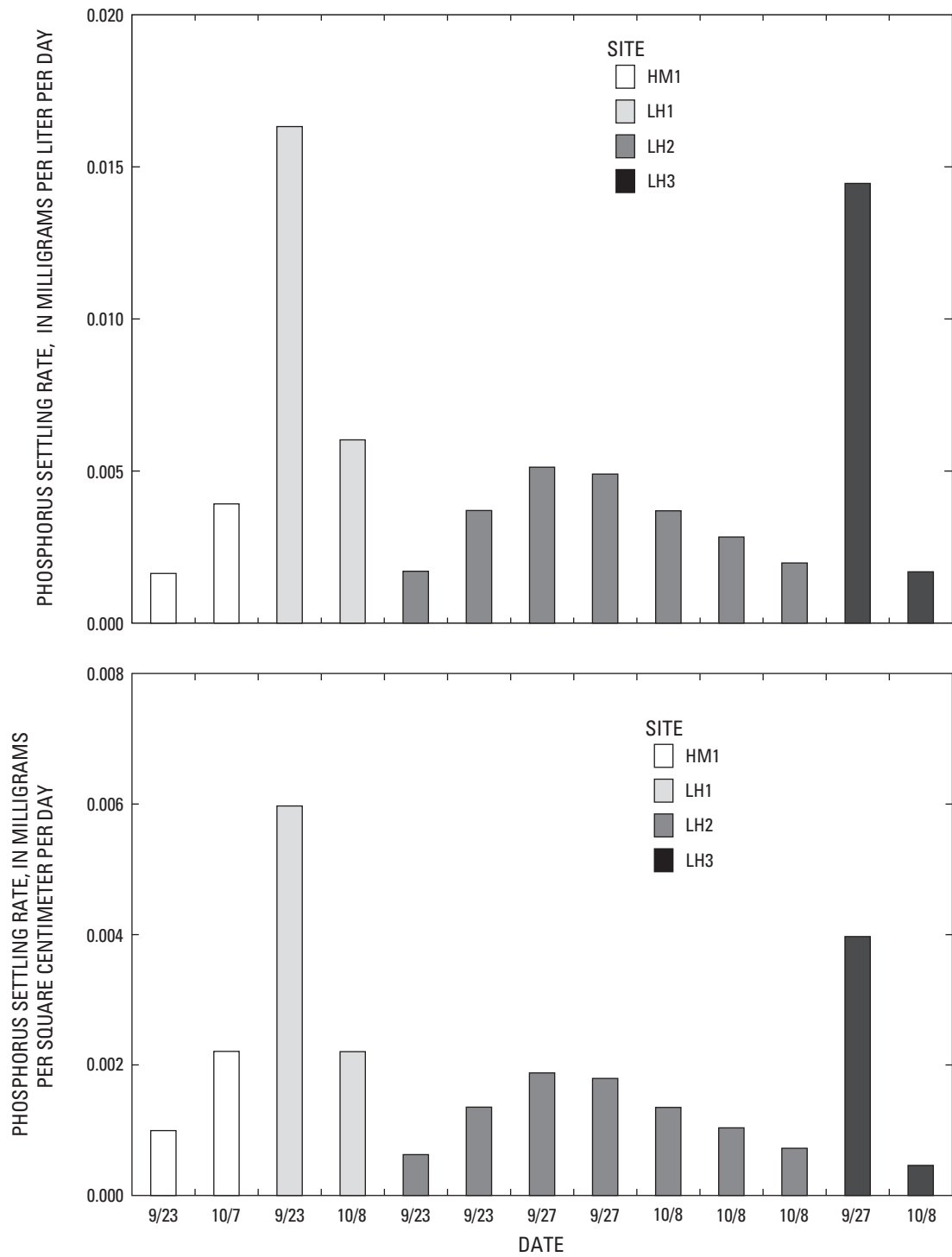
Bed-sediment and interstitial-water samples were collected from Lee Hall Reservoir on August 30, 2003; bed-sediment samples were collected from Harwoods Mill Reservoir on October 29, 2003. Bed sediment appeared to be physically similar in both reservoirs in many respects. The bed sediment present throughout both reservoirs when the reservoirs were constructed (original bed sediment) was a light gray, silty clay or clayey silt. Little additional sediment appeared to have been deposited over the original bed sediment near the shores of the reservoirs, probably because of the turbulence created by waves and other currents. Sediment that was deposited near the shore generally was sandy.

Vertical sediment profiles of deposited sediment also were similar at most locations at some distance from the shores in both reservoirs. The uppermost several inches of sediment consisted of a loose, fluffy, and almost fluid, dark gray, fine-grained deposit. Although this sediment was loose, it was more consolidated than the sediment deposited in the collectors during the phosphorus settling study. Sediment underlying the upper loose sediment was similar in color to the upper sediment but was extremely cohesive.

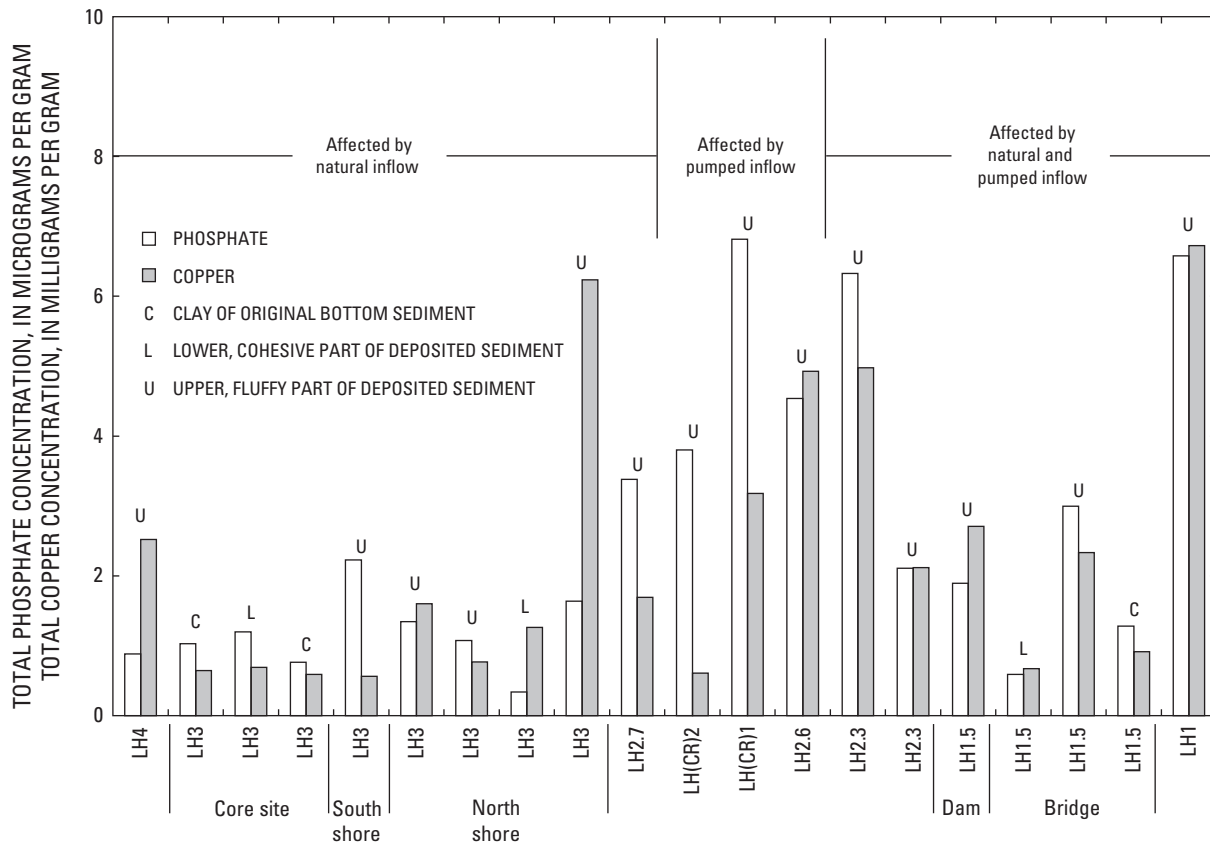
Of all the bed-sediment samples collected, benthic macroinvertebrates were observed in only two samples from Lee Hall Reservoir and in no samples from Harwoods Mill Reservoir during either sample collection or processing. One site having benthic macroinvertebrates was near the shore at site LH3 and the other was at site LH(CR)2. The near-shore sample at site LH3 was collected from a shallow cove where copper-sulfate application could have been limited. The LH(CR)2 sample was collected upstream from where copper-sulfate application appeared to have significant effects because the area contained abundant algal mats that were present nowhere else in areas of the reservoir visited. Although samples of aquatic vascular plants were collected from Lee Hall Reservoir near site LH3, none of the plants were rooted to the reservoir bottom. Of the several observed plant clusters, all were floating and appeared to have been blown by wind from other parts of the reservoir. No floating or rooted aquatic plants or algal mats were identified in the parts of Harwoods Mill Reservoir visited during sediment-sample collection.

The moisture content of the sediment reflects the difference in sediment consistency. Grab samples from Lee Hall Reservoir were collected primarily from the uppermost sediment layer. The moisture content of nine samples of upper sediment ranged from 29.9 to 85.6 percent with a median of 72.7 percent (table 5). Samples of both the upper fluffy and the lower cohesive sediment were collected from Harwoods Mill Reservoir. The moisture content of nine samples of upper sediment ranged from 58.2 to 89.0 percent with a median of 82.0 percent (table 6). The moisture content of five samples of the lower sediment ranged from 50.2 to 71.4 percent with a median of 55.9 percent. Thus, the fluffy upper sediment generally contained more water than the more cohesive, lower sediment, which could account for the differences in the consistency of these sediments.

Phosphate concentrations generally were less in grab and split-spoon samples of bed sediment from two sites in the upper part of the arm of Lee Hall Reservoir primarily affected by natural inflows (sites LH3 and LH4) than in bed sediment from the lower part of the arm (site LH2.7) and parts of the reservoir affected by the pumped inflow or both inflows (fig. 31). Phosphate concentrations from the part of the reservoir affected only by natural inflows ranged from 0.3 to 3.4 micrograms per gram ( $\mu\text{g/g}$ ). Only concentrations in samples from the south shore and near the causeway (site LH2.7) were greater than 1.6  $\mu\text{g/g}$ . Total phosphate concentrations in box-core samples from site LH3 decreased with depth from 3.4  $\mu\text{g/g}$  at the sediment surface (0.5 cm)



**Figure 30.** Rate of phosphorus settling during the copper-sulfate application study, September 17–October 8, 2002, at sites in Lee Hall (LH) and Harwoods Mill (HM) Reservoirs, Virginia.



**Figure 31.** Concentrations of phosphate and copper in grab and split-spoon samples of bed sediment collected at sites in Lee Hall Reservoir, Virginia.

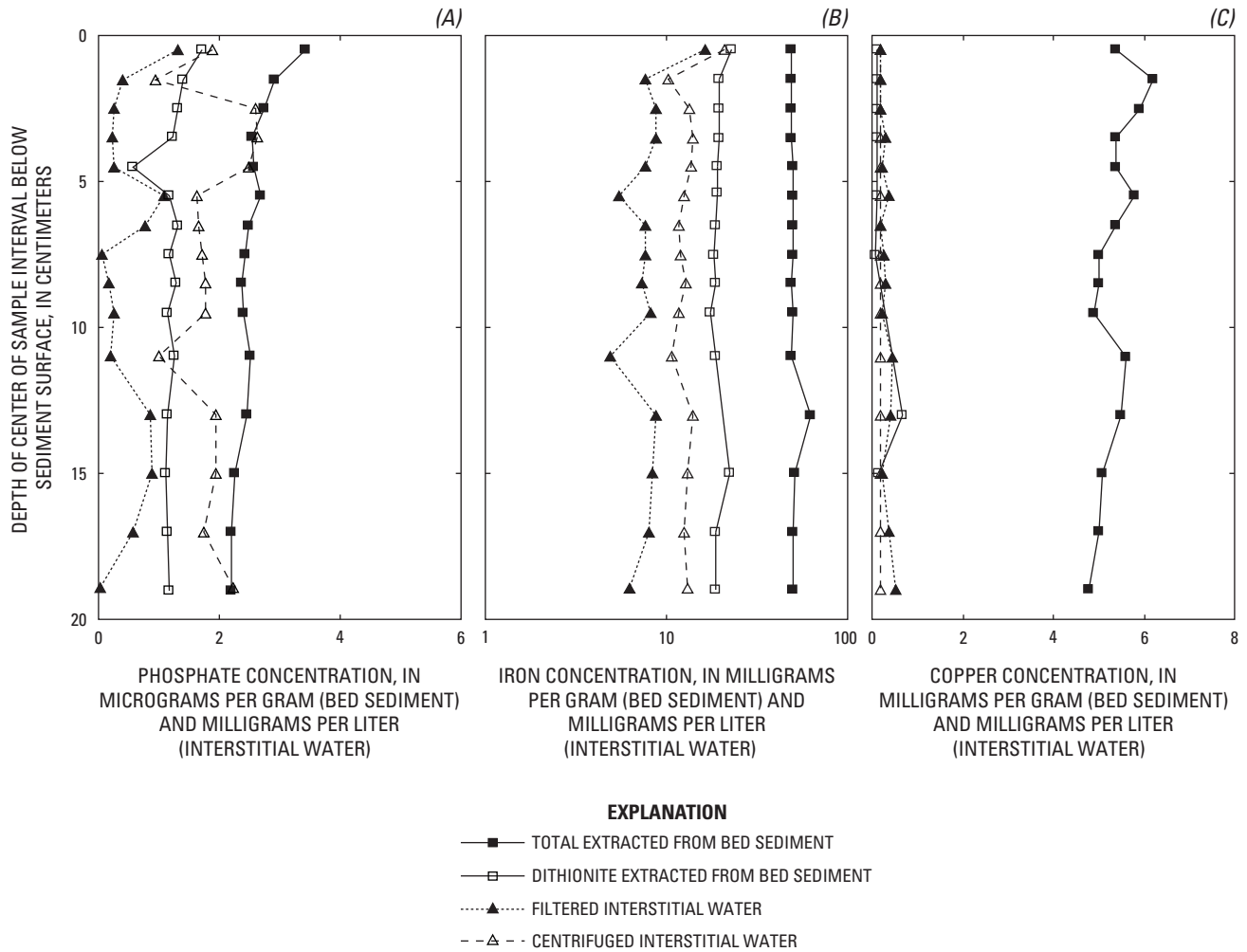
to 2.2 µg/g at a depth of 19 cm (fig. 32A; Note: Depths of box-core samples are for the centers of the sample intervals.). Dithionite-extracted phosphate concentrations generally reflect a similar vertical pattern (except at 4.5 cm) but average less than 50 percent of the total phosphate in the bed sediment.

Total phosphate concentrations in grab and split-spoon samples from the parts of the reservoir affected only by the pumped inflow were consistently the largest of any sections of Lee Hall Reservoir, ranging from 3.8 to 6.8 µg/g (fig. 31). Total phosphate concentrations in grab and split-spoon samples from the parts of the reservoir affected by both inflows varied substantially, ranging from 0.6 to 6.6 µg/g. Total phosphate concentrations in box-core samples collected at site LH1 (fig. 33A) generally were greater (ranging from 3.0 to 4.7 µg/g) than those from the site LH3 box core (fig. 32A). Concentrations decreased from 0.5 to 1.5 cm, increased to a peak concentration at 4.5 cm, decreased with depth to 11 cm, and changed little to 19 cm (fig. 33A). Concentrations in the box-core samples at site LH1 were less than the 6.6 µg/g in the grab sample collected at that site (fig. 31), but within the range of concentrations in grab samples collected in the lower part of the reservoir. Dithionite-extracted phosphorus concentrations reflect a similar pattern, except at 5.5 and 7.5 cm and averaged 70 percent of the total phosphorus in the bed sediment (fig. 33A).

Total phosphate concentrations in bed sediment of Harwoods Mill Reservoir were greater in the fluffy, upper sediment than in the cohesive, lower sediment where samples from both layers were collected, except for site HM1.3 near-shore samples and samples at site HM2 (fig. 34). Total phosphate concentrations in the upper bed sediment decreased from the upper part of the reservoir (site HM2.6) to site HM2 where the causeway crosses the reservoir and then increased down the reservoir to the water-treatment plant except at site HM1.3. Concentrations in the upper sediment at sites other than site HM1.3 ranged from 1.6 µg/g (site HM2) to 8.8 µg/g (site HM1).

The likelihood that bed sediment contributes appreciable amounts of phosphorus to the water column is better indicated by phosphorus concentrations in filtered rather than centrifuged samples of interstitial water from box-core samples. Centrifuged samples likely include colloidal and larger particles that contain phosphorus and, therefore, would over represent dissolved phosphorus concentrations that may diffuse through the interstitial water into the water column. The inability to filter sufficient water so that the first filtrate could be discarded may introduce uncertainty as to how well the filtered samples represent actual conditions. Because filtration was in a nitrogen atmosphere and a substantial concentration of particles was observed in centrifuged samples, however,





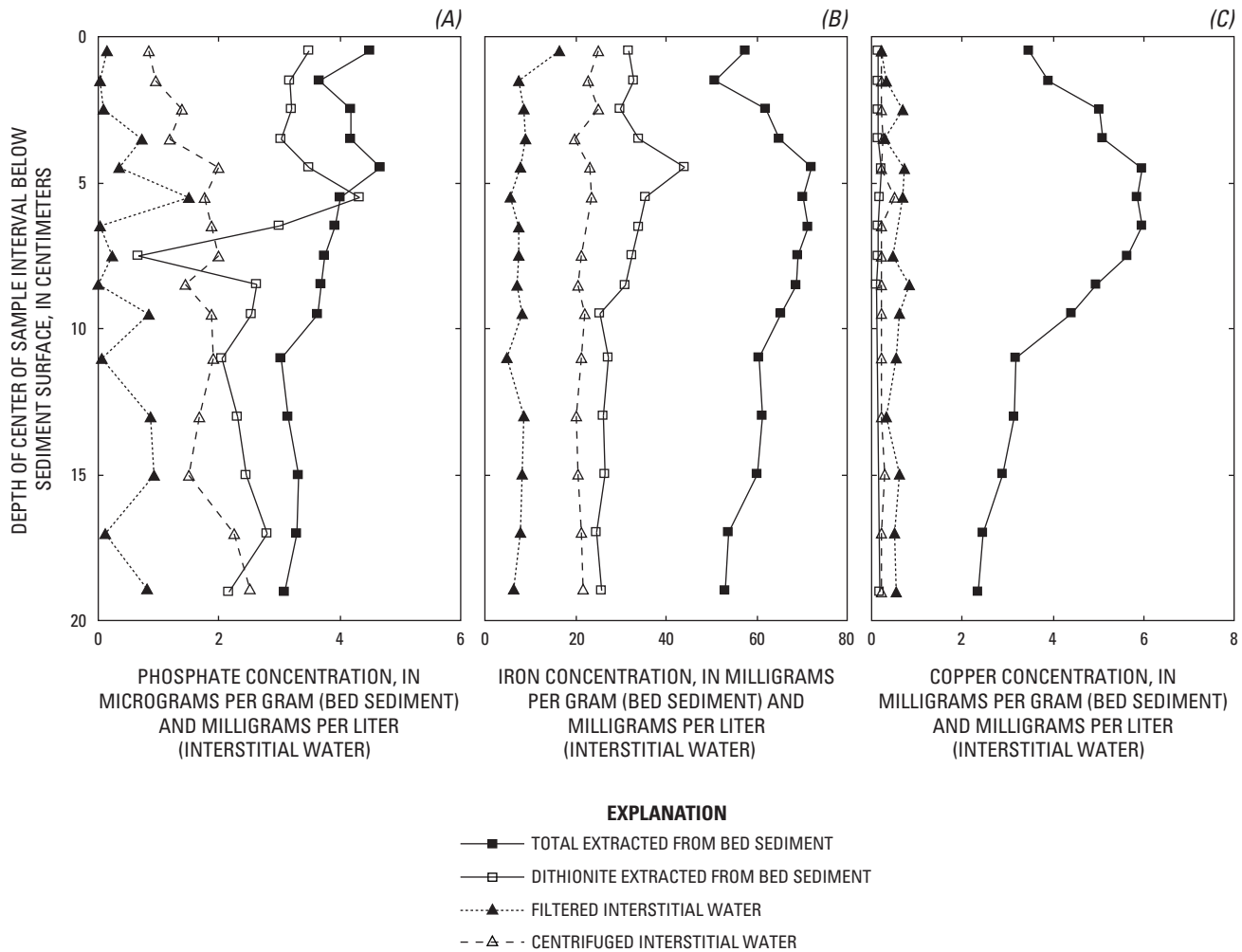
**Figure 32.** Vertical distributions of (A) phosphate, (B) iron, and (C) copper concentrations in box-core samples of bed sediment and interstitial water at site LH3, Lee Hall Reservoir, Virginia, August 2003.

the phosphate concentration of the filtered samples likely represents dissolved concentrations well.

Phosphate concentrations in both centrifuged and filtered samples at site LH3 show no distinct vertical gradient through the full interval of box-core samples (fig. 32A). Although the phosphate concentration of 1.3 mg/L in the filtered sample at the sediment surface is about 40–50 times the 0.025-mg/L median and 0.034-mg/L maximum concentrations (table 9, converted from phosphorus to phosphate) observed in the water column, the gradient in dissolved phosphorus is also downward in the interstitial water of the upper 4 cm of sediment. This gradient indicates a possible downward flux of phosphorus from the surface, and phosphorus contributions to the water column are only from the most recently deposited sediment. The surface sediment also is susceptible to resuspension because of its loose characteristics and could contribute phosphorus when resuspended.

Phosphate concentrations in centrifuged samples of interstitial water from site LH1 generally decreased from 2.5 mg/L at the bottom to 0.85 mg/L at the sediment surface

of the core (fig. 33A). The concentration at the sediment surface is greater than the 0.018-mg/L median and 0.036-mg/L maximum concentrations (table 9, converted from phosphorus to phosphate) measured in samples from the water column at this site. Phosphate concentrations in filtered samples of interstitial water had no clear vertical pattern, ranging from 0.003 mg/L at 8.5 cm to 1.5 mg/L at 5.5 cm. The concentration in the surface interval was 0.142 mg/L, greater than the median and maximum concentrations measured in the water column. The concentration in the second 1-cm interval was only 0.023 mg/L, near the median concentration observed in the water column. Thus, although no distinct gradient was present throughout the core, concentrations at the sediment surface were higher than in the water column and higher than in the next deeper sample, indicating that the greatest source of phosphorus from the bed sediment likely is the most recently deposited sediment; a flux from deeper sediment is not indicated. The indication that the bed sediment at sites LH1 and LH3 is not a likely major source of phosphorus to the water column is consistent with laboratory results of the



**Figure 33.** Vertical distributions of (A) phosphate, (B) iron, and (C) copper concentrations in box-core samples of bed sediment and interstitial water at site LH1, Lee Hall Reservoir, Virginia, August 2003.

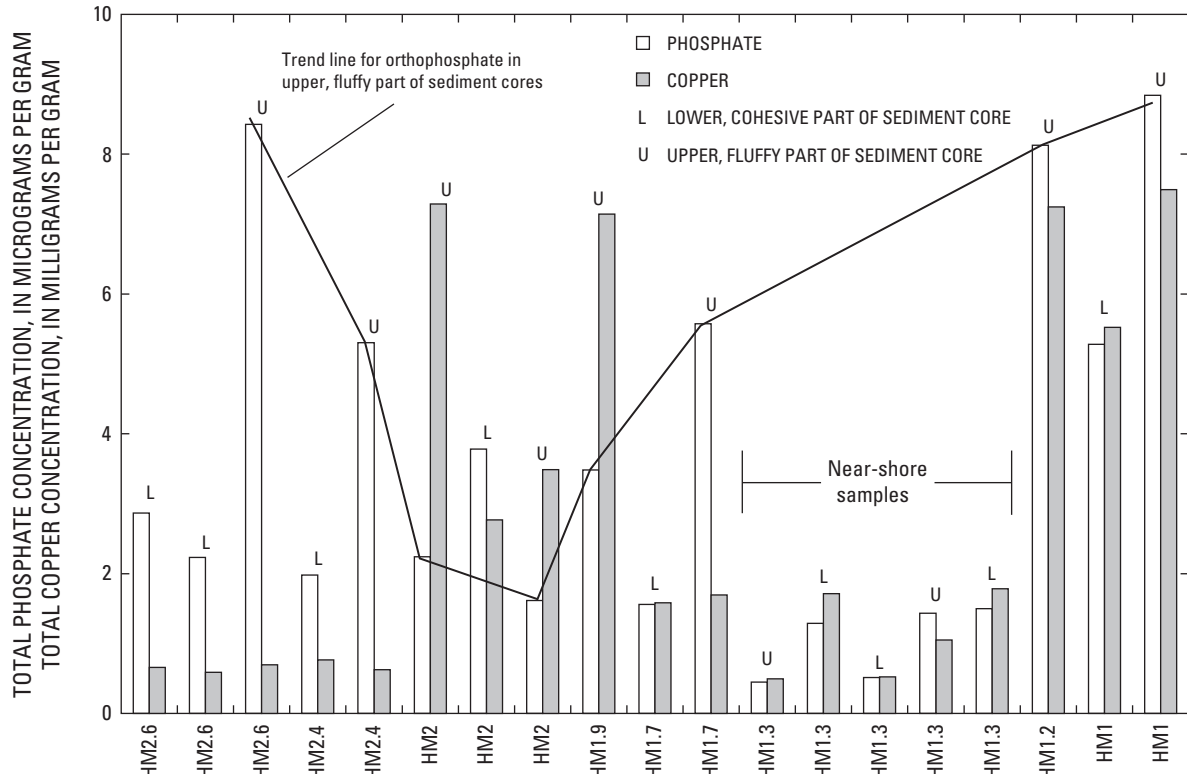
studies of the contribution of dissolved phosphorus from suspended particles in the water column.

Although phosphate concentrations in the bed sediment from box-core samples collected from site LH3 decreased with depth, total iron concentrations in the bed sediment were rather uniform with depth, ranging from 48 to 51 milligrams per gram (mg/g) except for the anomalous 62 mg/g at 13 cm (fig. 32B). Similarly, the dithionite-extracted iron concentrations generally were uniform, ranging from 17 to 23 mg/g. The dithionite-extracted iron concentrations averaged 39 percent of the total iron concentrations in the bed sediment. The centrifuged and filtered iron concentrations in interstitial water from site LH3 exhibited some variability but generally had no distinct vertical trend. The highest filtered iron concentration was at the sediment surface (fig. 32B).

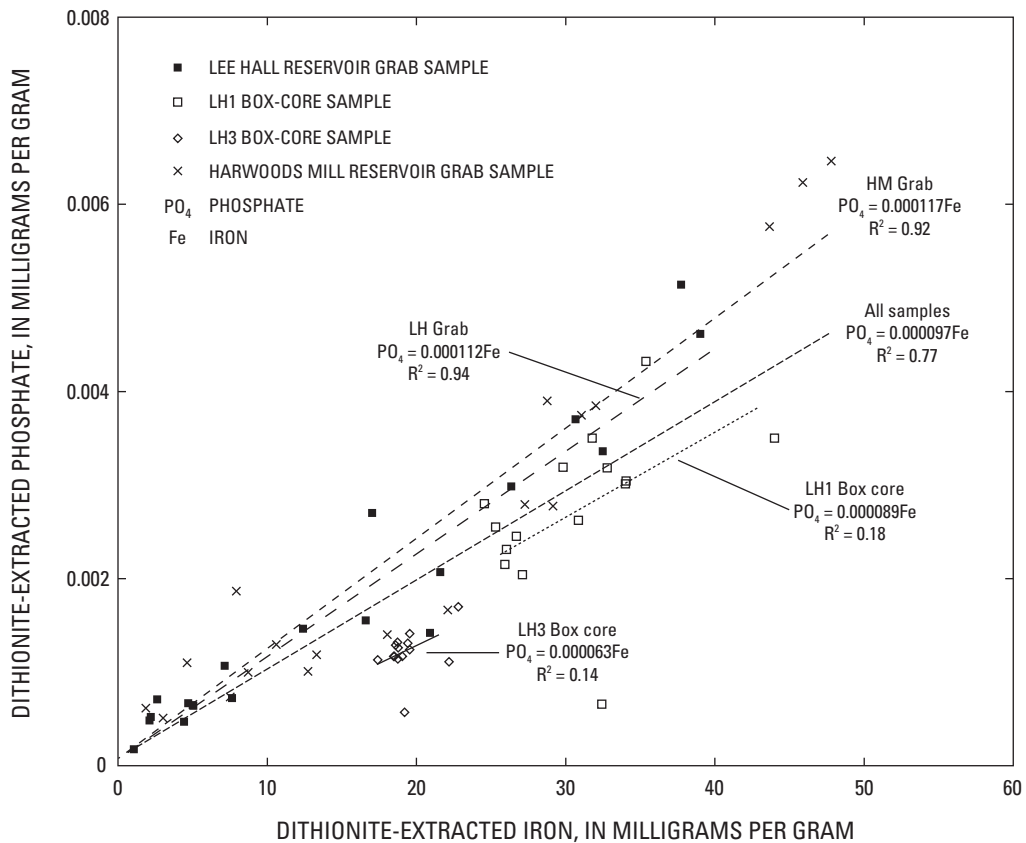
Total iron concentrations in sediment from the site LH1 box core reflect a pattern similar to that of the total phosphorus in the upper part of the core but differed slightly in the lower part of the core (fig. 33B). Concentrations decreased between 0.5 and 1.5 cm then increased to a peak of 72 mg/g at 4.5 cm.

Total iron concentrations decreased to 61 mg/g at 11 cm, then unlike total phosphorus concentrations that changed little below 11 cm, decreased at a lower rate to 53 mg/g at the bottom of the core (19 cm). Concentrations of dithionite-extracted iron averaged 49 percent of the total iron concentrations and had a pattern similar to that of total phosphorus concentrations. Concentrations of dithionite-extracted iron increased to a peak of 44 mg/g at 4.5 cm, decreased to 25 mg/g at 9.5 cm, and then changed little to the bottom, ranging from 24 to 27 mg/g. Concentrations of centrifuged and filtered iron concentrations in the interstitial water at site LH1 had no clear vertical trend. The highest filtered iron concentration was at the sediment surface.

A large part of the phosphorus in bed sediment appears to be bound to poorly crystallized iron oxides as indicated by the relation between dithionite-extracted phosphorus and iron concentrations (fig. 35). The relation for grab and box-core samples combined ( $R^2 = 0.77$ ) is better than that for only box-core samples from site LH3 ( $R^2 = 0.14$ ) and site LH1 ( $R^2 = 0.18$ ) but weaker than for only grab samples from Lee



**Figure 34.** Concentrations of phosphate and copper in grab and split-spoon samples of bed sediment collected near the center (except as noted) of the reservoir at sites in Harwoods Mill Reservoir, Virginia.



**Figure 35.** Dithionite-extracted iron and phosphate concentrations in grab and box-core samples of bed sediment collected from Lee Hall (LH) and Harwoods Mill (HM) Reservoirs, Virginia.

Hall Reservoir ( $R^2 = 0.94$ ) and Harwoods Mill Reservoir ( $R^2 = 0.92$ ). The weak relation for the box cores likely results from vertical heterogeneities or reduction of iron and release of phosphorus. The ratio of dithionite-extracted phosphorus to iron concentrations was approximately 0.0001 (fig. 35). If bed sediment were a major source of phosphorus to the water column, the ratio of dissolved phosphorus to dissolved iron concentrations in samples collected from site HM1B where dissolved constituents released from the bed sediment accumulate when the reservoir is stratified would be similar to this ratio. During the copper-sulfate application study, dissolved phosphorus concentrations were 0.043 and 0.060 mg/L as  $\text{PO}_4^{-3}$  in samples collected from site HM1B on September 17 and 23, 2002, respectively (fig. 28C). Dissolved iron concentrations were 19.8 and 2.09 mg/L in these samples on these dates, respectively (fig. 28D). Thus, the ratios of dissolved phosphorus to iron concentrations were 0.002 and 0.028 on these dates, respectively. Dissolved phosphorus concentrations, therefore, were about 20 and 290 times what concentrations would have been on these dates if dissolved phosphorus were derived entirely from reduction of poorly crystallized iron oxides in the bed sediment. This provides strong support for a source other than bed sediment being the major source of phosphorus to the water column. Although much of the phosphorus in the bed sediment appears to be bound to iron oxides, one reason that the phosphorus contribution from bed sediment to the water column may be limited could be the effects of low sulfate concentrations noted by Caraco and others (1989).

Copper concentrations in grab and split-spoon samples of bed sediment from Lee Hall Reservoir ranged from 0.56 to 6.7 mg/g and varied substantially in the different parts of the reservoir (fig. 31). Hanson and Stefan (1984) observed lower concentrations in five lakes in Minnesota to which copper sulfate had been applied for up to 58 years. Minimum, maximum, and mean copper concentration ranges were 0.093 to 0.370 mg/g, 0.173 to 1.593 mg/g, and 0.162 to 0.943 mg/g, respectively, for the five lakes. Thus, copper concentrations measured in many of the samples from Lee Hall Reservoir were greater than the maximum concentrations observed by Hanson and Stefan (1984).

Copper concentrations in the part of Lee Hall Reservoir affected only by the natural inflow ranged from 0.56 to 6.2 mg/g (fig. 31). Concentrations in the box-core samples collected at site LH3 generally decreased with depth from 6.2 mg/g at 1.5 cm to 4.8 mg/g at 19 cm (fig. 32C). This decrease in concentration with depth was similar to the pattern in total phosphorus but differed from the uniform total iron concentration. Dithionite-extracted copper generally was 0.2 mg/g or less because copper typically is not bound to poorly crystallized iron oxides. Copper concentrations in filtered pore water from this core were consistently below the detection level, substantiating that copper that binds to bed sediment remains bound in bed sediment and is not released to the water column as also noted in samples from the hypo-

limnion of Harwoods Mill Reservoir during the copper-sulfate application study.

Copper concentrations in grab and split-spoon samples of bed sediment from the part of the reservoir affected only by the pumped inflow increased in the direction of flow from 0.61 to 4.9 mg/g (fig. 31). This is consistent with the flushing of water containing copper from the upper part of the reservoir as water is pumped into the reservoir. Copper concentrations in grab and split-spoon samples of bed sediment from the part of the reservoir affected by both natural and pumped sources of water varied substantially, ranging from 0.67 to 6.7 mg/g. Although the highest concentrations are at both ends of this segment of the reservoir, this is not necessarily indicative of a spatial pattern because of uncertainty of the effects of the mixing of water from the natural and pumped sources, the causeways, and other factors.

Total copper concentrations in box-core samples collected at site LH1 may reflect changes in annual copper-sulfate application rates. Concentrations increased from 3.5 mg/g at the surface to 6.0 mg/g at 4.5 cm (fig. 33C). Concentrations changed little between 4.5 and 6.5 cm and then decreased sharply to 3.2 mg/g at 11 cm. Total copper concentrations decreased gradually from that depth to 2.4 mg/g at the bottom of the box core. The increase in copper concentration to 4.5 cm is consistent with the higher annual copper-sulfate application rates back to at least 1994 (fig. 9). Dithionite-extracted copper generally was 0.2 mg/g or less because copper typically is not bound to poorly crystallized iron oxides. Copper concentrations in filtered pore water from this core also were consistently below the 0.2-mg/L detection level, again indicating that copper remains bound to the bed sediment and is not released to the water column.

Total copper concentrations in the bed sediment of Harwoods Mill Reservoir also varied, ranging from 0.50 mg/g in a near-shore area at site HM1.3 to 7.5 mg/g in the upper sediment at site HM1 (fig. 34). The consistently lowest concentrations were in the upper part of the reservoir (sites HM2.4 and HM2.6). Water at these sites would be the first to flush into lower parts of the reservoir after application of copper sulfate, providing less opportunity for copper to settle from suspension. The highest concentrations were in sediment on both sides of the causeway that crosses the reservoir (sites HM1.9 and HM2) and in the lower part of the reservoir (sites HM1 and HM1.2). Although the profile studies indicated plug flow throughout the reservoir, the sample-collection sites on both sides of the causeway were away from the pipe that transmits water under the causeway. Thus, circulation patterns resulting from the causeway may retain water containing copper in parts of the reservoir around the causeway for longer periods than in open-water parts of the reservoir, or the causeway may shelter the reservoir from wind and allow particles to more readily settle from suspension. Water containing copper would flush last from the lower parts of the reservoir.

Combined results of the studies of the application of copper sulfate, bed-sediment quality, and interstitial-water quality indicate that much of the copper applied to the

reservoirs settles from the water column into the bed sediment and appears to remain immobilized in the sediment. Consequently, it is not likely that copper from reservoir bed sediment substantially affects the quality of the raw water withdrawn for public supply or downstream receiving waters unless the sediment becomes resuspended. Conversely, effects that copper in the bed sediment may have on benthic organisms and rooted aquatic plants will continue and only become mitigated as sediment containing little copper is deposited over copper-containing sediment. The presence of copper in bed sediment could account for the limited presence of benthic macroinvertebrates in the bed sediment.

## Implications for Alternative Management Strategies

Management strategies for reservoirs such as Lee Hall and Harwoods Mill Reservoirs depend on the nutrient that limits algal growth, the sources of the nutrient, and the processes that control its availability. The nitrogen-to-phosphorus ratios of total and dissolved species indicate that phosphorus most likely is the growth-limiting nutrient in the reservoirs (fig. 22). Consequently, knowledge of major sources and processes affecting phosphorus availability to algae is essential in managing the reservoirs for the control of algal growth. Although knowledge of annual phosphorus loads from different sources can be useful in reservoir management, late summer and early fall typically are the most critical times. Typically, late summer and early fall are when algal growth rates generally are the greatest (indicated by copper-sulfate

application intervals, fig. 8), Harwoods Mill Reservoir stratifies (figs. 16–18), and water demand is the greatest, thereby reducing hydraulic retention times.

Phosphorus loads to the reservoirs depend heavily on both the natural and pumped inflows as indicated by flow rates and calculated loads for the natural inflows, the pumped inflows, and raw-water withdrawals for Lee Hall Reservoir in 2002 (an extremely dry year) and 2003 (an extremely wet year; table 10). Pumped inflows and raw-water withdrawals were greater in 2002 than in 2003, whereas natural inflows were greater in 2003 than in 2002. Flow rates and possibly loads during these 2 years were among the most extreme that can be expected, based on current withdrawal rates because of the extreme hydrologic conditions.

The sum of the natural and pumped inflows was greater than the raw-water withdrawals during both years (table 10). This difference likely resulted from evaporation, leakage through the dams, and flow over the spillway. The smaller difference during 2002 likely resulted primarily from evaporation because little water flowed over the spillway. Much of the difference in 2003 likely was water that flowed over the spillway during extremely wet periods, particularly in the fall when several large storms, including Hurricane Isabel, passed through the area.

Hydrologic conditions partly determine which type of inflow is the major source of phosphorus to the reservoirs. The annual phosphorus load from the pumped inflow was about 2,390 lb, whereas the annual load from the natural inflows (using phosphorus concentrations at site LH3) was only about 600 lb during 2002. Thus, the pumped inflow contributed about 80 percent of the phosphorus during the dry year. Although the pumped inflow appears to be the greater

**Table 10.** Calculated loads of phosphorus to Lee Hall Reservoir through the pumped inflow and natural inflows and loads pumped from the reservoir in raw-water withdrawals during 2002 and 2003.

[Flow rates for pumped inflow and raw-water withdrawal from Ronald Harris, City of Newport News, written commun., 2004; —, no data]

Flow category	Flow rate		Phosphorus concentration, milligrams per liter	Phosphorus load		
	Million gallons per day	Fraction of total inflow		Pounds per day	Pounds per year	Grams per square meter per year
2002 (Dry year)						
Pumped inflow	22.4	0.81	0.035	6.54	2,390	0.54
Natural inflow	5.3	.19	.037	1.64	600	.14
Sum of inflows	27.7	1.00	—	8.18	2,990	.68
Raw-water withdrawal	26.2	.95	.018	3.94	1,440	.33
2003 (Wet year)						
Pumped inflow	11.4	0.33	0.047	4.47	1,630	0.37
Natural inflow	22.4	.66	.020	3.74	1,370	.31
Sum of inflows	33.8	1.00	—	8.21	3,000	.68
Raw-water withdrawal	23.9	.71	.027	5.39	1,970	.45



source of phosphorus during dry years, natural inflows can be a significant and possibly major source during wet years.

During 2003, the pumped inflow contributed about 1,630 lb of phosphorus, whereas the natural inflows contributed about 1,370 lb of phosphorus, using the median total phosphorus concentration of 0.020 mg/L at site LH3 for that year (Ronald Harris, City of Newport News, written commun., 2004). At a concentration of only 0.024 mg/L, phosphorus loads from the natural inflows would equal those from the pumped inflow. Phosphorus concentrations during base flow and stormflow at site BR1 were consistently above 0.024 mg/L (fig. 22), and likely were greater than the phosphorus concentrations of natural flows entering the reservoir because much of the stream between site BR1 and the reservoir has a lower slope than at site BR1; therefore, part of the suspended phosphorus likely settles before entering the reservoir. It is possible, however, that median concentrations in the natural inflows entering the reservoir were greater than 0.024 mg/L. Consequently, natural inflows would have been the dominant source of phosphorus during 2003.

Relations during wet and dry years could further translate into short-term and seasonal flow relations. During periods of high natural inflows that commonly occur in late winter and early spring, natural inflows likely are the major source of phosphorus to the reservoirs (figs. 6, 7). During periods of low natural inflow that commonly occur during summer and early fall, pumped inflow likely is the major source of phosphorus. Because of the short hydraulic retention times of the reservoirs, much of the phosphorus from either source flushes from the reservoirs in a short time, commonly less than a month, which results in a seasonal variability in the major source of phosphorus. The short hydraulic retention times and seasonal variability in sources requires management of both sources of phosphorus to the terminal reservoirs.

The higher loads in the combined sum of the natural and pumped inflows compared with the loads in the raw-water withdrawals (table 10) likely resulted from phosphorus that settled to the bed sediment or flowed over the spillway. Most of the 1,550-lb difference in 2002 likely was phosphorus that settled as bed sediment, because little water likely flowed over the spillway. A larger part of the 1,030-lb difference in 2003 likely flowed over the spillway because of the extremely wet conditions. If actual concentrations in the natural inflows are greater than 0.020 mg/L, flow of phosphorus over the spillway could be substantially greater.

Understanding the trophic state of reservoirs commonly is considered key to management of reservoirs and can be viewed in different ways. Because the normal trophic classification of reservoirs is extremely subjective, the use of Carlson's (1977) trophic state index (TSI) provides a more objective assessment of the trophic state of Lee Hall and Harwoods Mill Reservoirs. The average monthly TSI for total phosphorus (TP) for 2000 through 2003 was 44–55 at site LH2, 47–59 at site LH3 and 47–55 at site HM1 (Ronald Harris, City of Newport News, written commun., 2004). The TSI for chlorophyll *a* was 36–68 at site LH2, 34–57 at site LH3,

and 40–51 at site HM1. The TSI for chlorophyll at Lee Hall and Harwoods Mill Reservoirs shows the season fluctuations identified by Carlson (1977) but likely are lower than would naturally occur because of the application of copper sulfate. Carlson (1977) reported similar or higher values, averaging in the mid-50s to about 70 for three lakes in Minnesota.

Another perspective for evaluating the trophic state of reservoirs is phosphorus loads. Total phosphorus loads were 0.68 grams per square meter per year ( $\text{g/m}^2/\text{y}$ ) and exceeded both the permissible load of 0.07 ( $\text{g/m}^2/\text{y}$ ) and the dangerous load of 0.13 ( $\text{g/m}^2/\text{y}$ ) for a lake having a depth of 16.4 ft (5 meters) as classified by Wetzel (1975).

Comparison of total phosphorus and chlorophyll-*a* concentrations to the proposed criteria for reservoirs in Virginia (Virginia Department of Environmental Quality, 2006) reveals that median concentrations from April through October for 2000 through 2003 (Ronald Harris, City of Newport News, written commun., 2004) are below the 0.040-mg/L median criterion for total phosphorus and the 25- $\mu\text{g/L}$  median criterion for chlorophyll *a*. All monthly chlorophyll-*a* concentrations were less than the median 25- $\mu\text{g/L}$  criterion, much less below the 60- $\mu\text{g/L}$ , 90<sup>th</sup>-percentile criterion.

Comparison of the water quality of Lee Hall and Harwoods Mill Reservoirs to trophic indices, loads, or concentrations can be of somewhat questionable value, however, because of the effects of the pumped inflows, the short hydraulic retention times, and the application of copper sulfate. Although overall concentrations of phosphorus may be considered low, the pumped inflows cause high phosphorus loads (both dissolved and suspended) to the reservoirs. The high dissolved phosphorus loads likely are available to algae for photosynthesis. The high suspended phosphorus loads, however, likely are of limited availability to algae for photosynthesis because the short hydraulic retention times flush the phosphorus from the reservoirs, partly mitigating the effects of high loads. The use of chlorophyll *a* is of limited value because the application of copper sulfate alters the biological response in the reservoirs, likely preventing chlorophyll *a* from increasing in concentrations that may otherwise be achieved (Carlson, 1977; Virginia Department of Environmental Quality, 2006).

Although phosphorus in bed sediment is a possible source of phosphorus to the water column, data from a combination of interstitial-water, bed-sediment, and water-column samples collectively indicate that the bed sediment likely is only a limited source of phosphorus to the overlying water column in the reservoirs. Water-column data appear to provide the best indication of this. The strongest case is provided by data from the detailed, vertical nutrient distribution studies of August 2003 combined with the laboratory studies of phosphorus release and the copper-sulfate application studies of September 2002, particularly for Harwoods Mill Reservoir. Stratification during the detailed vertical distribution study appeared to limit vertical mixing of water in the epilimnion to depths above 6 to 10 ft, and dissolved phosphorus concentrations only increased vertically below a depth of 15 ft (fig. 24). Thus, phosphorus



would not diffuse from the hypolimnion to the epilimnion, and the hypolimnion would only be a source of phosphorus to the epilimnion upon the breakdown of stratification in the fall. Furthermore, the laboratory studies of phosphorus-release rates demonstrate that the peak phosphorus concentrations in the hypolimnion could be achieved by the release of phosphorus from particles in the water column within 30 to 40 days of stratification. This elevated concentration could have been attained easily in the nearly 90 days the reservoir was stratified. It is not likely that bed sediment also contributed significant amounts of phosphorus to the water column because of the absence of an upwardly decreasing gradient in phosphorus concentrations in the interstitial water of box cores from sites LH1 and LH3 (figs. 33 and 32, respectively). Additionally, the relations between the dithionite-extracted iron and phosphorus concentrations indicate that a large part of the phosphorus in bed sediment is bound by poorly crystallized iron oxides (fig. 35). This is a particularly important relation because it is so strong for the grab samples ( $R^2 = 0.94$  for Lee Hall Reservoir and  $R^2 = 0.92$  for Harwoods Mill Reservoir), which consisted of the near-surface sediment that would release phosphorus to the water column. The ratio of dissolved phosphorus to iron concentrations in samples from site HM1B, where phosphorus and iron released from the bed sediment accumulate, would be similar to the approximately 0.0001 ratio of the dithionite-extracted concentrations in the bed sediment if bed sediment were the main phosphorus source. The ratios observed in samples from site HM1B during the first part of the copper-sulfate application study, however, are about 20 to 290 times the ratio in the bed sediment and strongly indicate that a source other than bed sediment likely is the major source of phosphorus to the water column.

The anoxic conditions in the hypolimnion of Harwoods Mill Reservoir likely reduce the ferric iron in the iron oxides so that greater amounts of phosphorus are released from bed sediment in Harwoods Mill Reservoir than from bed sediment in Lee Hall Reservoir. It is unlikely that more phosphorus will release from bed sediment in Lee Hall Reservoir because low dissolved-oxygen concentrations are less persistent in Lee Hall Reservoir. Although the reason little phosphorus is released from the bottom sediment is uncertain, low sulfate concentrations in the water column may limit the release as cited by Caraco and others (1989).

The release of dissolved phosphorus from particles suspended in the water column, although an important process, is not the original source of phosphorus to the reservoirs. Phosphorus in these particles enters the reservoir through the natural and pumped inflows and then flows through the reservoirs to where it is withdrawn. Thus, control of phosphorus in these two sources likely is the best method to control the release of phosphorus from suspended particles.

Yet another consideration for reservoir management is the fate of copper applied to the reservoirs. As indicated by the study of the effects of copper-sulfate application, much of the copper appears to readily bind to particles (probably algae and other organic material) and settle from suspension (figs. 26–

30). The effectiveness of the binding and settling is evident in the copper concentrations in the bed sediment and interstitial water. Copper concentrations in the bed sediment ranged from 0.50 to 7.5 mg/g (figs. 31–34), generally higher than the 0.173- to 1.593-mg/g maximum concentrations observed by Hanson and Stefan (1984) in five lakes in Minnesota to which copper sulfate had been applied for up to 58 years. In contrast, copper concentrations in interstitial water from box-cores samples from sites LH1 and LH3 were near the detection level, indicating that copper strongly binds to organic particles and is not released into the water. Thus, release of copper into the water supply and downstream environment is not likely. The absence of macroinvertebrates and rooted aquatic vegetation, however, indicates possible toxic effects of the copper in the bed sediment that could affect the success of certain management alternatives in the reservoirs.

Management options will have different rates of success, costs, and environmental consequences. Options can control the growth of algae directly or control phosphorus availability in the reservoirs. Algal growth can be controlled directly by the application of algicides, which can include application of copper sulfate at lower rates than currently used or use of alternative algicides. The effectiveness and environmental consequences of either is uncertain. Because the reservoirs have short hydraulic retention times and release of dissolved phosphorus from suspended particles appears to be a greater pathway for recycling phosphorus into the water column than release from bed sediment, the continuous flow of water from natural and pumped sources ultimately appears to be the main sources of phosphorus to algae in the terminal reservoirs. Consequently, practices that control phosphorus in the natural and pumped inflow sources and not practices that sequester phosphorus in the bed sediment, such as application of alum or nitrate, likely will provide the most successful control of algal growth in the terminal reservoirs. Phosphorus in the pumped inflows not only can be managed by using the same practices as those used for the natural inflows but also by using additional practices. Water from outside watersheds can be pumped directly to the water-treatment plants to bypass the terminal reservoirs or be routed through Little Creek and Diascund Creek Reservoirs (fig. 1) to remove part of the phosphorus, as identified by Lynch (1992). These practices, however, cannot be used to manage phosphorus in the natural inflows. Control of phosphorus in natural inflows likely will be needed in the upper parts of the reservoirs because much of the phosphorus in the natural inflows appears to be derived from natural, nonpoint sources. Part of this control can be through re-establishing and enhancing natural biogeochemical processes, such as promoting benthic algae and rooted aquatic vegetation. Residual copper in the bed sediment, however, can inhibit such processes because of the large concentrations and persistence of the copper in the bed sediment, except in the uppermost parts of the reservoirs where little copper sulfate was applied.

These implications for alternative management strategies, although directed toward Lee Hall and Harwoods Mill

Reservoirs, have important implications for many other lakes and reservoirs across the Nation. This is particularly true for other small lakes and reservoirs, especially those in which pumpage appreciably affects the hydraulic retention times. In such reservoirs, pumpage from outside sources can have a continuing effect on phosphorus loads and algal growth. Although the literature commonly cites recycling of phosphorus from bed sediments as a source of phosphorus to lakes and reservoirs, the limited recycling of phosphorus from bed sediments observed in Lee Hall and Harwoods Mill Reservoirs can be important in small and large reservoirs and lakes alike. The observed accumulation of copper in the bed sediments and the limited release of copper from the bed sediments likely are similar to conditions that would be observed in many other lakes and reservoirs, regardless of size.

## Summary and Conclusions

Elevated phosphorus in freshwater systems can stimulate excessive growth of algae that, in turn, can impart tastes and odors when the water is treated for public supply. To help control algal growth and reduce these effects, water suppliers commonly apply copper sulfate to the source water bodies. Because copper has a maximum allowable concentration in drinking water and can be toxic to aquatic life, alternative management strategies might be needed. Investigations into the sources of phosphorus, the effects of phosphorus on algal growth, and the effects of copper-sulfate application on aquatic systems to help improve management strategies are appropriate studies for the U.S. Geological Survey (USGS) because algal growth and copper-sulfate application are nationwide issues and part of the mission of the USGS is to define and protect the quality of the Nation's water resources and better understand the physical, chemical, and biological processes in wetlands, lakes, reservoirs, and estuaries.

The City of Newport News, Virginia, provides an average 50 million gallons per day (Mgal/d) of treated water for public supply from Lee Hall and Harwoods Mill Reservoirs (the terminal reservoirs) to communities on the lower York-James Peninsula. Because of excessive algal growth in these reservoirs, city personnel apply about 3,500 pounds of copper sulfate to each reservoir at intervals of 3 to 99 days. These intervals typically are shortest during the summer and early fall. Consequently, city officials are seeking to develop a long-term alternative to the use of copper sulfate for managing algae in the reservoirs. This report describes results of research conducted from April 2002 through December 2003 by the USGS, in cooperation with the City of Newport News, on the effects of management practices and natural processes on phosphorus (the apparent growth-limiting nutrient), copper, and algal concentrations in the terminal reservoirs and implications for alternative management strategies.

A large part of the flow through the reservoirs is derived from pumpage from outside watersheds; the major outside

source is the Chickahominy River. This pumpage varies so that the combination of natural and pumped inflows generally meets but does not exceed the average needs for public supply, loss by evapotranspiration, and leakage through the dams. Water pumped from the reservoirs is processed in a treatment plant at the lower end of each reservoir. Although pumpage from Lee Hall Reservoir historically has been 50 percent greater than that from Harwoods Mill Reservoir, pumpage from both reservoirs was similar during the study as a result of failure of parts of the Lee Hall plant and construction to rebuild the entire plant. Pumpage from outside watersheds into each reservoir averaged about 17.1 Mgal/d, and raw-water withdrawals averaged about 24.7 Mgal/d from 2000 through 2003. Pumpage was greatest in 2001 and 2002, two extremely dry years, and least in 2003, a very wet year. Annual stream-flow of the Chickahominy River at Providence Forge (station 02042500) was the lowest on record in 2002 (record since January 1942) and the highest on record in 2003.

Lee Hall Reservoir is separated into two parts of similar volumes by the Interstate-64 causeway. Most natural flow enters the upper part of the reservoir through Beaverdam Creek and flows through the entire reservoir; pumped flow enters the reservoir downstream from the causeway. Thus, during periods of little natural inflow, flow through the reservoir is dominated by pumpage that only flows through the lower half of the reservoir. Harwoods Mill Reservoir is divided by the causeway for State Road 620; pumpage enters the reservoir above the causeway and flows through most of the reservoir. Depending on pumpage amounts, hydraulic retention times of the reservoirs can range from 35 to 11 days.

In background studies, circulation and possible stratification in the reservoirs were evaluated because these factors affect phosphorus availability to algae and, therefore, management decisions. A combination of physical and chemical characteristics and concentrations of sodium, calcium, iron, and the stable isotopes deuterium and oxygen-18 indicates that (1) water flows through both reservoirs in a plug-flow manner, (2) little water in the lower part of Lee Hall Reservoir flows into the upper part of the reservoir and mixes with that water, (3) Lee Hall Reservoir generally does not stratify, and (4) Harwoods Mill Reservoir does stratify. Stratification of Harwoods Mill Reservoir vertically separates the reservoir into an upper epilimnion that does not mix with water in the lower hypolimnion; the transition between these zones begins at a depth of 10 to 15 feet (ft) based on water-temperature gradients but 6 to 10 ft based on dissolved-oxygen concentration gradients, which appear to be the better transition indicator of the two. Harwoods Mill Reservoir first stratifies between April and June and remains stratified through September or October.

Although phosphorus commonly is the nutrient limiting the growth of algae in freshwater systems, nitrogen can limit growth in some lakes and reservoirs. Generally a nitrogen-to-phosphorus ratio (N:P) less than 7:1 indicates that nitrogen is the growth-limiting nutrient, whereas a ratio greater than 7:1 indicates that phosphorus is the growth-limiting nutrient. The N:P ratio of total nutrient concentrations commonly is

used in evaluating many reservoirs having extended hydraulic retention times (several months to years) because nutrients bound to particles that enter the reservoir in the spring can be released from the particles as dissolved orthophosphorus throughout the growing season and used by algae. Because of the short hydraulic retention times of the terminal reservoirs, the ratio of the dissolved species likely is a better indicator of nutrient limitation. The N:P ratio of dissolved nutrients for the reservoir sites and the pumped inflow generally was greater than 20:1, indicating that phosphorus likely is the growth-limiting nutrient in the terminal reservoirs.

Phosphorus typically was present predominantly as suspended rather than dissolved species except in the hypolimnion of Harwoods Mill Reservoir and the natural inflow. Orthophosphorus concentrations generally were less than the minimum reporting level of 0.007 milligram per liter (mg/L); dissolved phosphorus concentrations were 0.020 mg/L or less, and suspended phosphorus concentrations were less than 0.060 mg/L in all but 25 to 50 percent of the samples from these two sites. The higher dissolved phosphorus concentrations in the hypolimnion most likely resulted from release of phosphorus from suspended particles and the decomposition of organic material in the water column.

Because concentrations of most nutrient species differed near the bottom from those near the surface in both reservoirs, the detailed vertical distribution of nutrient concentrations was measured near the water-treatment plants at Lee Hall and Harwoods Mill Reservoirs in August 2003. In Lee Hall Reservoir, field-measured physical and chemical characteristics and concentrations of nitrogen and phosphorus species generally changed without large differences over short depth intervals. At site HM1, however, field-measured physical and chemical characteristics and several nutrient species changed sharply over short intervals. Dissolved phosphorus concentration increased from 0.015 to 0.057 mg/L from a depth of 15 ft to the reservoir bottom (depth of 18 ft), indicating the likely release of phosphorus from suspended particles in the hypolimnion or bed sediment. Because dissolved-oxygen concentrations indicate that the boundary between the epilimnion and the hypolimnion likely was between 6 and 10 ft, these sources would not contribute to the growth of algae in the epilimnion until the breakdown of stratification in the fall. Additionally, laboratory studies of the release of dissolved phosphorus from particles suspended in the water column indicate that these particles could account fully for the observed dissolved phosphorus concentrations within 30 to 40 days whereas phosphorus would have been released from particles over the nearly 90 days the reservoir had been stratified.

Studies of the effects of copper-sulfate application indicate that chlorophyll concentrations decreased then recovered, concentrations of phosphorus species changed little, and copper concentrations decreased after application. Thus, the die-off and settling of algae as a result of copper-sulfate application appeared to have little effect on phosphorus. Dissolved copper became bound to particles that settled as the bed sediment. The absence of dissolved copper and the

presence of high suspended copper concentrations in the hypolimnion of Harwoods Mill Reservoir indicate that copper is not released from particles once it becomes bound to the particles and, thus, is sequestered in the bed sediment.

Phosphorus and copper concentrations in bed sediment and interstitial water also indicate that although both phosphorus and copper settle as bed sediment, neither appears to be released from the sediment to the water column in appreciable amounts. Although phosphate concentrations in bed sediment ranged from 0.3 to 8.8 micrograms per gram, varied in spatially identifiable patterns, and generally decreased with depth, concentrations in interstitial water indicate that bed sediment likely is a limited source of dissolved phosphorus to the water column. Phosphorus concentrations in filtered samples of interstitial water did not reflect a consistent vertical gradient that would result in diffusion of phosphorus from the sediment to the water column. Because of a strong relation between dithionite-extracted phosphorus and iron concentrations, a large part of the phosphorus appears to be bound by iron oxides in the bed sediment. Low sulfate concentrations in the water column could account for phosphorus not being released from the iron oxides even when dissolved-oxygen concentrations are low in the sediment and overlying water, a relation identified by previous investigators. Additionally, because the ratios of dissolved phosphorus to dissolved iron in samples collected from the hypolimnion of Harwoods Mill Reservoir in September 2002 were 20 to 290 times the ratio of the dithionite-extracted concentrations, a source other than bed sediment appears to be the major source of phosphorus to the water column. Less than detectable concentrations of copper in the interstitial water also indicate that copper remains bound to the sediment and is not released to the water column.

## References

- American Public Health Association, 1998, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, American Water Works Association, and Water Environment Federation, p. 3-37—3-43.
- Andersen, F.Ø., and Jensen, H.S., 1992, Regeneration of inorganic phosphorus and nitrogen from decomposition of seston in a freshwater sediment: *Hydrobiologia*, v. 228, p. 71-81.
- Arar, E.J., and Collins, G.B., 1997, In vitro determination of chlorophyll *a* and pheophytin *a* in marine and freshwater algae by fluorescence, (rev. 1.2): U.S. Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development.

- Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of dissolved organic carbon by uv-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92–480, 12 p.
- Brockman, A.R., Nelms, D.L., Harlow, G.E., Jr., and Gildea, J.J., 1997, Geohydrology of the shallow aquifer system, Naval Weapons Station Yorktown, Yorktown, Virginia: U.S. Geological Survey Water-Resources Investigations Report 97–4188, 61 p., 1 pl.
- Brockman, A.R., and Richardson, D.L., 1992, Hydrogeologic framework of the shallow aquifer system of York County, Virginia: U.S. Geological Survey Water-Resources Investigations Report 92–4111, 36 p.
- Caraco, N.F., Cole, J.J., and Likens, G.E., 1989, Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems: *Nature*, v. 341, no. 6240, p. 316–318.
- Carlson, R.E., 1977, A trophic state index for lakes: *Limnology and Oceanography*, v. 22, p. 361–369.
- Clark, K.H., 1998, Grafton Ponds Natural Area Preserve resource management plan (1st ed.): Richmond, Virginia Department of Conservation and Recreation, Division of Natural Heritage, Natural Heritage Technical Report 98–04, 75 p.
- Commonwealth of Virginia, 2005, Waterworks regulations, Part II Operators regulations for waterworks, Article 1: Drinking water standards: Virginia Administrative Code, Chap. 590, 85 p.
- Cooke, D.G., and Kennedy, R.H., 1978, Effects of hypolimnetic application of aluminum sulfate to a eutrophic lake: *Internationale Vereinigung für Theoretische und Angewandte Limnologie*, v. 20, p. 486–489.
- Coplen, T.B., 1993, Uses of environmental isotopes, *in* Alley, W.M., ed., *Regional ground-water quality*: New York, Van Nostrand Reinhold, p. 227–253.
- Craig, H., 1961, Isotopic variations in meteoric water: *Science*, v. 133, p. 1,702–1,703.
- DeGasperi, C.L., Spyridakis, D.E., and Welch, E.B., 1993, Alum and nitrate as controls on short-term anaerobic sediment phosphorus release—An *in vitro* comparison: *Lake and Reservoir Management*, v. 8, no. 1, p. 49–59.
- Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of metals in water by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 92–634, 28 p.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determinations of inorganic and organic constituents in water and fluvial sediment: U.S. Geological Survey Open-File Report 93–125, 217 p.
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Focazio, M.J., 1997, Springs and seeps of Colonial National Historical Park: Yorktown, VA, National Park Service, 20 p.
- Foy, R.H., 1986, Suppression of phosphorus release from lake sediments by the addition of nitrate: *Water Research*, v. 20, no. 11, p. 1,345–1,351.
- Gächter, René, and Wehrli, Bernhard, 1998, Ten years of artificial mixing and oxygenation—No effect on the internal loading of two eutrophic lakes: *Environmental Science and Technology*, v. 32, no. 23, p. 3,659–3,665.
- Garbarino, J.R., and Struzeski, T.M., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of elements in whole-water digests using inductively coupled plasma-optical emission spectrometry and inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 98–165, 101 p.
- Gat, J.R., and Gonfiantini, R., eds., 1981, Stable isotope hydrology—Deuterium and oxygen-18 in the water cycle: Vienna, Austria, International Atomic Energy Commission, Technical Report Series no. 210, 399 p.
- Golosov, S.D., and Ignatieva, N.V., 1999, Hydrothermodynamic features of mass exchange across the sediment-water interface in shallow lakes: *Hydrobiologia*, v. 408–409, p. 153–157.
- Graber, K.J., and Hartman, R.T., 1985, Internal phosphorus loading to shallow Edinboro Lake in northwestern Pennsylvania: *Hydrobiologia*, v. 122, no. 1, p. 45–52.
- Hansen, P.S., Philips, E.J., and Aldridge, F.J., 1997, The effects of sediment resuspension on phosphorus available for algal growth in a shallow subtropical lake, Lake Okeechobee: *Lake and Reservoir Management*, v. 13, no. 2, p. 154–159.
- Hanson, M.J., and Stefan, H.G., 1984, Side effects of copper sulfate treatment of the Fairmont Lakes, Minnesota: *Water Resources Bulletin*, v. 20, no. 6, p. 889–900.
- Hoehn, R.C., 1985, A limnological study of the Harwood's Mill and Lee Hall Reservoirs: Blacksburg, VA, Virginia Polytechnic Institute and State University, Department of Civil Engineering, 141 p.



- Hoehn, R.C., Grizzard, T.J., Weand, B.W., and Randall, C.W., 1986, A preliminary evaluation of runoff-borne pollutants entering Newport News' water supply reservoirs—Final report: Blacksburg, VA, Virginia Polytechnic Institute and State University, Department of Civil Engineering, 87 p.
- Holz, J.C., and Hoagland, K.D., 1999, Effects of phosphorus reduction on water quality—Comparison of alum-treated and untreated portions of a hypereutrophic lake: *Journal of Lake and Reservoir Management*, v. 15, no. 1, p. 70–82.
- Hupfer, M., Pöthig, R., Brüggemann, R., and Geller, W., 2000, Mechanical resuspension of autochthonous calcite (seekreide) failed to control internal phosphorus cycle in a eutrophic lake: *Water Research*, v. 34, no. 3, p. 859–867.
- Jacoby, J.M., Lynch, D.D., Welch, E.B., and Perkins, M.A., 1982, Internal phosphorus loading in a shallow eutrophic lake: *Water Research*, v. 16, p. 911–919.
- James, W.F., Barko, J.W., Eakin, H.L., and Helsel, D.R., 2000, Distribution of sediment phosphorus pools and fluxes in relation to alum treatment: *Journal of the American Water Resources Association*, v. 36, no. 3, p. 647–656.
- Janus, L.L., and Vollenweider, R.A., 1984, Phosphorus residence time in relation to trophic conditions in lakes: *Verhandlung Internationale Vereinigung Limnologie*, v. 22, p. 179–184.
- Johnson, G.H., 1972, Geology of the Yorktown, Poquoson West, and Poquoson East quadrangles, Virginia: Virginia Division of Mineral Resources, Report of Investigations 30, 57 p.
- Johnson, G.H., Beach, Todd, Harris, M.S., and Herman, Julie, 1993, Late Cenozoic environments along the James River, southeastern, Virginia, in *Virginia Geological Field Conference Guidebook*, April 16–18, 1993: College of William and Mary, 36 p.
- Kleeberg, Andreas, and Kohl, J.G., 1999, Assessment of the long-term effectiveness of sediment dredging to reduce benthic phosphorus release in shallow Lake Muggelsee (Germany): *Hydrobiologia*, v. 394, p. 153–161.
- Koski-Vähälä, J., Hartikainen, H., and Kairesalo, T., 2000, Resuspension in regulating sedimentation dynamics in Lake Vesijärvi: *Archives Hydrobiologia*, v. 148, no. 3, p. 357–381.
- Lean, D.R.S., McQueen, D.J., and Story, V.A., 1986, Phosphate transport during hypolimnetic aeration: *Archiv für Hydrobiologia*, v. 108, no. 2, p. 269–280.
- Lynch, D.D., 1992, Water quality and evaluation of raw-water-routing scenarios, Chickahominy, Diascund Creek, and Little Creek Reservoirs, southeastern Virginia, 1983–86: U.S. Geological Survey Water-Resources Investigations Report 92–4043, 104 p.
- Meng, A.A., III, and Harsh, J.F., 1988, Hydrogeologic framework of the Virginia Coastal Plain: U.S. Geological Survey Professional Paper 1404–C, 82 p.
- Mitsch, W.J., and Gosselink, J.G., 1993, *Wetlands* (2d ed.): New York, NY, Van Nostrand Reinhold, 722 p.
- Moore, P.A., Jr., Reddy, K.R., and Fisher, M.M., 1998, Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida—Spatial and temporal variations: *Journal of Environmental Quality*, v. 27, p. 1428–1439.
- Panuska, J.C., and Robertson, D.M., 1999, Estimating phosphorus concentrations following alum treatment using apparent settling velocity: *Journal of Lake and Reservoir Management*, v. 15, no. 1, p. 28–38.
- Patton, C.J., and Truitt, E.P., 1992, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of total phosphorus by a Kjeldahl digestion method and an automated colorimetric finish that includes dialysis: U.S. Geological Survey Open-File Report 92–146, 39 p.
- Patton, C.J., and Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open-File Report 2000–170, 31 p.
- Peterson, S.A., 1982, Lake restoration by sediment removal: *Water Resources Bulletin*, v. 18, no. 3, p. 423–435.
- Pettersson, Kurt, 1998, Mechanisms for internal loading of phosphorus in lakes: *Hydrobiologia*, v. 373–374, p. 21–25.
- Reddy, K.R., Fisher, M.M., and Ivanoff, D., 1996, Resuspension and diffusive flux of nitrogen and phosphorus in a hypereutrophic lake: *Journal of Environmental Quality*, v. 25, p. 363–371.
- Richardson, D.L., 1994, Ground-water discharge from the Coastal Plain of Virginia: U.S. Geological Survey Water-Resources Investigations Report 93–4191, 15 p.
- Ruttenberg, K.C., 1992, Development of a sequential extraction method for different forms of P in marine sediments: *Limnology and Oceanography*, v. 37, p. 1,460–1,482.
- Simon, N.S., Kennedy, M.M., and Bricker, O.P., 1999, Geochemical data for sediment samples collected in 1997 and 1998 from the Popes Creek, VA, and Pocomoke River, MD, watersheds: U.S. Geological Survey Open-File Report 99–79, 18 p.
- Søndergaard, Martin, Jeppesen, Erik, and Jensen, J.P., 2000, Hypolimnetic nitrate treatment to reduce internal phosphorus loading in a stratified lake: *Lake and Reservoir Management*, v. 16, no. 3, p. 195–204.

- Speiran, G.K., 2000, Dissolved organic carbon and disinfection by-product precursors in water of the Chickahominy River Basin, Virginia, and implications for public supply: U.S. Geological Survey Water-Resources Investigations Report 00–4175, 60 p.
- Speiran, G.K., and Hughes, M.L., 2001, Hydrology and water quality of the shallow aquifer system, Yorktown Battlefield, Colonial National Historical Park at Yorktown, Virginia: National Park Service, 58 p.
- Stefan, H.G., and Hanson, M.J., 1981, Phosphorus cycling in five shallow lakes: *Journal of the Environmental Engineering Division of the American Society of Civil Engineers*, v. 107, no. EE4, p. 713–730.
- U.S. Environmental Protection Agency, 2000, Nutrient criteria technical guidance manual—Lakes and reservoirs (1<sup>st</sup> ed.): U.S. Environmental Protection Agency, EPA–822–B00–001, variously paged.
- U.S. Geological Survey, 1999, Virginia land cover data set, edition 1: Sioux Falls, SD; accessed January 30, 2003, at <http://edcwww.cr.usgs.gov/programs/lccp/nationallandcover.html>.
- Van der Does, Joop, Verstraelen, Pierre, Boers, Paul, Van Roestel, Jan, Roijackers, Rudi, and Moser, Gerard, 1992, Lake restoration with and without dredging of phosphorus-enriched upper sediment layers: *Hydrobiologia*, v. 233, no. 1–3, p. 197–210.
- Virginia Department of Environmental Quality, 2006, Basis for the development of nutrient criteria for lakes and reservoirs and guidance on monitoring, assessment and permitting [draft]: Richmond, VA, 21 p.
- Welch, E.B., and Cooke, G.D., 1995, Internal phosphorus loading in shallow lakes—Importance and control: *Journal of Lake and Reservoir Management*, v. 11, no. 3, p. 273–281.
- Welch, E.B., and Cooke, G.D., 1999, Effectiveness and longevity of phosphorus inactivation with alum: *Journal of Lake and Reservoir Management*, v. 15, no. 1, p. 5–27.
- Welch, E.B., DeSpari, C.L., and Spyridakis, D.E., 1986, Effectiveness of alum in a weedy, shallow lake: *Water Resources Bulletin*, v. 22, no. 6, p. 921–926.
- Welch, E.B., Michaud, J.P., and Perkins, M.A., 1982, Alum control of internal phosphorus loading in a shallow lake: *Water Resources Bulletin*, v. 18, no. 6, p. 929–936.
- Wetzel, R.G., 1975, *Limnology*: Philadelphia, PA, W.D. Sanders Company, 743 p.
- White, R.K., Hayes, D.C., Guyer, J.R., and Powell, E.D., 2003, Water-resources data, Virginia, water year 2002—Surface-water discharge and surface-water quality records: U.S. Geological Survey Water-Data Report VA–02–1, 538 p.
- White, R.K., Hayes, D.C., Guyer, J.R., and Powell, E.D., 2004, Water-resources data, Virginia, water year 2003—Surface-water discharge and surface-water quality records: U.S. Geological Survey Water-Data Report VA–03–1, 562 p.
- Wilde, F.D., ed., variously dated, Field measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6; accessed on various dates at <http://pubs.water.usgs.gov/twri9A6>.
- Wilde, F.D., Radtke, D.B., Gibb, Jacob, and Iwatsubo, R.T., eds., 1999, Processing of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A5, variously paged.
- Winter, T.C., Harvey, J.W., Franke, O.L., and Alley, W.M., 1998, Ground water and surface water—A single resource: U.S. Geological Survey Circular 1139, 79 p.
- Young, T.C., Collins, A.G., and Armstrong, A.A., 1988, A pilot-scale evaluation of alum treatments to reduce lake sediment phosphorus release: *Journal of Environmental Quality*, v. 17, no. 4, p. 673–676.
- YSI Incorporated, undated, YSI Environmental operations manual: 6 Series environmental monitoring systems: Yellow Springs, OH, YSI Incorporated, variously paged.



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