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

# Geohydrology and Limnology of Walden Pond, Concord, Massachusetts

Water-Resources Investigations Report 01-4137



Prepared in cooperation with the MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL MANAGEMENT



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By JOHN A. COLMAN and PAUL J. FRIESZ

Water-Resources Investigations Report 01-4137

Prepared in cooperation with the MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

Northborough, Massachusetts 2001

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#### CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	Ву	To obtain
cubic meter (m <sup>3</sup> )	35.31	cubic foot
cubic meter per year (m <sup>3</sup> /yr)	35.31	cubic foot per year
gram (g)	0.03527	ounce, avoirdupois
gram per square meter (g/m <sup>2</sup> )	0.003278	ounce, avoirdupois per square foot
hectare (ha)	0.003861	square mile
kilogram (kg)	2.205	pound
kilogram per year (kg/yr)	2.205	pound per year
kilometer (km)	0.6214	mile
liter per minute (L/min)	0.2642	gallon per minute
meter (m)	3.281	foot
meter per year (m/yr)	3.281	foot per year
micrometer (µm)	0.00003937	inch
millimeter (mm)	0.03937	inch
square centimeter per second (cm <sup>2</sup> /s)	0.1550	square inch per second
square kilometer (km <sup>2</sup> )	0.3861	square mile
square meter (m <sup>2</sup> )	10.76	square foot
Temperature is given in degrees (	Celsius (°C), whi	ch can be converted to degrees
Fahrenheit (°F) b	y use of the follo	wing equation:
°F	F = 1.8 (°C) + 32	

#### CONVERSION FACTORS

#### VERTICAL DATUM

**Sea level:** In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

#### ABBREVIATIONS

Abbreviated water-quality units used in this report: Chemical concentration in water solution is given in grams per liter (g/L), milligrams per liter (mg/L), micrograms per liter ( $\mu$ g/L), or nanograms per liter (ng/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand milligrams per liter is equivalent to one gram per liter. One thousand micrograms per liter is equivalent to one milligrams per liter is equivalent to one microgram per liter. Specific conductance is given in microsiemens per centimeter ( $\mu$ S/cm). One microsiemen is equivalent to one millionth of siemen.

# Geohydrology and Limnology of Walden Pond, Concord, Massachusetts

By John A. Colman and Paul J. Friesz

#### Abstract

The trophic ecology and ground-water contributing area of Walden Pond, in Concord and Lincoln, Mass., were investigated by the U.S. Geological Survey in cooperation with the Massachusetts Department of Environmental Management from April 1997 to July 2000. Bathymetric investigation indicated that Walden Pond (24.88 hectares), a glacial kettle-hole lake with no surface inlet or outlet, has three deep areas. The maximum depth (30.5 meters) essentially was unchanged from measurements made by Henry David Thoreau in 1846. The ground-water contributing area (621,000 square meters) to Walden Pond was determined from water-table contours in areas of stratified glacial deposits and from land-surface contours in areas of bedrock highs. Walden Pond is a flow-through lake: Walden Pond gains water from the aquifer along its eastern perimeter and loses water to the aquifer along its western perimeter. Walden Pond contributing area also includes Goose Pond and its contributing area. A water budget calculated for Walden Pond, expressed as depth of water over the

lake surface, indicated that 45 percent of the inflow to the lake was from precipitation (1.215 meters per year) and 55 percent from ground water (1.47 meters per year). The groundwater inflow estimate was based on the average of two different approaches including an isotope mass-balance approach. Evaporation accounted for 26 percent of the outflow from the lake (0.71 meters per year) whereas lake-water seepage to the ground-water system contributed 74 percent of the outflow (1.97 meters per year). The waterresidence time of Walden Pond is approximately 5 years.

Potential point sources of nutrients to ground water, the Concord municipal landfill and a trailer park, were determined to be outside the Walden Pond ground-water contributing area. A third source, the septic leach field for the Walden Pond State Reservation facilities, was within the ground-water contributing area. Nutrient budgets for the lake indicated that nitrogen inputs (858 kilograms per year) were dominated (30 percent) by plume water from the septic leach field and, possibly, by swimmers (34 percent). Phosphorus inputs (32 kilograms per year) were dominated by atmospheric dry deposition, background ground water, and estimated swimmer inputs. Swimmer inputs may represent more than 50 percent of the phosphorus load during the summer.

The septic-system plume did not contribute phosphorus, but increased the nitrogen to phosphorus ratio for inputs from 41 to 59, on an atomto-atom basis. The ratio of nitrogen to phosphorus in input loads and within the lake indicated algal growth would be strongly phosphorus limited. Nitrogen supply in excess of plant requirements may mitigate against nitrogen fixing organisms including undesireable blooms of cyanobacteria. Based on areal nutrient loading, Walden Pond is a mesotrophic lake. Hypolimnetic oxygen demand of Walden Pond has increased since a profile was measured in 1939. Currently (1999), the entire hypolimnion of Walden Pond becomes devoid of dissolved oxygen before fall turnover in late November; whereas historical data indicated dissolved oxygen likely remained in the hypolimnion during 1939. The complete depletion of dissolved oxygen likely causes release of phosphorus from the sediments.Walden Pond contains a large population of the deep-growing benthic macro alga Nitella, which has been hypothesized to promote water clarity in other clear-water lakes by sequestering nutrients and keeping large areas of the sediment surface oxygenated. Loss of Nitella populations in other lakes has correlated with a decline in water quality. Although the Nitella standing crop is large in Walden Pond, Nitella still appears to be controlled by nutrient availability. Decreasing phosphorus inputs to Walden Pond, by amounts under anthropogenic control would likely contribute to the stability of the Nitella population in the metalimnion, may reverse

oxygen depletion in the hypolimnion, and decrease recycling of phosphorus from the sediments.

#### INTRODUCTION

Walden Pond, the deepest lake in Massachusetts, has great historical, naturalistic, and limnological significance as the lake on which Henry David Thoreau lived from July 1845 to September 1847 and the subject of his well-known essay "Walden: or, Life in the Woods" (Thoreau, 1854). Since Thoreau's time, the uses of Walden Pond and environs have included a wood lot, an amusement park in the late 1800's, and a county park after 1922. In 1975 the area was designated a Massachusetts State Reservation. Walden Pond is located 24 km west northwest of Boston (fig. 1), in Concord, Mass., with a watershed that extends into Lincoln, Mass. Located in a large metropolitan area, Walden Pond potentially may be altered by factors common to urban development: a municipal landfill, septic leachate from the Walden Pond State Reservation bathhouse and headquarters, and high visitor use rates. Walden Pond retains clear, generally good water quality primarily because of conservation efforts that protect the woods and shore surrounding the lake. Questions remain whether these conservation efforts are enough to continue to maintain good water quality.

The cooperative investigation of the geohydrology and limnology of Walden Pond by the U.S. Geological Survey and the Massachusetts Department of Environmental Management was motivated by the historical significance of Walden Pond and by its unusual limnological characteristics: deepest natural lake in Massachusetts, protected drainage basin, and lack of surface inlet or outlet stream. This report documents present (1997–99) conditions and baseline data for Walden Pond that can be used to understand aquifer and lake water levels and water-quality conditions. The data also may be compared with data from other seepage lakes formed in glacial outwash and deltaic deposits in eastern Mass., many of which are stressed by high



Figure 1. Location and setting of Walden Pond, Concord, Massachusetts.

use or other development pressures. The cartographic, hydrologic, and limnologic results from the Walden Pond investigation are summarized in a map report (Friesz and Colman, 2001), depicting the entire ground-water contributing area at relatively high resolution.

The authors especially are indebted to Ariane Mercandante (U.S. Geological Survey) for help with field work, organization, and database management. Michelle Dumas and the staff at Walden Pond State Reservation always were helpful during the study. Also, the help of Mike Gildesgane (Massachusetts Department of Environmental Management) in initiating and supporting the project is greatly appreciated.

#### GEOLOGIC SETTING AND BATHYMETRY

Walden Pond is a kettle-hole lake, formed at the end of the last glaciation (Wisconsinan stage) about 15,000 years ago by the melting of a large block of ice that broke off from the retreating glacier. Initially resting on the bottom of glacial Lake Sudbury, the ice block eventually was surrounded by deltaic and outwash deposits (Koteff, 1963). These sorted, stratified deposits, which now form the shore and sides of the lake, range mainly in size from fine sand to coarse gravel (Koteff, 1964) (fig. 2). Lithologic and natural gamma logs, continuous seismic reflection, and fathometer data collected during the current investigation indicate that the lake and its associated finegrained lake sediments extend to the till and bedrock surface, which is granite (Zen, 1983), in the deepest areas of Walden Pond (fig. 2). Fine-grained lake sediments that extend about 6 m below the lake basins are approximately equal in thickness in each deep area.

The bathymetry of Walden Pond reflects the shape of the original ice block and the topography of the bedrock under the lake. Two historical bathymetric investigations by Thoreau (1854) in the winter of 1846 and by Deevey (1942) in August 1939, were less detailed than the bathymetry mapped for this investigation (fig. 3), which revealed a middle basin, previously unmapped. Fathometer-measured depths in this investigation were corrected to a common water-surface elevation of 48.27 m above sea level. Decreased depth, by comparison with the historical results (table 1), might indicate the recent rate of filling in (sedimentation) of the lake; however, differences in measurement techniques and unrecorded surface datums in previous investigations make direct comparisons invalid.

#### Table 1. Bathymetric surveys of Walden Pond, Concord, Massachusetts

[Data sources: Thoreau (1854) and Deevey (1942).  $m^3$ , cubic meter; m, meter;  $m^2$ , square meter; --, no data]

Invest- igator	Number of measurements	Area (m²)	Volume (m <sup>3</sup> )	Maximum depth (m)	Mean depth (m)
Thoreau	75	249,800		31.1	
Deevey	50	248,200	3,224,150	31.3	12.99
This investi- gation	1,700	248,800	3,211,450	<sup>1</sup> 30.5	12.91

<sup>1</sup>Lake level altitude of 48.27 m.



Figure 2. Generalized geologic cross section A-A' through Walden Pond, Concord, Massachusetts, and split-spoon interval, lithologic log, and natural-gamma log from monitoring well CTW214. (Line of section shown in fig. 4.)



Coordinates shown as 500 meter grid, Massachusetts State Plane Projection, 1983



#### HYDROLOGY

The aquifer underlying and surrounding Walden Pond, composed of stratified glacial deposits, is bordered by the Sudbury River and Concord River (fig. 1). Because there is no surface inlet or outlet to Walden Pond, the land-surface area contributing water to the lake is defined by its ground-water contributing area. Water from precipitation infiltrates the permeable surficial deposits, recharges the aquifer, then flows in the direction of decreasing water levels and discharges to a surface-water body. Thus, the surface topography does not necessarily define the area contributing water to the lake. Along steep shoreline areas sloping towards Walden Pond, including areas outside of the groundwater contributing area, small amounts of overland flow may occur after intense precipitation events. Knowledge of the land-surface area contributing ground water to Walden Pond can be used by waterresource planners in lake management. Knowledge of the water balance of Walden Pond can improve the understanding of lake hydrology and nutrient budget.

#### **Data-Collection Methods**

Water levels collected at 40 monitoring wells and 8 ponds (fig. 4) provided data on water-table fluctuations and ground-water flow directions in the Walden Pond vicinity. Monitoring wells were installed for this study and in addition, other wells were present in the vicinity of the Concord municipal landfill. The monitoring wells were screened at or near the water table with the exception of CTW165, which is part of the USGS long-term ground-water level network in Massachusetts. The altitude of the monitoring wells and pond-stage measuring points were surveyed to determine consistent water-level measurements related to sea-level altitude.

Water samples for isotopic analysis were stored in glass bottles with polyseal caps to prevent evaporation and were analyzed for isotopic values at a U.S. Geological Survey laboratory in Reston, Va. Precipitation samples for isotopic analysis were collected over the duration of specific precipitation events or over several-week periods from July 1998 to September 1999 in a wet-fall bucket. The wet-fall bucket was part of an atmospheric deposition station (fig. 4) and was sealed from the atmosphere except during precipitation events. Volume-weighted bulk samples were analyzed for each month, except for March and April 1999 when one volume-weighted sample was used to represent the 2-month period. Water samples for isotopic composition of ground water were collected from well LVW30 approximately monthly from July 1998 to June 1999 and less frequently from wells CTW203 and LVW33 (fig. 4). These ground-water samples were collected after an equivalent of at least three volumes of water in the well casing had been removed and temperature and specific conductance measurements had stabilized. Water samples for isotopic analysis were collected from the surface of Walden Pond at the east end deep area (fig. 4) approximately monthly during ice-free periods from June 1998 to June 1999. Atmospheric temperature and relative humidity, parameters used indirectly to calculate the atmospheric composition of evaporated water, were measured hourly by a sensor 2.7 m above the land surface at CTW205, and recorded by a data logger.

#### Water-Table Configuration and Extent of the Ground-Water Contributing Area

The altitude and configuration of the water table in areas of stratified glacial deposits surrounding Walden Pond on July 19, 1999, are shown in figure 4 (modified from Friesz and Colman, 2001). Water-table contours were drawn in English units at 1-foot intervals except in areas with shallow gradients, where 0.5-foot intervals were used. All ponds were assumed to be in direct hydraulic connection with the underlying aquifer and represent a surface-water expression of the water table. Total precipitation for the 12 days previous to the water-level measurements amounted to 2 mm. The direction of ground-water flow, shown by arrows in figure 4, can be determined in areas of stratified glacial deposits from the altitude and configuration of the water-table contours. In areas of bedrock highs, such as Emersons Cliff and Pine Hill, ground water flows downslope through the overlying saturated till in the direction of declining land-surface contours because the bedrock surface is relatively impermeable compared to surficial deposits. The boundary of the groundwater contributing area of Walden Pond, also shown in figure 4, was drawn based on the water-table contours and ground-water flow directions.



Base map created by using TERRAMODEL and Mass GIS DTMs, 1999, Coordinates shown as 500 meter grid, Massachusetts State Plane Projection, 1983 North American Datum; 1:5,000 Executive Office of Environmental Affairs (EOEA); Protected and Recreational Open Space data from MassGIS, 1989, Massachusetts State Plane Projection, 1983 North American Datum; 1:24,000 EOEA; Surficial Geology data from USGS, 1964, Massachusetts State Plane Projection, 1983 North American Datum; 1:24,000 EOEA; Surficial Geology data from towns of Concord and Lincoln, 1999 State Plane Feet, Zone 5176, 1983 North American Datum; 1:5,000

Figure 4. Altitude and configuration of the water table on July 19, 1999, extent of the ground-water contributing area, and



bathymetry, Walden Pond, Concord, Massachusetts.

The water-table map indicates that Walden Pond is a flow-through lake in which the aquifer serves as both a recharge and discharge zone for Walden Pond; ground-water flows into the lake along its eastern perimeter and lake-water flows into the aquifer along its western perimeter. The ground-water contributing area for Walden Pond also includes the contributing area and the surface area of Goose Pond. Precipitation that falls directly on the surface of Goose Pond and ground water from the direction of Pine Hill that enters Goose Pond on its upgradient side, leaves the pond either through evaporation or as pond water that enters the aquifer on the downgradient sides of the pond. Because the altitude of Goose Pond is higher than most of the ground-water levels in the aquifer surrounding it, pond water flows in a radially outward pattern from the pond; some of this pond-derived water that enters the aquifer flows west toward Walden Pond.

The Walden Pond ground-water contributing area is mainly within the Reservation Boundary and other conservation land except for that part of the contributing area that also is part of Goose Pond and its contributing area. Depending on subsurface transport processes, the Reservation septic leach field and the leach fields from residences on privately owned land located in the contributing area east of Walden Pond are potential source of nutrients to the lake (fig. 4). Ground water in the Reservation septic leach field area flows westward toward the eastern shore of Walden Pond. Leach fields from houses in the contributing area are located in areas where ground water flows towards Walden Pond directly or indirectly through Goose Pond. Ground water in the southeastern part of Walden Pond contributing area generally flows northwest from till-covered bedrock highs, Emersons Cliff and Pine Hill. Most of the ground water from till-covered areas probably enters the stratified glacial deposits before discharging to Walden Pond. Northeast of Walden Pond, the Concord municipal landfill and the trailer park are located on the north side of a ground-water divide; ground water north of the divide flows generally northward away from Walden Pond toward Fairyland Pond and Mill Brook, a tributary to the Concord River (fig. 1). North of Walden Pond near well CTW212, a localized ground-water high is present. The high may result because of the increased water levels resulting from a decrease in flow in the finegrained sediments in this area, thinner sediments than the surrounding area, or both.

Lake-derived ground water flows towards and discharges into the Sudbury and Concord Rivers or to wetlands and streams draining into these rivers (figs. 1 and 4). Southwest of Walden Pond, between the bedrock high of Fairhaven Hill and Emersons Cliff, ground water discharges to Heywoods Meadow and the Andromeda Ponds, which drain into the Sudbury River by way of Fairhaven Bay. The steep water-table gradient southwest of Walden Pond is caused by large waterlevel differences (14 ft) between Walden Pond, ground water discharges into an unnamed stream and wetlands draining into the Sudbury River or into the Mill Brook watershed that drains into the Concord River.

# Ground-Water and Lake-Stage Fluctuations

Ground-water levels in the aquifer surrounding Walden Pond fluctuate because of seasonal and longterm variations in recharge to the aquifer from precipitation. Water levels in Walden Pond also fluctuate seasonally and over the long-term because inflows and outflows to the lake vary. Hydrographs from the long-term network well CTW165 and from Walden Pond, along with precipitation amounts, are shown in figures 5 and 6 to illustrate these seasonal and long-term fluctuations.

Water levels in well CTW165, located about 400 m north of Walden Pond near the intersection of Routes 2 and 126, have been measured periodically since February 1965. CTW165 consists of a 0.6 m screen about 8 m below the water table in an area where the unsaturated zone is about 12 m thick; waterlevel fluctuations at this well are assumed to be similar to water levels in wells screened at the water table. Mean ground-water-level altitude for the period of record is 48.12 m. The stage of Walden Pond was measured during this study and historical stage data were available from water levels collected by Walden Pond State Reservation staff in 1956 and from 1959 to 1971 (Walker, 1971). Precipitation data for part of 1957 and from 1958 to 1999 are from a National Oceanic and Atmospheric Administration (NOAA) climatological station in Bedford, Mass., 5 km northeast of the study area, whereas precipitation data from 1953 to 1956 and part of 1957 are from the NOAA climatological station in Framingham, Mass, about 14 km south of the study



Figure 5. Water levels at well CTW165 and Walden Pond, Concord, Massachusetts, and annual precipitation amounts, Bedford and Framingham, Massachusetts, 1953–99.

area (U.S. Department of Commerce, National Oceanic and Atmospheric Administration, 1995–99; Hydrosphere Data Products, 1995). The mean annual precipitation over the ground-water contributing area from 1960 to 1999 is 1.151 m.

The hydrograph from CTW165 (fig. 6) indicates, in general, that water levels rise from winter through early summer when recharge to the aquifer exceeds ground-water discharge; therefore, water is added to aquifer storage. From summer through winter, water levels decline because ground-water discharge exceeds recharge and water is released from aquifer storage. Water is available to recharge the aquifer after the soil moisture deficit has been satisfied in autumn and before late spring when evapotranspiration exceeds precipitation. The annual cycle of water-level rises and declines



Figure 6. Water levels at well CTW165 and Walden Pond, Concord, Massachusetts, and monthly precipitation amounts, Bedford, Massachusetts, 1995–99.

lag climatic conditions because of the transit time for precipitation to recharge the water table through the unsaturated zone and because of storage in the aquifer.

Water levels from Walden Pond show a fluctuation pattern that is similar to the ground-water hydrograph for the common years of data because the lake is hydraulically connected to the surrounding aquifer. The magnitude of fluctuations in Walden Pond are less than the aquifer, however, because the lake has proportionally greater storage capacity than the aquifer. Water levels in the lake rise when inflows from ground water and precipitation exceed outflow to ground water and evaporation; water levels decline when these outflows exceed inflows.

Long-term variations in water levels, reflective of long-term storage changes in the aquifer and Walden Pond, also are evident from the hydrographs (fig. 5). The lowest water-level altitude for the period of record, 46.38 m at CTW165 and 46.34 m at Walden Pond, was in early 1967 after 4 successive years of below average precipitation; cumulative precipitation deficiency from 1963 to 1966, amounting to about 1.17 m, caused this depletion in storage. Two periods of relatively high water-level altitudes occurred in 1956 and 1984. The highest recorded altitude of Walden Pond of 49.8 m in 1956 resulted from 4 successive years of above average precipitation. The highest recorded ground-water altitude of 49.91 m in 1984 was due to 2 years of near normal precipitation. Water levels fluctuated over a range of about 3.5 m for the period of record from 1956 to 1999.

Water-level altitude in CTW165 and of Walden Pond, measured on July 19, 1999, to prepare the watertable map, are shown in figure 5. The ground-water altitude was 48.29 m, which is 0.17 m above the longterm average and indicates that the water-table map in figure 4 is representative of near-normal water-table conditions. In the eastern half of Massachusetts, ground-water levels and streamflows generally were below normal from autumn 1998 to late summer 1999 (Socolow and others, 2000). Water levels in Walden Pond and its contributing area, however, were at or above-average levels because of the large quantity of water in storage and because of the low outflow rates from the lake and aquifer.

#### Water Balance

A water balance is determined by measuring or estimating the inflows and outflows to a lake and the change, if any, in lake-volume storage ( $\Delta S$ ). Water enters the lake from precipitation (*P*) that falls directly on the lake surface and from ground water upgradient of the lake (ground-water inflow,  $GW_i$ ). Water discharges from the lake through evaporation (*E*) from the lake surface and from lake-water seepage to the aquifer (ground-water outflow,  $GW_o$ ). Thus, the water-balance equation for a lake, similar to Walden Pond, without surface inflows and outflows can be expressed as

$$\Delta S = P + GW_i - E - GW_o \quad , \tag{1}$$

with values expressed in consistent units of either volumetric flow rates or linear units.

The water balance for Walden Pond was defined based on average annual conditions during the 5-year period 1995-99. Preliminary water-balance calculations indicated that the water-residence time of Walden Pond was approximately 5 years; therefore, inflows and outflows to the lake should be reflective of the climatic conditions during this period. There was no change in long-term lake storage during 1995-99 based on the ground-water hydrograph at CTW165 (fig. 6). Precipitation, ground-water inflow, and evaporation were determined from both site-specific and regional data, whereas ground-water outflow was calculated indirectly as a residual of the water balance. Inflow and outflow values are approximate because of uncertainties in the water-balance components, which can be attributed to measurement errors and the use of indirect calculations and regional data for site-specific purposes, among other factors (Winter, 1981).

#### **Precipitation and Evaporation**

The average annual precipitation on Walden Pond and surrounding area during 1995–99 was 1.215 m, which is 0.064 m above the 40-year long-term average. Annual precipitation during this 5-year period ranged from 0.147 m below to 0.404 m above longterm average annual precipitation. An average annual evaporation of 0.71 m from the lake surface was estimated using regional-scale rates from Farnsworth and others (1982), which were based on pan evaporation and pan coefficient measurements.

#### **Ground-Water Inflow**

The ground-water inflow rate to Walden Pond was determined by using contributing-area and isotope mass-balance approaches. Quantifying ground-water inflow with the contributing-area approach requires knowledge of the recharge rate and the size of the contributing area where ground water flows directly to Walden Pond. In addition, because Goose Pond is within the contributing area, the quantity of pond water entering the aquifer from Goose Pond and flowing as ground water to Walden Pond must be considered. An assumption of the contributing-area approach is that no upgradient ground water flows beneath or by-passes the lake because deep areas of the lake extend to the till and bedrock surface.

The isotope mass-balance approach is based on stable isotopes of oxygen and hydrogen that naturally are present in water. Inflows and outflows to a lake, and the lake water can have different isotopic signatures; these isotopic differences, along with precipitation and evaporation rates, can be used to determine groundwater inflow to a lake using a technique described by Krabbenhoft and others (1990). This technique has been used successfully in climatic conditions of the Midwest (Krabbenhoft and others, 1990; LaBaugh and others, 1997) and the southern United States (Sacks and others, 1998). The isotopic composition of oxygen  $(\delta^{18}O)$  and hydrogen  $(\delta D)$  is defined in delta  $(\delta)$ notation and reported in parts-per-thousand (per mil) relative to Vienna Standard Mean Ocean Water (V-SMOW). Laboratory precision of the oxygen and hydrogen isotope results is  $\pm 0.2$  and  $\pm 2$  per mil, respectively, at the 95-percent confidence interval (Tyler Coplen, U.S. Geological Survey, written commun., 1999).

#### **Contributing-Area Approach**

Recharge to ground water was estimated based on mean annual runoff from watersheds drained by streams. Annual runoff, equivalent to precipitation minus evapotranspiration over the watershed, provides an estimate of maximum water available for recharge to ground water. Because the Walden Pond watershed lacks surface-water drainage, all water available to recharge the ground water should infiltrate the permeable surficial deposits. Randall (1996) constructed lines of equal mean annual runoff for the glaciated Northeast United States based on record from streamflow-gaging stations over the 30-year period, 1951-80; annual runoff averaged 0.58 m (depth of water over a watershed) when precipitation averaged 1.12 m. Watershed studies that have compared precipitation and runoff have found that annual evapotranspiration rates are not greatly affected by variations in annual precipitation (Lyford and Cohen, 1988); therefore, for this study, the recharge estimate was increased by 0.10 m to 0.68 m to account for the increased average precipitation during the 1995–99 period. The ground-water contributing area of Walden Pond that is not part of Goose Pond, 463,000 m<sup>2</sup>, was multiplied by the recharge value resulting in a ground-water inflow value of  $315,000 \text{ m}^3/\text{yr}$ .

The ground-water contribution to Walden Pond from Goose Pond for 1995-99 was determined by a water-balance analysis. Precipitation falling directly on Goose Pond, which has a surface area of  $46,000 \text{ m}^2$ , was computed to be 56,000  $\text{m}^3/\text{yr}$ . Ground-water inflow from the contributing area of Goose Pond, which covers an area of 112,000 m<sup>2</sup>, was calculated to be 76,000 m<sup>3</sup>/yr. Evaporation from the pond surface was equal to 33,000 m<sup>3</sup>/yr. The average annual groundwater outflow from Goose Pond of 99,000 m<sup>3</sup>/yr was determined by balancing the water budget on the basis of the above values. Because about 20 percent of the outflow perimeter of Goose Pond lies within the contributing area of Walden Pond, 20 percent of the average annual ground-water outflow from Goose Pond, or  $20,000 \text{ m}^3/\text{yr}$ , was assumed to flow toward Walden Pond.

The average annual ground-water inflow to Walden Pond totals  $335,000 \text{ m}^3/\text{yr}$  or, expressed as depth of water over the lake surface, 1.35 m/yr (volumetric flow rate,  $335,000 \text{ m}^3/\text{yr}$ , divided by

lake-surface area, 249,000 m<sup>2</sup>). The ground-water contribution from Goose Pond is 6 percent of this total ground-water inflow.

#### Isotope Mass-Balance Approach

The isotope mass-balance approach combines the water-balance equation (equation 1) with an isotopic mass-balance equation

$$\Delta S(\delta_L) = P(\delta_P) + GW_i(\delta_{GW_i}) - E(\delta_E)$$
$$- GW_o(\delta_{GW_o}), \qquad (2)$$

where  $\Delta S$ , P,  $GW_i$ , E, and  $GW_o$  have been defined previously and  $\delta_L$ ,  $\delta_P$ ,  $\delta_{GWi}$ ,  $\delta_E$ ,  $\delta_{GWo}$  are the isotopic composition of the lake, precipitation, ground-water inflow, evaporated water, and ground-water outflow, respectively. This approach assumes that the lake is at hydrologic and isotopic steady-state and that the isotopic composition of ground-water outflow is equivalent to the isotopic composition of a well-mixed lake. Because the water-balance equation is rearranged to solve for ground-water outflow and then substituted into the isotopic mass-balance equation, this component of the outflow drops out and, thus, does not need to be calculated directly. The isotopic mass-balance approach for a lake without surface-water inflow and outflow to determine ground-water inflow is expressed as (Krabbenhoft and others, 1990)

$$GW_1 = \frac{P(\delta_L - \delta_P) + E(\delta_E - \delta_L)}{\delta_{GW_1} - \delta_L},$$
(3)

where all parameters are defined previously. Average isotope values from water samples collected from July 1998 to June 1999 were assumed to represent the average isotopic values for the 5-year period of 1995–99.

The temporal distribution of the isotopic composition of precipitation, ground-water inflow, and lake water are illustrated using  $\delta^{18}$ O (fig. 7). The  $\delta$ D results have similar temporal trends and these values are listed in appendix A. The  $\delta^{18}$ O of precipitation varied seasonally ranging from -11.2 in December 1998 to -3.26 in July 1999. This seasonal variation in isotopic composition of precipitation is due primarily to changes in



Figure 7. Temporal variation in delta oxygen-18 of precipitation, ground-water inflow, and lake water, Walden Pond, Concord, Massachusetts, and monthly precipitation amounts, Bedford, Massachusetts, June 1998 to September 1999.

atmospheric temperature (Gat, 1980). Volumeweighted averages for the period July 1998 to June 1999 were -7.54 for  $\delta^{18}$ O and -42.8 for  $\delta$ D. Isotopic composition of ground-water inflow varied little spatially and temporally. Average values from LVW30, -9.35 for  $\delta^{18}$ O and -58.7 for  $\delta$ D, were used to represent the isotopic composition of ground-water inflow to Walden Pond. The average annual isotopic composition of ground water has lower values in  $\delta^{18}$ O and  $\delta$ D compared to the average annual isotopic composition of precipitation because precipitation recharges the aquifer primarily from autumn to spring, when atmospheric temperature is low. Evaporation from the lake surface enriches the lake water in oxygen-18 and deuterium compared to precipitation and ground-water inflow. The  $\delta^{18}$ O of lake water ranged from -4.14 to -3.61, which indicated minimal seasonal variation in the isotopic composition of the lake, as is typical of deep surface-water bodies with relatively long waterresidence times (Dincer, 1968). The variation in the isotopic composition of lake surface water that was present probably results because of the seasonal variation in evaporation rates and the seasonal variation in the isotopic composition of precipitation. The average isotopic composition of the lake water based on December 1998 and March 1999 isotope values, when Walden Pond was thermally and chemically mixed, was -3.94 for  $\delta^{18}$ O and -34.4 for  $\delta$ D.

Values of  $\delta^{18}$ O and  $\delta$ D of ground-water inflow, lake water, and rainfall-dominated precipitation samples, excluding the precipitation sample from July 1999, which may have been affected by evaporation, are shown in figure 8. The local meteoric water line (LMWL), determined from the rainfall-dominated precipitation samples, is defined by the regression equation

$$\delta D = 7.22\delta^{18}O + 8.52$$
 (n=11; R<sup>2</sup>=0.96).

This LMWL differs from the Global Meteoric Water Line (GMWL) of  $\delta D = 8\delta^{18}O + 10$  probably because of the limited number and range of data points used in the calculation. The isotopic composition of groundwater inflow plots along this LMWL, indicating that water recharging the aquifer was unaffected by evaporation. Lake water, which has been affected by evaporation, plots to the right of the LMWL because evaporation causes an increased enrichment of  $\delta^{18}$ O relative to  $\delta D$  in the lake water. An evaporation line of less steep slope than the LMWL was drawn from the midpoint between the average annual isotopic composition of precipitation and ground-water inflow, and through the lake samples. The midpoint between the source waters was used because, as explained in a subsequent section of this report, about 50 percent of the inflows to the lake are from each of these sources. This evaporation line indicates the isotopic evolution of lake water from its source waters (Krabbenhoft and others, 1990).



Figure 8. Relation between delta oxygen-18 and delta deuterium in precipitation, ground-water inflow, and lake water, Walden Pond, Concord, Massachusetts, June 1998 to September 1999.

The isotopic composition of evaporated lake water was calculated indirectly based on an equation derived by Craig and Gorden (1965)

$$\delta_E = \frac{\alpha^* \delta_L - h \delta_A - \varepsilon}{1 - h + 0.001 \Delta \varepsilon}, \qquad (4)$$

where  $\delta_E$  and  $\delta_L$  have been defined previously and  $\delta_A$  is the isotopic composition of atmospheric moisture; h is relative humidity normalized to the temperature of the lake surface water;  $\alpha^*$  is the equilibrium fractionation factor at the temperature of the air-water interface defined by Majoube (1971):  $\Delta \varepsilon$  is the kinetic fractionation factor estimated as 14.3(1-h) and 12.4(1-h) for  $\delta^{18}$ O and  $\delta$ D, respectively (Gilath and Gonfiantini, 1983), in units of per mil; and  $\varepsilon$  is the total fractionation factor equivalent to 1,000 (1 -  $\alpha^*$ ) +  $\Delta \epsilon$ , in units of per mil. The isotopic composition of atmospheric moisture was not measured directly as part of this investigation; however, this parameter can be estimated by assuming it is in isotopic equilibrium with precipitation. Krabbenhoft and others (1990) measured this parameter in their lake study and found that seasonal variation in the isotopic composition of atmospheric moisture parallels that of precipitation for most of the year with the poorest agreement during the warmest months of July and August. They also determined that most of the uncertainty in the isotope massbalance approach from their lake study was due to the uncertainties in  $\delta_E$  and evaporation.

Monthly average values of the isotopic composition of evaporated water were calculated for ice-free months with equation 4; an annual volume-weighted average was then determined based on estimated monthly evaporation rates. The monthly average values used to calculate the  $\delta^{18}$ O of evaporated water are shown in table 2. The volume-weighted average for the July 1998 to June 1999 period was -23.3 for  $\delta^{18}$ O and -98.4 for  $\delta$ D.

Ground-water inflow calculated with equation 3 resulted in 1.73 m/yr for  $\delta^{18}$ O and 1.45 m/yr for  $\delta$ D, which compare favorably to the estimate based on the contributing-area approach. An average of 1.59 m/yr was calculated for the  $\delta^{18}$ O and  $\delta$ D values.

#### Average Ground-Water Inflow

Ground-water inflow calculated on the basis of the contributing-area approach was 1.35 m/yr. Groundwater inflow determined on the basis of the isotope mass-balance approach was 1.59 m/yr. A ground-water inflow value of 1.47 m/yr (366,000 m<sup>3</sup>/yr), based on the average of the contributing-area and isotope massbalance approaches, was used in the water-balance analysis for Walden Pond.

#### Water-Balance Results

Average annual inflow to Walden Pond for the 5-year period 1995–99, from precipitation and ground water, totaled about 2.68 m/yr (667,000 m<sup>3</sup>/yr). The water-residence time for the lake, calculated by dividing the volume of the lake by the total inflow rate, was 4.8 years. A summary of the average annual water balance is shown graphically in figure 9 partitioned on the basis of the magnitude of inflow and outflow components. Precipitation on the lake surface accounted for about 45 percent of the inflow, whereas ground-water inflow contributed about 55 percent of the inflow.



Figure 9. Average annual water balance, Walden Pond, Concord, Massachusetts.

#### Table 2. Monthly average values used to calculate the delta oxygen-18 of evaporated water, Walden Pond, Concord, Massachusetts

[Temperature—Lake: Monthly or average of bimonthly temperature measurements of lake-surface water; March 1999 estimated from March 1998. Temperature—Air: July and August 1998 estimated from July and August 1999. Relative humidity: Normalized to the temperature of the lake-surface water. Isotopic composition of lake water: May 1999 is an average of April and June 1999. Evaporation: Average annual evaporation, distributed monthly is appoximated from the percentage of annual evaporation each month at Mirror Lake, New Hampshire, calculated for 1990–95 and 1997–98 (Mirror Lake data provided by Donald Rosenberry, U.S. Geological Survey, written commun., 2000). °C, degrees Celsius; δA, isotopic composition of atmospheric moisture; δP, isotopic composition of precipitation; --, not applicable]

	Tempe (°	erature C)	Relative	Equilibrium	Kinetic fraction-	Total fraction-	Isotopic composition	Equilibrium fractionation	Isotopic composition	Isotopic composi-	Isotopic composition	<b>F</b> ()
Date	Lake	hum Lake Air (frac		fraction- ation factor	ation factor (per mil)	ation factor (per mil)	of precip- itation (per mil)	factor between δP and δA	of atmo- spheric moisture (per mil)	tion of lake water (per mil)	of evapo- rated water (per mil)	Evaporation (meters)
July 1998	26.8	23.6	0.614	0.99086	5.52	14.66	-6.55	9.22	-15.8	-4.14	-23.2	0.15
August 1998	25.8	21.0	.573	.99078	6.11	15.33	-5.33	9.31	-14.6	-3.61	-24.3	.12
September 1998	22.8	18.2	.570	.99053	6.15	15.62	-7.87	9.56	-17.4	-3.78	-21.6	.10
October 1998	15.8	11.0	.551	.98994	6.42	16.48	-7.25	10.16	-17.4	-3.77	-23.3	.06
November 1998	9.4	5.3	.555	.98935	6.36	17.01	-7.46	10.76	-18.2	-3.84	-23.7	.02
December 1998	5.8	2.4	.547	.98901	6.48	17.47	-11.2	11.11	-22.3	-3.85	-19.7	.01
January 1999		-3.0										
February 1999		2										
March 1999	4.3	3.2	.598	.98886	5.75	16.89	-8.16	11.27	-19.4	-4.04	-22.7	.01
April 1999	10.5	9.1	.519	.98946	6.88	17.42	-8.16	10.65	-18.8	-4.03	-23.9	.04
May 1999	17.6	14.9	.603	.99010	5.68	15.58	-5.31	10.00	-15.3	-3.86	-25.2	.08
June 1999	23.2	21.2	.612	.99057	5.55	14.98	-6.42	9.52	-15.9	-3.68	-22.5	.12
Annual volume-weig	hted avei	age of th	e isotopic co	mposition of e	vaporated w	ater (per m	il)					-23.3

Outflow from the lake because of evaporation from the lake surface accounted for 26 percent of the outflow. Ground-water outflow (1.97 m/yr), calculated as the residual value of the water-balance equation, accounted for 74 percent. Ground water is the dominant pathway into and out of Walden Pond.

#### LIMNOLOGY

The primary public concern for Walden Pond relates to the trophic (nutritional) ecology of the lakewhether urban development or high public use at the Walden Pond State Reservation may have altered or will alter the relation between plant nutrient supplies and plant growth in the lake. Plant nutrient supplies, especially of growth-limiting nitrogen (N) and phosphorus (P), are key water-quality features of kettle-lake investigations because nutrients determine the type and quantity of lake biomass production, and plant growth, in turn, affects water clarity and controls the amount of summer dissolved oxygen (DO) present in the deep water. In addition, cycling of natural bioactive chemical constituents of the water is affected by plant production as is, to a degree, cycling of bioconcentrating pollutants like polychlorinated biphenyls and mercury. Trophic ecology, in turn, depends on hydrogeologysources, amounts, and cycling of water, and on chemical constituents carried by the water. The geohydrologic appraisal of Walden Pond limnology developed in this report leads to a determination of the ecological trophic state of the lake and to assessments of past and potential future ecological changes.

#### **External Inputs**

Sources and amounts of water that enter Walden Pond were described in the "Hydrology" section of this report. In the "Limnology" section, estimates are made of the chemical constituents contained in the water and of the constituent fluxes represented by flow of water into Walden Pond. Sources of nutrient inputs for Walden Pond, which lacks a stream input, are ground water, atmospheric deposition, avian, stocked fish, swimmers, and direct runoff from parking-lot and road pavement.

Nutrient inputs for Walden Pond were estimated recently by Baystate Environmental (1995). The present investigation remeasured ground-water and atmospheric-deposition inputs, which are important particularly for nutrient budgets of kettle-hole seepage lakes. Values for other nutrient budget components were taken directly or modified from Baystate Environmental (1995).

# Ground-Water Nutrient Inputs

Ground-water nutrient inputs were divided into point-source and background contributions. Depending on geochemical conditions in the aquifer, estimates of inputs from these sources can be determined from the product of ground-water flow and measured concentrations of nutrients.

### Sampling and Analytical Methods for Ground Water

Chemical-constituent concentrations in ground water were determined by sampling 12 monitoring wells open to the water table and 2 deeper wells, CTW 213 and CTW 214 (30.5 and 32.9 m, respectively, below ground surface) (fig. 10). The deeper well was screened 19 m below the water table. Wells were cased with PVC and 1.5-m screens were installed, appropriate for sampling for nutrients, major ions, iron (Fe), and manganese (Mn) (Lapham and others, 1995). Additional information on ground-water quality was obtained from steel, temporary-drive-point wells located along the beach within the ground-water contributing zone (fig. 10).

Water quality was monitored in wells monthly during November 1998 to September 1999. Samples were collected after pumping at least three well volumes and after conductance stabilized. Whole-water samples were collected first, followed by dissolved samples, which were collected using an in-line Gelman cartridge filter (0.4  $\mu$ m pore size). During the March 1999 sampling, four wells (CTW 213, 214, 205 and 216) were packed off above the well screen using a Keck pump and packer to avoid contamination with atmospheric oxygen. After packing, wells were pumped from 2 to 4 L/min, and DO, pH, and conductance were monitored with a flow-through cell, until stable values were obtained.

In October 1999, the 19 temporary drive-point wells (0.76 m below lake water level) were installed in shallow water (0.3 m) and sampled once at intervals along most of the shore bordering the contributing area of Walden Pond (fig. 10). The samples were referenced as "beach-perimeter samples." Before sampling, the drive-point wells were flushed for more than three casing volumes using a peristaltic tubing pump.



Figure 10. Specific conductance, nitrate concentrations, and estimated extent of the septic-system plume, in the area of the Walden Pond State Reservation septic leach field, Concord, Massachusetts.

Samples were collected by pumping directly to sample bottles, for whole-water samples, or through a capsule filter, for dissolved samples. In December 1998, two drive-point wells were installed in shallow water where contaminated ground water was thought to discharge to Walden Pond (fig. 10). Samples from these wells were obtained at 0.76 m intervals below the lake-water surface elevation continuing down to a depth of 4.6 m. These samples were referenced as "beach-depth samples."

With the exception of samples obtained for P analysis, total and dissolved samples were preserved in the field according to methods of Fishman (1989) and shipped to the U.S. Geological Survey National Water Quality Laboratory for analysis. N, major ions, Fe, and Mn were analyzed according to U.S. Geological Survey methods (Fishman, 1989). Care was taken with P samples to minimize contamination during sampling. Procedures included use of acid-rinsed polyethylene bottles, use of plastic gloves during sampling, and transport of sample bottles in clean plastic bags. P samples were preserved with ultra-pure, concentrated sulfuric acid, 20 drops acid (1 mL) dispensed from a teflon dropping bottle per 250 mL sample (Stauffer, 1983). In the laboratory, filtered and whole-water samples were digested using potassium persulfate (Menzel and Corwin, 1965) and analyzed by the phosphomolybdate method (Strickland and Parsons, 1968, as modified by Stauffer, 1983.) Digested whole-water and filtered sample results were reported as total phosphorus and total dissolved phosphorus, respectively. With the use of the methods and procedures described above, a detection limit of 1 µg P/L was achieved. Analysis of two 25 µg P/L USGS standard-reference water samples were within 1  $\mu$ g P/L of the standard value.

#### Geochemical Conditions in the Aquifer

Determination of nutrient speciation and geochemical environment of the ground water was an investigative priority in addition to determination of nutrient content of the ground water. Speciation and geochemical conditions affect nutrient conservation during ground-water transport through the aquifer and during crossing of the sediment-water interface at discharge to the lake. In particular, the presence or absence of DO in the aquifer may determine whether N species will be oxidized to nitrate (NO<sub>3</sub><sup>-</sup>) or reduced to ammonium (NH<sub>4</sub><sup>+</sup>), or whether Fe will form the reduced, soluble ferrous ion (Fe<sup>+2</sup>). Determination of these forms for N is important because anions are more nearly conserved in transport than are cations, and for Fe because Fe<sup>+2</sup> precipitates in the presence of oxygen—during discharge at the sediment-water interface—and the hydrous ferric oxide formed can sorb or coprecipitate phosphate (PO<sub>4</sub><sup>3-</sup>) (Ryden and others, 1987).

Geochemical conditions of the aquifer were determined by collection of samples from packer-sampled wells, where changes in samples during sampling caused by contact with atmospheric oxygen would be eliminated. The well sites selected for packer sampling were chosen on the basis of proximity to areas of the aquifer that might be most subject to reduced conditions if those conditions did exist. DO can be removed during ground-water flow in long, deep flow paths (DeSimone and others, 1995) and in flow paths where organic carbon, such as might be present in septic leachate, has been discharged (Walter and others, 1996). Selected were the two deep wells, CTW 213 and CTW 214, and two wells open to the water table near the Walden State Reservation septic leach field, CTW 203 and CTW 216 (fig. 10).

The four packer-wells sampled in March 1999 were aerobic; DO concentrations ranged from 7.0 to 10.7 mg/L (table 3). Redox sensitive constituents, such as N, Fe, and Mn, sampled for in these four as well as in nine other wells (table 3) also indicated that oxidizing conditions prevailed as indicated by the presence of  $NO_3^-$ , rather than  $NH_4^+$ , and low concentrations of dissolved Fe (below detection limit of 10 µg/L in all wells but two, with 150 and 200 µg/L). Only concentrations of dissolved Mn (4.2–1,000 µg/L) gave an indication of reducing conditions.

The results described above indicate that ground water in the aquifer was aerobic and ground-water transport of N would be as NO<sub>3</sub><sup>-</sup>, which moves conservatively, that is, without loss. Fe and P would not co-precipitate during passage through the interface, because Fe concentrations were too low to affect P. Nutrient loads from the aquifer to the lake, then can be determined by the product of dissolved-nutrient concentration and ground-water discharge.

#### Table 3. Ground-water quality constituents that indicate geochemical conditions in the aquifer of Walden Pond, Concord and Lincoln, Massachusetts

Local identifier	Station No.	Date	Time	Specific conduc- tance (µS/cm at 25°C)	Field pH (standard units)	Water temper- ature (°C)	Dissolved oxygen	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Potassium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Sulfate, dissolved (mg/L as SO <sub>4</sub> )
					PAC	KER-SAN	MPLED WE	LLS					
CTW 213	422627071195902	3-23-99	1225	33	6.1	9.3	8.8	2.5	0.75	1.1	2.1	6	3.0
CTW 214	422627071195903	3-23-99	1120	49	6.0	9.7	7.0	4.4	1.3	2.3	5.3	15	5.0
CTW 203	422622071195901	3-24-99	0820	124	5.9	8.7	8.9	9.8	2.0	1.1	8.6	8	11
CTW 216	422626071195901	3-24-99	1020	371	5.5	9.3	10.7	24	3.9	21	23	7	18
					SAMI	PLED WI	FHOUT PAC	CKER					
CTW 244	422625071195901	3-24-99	1138	537	5.3			37	6.2	24	26	5	6.3
CTW 205	422627071195901	3-24-99	1455	132	5.8			8.6	1.6	1.7	13	12	15
CTW 205	422627071195901	8-19-98	1330	436	5.4			37	6.8	4.4	24		4.3
CTW 217	422627071195904	3-24-99	1259	165	5.1	9.6		9.8	3.1	2.2	9.0	3	1.5
CTW 218	422628071195801	3-24-99	1325	176	5.7	10.5		13	2.2	6.9	8.7	10	7.7
LVW 30	422616071200301	3-24-99	0920	124	5.8	8.8		3.0	.88	.62	18	8	9.5
CTW 204	422627071195701	3-24-99	1400	58	6.5	9.5		4.2	.88	.57	4.4	10	7.4
CTW 206	422626071200401	3-24-99	1430	77	6.1			5.5	1.0	1.4	6.4	12	2.8
LVW 33	422613071201201	3-24-99	1540	60	5.9	8.5		2.2	.55	.35	8.1	5	6.7

[No., number; °C, degrees Celsius; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; mg/L, milligram per liter; <, actual value is less than value shown; --, not measured]

Table 3. Ground-water quality constituents that indicate geochemical conditions in the aquifer of Walden Pond, Concord and Lincoln, Massachusetts—Continued

Local identifier	Station No.	Date	Time	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Silica, dissolved (mg/L as SiO <sub>2</sub> )	Ammonia, nitrogen (mg/L as N)	NO <sub>2</sub> + NO <sub>3</sub> , nitrogen, dissolved (mg/L as N)	Phos- phorus, total dissolved (mg/L as P)	lron, dissolved (μg/L)	lron, total (μg/L)	Manga- nese, dissolved (µg/L)	Manga- nese, total (µg/L)
					PACK	ER-SAMP	LED WELL	S					
CTW 213	422627071195902	3-23-99	1225	2.7	< 0.10	9.9	0.144	0.39		150		158	
CTW 214	422627071195903	3-23-99	1120	3.3	<.10	16	.036	.37		<10		64	
CTW 203	422622071195901	3-24-99	0820	9.8	<.10	16	.024	4.8		<10		33	
CTW 216	422626071195901	3-24-99	1020	85	<.10	31	.024		0.027	<10	3,100	629	660
					SAMPI	LED WITH	OUT PACK	ER					
CTW 244	422625071195901	3-24-99	1138	43	0.11	24	<.020	45.6		<10	270	1,000	1,100
CTW 205	422627071195901	3-24-99	1455	6.9	<.10	18	.035	5.06		<10	10	11	11
CTW 205	422627071195901	8-19-98	1330	35	<.10	19	.092	36.1	<.010	<10		133	
CTW 217	422627071195904	3-24-99	1259	14	<.10	16	.570	12.2	.060	200	450	829	830
CTW 218	422628071195801	3-24-99	1325	13	<.10	20	<.020	8.36	.022	<10	1,500	270	300
LVW 30	422616071200301	3-24-99	0920	23	<.10	9.8				<10		16	
CTW 204	422627071195701	3-24-99	1400	4.3	<.10	14	.039	.32		<10		4	
CTW 206	422626071200401	3-24-99	1430	10	<.10	15	<.020	.43		<10		6	
LVW 33	422613071201201	3-24-99	1540	8.2	<.10	12	<.020	.05		<10		10	

#### **Ground-Water Point Sources**

Three large point sources were present that potentially could discharge nutrients to ground water in the Walden Pond area: the Concord municipal landfill, septic leach fields associated with a former trailer park, and the septic leach field of the Reservation bathhouse and headquarters (fig. 4). Input to Walden Pond by way of ground water from the first two sources was ruled out by delineation of the ground-water contributing area (fig. 4), whereas the septic leach field of the Reservation bathhouse and headquarters was within the ground-water contributing area.

Ground-water flow direction at the septic leach field, as determined by triangulation among water table wells, varied by as much as 30 degrees during the course of a year but generally was in the direction of the plume indicated in figure 10. The presence of a ground-water plume containing N was measured in wells immediately downgradient from the Walden Pond State Reservation leach field (fig. 10 and table 4) and in the drive-point wells at the northeast shore of Walden Pond (fig. 10 and table 5). NO<sub>3</sub><sup>-</sup> ranged from 2.5 to 45.6 mg N/L (one outlier at 0.21 mg N/L) in the within-plume monitoring wells and from 0.9 to 6.7 mg N/L (one outlier at <0.05 mg N/L) in the northeastshore beach samples. Repeated measurements at the monitoring well sites (table 4) indicated that conductance and N concentrations fluctuated in the plume wells, likely because of changes in the ground-water flow pattern or source variability (seasonal use).

Comprehensive water analysis of selected ground-water samples (table 3) confirmed the plume presence by analogy with water-quality constituents in other sewage-related plumes. In coarse-grained, glacial drift aquifers in eastern Massachusetts, sewage plumes typically contain high levels of conductance, chloride (Cl), sodium (Na), and species of sulfur (S) and N, compared to ground water outside the plume. DO generally is present at low concentrations in the plumes and reducing conditions may develop (DeSimone and Howes, 1996; LeBlanc, 1984). Some of these characteristics of sewage plumes occur in the samples from the wells that are downgradient of the septic leach field between the leach field and Walden Pond. Calcium (Ca), magnesium (Mg), Mn, potassium (K), Na, Cl, sulfate  $(SO_4^{2^-})$ , and specific conductance, were higher in wells CTW 205, 216, 217, 218, and 244 downgradient of the leach field, compared to concentrations of these constituents in the deep wells CTW 213 and CTW 214 and wells CTW 204.

CTW 206, LVW 30, and LVW 33, which were outside of the plume (table 3). Well CTW 203 appears to be located south of the plume (fig. 10), but contained various constituents including N at concentrations similar to that of plume water. A possible explanation is that elevated N concentrations were reaching this well because it is adjacent to a corral containing 5–10 horses during the summer.

Nutrient load transported in the plume to Walden Pond could be estimated from the product of the nutrient concentration in the leach-field feed water (table 4, septic tank) and water use at the bathhouse and Reservation headquarters, provided that no nutrient loss occurred during transport. The possibility of nutrient loss is considered separately for N and P.

N loss during leachate infiltration and transport can be determined by comparison of N concentration with specific conductance, which generally is conservative in waste water, in samples from the septic tank, the water-table wells, and the beach drive-point wells. N was present in the septic tank as NH<sub>4</sub><sup>+</sup> and organic N and converted to NO<sub>3</sub><sup>-</sup> during infiltration from the septic leach field to the water table (table 4). Conductance and N were an order of magnitude higher in the septic-tank samples than in water-table wells immediately downgradient, indicating that the sewage leachate was diluted during infiltration and transport to the wells. Assuming end-member mixing of N in the plume with background ground water, the relation of N to conductance should be linear if N is transported conservatively and given as

$$N_{s} = \frac{C_{s}(N_{l} - N_{b})}{(C_{l} - C_{b})} - \frac{C_{b}(N_{l} - N_{b})}{(C_{l} - C_{b})} + N_{b}, \qquad (5)$$

where *N* and *C* refer to nitrogen concentration and conductance, respectively, and the subscripts *b*, *l*, and *s* refer to concentrations in the background wells, the septic tank, and plume wells, respectively.

A plot of all the data and the theoretical endmember mixing line (fig. 11) indicates that the upgradient samples (samples out of the plume), and many of the downgradient well data, fall near the end-member mixing line, but the beach-depth samples and beachperimeter samples, with one exception, do not. The divergence of the first two data types from the endmember mixing dilution line could result from loss of N in transport, or from a sewage N:conductance ratio that fluctuates from the measured septic-tank values. Assuming that the divergence represents N loss, the degree of loss is not more than about 20 percent for the downgradient wells (fig. 11).

### Table 4. Ground-water concentrations of nutrients and specific conductance from water monitoring wells in the aquifer of Walden Pond, Concord and Lincoln, Massachusetts

Ammonia Ammonia	
[E, estimated; No., number; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligram per liter; <, actual value is less than value shown;, not measured]	
Massachusetts	

Local identifier	Station No.	Dates	Time	Specific conduc- tance (µS/cm at 25°C)	Field pH (standard units)	Water temper- ature (°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Ammonia nitrogen, dissolved (mg/L as N)	Ammonia plus organic nitrogen, dissolved (mg/L as N)	Ammonia plus organic nitrogen, total (mg/L as N)	NO <sub>2</sub> + NO <sub>3</sub> , nitrogen, dissolved (mg/L as N)	Phos- phorus, total (mg/L as P)	Phos- phorus, total dis- solved (mg/L as P)
						S	SEPTIC TANK	K					
		5-28-99		4,040				460		460	0.05	60.2	
		7-21-99	1248		5.6	11.2	9	110		100	<.05	10.5	11.4
		9-14-99	1315	1,907				150		160	<.05	13.1	17.5
				UPGRAD	IENT OR OU	TSIDE OF 1	THE SEPTIC	-SYSTEM LEA	CH-FIELD P	LUME			
LVW 33	422613071201201	2-18-99	1328	70	8.5	8.5							
	422613071201201	3-24-99	1540	60	5.9	8.5	5	< 0.02			0.05	0.048	0.008
	422613071201201	4-26-99	1514	65		8.9							
	422613071201201	6-04-99	1020	79	5.9	9	7	<.02			<.05	.105	.013
	422613071201201	7-22-99	1015	62	5.9	9	6	<.02			.18	.062	.009
	422613071201201	9-14-99	1232	63	5.9	8.8	7	<.02			<.05		.002
LVW 30	422616071200301	7-10-98	1549	163		10.4							
	422616071200301	8-12-98	1425	121		8.9							
	422616071200301	9-18-98	1436	96		8.9							
	422616071200301	10-20-98	1030										
	422616071200301	11-04-98	1420						<.1		.01	.021	.001
	422616071200301	11-20-98	0956	99		9.1							
	422616071200301	12-11-98	1131	97		8.6							
	422616071200301	1-20-99	1035	99		8							
	422616071200301	1-20-99	1051						<.1		.02		
	422616071200301	2-18-99	1205	116		8.5							
	422616071200301	3-24-99	0913	124	5.8		6	.03			.05	.053	.004
	422616071200301	3-24-99	0920	124	5.8	8.8	8						
	422616071200301	3-24-99	1140	537	5.3	9.2	6						
	422616071200301	3-24-99	1459	132	5.8	9.5	14						
	422616071200301	4-26-99	1028	131		9							
	422616071200301	6-04-99	1215	156		9.3							
	422616071200301	6-04-99	1220	156	5.8	9.3	8	<.02			<.05	.067	.004
	422616071200301	7-22-99	0935	114	5.8	9.3	7	<.02			<.05	.018	.004
	422616071200301	9-14-99	1052	105	5.8	9.1	17	<.02			<.05		.003

# **Table 4.** Ground-water concentrations of nutrients and specific conductance from water monitoring wells in the aquifer of Walden Pond, Concord and Lincoln, Massachusetts—Continued

Local identifier	Station No.	Dates	Time	Specific conduc- tance (µS/cm at 25°C)	Field pH (standard units)	Water temper- ature (°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Ammonia nitrogen, dissolved (mg/L as N)	Ammonia plus organic nitrogen, dissolved (mg/L as N)	Ammonia plus organic nitrogen, total (mg/L as N)	NO <sub>2</sub> + NO <sub>3</sub> , nitrogen, dissolved (mg/L as N)	Phos- phorus, total (mg/L as P)	Phos- phorus, total dis- solved (mg/L as P)
			UP	GRADIENT	OR OUTSID	E OF THE S	EPTIC-SYST	EM LEACH-F	TELD PLUM	E—Continued			
CTW 227	422624071201101	1-27-99	1600						< 0.1		0.01		
	422624071201101	9-14-99	1015	77	6		11	< 0.02			<.05		< 0.001
CTW204	422627071195701	11-04-98	1230						<.1		.13	0.022	.022
	422627071195701	1-27-99	1110						<.1		.18		.025
	422627071195701	3-24-99	1400	58	6.5	9.5	10	.04			.32	.027	.025
	422627071195701	6-04-99	1105	70	6.1	10.1	11	<.02			.27	.027	.027
	422627071195701	7-21-99	1455	58	6	10	10	<.02			.36	.027	.025
	422627071195701	9-13-99	1445	57	6.1	9.8	8	<.02			.31		
CTW 206	422626071200401	11-04-98	1545						<.1		.32	.027	.005
	422626071200401	1-27-99	1200						<.1		.29		.016
	422626071200401	3-24-99	1430	77	6.1		12	<.02			.43	.045	.019
	422626071200401	6-04-99	1325	75	6.5	11.7	8	<.02			.26	.028	.018
	422626071200401	7-22-99	0904	66	6.2	11.5	14	<.02			.27		
	422626071200401	9-13-99	1510	99	6	11.5	13	<.02			.16		.004
CTW 207	422628071200801	11-04-98	1440						<.1		.02	.055	.006
CTW 213	422627071195902	3-23-99	1225	33	6.1	9.3	6	.14			.39	.053	.013
	422627071195902	5-28-99	0946	46	5.8	10.1	8	.11			.47	.038	.011
	422627071195902	7-21-99	1320	51	6.2	10.1	10	.09			.41		.032
	422627071195902	9-13-99	1415	54	6.2	9.8	10	.02			.50	.021	.004
CTW 214	422627071195903	1-27-99	1530						<.1		.32		
	422627071195903	3-23-99	1120	49	6	9.7	15	.04			.37	.021	.016
	422627071195903	6-04-99	1015					<.02			.36	.016	.015
	422627071195903	7-21-99	1220	65	6.8	9.8	17	<.02			.39		.032
	422627071195903	9-13-99	1130	65	6.7	10	16	.02			.47	.121	.003
CTW 203	422622071195901	10-20-98	1125										
	422622071195901	11-04-98	1340						<.1		3.14	.024	.021
	422622071195901	12-11-98	1209	170		9							
	422622071195901	2-18-99	1230	153		9.1							
	422622071195901	3-24-99	0820	124	5.9	8.7	8	.02			4.80	.030	.027

**Table 4.** Ground-water concentrations of nutrients and specific conductance from water monitoring wells in the aquifer of Walden Pond, Concord and Lincoln,

 Massachusetts—Continued

Local identifier	Station No.	Dates	Time	Specific conduc- tance (µS/cm at 25°C)	Field pH (standard units)	Water temper- ature (°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Ammonia nitrogen, dissolved (mg/L as N)	Ammonia plus organic nitrogen, dissolved (mg/L as N)	Ammonia plus organic nitrogen, total (mg/L as N)	NO <sub>2</sub> + NO <sub>3</sub> , nitrogen, dissolved (mg/L as N)	Phos- phorus, total (mg/L as P)	Phos- phorus, total dis- solved (mg/L as P)
			UP	GRADIENT	OR OUTSID	E OF THE S	EPTIC-SYST	EM LEACH-F	IELD PLUME	—Continued			
CTW 203	422622071195901	4-26-99	1102	108		9.6							
	422622071195901	6-04-99	1235	140	5.9	9.5	12	< 0.02			3.89	0.227	0.027
	422622071195901	7-21-99	1520	127	5.8	9.7	14	.03			4.66		.039
	422622071195901	9-14-99	1115	131	5.8	9.6	13	<.02			4.88		.024
													.013
				DOWNGRA	ADIENT FRO	M SEPTIC-	SYSTEM LE	ACH-FIELD, V	VITHIN THE	PLUME			
CTW 244	422625071195901	1-20-99	1343						<0.1		25.6		
	422625071195901	3-24-99	1138	537	5.3		5	< 0.02			45.6	0.019	0.015
	422625071195901	6-04-99	0845	469	5.4	9.5	6	<.02			13.5	.034	.028
	422625071195901	7-21-99	1046	457	5.2	15.1	6	.25			30.4		.055
	422625071195901	9-13-99	1000	438	5.2	9.5	4	.42			24.8	.017	.004
CTW 216	422626071195901	1-20-99	1428						<.1		30.4		
	422626071195901	3-24-99	1020	371	5.5	9.3	7	.02				.225	.027
	422626071195901	6-04-99	0910	475	5.3	9.8	8	<.02			26.3	.044	.030
	422626071195901	7-21-99	1235	570	5.2	10.1	5	<.02			38.5	.032	.052
	422626071195901	9-13-99	1025	644	5.1	10.2	5	.12			37.8	.015	.008
CTW 205	422627071195901	8-19-98	1330	394	5.4			.09			36.1		<.01
	422627071195901	11-05-98	1045						.2			.013	.016
	422627071195901	2-02-99	1055	124	5.8	9.1			<.1		5.25		
	422627071195901	3-24-99	1455	132	5.8		12	.04			5.06	.026	.025
	422627071195901	6-04-99	0945	260	5.7	11	11	<.02			12.9	.020	
	422627071195901	7-21-99	1425	208	5.7	11.5	11	<.02			11.9		.047
	422627071195901	9-13-99	1150	162	5.8	11.3	12	<.02			6.44		
CTW 217	422627071195904	1-20-99	1524						.1		.21		
	422627071195904	3-24-99	1259	165	5.1	9.6	3	.57			12.2	.071	.060
	422627071195904	5-28-99	0820	173	5.3	10.3	9	.27			12.1	.314	.062
	422627071195904	9-13-99	1212	162	5.5	10.8	10	.06			8.68		.055
CTW 218	422628071195801	1-21-99	1033						<.1		2.56		
	422628071195801	3-24-99	1325	176	5.7	10.5	10	<.02			8.36	.046	.022
	422628071195801	6-04-99	1040	174	5.6	10.7	10	<.02			8.72	.032	.026
	422628071195801	7-21-99	1405	158	5.6	10.9	10	<.02			8.95		.044
	422628071195801	9-13-99	1330	226	5.5	10.6	7	.03			13.6	.032	.007

 Table 5. Ground-water concentrations of nutrients and specific conductance in the beach-depth temporary drive-point wells,

 Walden Pond, Concord, Massachusetts

Figure 10 identifier	Station No.	Date	Time	Depth below surface (m)	Specific conductance (µS/cm at 25°C)	Nitrogen NO <sub>2</sub> + NO <sub>3</sub> , dissolved (mg/L as N)	Phosphorus, total dissolved (mg/L as P)
Beach depth 1	422624071200601	12-04-98	1515	0.76	227	6.39	0.002
	422624071200601	12-04-98	1445	1.52	237	2.81	
	422624071200601	12-04-98	1420	2.29	174	1.20	
	422624071200601	12-04-98	1400	3.05	164	1.68	
	422624071200601	12-04-98	1326	3.81	157	5.21	.007
	422624071200601	12-04-98	1230	4.57	155	.90	
Beach depth 2	422623071200501	12-07-98	1105	.76	190	4.02	.001
	422623071200501	12-07-98	1135	1.52	190	3.96	.002
	422623071200501	12-07-98	1205	2.29	181	4.54	.007
	422623071200501	12-07-98	1245	3.05	187	6.24	.010
	422623071200501	12-07-98	1320	3.81	160	3.42	.008
	422623071200501	12-07-98	1400	4.57	145	2.66	.010

[No., number; °C, degrees Celsius; m, meter; µS/cm, microsiemens per centimeter; mg/L, milligram per liter;--, no data]



#### **EXPLANATION**

- BEACH-DEPTH DRIVE POINT
- BEACH-PERIMETER
   DRIVE POINT
- AWAY FROM PLUME MONITORING WELLS
- WITHIN PLUME MONITORING WELLS



Sorption of the NH<sub>4</sub><sup>+</sup> onto negatively charged solids in the aquifer can cause losses from the septictank N. Investigation of this process at septage-system infiltration beds in Orleans, Mass. (DeSimone and Howes, 1998), indicated that 80 percent of the N discharged to the beds arrived at the water table. The NH<sub>4</sub><sup>+</sup> that is not lost through sorption, but rather converted to NO<sub>3</sub><sup>-</sup> during passage through the unsaturated zone, likely will continue in transport through the saturated zone. NO<sub>3</sub><sup>-</sup> in aerobic ground water is not readily converted to other forms, nor are anions such as NO<sub>3</sub><sup>-</sup> retarded in flow by interaction with the aquifer solid phase (Desimone and Howes, 1996; DeSimone and Howes, 1998).

Deviation from end-member mixing occurs for the beach-perimeter samples where the relation between conductance and NO<sub>3</sub><sup>-</sup> appears to breakdown. Results from the beach-perimeter sampling indicated that high N values were restricted to the northeast corner of the lake (fig. 10). Beach-depth sampling in the northeast location indicated the high N values extended some distance (up to about 4.5 m) below the surface (table 5). Although the nitrogen values indicated the discharge of plume water, the conductance:N values from the beach-depth and perimeter sampling generally were greater than those associated with dilution of plume water (fig. 11). The wide distribution of high conductance in the beach sampling may result from highway salt applied to State Route 126 (fig. 10), which likely moves downgradient toward the lake. Only in the western-most sample on the south side of the lake does specific conductance approach values (less than 80  $\mu$ S) from wells upgradient of the highway outside of the plume. The specific conductance at this site likely results from ground-water flow on a path from Emersons Cliff (fig. 4), which would not be affected by highway runoff. Consideration of highway salt explains how high conductance could be present on the shore without high NO<sub>3</sub><sup>-</sup> concentrations.

Assuming 20-percent loss of N after discharge from the septic tank, concentration for the load computation is 0.8 times the average of the three septic-tank nitrogen measurements (table 4). Water use at the bathhouse and Reservation headquarters averaged 1,350 m<sup>3</sup>/yr from 1996 to 1998. The product of the N concentration and water use delivered to Walden Pond in the plume is 260 kg N/yr (table 6).

In contrast to N, loss rates for P that occurred between the septic tank and ground water approached 100 percent. Whole-water P concentrations were high in the leach-field feed water (10 to 60 mg/L, n=3), but P apparently adhered to aquifer solids during passage through 12 m of unsaturated sands underlying the beds. Whereas N concentration was about 10 times less in the plume water adjacent to the leach field than in the septic tank, P was 1,000 times less. Background P concentrations tended to be greater from samples at wells between Goose Pond and Walden Pond (CTW 204, CTW 206, and CTW 203) than at those north and south of Walden Pond (LVW 30, LVW 33 and CTW 227). P concentrations in the plume wells were approximately the same as the background concentrations in wells between Goose Pond and Walden Pond. P in water from the beach samples was not correlated with N in those samples (table 5); there was not a tendency towards high P concentration in the northeast corner of the lake where high N was detected. Thus, P transport in the plume above that of background transport did not appear to be significant and was not estimated separately.

Seventeen residential point sources (houses on septic systems) are in the Walden Pond contributing area (buildings are shown in fig. 4). N inputs from all but two of these would enter Goose Pond first and contribute to Walden Pond input only as mediated by the output from Goose Pond. Nitrogen output from Goose Pond (and lakes in general) would be expected to be substantially less than inputs because of denitrification in lake sediments (Dillon and others, 1990). The movement of P from the residences to Walden Pond is unlikely because of the low sewage loading of domestic septic systems and because of the long flow paths involved from the septic systems to the lake.

#### **Ground-Water Background Source**

Nutrient loads from background ground water were determined by the product of an average background concentration and ground-water discharge. The ground-water discharge value used (366,000 m<sup>3</sup>/yr), determined in the "Hydrology" section, was an average of the watershed-area and isotopic method results.

# Table 6. Annual and summer nutrient budgets for Walden Pond, Massachusetts, based on 1995–99 average ground-water and precipitation inflows and 1998–99 average nutrient concentration data

EN	T	D1	1 1.	- 12	1-11 6	2 41 1 /-			- /T			
[II	N, mitrogen	; Р, рпс	ospnorus; k	.g/3 mo.	, knogram for	5 months; kg/y	/r, knogram	per year; m	g/L, 1	minigram j	per year;	, not measured

	Annual								Summer				
Source	P concen- tration (mg/L)	P load (kg/yr)	Percent of total load	N concen- tration (mg/L)	N load (kg/yr)	Percent of total load	N:P ratio (atomic)	P load (kg/3 mo)	Percent of total summer load	N load (kg/3 mo)	Percent of total summer load	N:P ratio (atomic)	
Background ground water	0.015	5.5	17	0.18	66	7.7	27	1.4	9	16	4	27	
Plume ground water					260	30				65	15		
Atmospheric wet	.0027	.8	3	.50	152	18	412	.2	1	38	9	412	
Atmospheric dry		15	47		75	8.7	11	3.8	23	19	4	11	
Swimmers		8.7	27		290	34	74	8.7	54	290	67	74	
Waterfowl		.6	2		4	.5	15	.6	4	1	0	4	
Fish stocking		.7	2		6	.7	19	.7	4	2	0	5	
Direct runnoff		.8	2		6	.7	16	.8	5	1	0	4	
Total		32	100		858	100	59	16	100	432	100	59	
Total without plume		32			598		41	16		367		50	
Total without swimmers		23			568		54	7.4		142		43	

NO3<sup>-</sup>-N background concentrations were measured in 39 samples from 9 wells located upgradient or outside of the septic-system leach-field plume (table 4). Concentrations in samples from CTW213 and 214 (deep wells) and CTW 204, CTW 206, and CTW 207 were consistently higher (average 0.32 mg/L) than in the other three wells (average 0.05 mg/L). Values of <0.05 mg/L listed for some of the samples (table 4) resulted from a high-detection limit method, and these values were not included in the average. CTW 203 was not used in averages because of anomalously high concentrations as already discussed. The wells with higher concentrations of N were in the zone between Goose Pond and Walden Pond, whereas the wells with lower concentrations of N were in flow paths originating from local highs in the ground water north or south of Walden Pond (table 4 and fig. 4). The reason for the difference in concentrations is unknown. An intermediate background concentration was computed as the grand mean (0.18 mg/L) of the means of the high and low concentration wells. A background N of 66 kg N/yr load was estimated by taking the product of average concentration and ground-water discharged to the lake .

Because P concentration was not significantly different in samples from the septic plume wells compared to samples from wells upgradient or outside of the plume, all well data were used to compute average P concentration in the ground water. The average was computed by analogy with N as the grand mean (0.015 mg/L) of the mean from wells between Goose Pond and Walden Pond (0.024 mg/L) and the mean of wells north and south of Walden Pond (0.005 mg/L). Dissolved P data, rather than whole-water P data were used in the analysis, because substantial amounts of P could be leached off large particles (sand) in the wholewater samples by the acid preservation method used. The particles were assumed not to transport in the aquifer. The P contribution to Walden Pond from groundwater inflow was determined to be 5.5 kg/yr, the product of the average dissolved concentration and the volume of ground water discharged to the lake.

#### **Atmospheric Deposition Source**

Atmospheric sources, especially dryfall, often are ignored in lake nutrient budgets or estimated without local data because of technical or logistical difficulties associated with the collection or interpretation of the data. In this investigation, local atmospheric deposition measurements were included. Dryfall of P was shown to be substantial in this investigation as also has been shown for a small lake investigated in New Hampshire (Cole and others, 1990).

Atmospheric inputs for both N and P were measured separately for wet deposition and dry deposition inputs using an Aerochem atmospheric deposition collector at the station northeast of Walden Pond (fig. 4). The collector was in an open area on a platform with the collection height positioned 3.4 m above the ground with approximately 50-degree angle from horizontal to the 17.5-m-tall tree canopy located 11.9 m distant. The sampler consisted of two buckets and one cover, which moved automatically to cover the dry or wet bucket according to signals from a precipitation sensor.

Dryfall was collected in a precleaned, acid and deionized water rinsed plastic bucket (28.3 cm diameter) filled to a depth of approximately 5 cm with deionized water. The water was used as the collection surface to mimic the surface of the lake (Cole and others, 1990). After the deployment period, usually two weeks, the bucket was covered and brought back to the laboratory. The water amount was measured gravimetrically, insects were screened out (2 mm screen plastic sieve), and N and P concentrations were measured, as described previously in "Sampling and Analytical Methods for Ground Water." Based on concentration in the water and water volume, a weight of nutrient collected was computed. Time-weighted average collection during 16 collection periods, July 1998 through June 1999, adjusted to annual amount per lake area was 75 kg/yr for N and 15 kg/yr for P. On a percentageinput basis, the dryfall P load was large (table 6). Given the time dependency of dryfall deposition (fig. 12) and visual observations of pollen in the collection bucket, the dryfall P input appeared to be dominated by pollen.

Wetfall samples were collected in an analogous processing, except that the buckets were put out dry and the water analyzed came from precipitation. Precipitation samples were not screened because insects generally were not present in the collected water. Annual wetfall loads were determined by adjusting the volume-weighted-average concentration from 19 water-collection intervals from July 1998 through June 1999 by annual rainfall and the area of Walden Pond. Volume-weighted concentrations were 500  $\mu$ g/L of N and 2.7  $\mu$ g/L of P. Loads were 152 kg/yr of N and 0.8 kg/yr of P.



**Figure 12.** Dryfall deposition of phosphorus from June 1, 1998, to September 1, 1999, collected on a water surface in a collector near Walden Pond, Concord, Massachusetts. [Width of bar indicates interval of sample composite.]

#### **Swimmer Source**

Walden Pond receives about 500,000 visitors per year, concentrated during the summer months. The percentage of visitors who swim also increases on the hottest days during the summer. Swimmers have been found to be a large source of nutrients in other lakes (Schultz, 1981). Urine is the source of nutrients from swimmers (Caraco and others, 1992). Human output of nutrients in urine is well known and averages 27 g N/d (computations from Guyton, 1971) and 0.81 g P/d (Caraco and others, 1992). Assuming 270,000 visitors during June, July and August (as in 1996), that 80 percent are swimmers, and that 50 percent of the swimmers urinate in the lake in the amount of 10 percent of their daily urine output, then the swimmer input of N and P to Walden Pond would amount to 290 kg/yr of N and 8.7 kg/yr of P.

#### **Other Nutrient Sources**

Previous avian input estimates, which were substantial when the nearby Concord Landfill was active, were 33 kg N/yr and 4.8 kg P/yr (Baystate Environmental, Inc., 1995). The previous estimate was weighted heavily towards winter gull presence (88 percent input) and away from summer ducks and geese (12 percent input). Gulls mainly were associated with the active landfill. Retaining the ducks and geese component, the estimates used in this study are 4 kg/yr of N and 0.6 kg/yr of P, which better reflect the current absence of gulls because of the closing of the Concord landfill. Nutrient input from stocking of trout was determined from a previous study to be 6.0 kg/yr of N and 0.7 kg/yr of P (Baystate Environmental, Inc., 1995). Previous estimates of annual nutrient loads from direct road runoff were 5.8 kg/yr of N and 0.8 kg/yr of P (Baystate Environmental, Inc., 1995). These may be lower-bound estimates because they did not account for the amount of impervious surface in the Reservation parking lots.

#### Nutrient Limitation, Ratios, Source Size, Timing, and Disposal Strategies

Often in aquatic ecosystems, all algal nutrients are in excess supply for algal growth except one, termed the (growth) limiting nutrient (Rutner, 1973). The average ratio in which algae require N and P, established by Redfield and others (1963), is 16:1 on an atom-to-atom basis. The N to P ratios in Walden Pond nutrient inputs (59 overall, see table 6) indicate that N is in excess and P would be the limiting nutrient provided that the nutrients were not subject to differential loss in the lake. N to P ratios are greater than 16 in precipitation, estimated swimmer input, and in the septic leach-field plume water (table 6). Without the septic leach-field plume, which contains 30 percent of the total N input, the N to P ratio would decrease to 41—still well above the Redfield ratio.

Nutrient sources in which N is substantially in excess may mitigate against blooms of cyanobacteria, which have the capability to satisfy their N requirement by using (fixing) N from the atmosphere. A selective advantage of cyanobacteria over algae, which cannot fix atmospheric N, may be removed when N is in excess supply (Levine and Schindler, 1999). As cyanobacteria blooms often form nuisance surface scums and even may develop toxins, a high N to P ratio, and sources that contribute to it, such as the leach-field plume, may be desirable.

Control over the amount of algal biomass produced is exerted by the input load of the limiting nutrient (P). The "percent of total load" column for the limiting nutrient P (table 6) indicates that the biggest sources are atmospheric dryfall (47 percent), swimmers (estimated at 27 percent), and background ground water (17 percent). Of the large sources, the estimated swimmer source is perhaps the most subject to regulation.

The swimmer source greatly affects the summer nutrient budget. If the nutrient budget is recomputed for the 3-month summer period and ground-water and atmospheric-deposition sources are added in at one quarter of their annual value, estimated swimmer input becomes over 50 percent of the total summer P budget (table 6).

From perspectives of the amount and type of algal growth, an advantage was realized by routing waste from the State Reservation bathhouse located on the shore of Walden Pond to the thick (14 m) unsaturated zone underlying the leach field (figs. 4 and 10). P partitions away from the mobile water phase and absorbs to grain surfaces in the unsaturated zone. This results in an increase in the N to P ratio of groundwater nutrient inputs without (currently) increased P load. Prospects for long-term (greater than 100 years) sequestration of P in the unsaturated zone are less certain. P is not transported in the unsaturated zone only because it moves from water to solids in the aquifer; P does not degrade or volatilize. Depending on the nature of the aquifer solid phase and quality and quantity of disposed waste, P can be transported eventually with the water phase, as it has been in a sewage plume in glacial outwash materials that are upgradient to Ashumet Pond on Cape Cod (Walter and others, 1996). The unsaturated zone was thinner at the Cape Cod sewage disposal site (6 to 11 m) than at the Walden State Reservation site (14 m). Also, the Cape Cod site handled a much greater waste load (varying from 140,000 to 2,200,000  $\text{m}^3/\text{yr}$  from 1936 through 1995) than the waste load handled by the leach field at Walden Pond (1,350  $m^3/yr$ ). Both of these conditions would likely cause increased subsurface transport at the Cape Cod site compared to the Walden site. Another strategy for waste disposal without affecting the lake would be to locate disposal facilities downgradient from Walden Pond (at the west end or to the north), that is, outside the ground-water contributing area (fig. 4).

# Nutrient Loading Trophic Index

Nutrient transport and ways of decreasing nutrient inputs were presented in the previous section without determination of whether decreases for Walden Pond were necessary. To assess the relative effect of decreasing inputs on the lake, nutrient budgets expressed on an areal basis can be compared among lakes, using comparison relations established by Vollenweider (1975). Walden Pond, at 0.13 g  $P/m^2/yr$ , is approaching a eutrophic state between "permissible and critical P loads," 0.084 and 0.17 g P/m<sup>2</sup>/yr, respectively, which apply for a lake with mean depth of 12.9 m and hydraulic residence time of 5 yr Vollenweider (1975). By comparison, more eutrophic Ashumet Pond on Cape Cod, mentioned in the previous section, is estimated to receive between 0.24 to  $0.29 \text{ g P/m}^2/\text{yr}$  (Jacobs Engineering Group, 2000). The Vollenweider loading concept usually is based on loads to drainage lakes, such as from sewage-treatment outfalls and riverine inputs. Correspondence to loads from the important nutrient sources for Walden Pond, ground water, dry deposition and, possibly, swimmers is unknown.

Although the nutrient budget comparison indicated that Walden Pond was in a mesotrophic state when compared with other lakes, it does not indicate whether Walden Pond has changed or is at an appropriate state for an ecologically "healthy" kettle-hole lake. Usefulness of the nutrient budget assessment also is limited because two sources (swimmers and runoff) are uncertain and the large dry-deposition term is difficult to extrapolate from the collector location to lake. Inlake response to nutrients in terms of plant growth also must be considered to determine if a kettle-hole lake is in a desirable trophic state.

#### Plant Growth and Internal Cycling of Chemical Constituents

Nutrient budgets are important to trophic ecology because they control plant growth; however, uncertainties regarding budget terms and nutrient processing in a given lake system make desirable actual measurements of the growth response of plants. In this section, plant growth in Walden Pond is examined as well as the chemical constituents in water that affect and are affected by plant growth.

#### Methods of Sampling and Analysis of the Water Column

Secchi-disk depth and in-lake depth-profile data for pH, DO, conductance, and temperature were collected every 2 weeks during temperature stratification and occasionally during winter from March 1997 to July 1999 at the deep-hole station in the western basin of the Walden Pond (fig. 4). These properties and constituents also were measured monthly at the east basin station (fig. 4) during 1997 and 1998. Water samples were collected at 1-m intervals by peristaltic pump and tubing at the deep-hole station for nutrient and chlorophyll-*a* analysis on a monthly basis. Samples were taken for complete ion analysis, on September 10, 1997, and to measure levels of dissolved Fe and Mn, on August 19 and September 10, 1997.

During 1998, samples of benthic algae (primarily the macroalga Nitella) were collected along eight transects perpendicular to the shoreline from depths shallower to depths deeper than that of Nitella growth. Samples were collected at the transects by divers during May and again, by Ekman dredge ( $225 \text{ cm}^2$ ), during October. The diving procedure involved pushing plastic buckets, from which the bottoms had been cut away, into the sediment substrate and scooping the plants from the ring interior (surface area  $531 \text{ cm}^2$ ). Comparisons between diver and dredge sampling indicated similar results were obtained by both methods. At the surface, plants were rinsed in lake water to remove attached sediment, blotted dry with paper tissue, wrapped in tared aluminum foil, and stored on ice in a cooler.

Methods of water analysis used were as described for ground-water analysis except for the field parameters of pH, DO, and conductance, which were measured *in situ* using a Hydrolab with a 30 m cable. The Hydrolab was calibrated using standard solutions for pH and conductance, and by air calibration for oxygen, at the beginning of each data-collection day. The Hydrolab thermistor probe was checked once per year by comparison with a National Institute of Standards and Technology traceable thermometer and determined to be accurate to within the precision of the thermometer ( $0.01^{\circ}$ C).

Chlorophyll-*a* samples were filtered through a glass-fiber filter, dried (Godfrey and Kerr, 2000), and analyzed by spectrometric methods (APHA, 1995).

*Nitella* biomass was determined by weighing samples from a known area of sediment surface that had been oven-dried  $(100^{\circ}C)$  to a constant weight.

#### **Temperature Stratification**

Distribution of constituents within Walden Pond, such as nutrients, DO, and even biomass is controlled in part by annual thermal stratification of the lake (fig. 13). Warm water is less dense than cold water so that the sharp temperature gradient that forms at around 6 m every summer (the thermocline) is a barrier to vertical mixing of the water. The short fetch and forested, steep banks of Walden Pond further restrict the water mixing action of wind. In small New England lakes, vertical mixing in the zone above the thermocline (the epilimnion) continues during the stratified period, but vertical mixing in and below the thermocline is restricted. In the zone of steep temperature gradient (the metalimnion) vertical mixing probably approaches that of molecular diffusion, although in the zone below the temperature-gradient zone (the hypolimnion) vertical mixing may be up to two orders of magnitude greater than molecular diffusion (Quay and others, 1980; Benoit and Hemond, 1996).

# Phytoplankton, *Nitella*, and Light

Phytoplankton amounts can be determined from profiles of chlorophyll *a* (fig. 14). The conversion factor between chlorophyll *a* and plant biomass varies according to species and nutritional status but averages about 30, on a chlorophyll-to-carbon basis (Strickland, 1960), or 67, on the basis of chlorophyll to dry-weight organic matter (APHA, 1995).

The epilimnetic chlorophyll-*a* average, often used to assess trophic state, was 1.2 and 1.6  $\mu$ g/L in 1997 and 1998, respectively. The chlorophyll-a profiles are somewhat variable (fig. 14), indicating changing phytoplankton bloom conditions. A metalimnetic peak concentration at about 10 m occurred during most of the sampling dates in the stratified period. In 1998, when profiles are available for spring and summer, there was a tendency for low chlorophyll-a concentrations in the epilimnion (0 to 6 m) in the spring, which increased by the last sampling in June. Using average values for 1997 and 1998 for epilimnetic and metalimnetic chlorophyll of 1.4 and 2.4 µg/L, respectively, and volumes from table 7, the average summer standing crop of phytoplankton, is 103 kg in the epilimnion and 182 kg in the metalimnion, dry-weight basis.



Figure 13. Thermal stratification of Walden Pond, Concord, Massachusetts: (*A*) Contour plot of temperature versus time and depth, from March 1997 to August 1999, and (*B*) Example temperature-depth profiles for 1998. (White dots in *A* indicate temperature measurement points. Horizontal white lines indicate Secchi disk depth; blue bars above axis indicate ice cover.)



**Figure 14.** Chlorophyll-*a* concentration-depth profiles from the deep-hole station of Walden Pond, Concord, Massachusetts, June 1997–June 1998.

**Table 7.** Surface area and volume data at 1-meter increments

 for Walden Pond, Concord, Massachusetts

$[m^{3},$	cubic	meter;	m,	meter;	m²,	square	meter]
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Depth below water surface (m)	Area at given depth (m <sup>2</sup> )	Volume of 1-meter slice (m <sup>3</sup> )
0	248,776	248,776
1	233,493	233,493
2	220,868	220,868
3	210,993	210,993
4	200,261	200,261
5	191,540	191,540
6	183,134	183,134
7	174,403	174,403
8	164,679	164,679
9	154,292	154,292
10	140,916	140,916
11	128,608	128,608
12	117,184	117,184
13	103,949	103,949
14	95,523	95,523
15	88,267	88,267
16	81,022	81,022
17	72,521	72,521
18	63,675	63,675
19	54,532	54,532
20	46,886	46,886
21	41,443	41,443
22	37,892	37,892
23	34,262	34,262
24	30,039	30,039
25	26,118	26,118
26	22,533	22,533
27	18,712	18,712
28	14,125	14,125
29	8,743	8,743
30	2,065	2,065

Phytoplankton are not the only source of plant biomass in Walden Pond. Large stands of the macroalgae *Nitella* grow on the bed-sediment surface. Only tentative field identification of species, *Nitella flexilis* in deeper and *Nitella gracilis* in the shallower zones of the *Nitella* growing range, were made during this investigation (Ray Stross, State University of New York– Albany, oral commun., 1997). No species differentiation was made in the biomass determinations and results are referred to by the genus name.

*Nitella* biomass data are plotted as a function of depth for each transect (fig. 15). *Nitella* grows from 6 to 13 m depth in Walden Pond. In several of the transects, a biomass peak was measured at a depth of 10 m. Transects that were sampled multiple times show *Nitella* biomass did not change substantially between May and October–November samplings. *Nitella* biomass varied with location in Walden Pond. Highest biomass transects were associated with soft substrates and relatively flat sediment surface at the eastern end of the lake (figs. 15 and 16). On the north and south sides of Walden Pond, the lake bed is steep, the sediment substrate usually is cobbley, and *Nitella* biomass is low. On the south side at transect 4, no *Nitella* was observed in the 6 to 13 m zone. Shading in these depths on a bathymetric map indicates the *Nitella* growth zone (fig. 16). Bathymetry data (table 7) indicate the bedsediment surface area within these depths is 32 percent of the total pond surface area, or 79,200 m<sup>2</sup>.

Total biomass of *Nitella* can be estimated as the product of square meters covered and an average biomass per square meter. An average of 63 g/m<sup>2</sup> (n=203) was computed from the *Nitella* transect data, so that biomass is about 5,000 kg, or more than 17 times greater than the phytoplankton biomass. Assuming conversion from biomass to carbon is a factor of 2, *Nitella* represents 2,500 kg carbon.

The *Nitella* biomass of Walden Pond is large on a per-area-basis in comparison to other lakes that have been investigated in North America and Europe. Average summer biomass in a Danish lake (Grane Langso) where metalimnetic production was determined to be dominated by *Nitella flexilis* was 26 g/m<sup>2</sup> (Nygaard and Sand-Jensen, 1981). *Nitella flexilis* biomass reported for Lake George, New York, was 51 g/m<sup>2</sup> in the north basin and 90 g/m<sup>2</sup> in the more eutrophic south basin (Stross and others, 1988).

The deep planktonic chlorophyll-a and Nitella maxima likely are associated with the clarity of water in Walden Pond. For deep growing plants like Nitella, light, in addition to nutrients, can become limiting to plant growth. Light incident to Walden Pond varies with season, and light penetration into the lake varies with clarity of the water. With a ground-water contributing area underlain by a thick unsaturated zone devoid of wetlands and humic substances, Walden Pond has unusually clear water. Light penetration and plant growth occurs at greater depth than in many lakes. Nitella requires clear-water conditions to grow and also may contribute to water clarity: large stands of Nitella tie up a large amount of P and may intercept P that might recycle from the sediments before mixing into the water column thus decreasing the P available for phytoplankton growth (Nygaard and Sand-Jensen, 1981).



Figure 15. Nitella biomass measured along transects in Walden Pond, Concord, Massachusetts, 1998. (See fig. 16 for location of transects.)



Coordinates shown as 500 meter grid, Massachusetts State Plane Projection, 1983

Figure 16. Bathymetry with sampling transects and zone of *Nitella* growth, Walden Pond, Concord, Massachusetts, 1998.

Interception of light by phytoplankton in the shallow depths decreases the light available for Nitella. Light penetration in the lake, as determined by Secchidisk depth (fig. 13), indicated phytoplankton bloomed during early spring, that phytoplankton decreased (increase in water clarity) in the late spring, and that a second increase in phytoplankton occurred during the summer stratification period. Light penetration to the deep-dwelling Nitella would be greatest during the late-spring clear-water period. The light penetration period correlated with pale green shoots on Nitella samples, indicative of new growth (R.G. Stross, State University of New York-Albany, oral commun., 1997), which were present on Nitella harvested during early May and not present on plants harvested in late summer.

Data on phytoplankton and macrophyte standing crops do not indicate the amount of growth, because continual grazing of the crop by zooplankton and other organisms may occur, decreasing standing crop but stimulating growth. More exact determination of growth can be determined by considering the nutrients used in growth and DO generated by growth.

#### **Dissolved Oxygen**

Plant production and internal cycling of nutrients are coupled directly to DO, which is a product of photosynthesis and is consumed in respiration. Analysis of changes in DO and nutrient content in lake zones defined by water stratification can be used to augment nutrient-budget estimates of lake trophic status.

During cold weather every year, Walden Pond, and most temperate-zone lakes, mix oxygen from the atmosphere into the water column. Therefore, lakes are nearly saturated with DO in the early spring (fig. 17). After this cold weather "inhalation" of oxygen and as the surface water warms, the deep water is cut off from the surface by thermal stratification, so that internal processes of photosynthesis and respiration alone determine DO concentration in the deep, colder water zone during the summer. Even the continuous discharge of oxygenated ground water does not affect the DO balance below the thermocline zone. Ground water from unconfined aquifers mostly enters lakes near the shoreline, in shallow water (Pfannkuch and Winter, 1984). In late fall, wind and cooling temperatures break down the thermal stratification, and whole-lake circulation begins again.

Interpretation of DO profiles requires knowledge of their spatial and temporal variability. Horizontal mixing, unencumbered by density stratification, is much greater than vertical mixing (Fischer and others, 1979), so that points on a vertical DO profile may be representative of water extending across the entire lake. Comparison of profiles measured the same day in opposite ends of Walden Pond (deep-hole and east-end stations) indicate that DO concentrations are horizontally uniform, at least to the depth of the sill between basins (fig. 18). Horizontal mixing is blocked by the sill so that different DO concentrations develop within each basin below the depth of the sill (12.6 m).

Temporal variability that may occur on a diurnal basis also must be considered before interpretation of the DO profiles in terms of seasonal change. Because DO generation can occur through photosynthesis only during the light period, DO profiles in the sunlit part of the water column may change from sunrise to midafternoon. Diurnal variation is unlikely to have contributed to the variation between profiles at opposite ends the Walden Pond, since only about 1 hour elapsed during measurements at each station. To quantify diurnal variability, DO profiles were measured at the deep-hole station in morning (0640-0730) and midafternoon (1400-1450) on September 17, 1997, which was a cloudless day. The profiles indicated very little difference during the day (fig. 18). Apparently, the differences in DO profiles measured through time result from cumulative changes that were small day to day, and were not affected greatly by variations associated with the time of day when the profiles were measured.

#### Dissolved Oxygen in the Epilimnion

DO concentrations in the epilimnion of Walden Pond generally were in equilibrium with oxygen in the atmosphere (fig. 17). Except during and following destratification (lake turnover), none of the 44 profiles measured in open water (without ice cover) were more than 5 percent away from saturation in the top 5 m of the lake. Because the surface waters warmed during March to late July each year, DO became less soluble and concentrations decreased from about 12 to 8 mg/L.



**Figure 17.** Distribution of dissolved oxygen in Walden Pond, Concord, Massachusetts, March 1997–August 1999 (*A*) Contour plot of dissolved oxygen in relation to depth and time (white dots indicate dissolved oxygen measuring points), and (*B*) Dissolved oxygen in relation to depth on selected dates.



Figure 18. Dissolved oxygen profiles from the deep-hole station compared with those from the east-end station, Walden Pond, Concord, Massachusetts, (1997); and morning profiles compared with afternoon profiles (September 17, 1997).

In August and September, the surface water cooled, and DO concentrations increased, reaching more than 10 mg/L by late October. Although surface water continued to cool through November and December (5.8°C on December 21, 1998), DO concentrations decreased slightly during the fall (9.5 mg/L on December 21, 1998), and the surface water became undersaturated (76 percent saturation, December 21, 1998). DO moved into the surface water from the atmosphere during this period, but the rate was not sufficient to keep up with the cooling of the water and the upward mixing of low-DO water caused by a deepening thermocline.

#### **Dissolved Oxygen in the Metalimnion**

Unlike the epilimnion, the metalimnion is isolated from the atmosphere by the thermocline during the stratified period. Because of the pronounced thermal stratification present in the upper metalimnion, vertical mixing is restricted to molecular diffusion rates (Quay and others, 1980), and vertical solute flux would equal the product of solute gradient and molecular diffusivity, which is  $2.35 \times 10^{-5} \text{ cm}^2/\text{s}$  at  $25^{\circ}\text{C}$  for DO (Thibodeaux, 1996). The sum of upward molecular diffusive flux of DO to the epilimnion and downward flux to the hypolimnion, assuming DO gradients of 3 mg/L/m, would reduce DO in the 8-m thick metalimnion by about 0.01 mg/L over a period of 3 months. Thus, DO concentrations in the metalimnion are not affected materially by vertical transport and DO generated (or consumed) in the metalimnion accrues until the thermocline deepens in the fall.

Plants respire continuously through light and dark periods, but conduct photosynthesis only during light portions of the day. Plant growth occurs when photosynthesis minus respiration, its chemical opposite reaction, is positive according to the reaction

photosynthesis 
$$\rightarrow$$
  
 $6CO_2 + 6H_2O \Leftrightarrow C_6H_{12}O_6 + 6O_2 \quad . \quad (6)$   
 $\leftarrow respiration$ 

The difference between photosynthesis and respiration is also called net photosynthesis. Changes in DO concentration in the metalimnion during the stratified period can be interpreted as net production of the metalimnetic ecosystem. This interpretation is analogous to incubating light and dark bottles at depth to determine production of the water contained in the bottle. The assumption is that rate of DO diffusion through the top and bottom planes of the metalimnion is negligible because of temperature stabilization of the water column.

Net ecosystem production in the metalimnion as determined from changes in DO includes any contribution from *Nitella* and deep-growing algae that inhabit this zone. Metalimnetic DO concentrations increased substantially between March 20 and April 23, 1998 (fig. 17*B*), generating 3.6 g  $O_2/m^2/day$ , which amounts to 1,300 kg DO in the metalimnion. The metalimnion receives the most light during this period. Subsequent metalimnetic DO changes (after April) were minimal (fig. 17*B*). During the 1998 stratified period, maximum DO concentrations increased from 12.0 to 13.6 mg/L between March 20 and April 23, dropped as low as 13.0 mg/L on June 23 and reached 14.2 mg/L in September. Similar patterns were observed in 1997 and 1999.

Given the possibility of independent rates of photosynthesis and respiration that could occur, control of DO concentration in the metalimnion between 13 and 14 mg/L during the 6-month stratified period likely was the result of some identifiable mechanism, rather than by chance. The mechanism appears to be other than control through oxygen solubility. The saturation concentration for oxygen (not air) computed from Henry's Law (Stumm and Morgan, 1996) for DO at a depth of 8 m (1.8 atmospheres) and 25°C is approximately 60 mg/L and would be greater still at metalimnetic temperatures. Neither are DO concentrations limited by the physiology of plants, which are capable of generating DO concentrations greater than 14 mg/L, as has been observed below the thermocline of other lakes (Cole, 1975).

A conceptual model was formulated during this investigation that metalimnetic DO was controlled by nutrient limitation and supply. Relations between N, P, DO, and organic carbon were assumed, for the purposes of the model, to be fixed by the stoichiometry of photosynthesis and respiration, expanded from equation (6), as given by Stumm and Morgan (1996) of

$$106 \text{ CO}_2 + 16 \text{ NO}_3 + \text{HPO}_4^{2-} + 122 \text{ H}_2\text{O} + 18 \text{ H}^+$$

+ trace elements and energy

 $= (C_{106} H_{263} O_{110} N_{16} P) + 138 O_2.$  (7)

These stoichiometric ratios, on average, are measured in analyses of phytoplankton and have been found on average in many analyses of deep seawater (Broecker and Peng, 1982) and lake water (Stumm and Morgan, 1996), where phytoplankton constituents are metabolized by bacteria and returned to solution.

According to the conceptual model, plant growth in the spring in the metalimnion exhausts available supplies of nutrients, especially P, which is growth limiting. The metalimnetic plant growth likely begins before thermal stratification because of increased light penetration through the water surface in the spring and continues into the beginning of thermal stratification. The plant growth generates DO, which builds up after stratification, accounting for the high DO concentrations in the metalimnion during April (fig. 17B). The DO concentration does not exceed about 13.5 mg/L because available P in the metalimnion-from storage in overwintering *Nitella*, remineralization of the early spring algae, or other sources-becomes exhausted. Once P is depleted in the metalimnion, DO can not increase, because continued plant growth, which is what results in DO increase, would require more nutrients.

External sources of nutrients from, atmospheric deposition, and swimmers—enter the lake primarily through the epilimnion. Ground water, from unconfined aquifers, is discharged preferentially to lakes at the water table (Pfannkuch, and Winter, 1984). Transport of dissolved nutrients from above or below the metalimnion is blocked by thermal stratification restrictions on vertical mixing. Even though dissolved sources of nutrients are blocked during stratification, nutrients from degrading particulates continue to

supply the metalimnion. But respirative degradation of particulates, whether present on the bed-sediment surface or descending from the surface as detritus, consumes DO. Under the conceptual model, a series of cloudy days or turbid water might cause negative net metalimnetic production, that is more respiration than photosynthesis, and result in a decrease in DO and a release of nutrients. Similar decrease might be caused by respirative degradation of a heavy detrital fall. When light penetrated again, however, net production and DO generation could advance, but only in proportion to the amount of P released by respiration, generating photosynthetic DO in the process equivalent to the DO amount lost in respiration.

The conceptual model described here is consistent with available data, but has not been verified by, for example, direct measure of nutrient limitation in *Nitella*. An alternative model for DO control is light limitation of plant growth. Light limitation is consistent with the correlation of new plant shoots and Secchi disk depth, but does not provide a mechanism for maintaining DO at a particular value. Although the cause of constant metalimnetic DO remains uncertain, the implication of constant DO, that net metalimnetic production after April is zero remains essentially true.

#### Dissolved Oxygen in the Hypolimnion

During stratification, DO decreases in the hypolimnion, where bacterial respiration dominates, in proportion to the amount of algal biomass that settles down from the sunlit surface water. By late fall, virtually all the of the DO stored below a depth of 15 m in Walden Pond has been consumed (fig. 17*A*).

#### Conductance, pH, Nitrogen, Phosphorus, Iron, Manganese, and Internal Nutrient Recycling

Conductance varied during the investigation from 83 to 92  $\mu$ S. These relatively low values are indicative of the relatively insoluble crystalline rock materials in the aquifer constituting the drainage area. As noted previously, the conductance is increased somewhat by the septic plume water and runoff from State Route 126 (fig. 4).

Measured pH varied from about 6.5 throughout the water column during winter and spring mixing to about 8.5 in the metalimnion during the temperature stratified period (fig. 19). Measurements of pH in the hypolimnion decreased slightly during stratification from about 6.5 to 6.0. Changes in and vertical stratification of pH values result from generation and use of CO<sub>2</sub> during photosynthesis and respiration. The wellknown relation is caused by CO<sub>2</sub> formation of carbonic acid,  $CO_2 + H_2O \rightarrow H_2CO_3$ , which in turn can dissociate and contribute hydrogen ion to solution (Stumm and Morgan, 1996). Because of the connection of pH with CO<sub>2</sub>, initial production and subsequent balance in the metalimnion can be tracted by pH. As documented in figure 19, the seasonal pattern of pH change is similar to that of DO, which as discussed is indicative of net primary production.

The cycling of N, P, Fe, and Mn is affected by a combination of thermal stratification, and by plant growth in the epilimnion and metalimnion, plant settling, and plant remineralization in the hypolimnion. The dissolved concentration of these elements can indicate the effect of geochemical redox state on nutrient release or sequestration by the bed sediments.

Measurements of N in the water column were analyzed as total combined organic-and-ammonia  $(NH_3)$  N, and as dissolved NO<sub>3</sub><sup>-</sup>-plus-nitrite  $(NO_2^{-})$  N. Organic N, a component of biomass, indicates where phytoplankton is abundant. NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are the forms that dissolved N takes in reducing conditions, and NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> are the dissolved forms of N present under aerobic conditions. A series of plots of N concentration and depth (fig. 20) indicates the effect of stratification and DO depletion on the N species. In March, before temperature stratification, NO<sub>3</sub><sup>-</sup> and organic-plus-NH<sub>3</sub> N were uniform in the water column, with NO<sub>3</sub><sup>-</sup> about one third the concentration of the organic-plus-NH<sub>3</sub> N. During the stratified period, NO<sub>3</sub><sup>-</sup> and organic-plus-NH<sub>3</sub> N began to build up in the hypolimnion but diverged in the upper water, where NO3<sup>-</sup> was depleted and organic-plus-NH<sub>3</sub> N followed the biomass concentrations. Later in the stratified period, (August and September), denitrification and reduction of NO<sub>3</sub><sup>-</sup>, and ammonification of organic matter in the deepest 5 m of the lake, where oxygen became completely exhausted, resulted in depleted NO<sub>3</sub><sup>-</sup> and increased levels of organic-plus-NH<sub>3</sub> N.

P was measured as total P and as total dissolved P (fig. 21). The total P--total-dissolved P couple (fig. 21) corresponds to a degree to the organic-plus-NH<sub>3</sub> N—NO<sub>3</sub><sup>-</sup> couple. Like N, P is a component of biomass and total P indicates the abundance of phy-toplankton. Like NO<sub>3</sub>, total dissolved P is increased by the remineralization of phytoplankton. The effect of DO is different on P than on N however, because total dissolved P does not change form where DO is depleted. In fact, total dissolved P concentration increased in the deep water in the stratified period, where DO depletion occurred. The increase may be associated with reductive dissolution of sediment Fe (Stauffer, 1986), with which PO<sub>4</sub><sup>-3</sup>, a component of total dissolved P, associates.

The N to P ratio for annual input of nutrients, as previously stated, was 59. Comparison with the Redfield ratio of 16 indicated phosphorus limitation. Monitoring the N to P ratio in the epilimnion is more directly indicative of potential limiting nutrient, because variable recycle may alter ratios there from the ratio of input. The pattern of total nutrient concentrations in the epilimnion during the summer—about 0.2 mg/L for organic-plus-NH<sub>3</sub> N and about 0.006 to 0.010 mg/L for total P—did not change substantially during the years of summer sampling. These concentration ranges correspond to atomic N to P ratios of 44 to 74, similar to the ratio of inputs, and confirm that P limited plant growth in the water column.

The interaction of N, P, Fe, and Mn with DO and the effects of temperature stratification were apparent in the late-stratification period (September, fig. 22).  $NO_3^-$ , P, Fe, and Mn were depleted in the epilimnion and the metalimnion. The nutrients likely were absorbed by phytoplankton and *Nitella* in those zones; Fe and Mn were not present because high pH and concentrations of DO keep these elements in insoluble oxide forms. In the upper hypolimnion,  $NO_3^-$  concentration reached a maximum value, but P concentration remained low. In the lower hypolimnion, where DO was completely depleted, P, Fe, and Mn concentrations increased, but  $NO_3^-$  concentration decreased because of denitrification and reduction to NH<sub>3</sub>.



Figure 19. Distribution of pH in Walden Pond, Concord, Massachusetts, March 1997–August 1999. (White dots indicate pH measuring points.)



**Figure 20.** Total organic-plus-ammonia nitrogen, and dissolved nitrate-plus-nitrite nitrogen concentration-depth profiles in Walden Pond, Concord, Massachusetts, March–September 1998. [For profiles of May 27, 1998, June 23, 1998, nitrate values below the detection limit (<0.05 mg/L) were plotted at 0.025 mg/L. For profiles of July 22, 1998, August 18, 1998, nitrate values below the detection limit (<0.005 mg/L) were plotted at 0.0025 mg/L.]



Figure 21. Total phosphorus and total dissolved phosphorus concentration-depth profiles in Walden Pond, Concord, Massachusetts, 1997–1998.



**Figure 22.** Depth distribution of nitrogen, phosphorus, dissolved oxygen, and temperature from September 23, 1998; and iron, sulfate, and manganese from September 10, 1997, in Walden Pond, Concord, Massachusetts.

The ratio of S to Fe is thought to determine the relative availability of Fe for interaction with P in lakes. Under reducing conditions, sulfide forms and ties up Fe<sup>2+</sup> in FeS precipitate. Hard-water lakes with abundant SO<sup>-2</sup><sub>4</sub> from dissolution of carbonate rocks generally have little Fe available for association with P (Stauffer, 1987). Walden Pond, although soft water, has several additional sources of SO<sup>-2</sup><sub>4</sub> including the septic plume and swimmers. Fe concentrations in the anaerobic layer of about 3 mg/L were intermediate between those measured in hard (0.06 mg/L) and softwater (20 mg/L) systems (Stauffer, 1987). Where Fe is tied up by S, P is thought to recycle more efficiently in aerobic conditions, because Fe-hydroxides, on which P adsorbs, are not available—and in anaerobic conditions, because Fe is not released with the P to precipitate upon oxidation (Stauffer, 1987).

Analysis of the concentration profiles in figure 22 also indicates the degree to which internal cycling of nutrients takes place. That N was recycled clearly was indicated by the increased concentrations of N species throughout the hypolimnion. Increases in total dissolved P, by contrast, were restricted to the anaerobic zone in the deepest water. During most of the stratified period, the anaerobic zone was so far removed from the euphotic zone that none of the released P could be reused. Even when thermal destratification reaches this zone usually sometime after mid-December, associated DO would likely precipitate Fe and a portion of the  $PO_4^-$ .

Nutrient recycling in Walden Pond at the end of stratification may be greater than recycling that occurs during the stratification period. Near the end of stratification, the annual recycling of P may be substantial in that DO decreased to zero in the entire hypolimnion just prior to turnover (fig. 17). This condition likely released the Fe-bound P that had been accumulating in the sediment during the summer.

#### Historical and Between-Lake Trophic Assessments

The relations between plant growth and cycling of water-column chemical constituents can be used in comparative investigations of trophic ecology. These assessments include historical comparisons within a specific lake and comparisons among lakes.

#### Trophic State from Water-Column Assessment

Trophic state can be measured on the basis of DO consumption in the hypolimnetic water during stratification. The rate at which lakes consume DO in their deep water during respiratory degradation of the particulate organic carbon (largely dead phytoplankton) that falls from the epilimnion has been quantified as the hypolimnetic oxygen deficit (HOD) and compared among lakes (Hutchinson, 1975). The measurement of HOD can be used, as are nutrient budgets and standing crops, to establish trophic state (Walker, 1979). HOD is most informative in lakes like Walden Pond that are deep and relatively oligotrophic, because their deep-stored DO content is large and not consumed too quickly after stratification, in which case the HOD record ends. In addition, lakes low in organic carbon (humic substances) derived from the watershed, like Walden Pond, are favored for HOD interpretation because consumption of DO by humic substances would obscure the relation between HOD and in-lake productivity. Comparison of HOD at different times during a season indicates when respiratory degradation of the organic matter in plankton is greatest. Annual comparisons are useful in identifying trends in production of water-column organic matter through time. HOD is a stable and sensitive measurement, because it reflects the summed phytoplankton production occurring during the entire stratified period (contrasting chlorophyll concentration data, which are more

representative of current bloom conditions), and thus is a useful measure to establish baseline data on productivity of Walden Pond.

Investigators have computed HOD in various ways to determine actual, absolute, relative, apparent, and real oxygen deficits (Hutchinson, 1975). These various computations consider whether the lake is assumed to be at oxygen saturation in the spring, whether measured spring DO values are used, and whether the volume of the hypolimnion at each depth or simply a column of water is used in the computation. HOD based on measured spring conditions and horizontal volume elements of the hypolimnion associated with each DO concentration in a profile most closely connects the amount of DO used with the amount of plankton falling from the epilimnion in a given growth season. When calculated by these methods and expressed in units of time per surface area of the top of the hypolimnion surface, HOD is termed the relative hypolimnetic areal deficit (Hutchinson, 1975).

The degree of interconnectedness among the three basins of Walden Pond must be considered in the computation of HOD from DO profiles that were measured only at the deep-hole station, because DO profiles from the east-end basin diverge at depths below the sill from DO profiles from the deep-hole basin. The top of the hypolimnion used in the HOD computations was taken at 13.5 m, approximately the level of the sill between the east and middle basins, so the HOD can be calculated on the basis of a hypolimnion area and DO content exclusive of the east-end basin. No DO profiles were measured in the middle basin, because its existence was not known until well into the investigation. For the purposes of HOD calculation, deep-hole station DO concentrations were applied to volumes in the middle basin at the same level.

The May through July HOD values computed during the 3 years of biweekly monitoring and additional 2000 data are nearly identical (0.049, 0.050, 0.051, 0.048 mg  $O_2/cm^2/d$ ) from 1997 through 2000. The small difference in values at Walden Pond can be compared with eutrophic Lake Mendota (0.11 g  $O_2/cm^2/d$ ) in Wisconsin (Hutchinson, 1975). The constant values at Walden Pond result despite potential changes in P input during measurement years. For example, the swimming beach at Walden Pond was closed during the July 4th weekend in 1997. In addition, substantial amounts of phosphate fertilizer equivalent to the entire annual P budget for the lake—were applied to shoreline plantings in connection with a bank stabilization program in 1997 and 1998. A better understanding of variation in HOD is obtained by considering the DO content of the hypolimnion on a week-to-week basis during this time period.

HOD and variation in development of HOD are indicated by hypolimnetic DO content plotted with time (fig. 23). The slope of the curve represents the HOD. During the 3 years of biweekly monitoring, 1997–99, hypolimnetic DO content was similar at the beginning of April. DO in the hypolimnion was completely consumed by the end of stratification in the fall. As a consequence, the curves start together in April diverge and then converge after August as complete consumption of DO is approached. During 1997, the slope in April was less than that of April 1998 and 1999. After April, slopes were approximately the same during the three years studied. The offset of the 1997 data from that of 1998 and 1999 apparently was caused by differences in DO use (or resupply in the poorly stratified April water column) before May.

# Historical Dissolved-Oxygen Profiles

Historical DO profiles from Walden Pond provide an indication of how nutrient cycling and trophic state may have changed through time. Four historical summer profiles (data and data sources fig. 24) are available (1939, 1992, 1994, and 1996). These profiles indicate that oxygen depletion is more advanced in late summer in 1994 and 1996 than in previous years and indicate progressively greater metalimnion DO production than do the earlier profiles. The increased hypolimnetic DO depletion could be interpreted as a greater settling of phytoplankton biomass that resulted from growth of a larger biomass and a greater supply of nutrients to support the growth. The increased metalimnetic production would follow from the hypothesized greater availability of plant nutrients.

Historical changes in HOD can be estimated from a few historical DO profiles available for Walden Pond. The biweekly DO data used to establish the 1997–99 HOD baseline (fig. 23) give a context for historical profiles (one per summer) from 1939, 1992,



**Figure 23.** Dissolved oxygen content of the hypolimnion of Walden Pond, Concord, Massachusetts, during summers of 1997, 1998, and 1999 (lines); dissolved oxygen content from single profiles in 1939, 1992, 1994, 1996, and 2000 (blue symbols); and lines projecting dissolved oxygen content for summer of 1939 (A-B and C-D).



**Figure 24.** Historical dissolved oxygen profiles for Walden Pond, Concord, Massachusetts. [1939 data are from Deevey (1940); 1992 data are from Arthur Screpetis, Massachusetts Department of Environmental Management, written commun. (1994); 1994 data are from Baystate Environmental, Inc. (1995); and 1996 data are from this investigation.]

1994, and 1996 (fig. 23). Depending on spring conditions, the 1992 through 1996 profiles may represent conditions similar to those measured during the detailed monitoring. The 1939 profile deviates more substantially from the others. This profile, measured before membrane-electrode oxygen probes were available, was based on the accurate Winkler titration method as described in Deevey (1940). The 1997-1999 data indicated that DO was consumed at an approximately constant rate during the summer. If early spring conditions were similar in 1939 to 1997–1999, then a constant depletion rate would run along line A-B, and 1939 HOD would be 0.015 mg/cm<sup>2</sup>/d, or 30 percent of the current rate. Lower HOD in the past, however, may be associated with higher spring hypolimnetic oxygen content, so that line C-D, (HOD of  $0.021 \text{ mg/cm}^2/\text{d})$ may be more accurate. Both projected lines run through the historical August 1939 point and indicate that DO in the 1939 hypolimnion would not have been exhausted if Walden Pond stratified and turned over historically, at the same times as in the present. Later stratification and earlier turnover result in less DO depletion because there is less time for DO depletion to occur. As indicated by freeze and breakup dates of ice on lakes in the Northern Hemisphere, stratification duration may have increased by 12 days per 100 years from 1846 through 1995, or about 8 days since 1939 (Magnuson and others, 2000).

According to the analysis described above, HOD has doubled since 1939, which implies that historical inputs of nutrients were less than present inputs. But the relation between nutrient supply and plant growth is not necessarily linear and can temporally lag, in part because of buildup and release of P in the lake bed sediments. Although pre-recreational Walden Pond may have received less nutrient input, nutrient inputs may have been large in the past. One thousand swimmers were observed at the 1939 sampling (Deevey, 1942). The Concord Herald newspaper reported on September 5, 1935, that summer Sunday afternoon crowds reached 25,000 at Walden Pond and that total summer attendance was 485,000. The effect of initial increases in nutrient supply would be decreased because of P sequestration by the sediments. As the sedimentbinding sites for P became filled, an increasingly larger fraction would have been included in internal recycling. To the extent that DO in the hypolimnion became depleted, sequestered P would be released by reductive dissolution of Fe minerals on which P was adsorbed. The first occurrence of DO depletion at a given level in the hypolimnion may have been associated with a substantial bed-sediment release of P, which had accumulated with Fe, since the formation of the lake.

If HOD could be reduced to the rate present in 1939 so that DO was not exhausted in the final weeks before turnover, then annual accumulation of P in the hypolimnetic sediments might begin again, with consequent increase in water clarity. Because some DO remains in the hypolimnion until nearly the end of stratification, the degree of P input decrease necessary to sustain aerobic conditions may not be too large.

## Comparisons of Dissolved Oxygen Among Lakes

Simple comparison of DO profiles among lakes indicates the consequences of the variability in HOD among lakes (fig. 25). Regarding deep DO in kettlehole lakes in eastern Massachusetts, Gull Pond in the National Seashore Cape Cod (Portnoy, 1990) and White Pond in Concord (Walker, 1989) show similar DO concentrations in the metalimnion to Walden Pond and similar DO deficits in the hypolimnion. Ashumet



**Figure 25.** Comparison dissolved oxygen profiles for eastern Massachusetts kettle-hole lakes: Ashumet Pond, Falmouth and Mashpee; Walden Pond, Concord; White Pond, Concord; and Gull Pond, Wellfleet.

Pond, also on Cape Cod, differs with dissolved oxygen depletion in the metalimnion and the hypolimnion (Jacobs Engineering, 2000). Nutrient inputs are from water fowl, swimmers and septic leach fields of 21 summer residences at Gull Pond, swimmers and residences on White Pond, Concord, and ground-water discharge of P and N from a sewage plume (with P transport) and residences at Ashumet Pond. These comparisons verify the sensitivity of HOD to trophic state and highlight a key aspect of trophic variability among lakes in the oligotrophic to mesotrophic classification: the depth of the oxygenated zone.

#### **Trophic Stability**

Walden Pond may have become more eutrophic since 1939, but the water still is clear and the lake remains attractive to the public. Metalimnetic DO levels remain high throughout the stratified period so conditions for trout are favorable and the principal plant biomass consists of deep-growing macroalgae. Does the ecologic health of Walden Pond require a decrease in nutrient input in an attempt to achieve more oligotrophic conditions? The answer depends on the stability of the present condition.

Other kettle-hole lakes in eastern Massachusetts have degraded episodically in water quality. In November 1998, the kettle-hole lake Cliff Pond in Nickerson State Park on Cape Cod, Mass., developed a substantial cyanobacterial bloom that was blown to the shore by the wind. The decaying biomass smelled bad and contained naturally occurring toxins (S. Nichol, Massachusetts Department of Environmental Management, oral commun., 2000). Two dogs that drank water from the downwind shore died, a confirmed consequence of cyanobacterial poisoning. The bloom, which did not recur in 1999 or 2000, was unexpected in that Cliff Pond is a deep (26 m), generally clear-water lake, surrounded by park land. It is assumed that Cliff Pond probably does not have a large P-input budget on a lake-area basis. Complaints regarding increased plant growth have been registered for Ashumet Pond and fish kills have occurred, although not with yearly frequency (K-V Associates, Inc., 1991). Although loading of P to Ashumet Pond (estimated 208 to 255 kg/yr, Jacobs Engineering, 2000), is probably much larger than to Cliff Pond, there are no recorded poisonings from cyanobacteria blooms for Ashumet Pond. The kettle-hole lakes appear to be subject to episodic water-quality degradation even when external nutrient loading, such as from ground-water sources, appear to be constant. The question remains whether Walden Pond could develop a substantial bloom of cyanobacteria such as in Cliff Pond in 1998 or become subject to fish kills, as has Ashumet Pond, without receiving the considerably greater per-area nutrient loading of Ashumet Pond.

The consequences of eutrophication, present in Cliff Pond and Ashumet Pond, likely could be prevented in Walden Pond by maintenance of DO in the metalimnion. An oxygenated metalimnion decreases internal recycling of phosphorus. Currently (2000), the high, constant concentration of DO of the metalimnion is a prominent feature of stratification in Walden Pond. According to the conceptual model developed in the section "Dissolved Oxygen in the Metalimnion," metalimnetic DO in Walden Pond is increased at the onset of stratification by spring expansion of the metalimnetic plant biomass that proceeds until nutrient limitation. DO is maintained at a high level through a nutrient regulated balance of biomass degradation and regrowth until destratification in the fall. According to the conceptual model, stability would be altered if shading of the metalimnion, such as from increased

growth of phytoplankton, switched control over metalimnetic plant growth from nutrient to light. The conceptual model has not been tested, however, nor is the stability of the proposed regulatory mechanism known.

On the basis of plant biomass alone, the stability of the present trophic condition of Walden Pond likely involves the ecology of the macroalgae Nitella, which grows in the metalimnion of Walden Pond with a biomass 17 times greater than that of the phytoplankton in the epilimnion and metalimnion combined. Stross and Rottier (1989) hypothesized that Nitella helps maintain good water quality by uptake of nutrients, transfer of nutrients to the sediment at die-off, prevention of fine-particle resuspension, and facilitation of coagulation of colloids. Nygaard and Sand-Jensen (1981) hypothesized that the deep-growing charophyte species prevent release of Fe-bound phosphate to the water column by releasing oxygen near the sedimentwater interface. In two European studies (Melzer, 1999; Riis and Sand-Jensen, 1998), presence of Nitella has been associated with clear-water conditions and later absence of *Nitella* with more turbid, eutrophic conditions. In Lake George, N.Y., lower biomass density of Nitella was associated with the oligotrophic northern basin, compared to larger biomass density in the more eutrophic southern basin (Stross and others, 1988) and eventual disappearance in the formally most productive areas (R.G. Stross, State University of New York-Albany, oral commun., 1997). Whereas investigation is lacking that establishes a cause-and-effect relation between Nitella and water quality, cause and effect has been established for shallow-growing benthic-algal charophytes, with more completed experimentation (Scheffer, 1998). Charophytes, of which Nitella is a deep-growing member, have been reintroduced in turbid shallow ponds to reestablish clearwater conditions that were lost because of shading of former benthic algal populations.

Without further investigation, the role, mechanism, and, thus, the stability of *Nitella* for maintaining DO in the metalimnion remain a matter of conjecture. Given the uncertainty over current metalimnetic regulation, the importance of the nutrient budget and historical data is increased. Substantial eutrophication has occurred since the historical DO data collection at Walden Pond in 1939. The principal anthropogenic perturbation causing eutrophication is the hypothesized swimmer input of nutrients. Because of the long recreational history at Walden Pond, increased nutrient input may have resulted over a period of more than 100 years. There is insufficient HOD data between 1939 and the present to estimate whether the present level of eutrophication has reached a new steady state or rather that HOD has increased continuously since 1939. Unlike the trophic perturbations in many lakes, which result in part from alteration of drainage, hypothesized anthropogenic nutrient inputs to Walden Pond potentially could be controlled.

#### Trophic Ecology and Management Options

At present, the water quality of Walden Pond appears to be desirable and may not require management. Managing Walden Pond and its ground-water contributing area in a nutrient flux/eutrophication context could be needed only with changing conditions. These conditions could include long-term changes in septic-system P retention by the aquifer, delayed eutrophication effects from past or current nutrient loads, or concern regarding potential water-quality instability and the size of the *Nitella* biomass.

Concerns about desorption of P from the aquifer can be addressed by monitoring ground water in the wells just downgradient from the septic leach field. As long as P concentrations in the septic plume remain at background levels in those wells, plume associated transport is not occurring.

Other concerns about delayed effects of current nutrient loads, water-quality instability, and Nitella biomass all could be addressed by decreasing P load. The effect of decreasing P load could be monitored by HOD assessment. If HOD is seen to decrease, then the delayed effects of nutrient load necessarily would have been overcome. Decreased P load would minimize the hypothesized tendency toward instability, by increasing water clarity and depth of DO generation, and decreasing the amount of phytoplankton sedimentation and DO consumption. Decreased P load should decrease the thickness of DO depleted water in the hypolimnion and decrease the amount of P recycled from the sediments. The Nitella population should grow less and, thus, be less subject to die-off from self shading. Because the principal source of anthopogenic nutrients is from swimmers, decrease of the source might be possible through a swimmer-education program.

If nutrient input can not be decreased, management efforts could concentrate on prevention of other circumstances that would decrease water clarity and light penetration to the metalimnion. Road runoff and bank erosion should be avoided. Rerouting runoff from State Route 126 would decrease turbidity associated with storm runoff. Any runoff water rerouted from direct discharge to Walden Pond to infiltrate to the ground water instead would have turbidity and P largely removed. The bank stabilization program completed in 1997 through 1998 had a potential for temporarily increasing turbidity because soil was moved at the shore and in some cases heavy equipment was driven into shore water. The turbidity curtain which was installed to restrict sediment movement to nearshore areas was an important precaution.

Continued monitoring of HOD, and the amount and distribution of *Nitella* would be useful with or without a nutrient-reduction program. HOD is likely the most sensitive measure of trophic state available for Walden Pond.

# SUMMARY AND CONCLUSIONS

Walden Pond, the deepest lake in Massachusetts, has historical, naturalistic, and limnological importance. Walden Pond is a kettle-hole lake, 30.5 m deep, with 249,000-m<sup>2</sup> surface area, located 24 km west northwest of Boston, in Concord, Mass., with a watershed that extends into Lincoln. Mass. Located in a large metropolitan area, the pond potentially is threatened by factors common to urban development. That Walden Pond retains clear, generally good water quality attests to conservation efforts that protect the woods and shore surrounding the pond. Questions remain whether these conservation efforts will continue to preserve lake-water quality. The U.S. Geological Survey, in cooperation with the Massachusetts Department of Environmental Management, began an investigation in 1997 to document present water-quality conditions and collect baseline data for Walden Pond.

The ground-water contributing area (621,000 m<sup>2</sup>) of Walden Pond was determined from water-table information in areas of stratified glacial deposits, measured at near-normal levels in 40 monitoring wells and 8 ponds on July 19, 1999, and from land-surface contours in areas of bedrock highs. Results indicate Walden Pond is a flow-through lake. Ground water flows into Walden Pond along the eastern perimeter and lake water flows into the aquifer along the western perimeter. The Walden Pond contributing area includes Goose Pond, also a flow-through pond, and its ground-water contributing area. Approximately 6 percent of the inflow from ground water is derived from Goose Pond. Lake-derived ground water from Walden Pond discharges into the Sudbury and Concord Rivers or to wetlands and streams draining into these rivers.

A water balance for Walden Pond, used to derive a nutrient budget, was based on average annual conditions from 1995 through 1999 because the waterresidence time of the lake was calculated to be about 5 years. There was no change in long-term lake storage during this 5-year period. Precipitation on the lake surface accounted for 45 percent of the inflow (1.215 m/yr) whereas ground-water inflow contributed 55 percent (1.47 m/yr expressed as depth of water over the lake surface). The ground-water inflow estimate was based on the average of two different approaches. One approach used the size of the contributing area and the recharge rate to the aquifer from precipitation. A second approach was based on an isotopic massbalance, which uses the stable isotopes of oxygen and hydrogen that naturally occur in water. Outflow from evaporation from the lake surface accounted for 26 percent (0.71 m/yr) and lake-water seepage to the aquifer, calculated as the residual value of the water balance. accounted for 74 percent of the outflow (1.97 m/yr). Ground water is the dominant pathway into and out of Walden Pond.

Walden Pond contributing area excludes nearby potential sources of nutrients to the lake from a landfill and a trailer park, but the Reservation septic leach field and leach fields from private residences are within the contributing area. At present, nitrogen from the septic leach field of the Walden Pond State Reservation headquarters and bathhouse reaches Walden Pond, but phosphorus is removed during transport with the net effect of increasing the nitrogen to phosphorus ratio of nutrient inputs. Nutrient budgets for the lake indicated that nitrogen inputs (858 kg/yr) were dominated (30 percent) by plume water and, possibly, by swimmers (34 percent). Phosphorus input (32 kg/yr) was dominated by atmospheric dry deposition, background ground water, and estimated swimmer inputs. Swimmer inputs may represent more than 50 percent of the phosphorus load during the summer.

Walden Pond has become more eutrophic in this century and loses dissolved oxygen in deep water that historical dissolved oxygen measurements indicate remained aerobic 60 years ago. Historical, and interlake comparisons of plant production, and estimated loads of nutrients to Walden Pond indicate the eutrophication of Walden Pond possibly could be reversed through management action and deep-water dissolved oxygen increased if phosphorus input to the lake were decreased, possibly through a swimmer-education program. This may benefit a population of a deepgrowing macroalgae *Nitella*, which is hypothesized to maintain water quality by tying up nutrients in deep plant biomass, generating metalimnetic dissolved oxygen at the onset of stratification, and maintaining high metalimnetic dissolved oxygen concentrations during stratification.

#### **REFERENCES CITED**

- Andersen, F.O., and Ring, P., 1999, Comparison of phosphorus release from littoral and profundal sediments in a shallow, eutrophic lake: Hydrobiologia, v. 408-409 p. 175–183.
- APHA, (American Public Health Association, American Water Works Association, Water Environment Federation), 1995, Standard methods for the examination of water and wastewater: Washington, D.C., American Public Health Association, variable pagination.
- Baystate Environmental, Inc., 1995, Study of trophic level conditions of Walden Pond, Concord, Massachusetts: Massachusetts Department of Environmental Management, Division of Resource Conservation, 111 p.
- Benoit, G., and Hemond, H.F., 1996, Vertical eddy diffusion calculated by the flux gradient method—significance of sediment—water heat exchange: Limnology and Oceanography, v. 41, p.157–168.
- Broecker, W.S., and Peng, T.-H., 1982, Tracers in the sea: Palisades, N.Y., Lamont-Doherty Geological Observatory, Columbia University, 690 p.
- Carlson, R.E., 1977, A trophic index for lakes: Limnology and Oceanography, v. 2, p.361–369.
- Caraco N.F., Cole, J.J., and Likens, G.E., 1992, New and recycled primary production in an oligotrophic lake insights for summer phosphorus dynamics: Limnology and Oceanography, v. 37, p. 590–602.
- Cole, J.J., Caraco, N.F., Likens, G.E., 1990, Short-range atmospheric transport—A significant source of phosphorus to an oligotrophic lake: Limnology and Oceanography, v. 35, p. 1230–1237.
- Cole, G.A., 1975, Texbook of limnology: Saint Louis, Mo., Mosby, 283 p.

- Craig, H., and Gorden, L.I., 1965, Deuterium and oxygen 18 variations in the ocean and the marine atmosphere, *in* Tongiorgi, E., ed., Stable Isotopes in Oceanographic Studies and Paleotemperatures: Pisa, Italy, Spoleto, Consiglio Nazionale delle Ricerche, p. 9–130.
- Deevey, E.S., 1940, Limnological studies in Connecticut. V. A contribution to regional limnology: American Journal of Science, v. 238, p. 717–741.
- Deevey, E.S., 1942, A re-examination of Thoreau's Walden: The Quarterly Review of Biology, v. 17, no. 1, p. 1–11.
- DeSimone, L.A., Barlow, P.M., Howes, B.L., 1995, A nitrogen-rich septage-effluent plume in a glacial aquifer, Cape Cod, Massachusetts, February 1990 through December 1992: U.S. Geological Survey Open-File Report 95-290, 92 p.
- DeSimone, L.A. and Howes, B.L. 1996, Denitrification and nitrogen transport in a coastal aquifer receiving wastewater discharge: Environmental Science & Technology, v. 30, p. 1152–1162.
- DeSimone L.A. and Howes B.L., 1998, Nitrogen transport and transformations in a shallow aquifer receiving wastewater discharge—A mass balance approach: Water Resources Research, v. 34, p. 271–285.
- Dillon, P.J., Evans R.D., and Molot, L.A., 1990, Retention and resuspension of phosphorus, nitrogen, and iron in a central Ontario lake: Canadian Journal of Fisheries and Aquatic Sciences, v. 47, p. 1269–1274.
- Dincer, T., 1968, The use of oxygen 18 and deuterium concentrations in the water balance of lakes: Water Resources Research, v. 4, no. 6, p. 1289–1306.
- Farnsworth, R.K., Thompson, E.S., and Peck, E.L., 1982, Evaporation atlas for the contiguous 48 United States: U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Technical Report NWS 33, 26 p., 4 pls.
- Fischer, H.B., List, E.J., Koh, R.C.Y.H., Imberger, J., and Brooks, N.H., 1979, Mixing in inland and coastal waters: New York, Academic Press, 483 p.
- Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations Report, book 5, chap. A1, 545 p.
- Friesz, P.J., and Colman, J.A., 2001, Hydrology and trophic ecology of Walden Pond, Concord, Massachusetts: U.S. Geological Survey Water-Resources Investigations Report 01-4153, 1 sheet.
- Gat, J.R., 1980, The isotopes of hydrogen and oxygen in precipitation, *in* Fritz, P. and Fontes, J.Ch., eds., Handbook of environmental isotope geochemistry, vol. 1, The terrestrial environment A: New York, Elsevier, p. 21–47.

Gilath, C., and Gonfiantine, R., 1983, Lake dynamics, *in* Guidebook on Nuclear Techniques in Hydrology: International Atomic Energy Agency, technical report series no. 91, p. 129–161.

Godfrey, P.J., and Kerr, P.A., 2000, Preliminary evaluation of a promising forced air-drying technique for preserving chlorophyll on glass fiber filters: Lake and Reservoir Management, v. 16, p. 222–234.

Guyton, A.C., 1971, Texbook of medical physiology (4th ed.): Philadelphia, Pa., Saunders Company, 1032 p.

Hutchinson, G.E., 1975, A treatise on limnology— Chemistry of Lakes: New York, Wiley, v. I, Part 2, 541– 1015 p.

Hydrosphere Data Products, Inc., 1995, Climate data: Boulder, Colo., National Climatic Data Center Summary of the Day, 1 CD-ROM.

Jacobs Engineering, 2000, Ashumet Pond Trophic Health Technical Memorandum: Massachusetts Military Reservation, v. 1, AFC-J23-35S18402-M17-0005, variable pagination.

Koteff, Carl, 1963, Glacial lakes near Concord, Massachusetts, Article 96, *in* U.S. Geological Survey Professional Paper 475-C: Washington, D.C., p. C142– C144.

Koteff, Carl, 1964, Surficial geology of the Concord Quandrangle, Massachusetts: Washington D.C., U.S. Geological Survey Map GQ-133., 4 p., 1 pl.

Krabbenhoft, D.P., Bowser, C.J., Anderson, M.P., and Valley, J.W., 1990, Estimating groundwater exchange with lakes 1—The stable isotope mass balance method: Water Resources Research, v. 26, no. 10, p. 2445–2453.

K-V Associates, Inc., 1991, Ashumet Pond Falmouth/Mashpee, Massachusetts, A diagnostic/feasibility study: Towns of Falmouth and Mashpee, 158 p.

LaBaugh, J.W., Winter, T.C., Rosenberry, D.O., Schuster, P.F., Reddy, M.M., and Aiken, G.R., 1997, Hydrological and chemical estimates of the water balance of a closed-basin lake in north central Minnesota: Water Resources Research, v. 33, no. 12, p. 2799–2812.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data collection protocols and procedures for the National Water-Quality Assessment Program— Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

LeBlanc, D.R., 1984, Sewage plume in a sand-and-gravel aquifer, Cape Cod, Massachusetts: U.S. Geological Survey Water-Supply Paper 2218, 28 p. Levine, S.N., and Schindler, D.W., 1999, Influence of nitrogen to phosphorus supply ratios and physicochemical conditions on cyanobacteria and phytoplankton species composition in the Experimental Lakes Area, Canada: Canadian Journal of Fisheries and Aquatic Sciences, v. 56, p. 451–466.

Lyford, F.P., and Cohen, A.J., 1988, Estimation of water available for recharge to sand and gravel aquifers in the glaciated northeastern United States, *in* Randall, A.D., and Johnson, A.I., eds., The Northeast glacial aquifers: American Water Resources Association Monograph Series, no. 11, p. 37–62.

Majoube, M., 1971, Fractionnement en oxygene-18 et en deuterium entre l'eau et sa vapeur: Journal of Chemistry and Physics, v. 197, p. 1423–1436.

Melzer, A., 1999, Aquatic macrophytes as tools for lake management: Hydrobiologia, v. 395-396, p. 181-190

Menzel, D.W., and Corwin, N.C., 1965, The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation: Limnology and Oceanography, v. 10, p. 280–282.

Nygaard, G., and Sand-Jensen, K., 1981, Light climate and metabolism of *Nitella flexilis* (L.) Ag. in the bottom water of oligotrophic Lake Grane Langso, Denmark: Internationale Revue Der Gesamten Hydrobiologie, v. 66, p. 685–699.

Pfannkuch, H.O., and Winter, T.C., 1984, Effect of anisotropy and groundwater system geometry on seepage through lakebeds, 1—Analog and dimensional analysis: Journal of Hydrology, v. 75, p. 213–237.

Portnoy, J.W., 1990, Gull contributions of phosphorus and nitrogen to a Cape Cod kettle pond: Hydrobiologia, v. 202, p. 61–69.

Quay, P.D., Broecker, W.S., Hesslein, R.H., and Schindler, D.W., 1980, Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes: Limnology and Oceanography, v. 25, p. 201–218.

Randall, A.D., 1996, Mean annual runoff, precipitation, and evapotranspiration in the glaciated Northwestern United States, 1951–80: U.S. Geological Survey Open-File Report 96-395, 2 sheets.

Redfield, A.C., Ketchum, B. H., and Richards, F. A., 1963, The influence of organisms on the composition of seawater, *in* Hill, M.N., ed., In The Sea: New York, Wiley Interscience, v. 2, p. 26–77.

Riis, T. Oa, and Sand-Jensen, K., 1998, Development of vegetation and environmental conditions in an oligotropic Danish lake over 40 years: Freshwater Biology, v. 40, p. 123–134.

Ruttner, F., 1973, Fundamentals of limnology (3d ed): Buffalo, N.Y., University of Toronto Press, p. 295. Ryden J.C., Syers J.K., Tillman R.W., 1987, Inorganic anion sorption and interactions with phosphate sorption by hydrous ferric oxide gel: Journal of Soil Science, v. 38, p. 211–217.

Sacks, L.A., Swancar, A., and Lee, T.M., 1998, Estimating ground-water exchange with lakes using water-budget and chemical mass-balance approaches for ten lakes in ridge areas of Polk and Highlands Counties, Florida: U.S. Geological Survey Water-Resources Investigation Report 98-4133, 52 p.

Scheffer, M., 1998, Ecology of shallow lakes: New York, Chapman and Hall, p. 357.

Schultz, L., 1981, Nutrient input in lakes by bathers: Zentralblatt f
ür Bakteriologie, Mikrobiologie, und Hygiene Ser. B Umwelthyg. Krankenhaushyg. Arbeitshyg. Praev. Med. v. 173, p. 528–548.

Socolow, R.S., Zanca, J.L., Murino, Dominic, Jr., and Ramsbey, L.R., 2000, Water resources data for Massachusetts and Rhode Island, water year 1999: U.S. Geological Survey Water-Data Report MA-RI-99-1, 401 p.

Stauffer, R.E., 1983, Determination of arsenic and phosphorus compounds in groundwater with reduced molybdenum blue: Analytical Chemistry, v. 55, p. 1205–1210.

\_\_\_\_1986, Cycling of manganese and iron in Lake Mendota, Wisconsin: Environmental Science and Technology, v. 20, p. 449–457.

\_\_\_\_\_1987, A comparative analysis of iron, manganese, silica, phosphorus, and sulfur in the hypolimnia of calcareous lakes: Water Research, v. 21, p. 1009–1022.

Strickland, J.D.H., 1960, Measuring the production of marine phytoplankton: Fisheries Research Board of Canada Bulletin, v. 122, 172 p.

Strickland, J.D.H., and Parsons, T.R., 1968, A practical handbook of seawater analysis: Fisheries Research Board of Canada, Ottawa, Special Publication No. 167, 311 p.

Stross, R.G., Huvane, J., and Sokol, R.C., 1988, Internal structure of deep-dwelling *Nitella* meadows: Aquatic Botany, v. 29, p. 329–345. Stross, R.G., and Rottier, B., 1989, Protecting water clarity in Lake George: The Conservationist, v. September– October, p. 44–46.

Stumm, W., and Morgan, J.J., 1996, Aquatic chemistry (3d ed.): New York, Wiley Interscience, 1022 p.

Thibodeaux, L.J., 1996, Environmental chemodynamics (2d ed.): New York, Wiley Interscience, 593 p.

Thoreau, H.D., 1854, Walden; or, life in the woods, *in* Bode, Carl, ed., The Portable Thoreau: New York, The Viking Press, 1964, p. 258–591.

U.S. Department of Commerce, National Oceanic and Atmospheric Administration, 1995–99, Climatological data annual summary—New England, (published annually): Asheville, N.C., National Climatic Data Center, variously paged.

Vollenweider, R.A., 1975, Input-output models with special references to the phosphorus loading concept in limnology: Schweizerische Zeitschrift Fuer Hydrologie, v. 37, p. 53–62.

Walter, D.A., Rea, B.A., Stollenwerk, K.G., Savoie, J., 1996, Geochemical and hydrologic controls on phosphorus transport in a sewage-contaminated sand and gravel aquifer near Ashumet Pond, Cape Cod, Massachusetts: U.S. Geological Survey Water-Supply Paper 2463, 89 p.

Walker, E.H., 1971, Walden's way revealed: Man and Nature, p. 11–20.

Walker, W.W., 1979, Use of hypolimnetic oxygen depletion rate as a trophic state index for lakes: Water Resources Research, v. 15, p. 1463–1470.

Walker, W.W., 1988, White Pond water quality studies: Concord, Mass., White Pond Advisory Committee, 28 p.

Winter, T.C., 1981, Uncertainties in estimating the water balance of lakes: American Water Resources Association Water Resources Bulletin, v. 17, no.1, p. 82–115.

Zen, E-an, Goldsmith, G.R., Ratcliffe, N.L., Robinson, Peter, and Stanley, R.S., 1983, Bedrock geologic map of Massachusetts: Washington D.C., U.S. Geological Survey, scale 1:250,000, 3 sheets. APPENDIX A: Delta Deuterium and Delta Oxygen-18 of Lake Water, Ground-Water Inflow, and Precipitation, Walden Pond, Concord, Massachusetts

water, ground-wa Concord, Massad	iter inflow, and precipit chusetts	ation, Walden Pond,
Date	Delta deuterium (per mil)	Delta oxygen-18 (per mil)
Wa	alden Pond, East End D	eep Area
6-09-98	-33.5	-3.98
7-06-98	-35.6	-4.14
8-04-98	-33.8	-3.61
9-08-98	-32.8	-3.78
10-20-98	-34.3	-3.77
11-18-98	-34.3	-3.84
12-21-98	-34.4	-3.85
	2 4 2	

**Appendix A.** Delta deuterium and delta oxygen-18 of lake water, ground-water inflow, and precipitation, Walden Pond,

6-09-98	-33.5	-3.98
7-06-98	-35.6	-4.14
8-04-98	-33.8	-3.61
9-08-98	-32.8	-3.78
10-20-98	-34.3	-3.77
11-18-98	-34.3	-3.84
12-21-98	-34.4	-3.85
3-18-99	-34.3	-4.04
4-30-99	-34.0	-4.03
6-07-99	-32.3	-3.68
	Well LVW 30	
7-10-98	-59.7	-9.57
8-12-98	-60.4	-9.68
9-18-98	-60.1	-9.60
10-20-98	-60.1	-9.63
11-20-98	-61.7	-9.56
12-11-98	-60.4	-9.71
1-20-99	-60.6	-9.54
2-18-99	-59.5	-9.39
3-24-99	-57.7	-8.95
4-26-99	-53.5	-8.63
6-04-99	-52.5	-8.56
	Well LVW 33	
2-18-99	-60.9	-9.64
4-26-99	-58.3	-9.12
	Well CTW 203	
10-20-98	-59.0	-9.20
12-11-98	-58.2	-9.27
2-18-99	-56.3	-9.10
4-26-99	-58.1	-9.28
Precip	itation, monthly bu	lk sample
July 1998	-40.4	-6.55
August	-29.2	-5.33
September	-50.4	-7.87
October	-40.7	-7.25
November	-41.9	-7.46
December	-72.9	-11.23
January 1999	-41.7	-7.90
February	-47.4	-8.89
March and April	-47.2	-8.16
May	-29.5	-5.31
June	-41.2	-6.42
July	-19.8	-3.26
August	-37.2	-6.21
September	-55.8	-8.63