Lake and Reservoir Management 16(4):268-280, 2000

Trophic Conditions and Water Chemistry of Lakes on Cape Cod, Massachusetts, USA

Toby D. Ahrens[1]
Botany Department
Connecticut College
270 Mohegan Ave.
New London, CT 06320

Peter A. Siver[2]
Botany Department
Connecticut College
270 Mohegan Ave.
New London, CT 06320

ABSTRACT

Ahrens, T. D. and P. A. Siver. 2000. Trophic conditions and water chemistry of lakes on Cape Cod, Massachusetts, USA. Lake and Reserv. Manage. 16(4):268-280.

Sixty lakes and ponds distributed throughout the Cape Cod peninsula were each sampled three times during 1996-1998 in order to determine the chemical conditions of the waterbodies. The study lakes, situated on either glacial moraine, glacial outwash plain or post-glacial sand accumulations, ranged in surface area from 3.6 ha to 301 ha and in maximum depth from 1 m to 26 m. The dominant ionic species in all lakes were Na^+ and Cl^-, likely due to inputs from sea spray. Conductivity and the relative charge contribution from Na^+, Cl^- and Mg^{2+} increased with distance out onto the peninsula, whereas the contribution due to Ca^{2+} decreased along the same distance gradient. Concentrations of Mg^{2+} were greater than those of Ca^{2+} in the study lakes, and the concentrations of the latter cation were very low compared to other areas in the northeast U.S. Except for the eutrophic lakes situated on the post-glacial sand accumulations on the outer tip of Cape Cod, the waterbodies were, in general, low in total phosphorus, total nitrogen and chlorophyll-a levels, had high Secchi disk depths, and were best classified as oligotrophic. The pH and alkalinity (except for lakes situated on the post-glacial sand accumulations) declined with distance out onto the peninsula. The mean pH and alkalinity of waterbodies located closest to the mainland were 6.8 and 71 $\mu eq \cdot L^{-1}$, respectively, but declined to only 5.3 and -7.5 $\mu eq \cdot L^{-1}$ on the outer Cape. Findings are compared to other studies in the northeast U.S.

Key Words: Cape Cod, lakes, pH, alkalinity, eutrophication, sodium, chloride, conductivity.

Cape Cod is a 65-mile long peninsula located between 41°30' to 42°00' North latitude and 70°45' to 69°55' West longitude in southeastern Massachusetts that extends into the Atlantic Ocean. Cape Cod is separated from the Massachusetts mainland by a 17.5 mile-long man-made canal known as the Cape Cod Canal, and varies in breadth between 1 and 20 miles. Approximately 343 freshwater lakes and ponds are located on the peninsula, ranging in surface area from less than 4 ha to 301 ha (Massachusetts Lakes Classification Program 1989). The lakes are predominantly glacial kettle ponds, and many are true seepage lakes that are fed by groundwater and lack outlets.

The Cape Cod peninsula is thought to have formed during the Wisconsin glaciation approximately 15,000 to 10,000 years BP (Strahler 1966). The geology of the Cape varies from glacial moraine to outwash plains to post-glacial dune accumulations (Oldale and Barlow 1986). Two bands of glacial moraine deposits, the Buzzards Bay moraine and the Sandwich moraine, are located in the western-most portion of Cape Cod and along the northwestern shore along Cape Cod Bay, respectively (Strahler 1966, Oldale and Barlow 1986).

[1] currently with Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543.
[2] author to whom correspondence should be addressed.

Both moraine deposits consist of till, sand, gravel, and fine clay (Oldale and Barlow 1986). Four outwash plains, the Mashpee pitted plain deposits, Barnstable plain deposits, Eastham plain deposits, and Wellfleet plain deposits, occupy much of the remainder of Cape Cod. Most of the outwash plains consist of fine or gravely sand, fine silt, clay, and till (in lower concentrations than in the moraines), and portions of the Wellfleet plain deposits contain beds of clay (Oldale and Barlow 1986). The Provincetown region at the outer tip of the peninsula was formed by post-glacial dune deposits consisting mostly of sand.

The most in-depth study of lakes on Cape Cod was done by Mattson et al. (1992). In that study, based largely on data collected in the 1980's, the authors grouped all lakes on Cape Cod and critically compared them to waterbodies in the five additional geologic zones identified in Massachusetts. Mattson et al. (1992) characterized the lakes on Cape Cod as low in pH, alkalinity, and mineral content. They also observed that Cape Cod lakes were comparatively high in sodium, chloride, and magnesium levels, presumably due to the effects of sea spray. Mattson et al. (1992) further suggested that the slow weathering of the glacial sand deposits surrounding the lakes was likely contributing to the low pH and poorly buffered condition of many of the lakes. Lakes on Cape Cod were significantly different from lakes in other regions in Massachusetts due, in large part, to the extent of the glacial deposits that lie between the surface waterbodies and the bedrock (Mattson et al. 1992).

Over the last two decades, lake acidification caused by acidic deposition has been a concern in the northeastern United States (e.g., Brakke et al. 1988, Husar et al. 1991). A number of studies, the most extensive of which was conducted by the EPA in the early 1980s (Brakke et al. 1988), have been undertaken in order to document the current pH status of lakes in the northeastern U.S. (e.g., Omernik et al. 1988, Godfrey et al. 1996). Studies subsequent to the EPA survey of the 1980's done in the Adirondacks (Kretser et al. 1989) and Connecticut (Canavan and Siver 1994) suggested that the EPA study may not have accurately represented the status of lake acidity in these regions. In addition, Mattson et al. (1992) found that if small ponds (< 4 ha) were included in estimates of the number of acidic waterbodies (defined as lakes with an alkalinity $< 0\ \mu eq \cdot L^{-1}$) that there were twice as many acidic lakes in Massachusetts than estimated in the EPA study; many of these acidic ponds were situated on Cape Cod.

In addition to atmospheric deposition, anthropogenic influences within the watershed can also greatly alter lake water chemistry (Field et al. 1996). In many areas of the northeast U.S. use of winter road deicing salts can significantly increase sodium and chloride levels in lakes (Brakke et al. 1988, Mattson et al. 1992, Canavan and Siver 1994). Other activities associated with conversion of forests to residential lands, such as liming of lawns and use of fertilizers, can significantly change lake water chemistry (Field et al. 1996), especially concentrations of phosphorus (Norvell et al. 1979) and nitrogen (Frink 1991).

Although there have recently been attempts to document changes in pH, alkalinity, and major ion concentrations in Massachusetts lakes (Godfrey et al. 1996), little is known about how the lakes have changed over the past 100 to 200 years. Over the past two decades paleolimnological methods employing the use of algal microfossils to reconstruct historical conditions of lakes have become well established (e.g., Smol 1992, 1995). Except for several paleolimnological studies that focused on a few waterbodies in the outer Cape Cod region (Winkler 1985, 1988), paleolimnological work is lacking on Cape Cod. Reconstructing lake histories using remnants of siliceous algae is highly dependent on an up-to-date and accurate chemical database documenting the current conditions of lakes in the area being studied (Siver 1993).

The primary objective of this study was to determine the current chemical status of lakes and ponds on Cape Cod relative to geographic location on the peninsula.

Materials and Methods

Study Site

The Cape was divided into four regions based on geology and geographic location, and named for the purpose of this paper as follows: 1) "Provincetown," post-glacial dune deposits, 2) "Forearm," Wellfleet outwash plain deposits, 3) "Elbow," Eastham and Harwich outwash plain deposits, and 4) "Bicep," Mashpee Pitted outwash plain deposits and Sandwich moraine deposits (Fig. 1 and Table 1). Many of the lakes in the Forearm region are located in the Cape Cod National Seashore, a national park established in 1961.

Sixty lakes and ponds were selected from over 340 freshwater waterbodies found on Cape Cod: 19 in the Bicep region, 21 in the Elbow region, 16 in the Forearm region, and 4 in Provincetown (Fig. 1 and Table 1). This study included lakes of all sizes, ranging in surface area from 3.6 ha to 301 ha and in maximum depth from 1 m to 26 m. The study lakes were distributed throughout the peninsula from the towns of

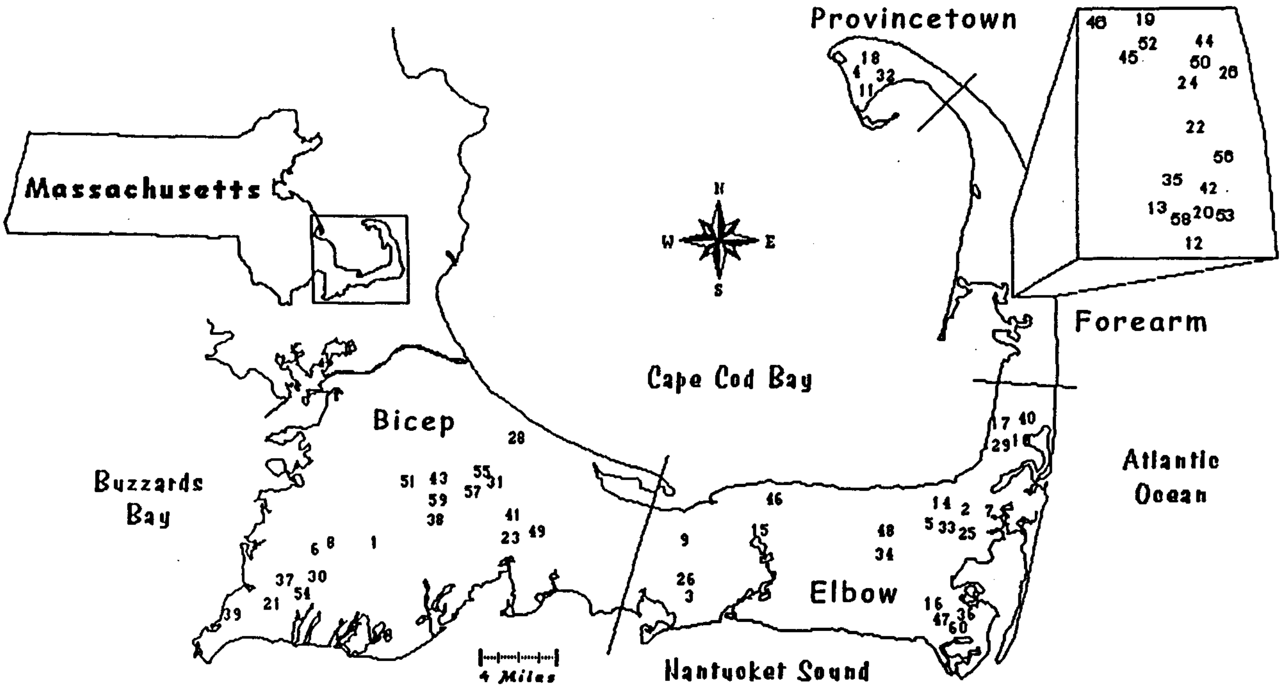

Figure 1.–The locations and grouping of the 60 study lakes. The numbers correspond with those on Table 1.

Falmouth and Sandwich situated nearest the mainland to Provincetown on the outer Cape, and were selected, in part, based on their inclusion in previous studies.

All but the four study lakes situated in Provincetown are believed to be glacial in origin and most likely are true kettle ponds (Strahler 1966). The four waterbodies found in Provincetown were formed post-glacially (Oldale and Barlow 1986), and are shallow depressions on sand dune deposits. Most are seepage lakes, however a few, including Lovers Lake, Mashpee Lake, Crystal Lake, Big Sandy Pond, and Horse Pond, are not true seepage lakes, as they have either an inlet, outlet, or both.

Methods

All lakes were sampled in June 1997 (except the Forearm lakes, which were sampled in October 1996), July 1997, and July 1998. All variables were analyzed on each collection date except for total nitrogen (TN) which was measured only in July 1997 and July 1998. Profiles of conductivity (SC) and Secchi disk depth were measured *in situ*. All other analyses were done on water samples taken from a one meter depth using a 2.2-liter horizontal van-Dorn water sampler. Water samples were collected in polyethylene bottles, and all bottles except those used to collect water for chloride analysis were acid-washed and triple rinsed prior to use. Water samples taken for pH and alkalinity analysis were kept in bottles with air-excluding lids until analysis. Water was collected over the deep basin in each lake, determined from bathymetric maps (Butterworth Co. 1993), and refrigerated until analysis.

Secchi disk depth was measured with a 20 cm black and white disk. Specific conductivity was measured with a YSI 33 SCT meter calibrated using a sodium chloride standard as per the manufacturer's directions. Measurements were taken at the surface, 0.5 meters, and every meter to the bottom. Specific conductance was standardized to 25°C. The pH was measured on the same day as collection with a Fisher Acumet 640-A pH meter; a two-point calibration of the meter was made before each use. The Gran Titration method was used to measure alkalinity (Wetzel and Likens 1991). A reagent-grade 0.02N acid titrant purchased from Fisher Scientific was used for all alkalinity measurements. Chlorophyll-*a*, -*b*, and -*c* were extracted in acetone and measured using spectrophotometry (APHA 1985). Total phosphorus (TP) levels were determined using a stannous chloride–ammonium molybdate colorimetric assay following a persulfate digestion (APHA 1985). A standard curve based on a dilution series using a reagent grade standard solution was prepared for each set of total phosphorus samples processed, and ten-cm cuvettes were used to enhance measurements of low TP concentrations. Standard curves for total phosphorus measurements had r^2 values above 0.9, and blanks and known standards were inserted after every tenth sample.

Table 1.–The 60 study lakes with town locations in Massachusetts, USA, and with lake numbers that correspond with those on Figure 1.

	LAKE	TOWN		LAKE	TOWN
1	Ashumet	Mashpee	31	Lawrence	Sandwich
2	Baker	Brewster	32	Little Bennett	Provincetown
3	Big Sandy	Yarmouth	33	Little Cliff	Brewster
4	Clapps	Provincetown	34	Long	Brewster
5	Cliff	Brewster	35	Long	Wellfleet
6	Crooked	Falmouth	36	Lovers	Chatham
7	Crystal	Orleans	37	Mares	Falmouth
8	Deep	Falmouth	38	Mashapee	Mashpee
9	Dennis	Yarmouth	39	Miles	Falmouth
10	Depot	Eastham	40	Minister	Eastham
11	Duck	Provincetown	41	Mystic	Barnstable
12	Duck	Wellfleet	42	Northeast	Wellfleet
13	Dyer	Wellfleet	43	Peters	Sandwich
14	Flax	Brewster	44	Round	Eastham
15	Flax	Dennis	45	Ryder	Truro
16	Goose	Chatham	46	Scargo	Dennis
17	Great	Eastham	47	Schoolhouse	Chatham
18	Great	Provincetown	48	Sheep	Brewster
19	Great	Truro	49	Shubael	Barnstable
20	Great	Wellfleet	50	Slough	Truro
21	Grews	Falmouth	51	Snake	Sandwich
22	Gull	Wellfleet	52	Snow	Truro
23	Hamblin	Barnstable	53	Southeast	Wellfleet
24	Herring	Wellfleet	54	Spectacle	Falmouth
25	Higgins	Brewster	55	Spectacle	Sandwich
26	Horse	Yarmouth	56	Spectacle	Wellfleet
27	Horseleech	Truro	57	Triangle	Sandwich
28	Hoxie	Sandwich	58	Turtle	Wellfleet
29	Jemima	Eastham	59	Wakeby	Mashpee
30	Jenkins	Falmouth	60	White	Chatham

Total nitrogen was analyzed by the Environmental Research Institute (ERI) at the University of Connecticut using spectrophotometry after the sample was oxidized, reduced, diazotized with sulfanilamide, and combined with N-(1-napthyl)-ethylenediamine dihydrochloride (U.S. EPA 1983). Sulfate levels were also analyzed by the ERI at the University of Connecticut using anion chromatography (U.S. EPA 1983). Chloride was analyzed using the argentometric method (APHA 1985).

Cation concentrations (K^+, Na^+, Ca^{2+}, Mg^{2+}) were measured using a Perkin Elmer 2380 flame atomic absorption spectrophotometer. Standard curves based on a dilution series using reagent grade standard solutions were prepared for each base cation before each set of samples were processed. Standard curves for each base cation routinely had r^2 values above 0.97. Blanks were run between each sample, and known standards were inserted after every tenth sample. Triplicate readings were taken for each sample. All samples were filtered through Whatman glass microfiber filters and acidified with 50% HNO_3 to pH < 2 prior to analysis. Lanthanum chloride was added to the Ca^{2+} and Mg^{2+} samples to reduce potential interferences caused by phosphorus, sulfur, and aluminum.

A principle component analysis (PCA) was conducted using CANOCO (ter Braak 1990) for the 60 sample lakes on Cape Cod based on 13 parameters: SD, TP, TN, Chl-a, SC, pH, alkalinity, Cl^-, SO_4^{2-}, K^+, Na^+, Ca^{2+}, and Mg^{2+}. Additional PCA analyses were also conducted using only the trophic parameters (SD, TP, TN, and Chl-a) or only the chemical parameters (SC, pH, alkalinity, Cl^-, SO_4^{2-}, K^+, Na^+, Ca^{2+}, and Mg^{2+}). The principle component analyses were done on a correlation matrix using centered and standardized data, and the PCA scores of the first two extracted axes were plotted in an XY coordinate plane where the Euclidean distances were preserved. Since we observed no obvious trends between the data sets for each year for the variables measured, we used all data in calculating means, median values, and in the PCA analysis.

Results

pH and Alkalinity

The pH values ranged from 4.4 in Flax Pond in Dennis, to 8.0 in Lovers Pond in Chatham. The mean and median pH values were 6.2 and 6.4, respectively. Eighteen percent of the lakes had pH values less than 5, 38% less than 6, and 80% less than 7. In general, the pH of the lakes decreased with distance from the Cape Cod Canal (farther away from the glacial moraine deposits in western Cape Cod) (Fig. 2). The mean pH values in the Bicep, Elbow, Forearm, and Provincetown regions were 6.8, 6.3, 5.3, and 5.4, respectively. There were no lakes in the Forearm and Provincetown regions with pH values greater than 7.0.

The mean and median alkalinity values of the 60 study lakes were 39 $\mu eq \cdot L^{-1}$ and 23 $\mu eq \cdot L^{-1}$, respectively. The high mean alkalinity (relative to the median) is due in large part to a few lakes with uncharacteristically high alkalinity values (Fig. 3). Lovers Lake in Chatham, Duck Pond in Provincetown, and Mystic Lake in Barnstable had alkalinity values of 204 $\mu eq \cdot L^{-1}$, 161 $\mu eq \cdot L^{-1}$, and 151 $\mu eq \cdot L^{-1}$, respectively. Thirty-seven percent of the lakes in this study had an alkalinity < 0 $\mu eq \cdot L^{-1}$, and 63% had an alkalinity < 50 $\mu eq \cdot L^{-1}$. Many of the lakes with an alkalinity < 0 $\mu eq \cdot L^{-1}$ were concentrated in the Forearm region (Wellfleet outwash plain), as 75% of the lakes in that area had an alkalinity < 0 $\mu eq \cdot L^{-1}$ (Fig. 3).

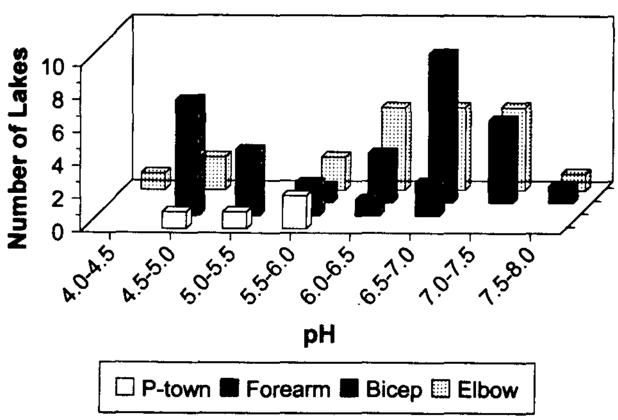

Figure 2.–The distribution of lakes along a pH gradient by region.

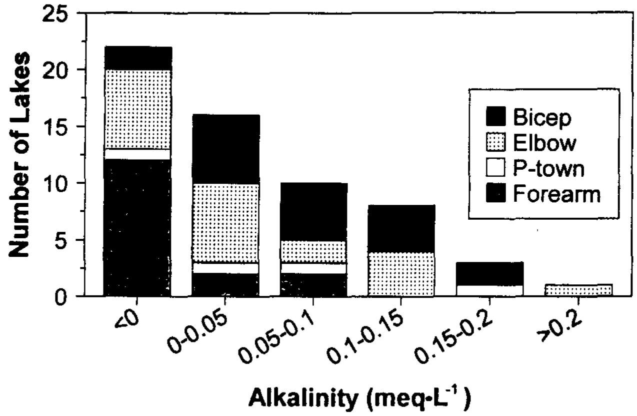

Figure 3.–The distribution of lakes along an alkalinity gradient by region.

Dissolved Salts

Sodium was the cation found in the greatest concentration in all lakes, and K^+ the least prevalent cation. The mean Na^+, Mg^{2+}, Ca^{2+}, K^+, and H^+ concentrations were 520 $\mu eq \cdot L^{-1}$, 154 $\mu eq \cdot L^{-1}$, 78 $\mu eq \cdot L^{-1}$, 18 $\mu eq \cdot L^{-1}$, and 4 $\mu eq \cdot L^{-1}$, respectively. Median Na^+, Mg^{2+}, Ca^{2+}, K^+, and H^+ concentrations were 461 $\mu eq \cdot L^{-1}$, 149 $\mu eq \cdot L^{-1}$, 67 $\mu eq \cdot L^{-1}$, 17 $\mu eq \cdot L^{-1}$, and 1 $\mu eq \cdot L^{-1}$, respectively (Table 2). Sodium ions accounted for 68% and 67% of the total cation charge according to the mean and median values, respectively. Several lakes, including Minister Pond in Eastham, White Pond in Chatham, and Lovers Pond in Chatham, had exceptionally high mean concentrations of Na^+. On average, the H^+ concentration accounted for only 0.1%, 0.8%, 1.2%, and 0.7% of the total cation charge in the Bicep, Elbow, Forearm, and Provincetown regions, respectively. The largest concentration of H^+ ions was 41.1 $\mu eq \cdot L^{-1}$ found in Flax Pond in Dennis, accounting for 8% of the total cation charge in that lake.

Sodium was the dominant cation in the study lakes, and concentrations ranged from 249 $\mu eq \cdot L^{-1}$ in Grews Pond in Falmouth, to 1,552 $\mu eq \cdot L^{-1}$ in Minister lake in Eastham. Sodium levels increased to the east and north, as the mean level in the Forearm region was almost double the mean level in the Bicep region (Table 3). Calcium concentrations ranged from 35 $\mu eq \cdot L^{-1}$ in Snow Pond in Wellfleet, to 198 $\mu eq \cdot L^{-1}$ in Lovers Lake in Chatham. Calcium concentrations were the lowest in the Forearm region, where more than 80% of the lakes had levels lower than the median value for all lakes (Fig. 4). Magnesium concentrations tended to increase to the east and north (Fig. 4). Magnesium and Ca^{2+} were not correlated ($r^2 = 0.15$), however, Ca^{2+} and alkalinity had a correlation (r^2) of 0.81.

The mean Cl^-, SO_4^{2-}, and alkalinity concentrations

Table 2.–Mean, median, minimum, and maximum values for all lakes in the study based on average values of the three sampling dates for each lake. All lakes were sampled in June 1997 (except for the Forearm lakes, which were sampled in October 1996), July 1997, and July 1998. Water samples were taken from 1 m.

Parameter	Units	Mean	Median	Minimum	Maximum
SD	meters	4.4	4.4	0.3	9.4
ALK	$\mu eq \cdot L^{-1}$	39	23	-47	204
TEMP	° C	22.7	22.9	17.9	26
pH	pH units	6.1	6.4	4.4	8.0
SC	$\mu S \cdot cm^{-1}$	106.3	99.8	54.3	206.3
CHL-a	$\mu g \cdot L^{-1}$	3.07	2.11	0.51	19.25
TP	$\mu g \cdot L^{-1}$	14.19	10.23	4.73	82.17
TN	$\mu g \cdot L^{-1}$	249	236	55	615
N:P		20.5	20.3	7.5	48.3
Cl^-	$meq \cdot L^{-1}$	0.597	0.546	0.253	1.368
$SO4^{-2}$	$meq \cdot L^{-1}$	0.110	0.115	0.020	0.198
Na^+	$meq \cdot L^{-1}$	0.520	0.461	0.249	1.552
Mg^{+2}	$meq \cdot L^{-1}$	0.154	0.149	0.078	0.281
Ca^{+2}	$meq \cdot L^{-1}$	0.078	0.067	0.035	0.198
K^+	$meq \cdot L^{-1}$	0.018	0.017	0.007	0.044
H^+	$meq \cdot L^{-1}$	0.004	0.000	0.000	0.041
Na:Cl		0.89	0.90	0.68	1.13

were 597 $\mu eq \cdot L^{-1}$, 110 $\mu eq \cdot L^{-1}$, and 39 $\mu eq \cdot L^{-1}$, respectively. The median Cl^-, SO_4^{2-}, and alkalinity concentrations were 546 $\mu eq \cdot L^{-1}$, 115 $\mu eq \cdot L^{-1}$, and 23 $\mu eq \cdot L^{-1}$, respectively. The Cl^- concentration ranged from 253 $\mu eq \cdot L^{-1}$ in Snake Pond in Sandwich, to 1,368 $\mu eq \cdot L^{-1}$ in Minister Pond in Eastham, and chloride concentrations accounted for 80% of both the mean and median total anion charge. Chloride concentrations increased with distance from the Cape Cod Canal (Fig. 5), as mean concentrations in the Bicep, Elbow, Forearm, and Provincetown regions were 350 $\mu eq \cdot L^{-1}$, 615 $\mu eq \cdot L^{-1}$, 822 $\mu eq \cdot L^{-1}$, and 787 $\mu eq \cdot L^{-1}$, respectively (Table 3). All lakes in the Bicep region had Cl^- concentrations lower than the mean for all of the study lakes, and all but one of the lakes in the Forearm region had Cl^- concentrations greater than the mean for all of the study lakes. Concentrations of Cl^- were closely correlated with those of Na^+, with an r^2 of 0.85, and concentrations of Na^+ and Cl^- were both highly correlated with conductivity ($r^2 = 0.81$ and $r^2 = 0.93$, respectively). Magnesium was also highly correlated with Cl^- ($r^2 = 0.61$) and conductivity ($r^2 = 0.71$).

The Na:Cl ranged from 0.68 to 1.13 with mean and median values of 0.89 and 0.90, respectively (Table 2). All lakes in the Forearm and Provincetown region had Na:Cl values below 0.86, while none of the lakes in the Bicep region had Na:Cl values below 0.86. Five of the 21 lakes in the Elbow region had Na:Cl values less than 0.86.

The mean and median conductivity values of the study lakes were 106 $\mu S \cdot cm^{-1}$ and 100 $\mu S \cdot cm^{-1}$, respectively, and the values ranged from 54 $\mu S \cdot cm^{-1}$, in Grews Pond (Falmouth) to 206 $\mu S \cdot cm^{-1}$, in both Minister Pond (Eastham) and Horseleech Pond (Wellfleet). As was observed for concentrations of Na^+ and Cl^-, specific conductivity increased in waterbodies with distance from the Cape Cod Canal out onto the peninsula. The mean conductivity level of lakes located closest to the Cape Cod Canal was 76 $\mu S \cdot cm^{-1}$ (Bicep region), whereas those in the Forearm and Provincetown region had mean conductivity values of 137 $\mu S \cdot cm^{-1}$ and 128 $\mu S \cdot cm^{-1}$, respectively (Table 3). No lakes in the Forearm region had conductivity values less than 100 $\mu S \cdot cm^{-1}$. Lakes with conductivity levels greater than 150 $\mu S \cdot cm^{-1}$ included Minister Pond (Eastham), Round Lake (Wellfleet), Horseleech Pond (Wellfleet), Spectacle Pond (Wellfleet), White Pond (Chatham), and Lovers Pond (Chatham).

Sulfate concentrations ranged from 20 $\mu eq \cdot L^{-1}$ in Great Pond in Provincetown, to 198 $\mu eq \cdot L^{-1}$ in Ryder

Table 3.–Mean values for major trophic and chemical characteristics in each of the four regions of Cape Cod. Refer to Table 2 for depth, season, and year of sampling. Regions are shown in Figure 1.

Parameter	Units	Bicep	Elbow	Forearm	P-town
SD	meters	4.5	4.5	5.0	0.5
ALK	$\mu eq \cdot L^{-1}$	71	41	-7.5	60
TEMP	°C	22.8	24.6	20.2	22.6
pH	pH units	6.8	6.3	5.3	5.4
SC	$\mu S \cdot cm^{-1}$	76	106	137	128
CHL-a	$\mu g \cdot L^{-1}$	2.58	3.16	2.05	9.07
TP	$\mu g \cdot L^{-1}$	11.6	12.2	10.4	52.1
TN	$\mu g \cdot L^{-1}$	250	246	173	567
N:P		23.5	21.9	16.6	14.7
Cl^-	$meq \cdot L^{-1}$	0.350	0.615	0.822	0.787
$SO4^{-2}$	$meq \cdot L^{-1}$	0.112	0.110	0.126	0.039
Na^+	$meq \cdot L^{-1}$	0.347	0.581	0.625	0.592
Mg^{+2}	$meq \cdot L^{-1}$	0.133	0.148	0.182	0.172
Ca^{+2}	$meq \cdot L^{-1}$	0.090	0.088	0.052	0.079
K^+	$meq \cdot L^{-1}$	0.016	0.016	0.021	0.027
H^+	$meq \cdot L^{-1}$	0.000	0.004	0.010	0.006
Na:Cl		1.00	0.92	0.76	0.75

Pond in Wellfleet. Mean sulfate concentrations in the Bicep, Elbow, and Forearm regions were 112 $\mu eq \cdot L^{-1}$, 110 $\mu eq \cdot L^{-1}$, and 126 $\mu eq \cdot L^{-1}$, respectively, significantly higher than those in the Provincetown region which averaged only 39 $\mu eq \cdot L^{-1}$ (Fig. 5).

Trophic parameters

Secchi disk depths ranged from 0.31 m in Duck Pond in Provincetown to 9.35 m in Sheep Pond in Brewster (Table 2). Thirty-six percent of the lakes had a mean Secchi disk depth greater than 5.0 m. There was a greater range of Secchi depths in both the Forearm and Elbow region as compared to the Bicep region. All four Provincetown lakes had Secchi disk depths of less than 1 m due primarily to high humic acid contents. Due to the sampling schedule, Secchi depth readings were sometimes taken in undesirable conditions (in light rain or late in the day). For this reason, variations in Secchi depths for a given lake between different sampling dates may be due to variable physical conditions as well as different trophic conditions.

The Chl-a levels ranged from 0.51 $\mu g \cdot L^{-1}$ in Flax Pond in Dennis, to 19.25 $\mu g \cdot L^{-1}$ in Duck Pond in Provincetown. The mean and median Chl-a concentrations were 3.06 $\mu g \cdot L^{-1}$ and 2.17 $\mu g \cdot L^{-1}$, respectively. The Provincetown lakes had the highest Chl-a concentrations, with two lakes having concentrations greater than 10 $\mu g \cdot L^{-1}$. Long Pond (Brewster), Spectacle Pond (Sandwich), and Cliff Pond (Orleans) had one sampling date where Chl-a concentrations were 5.0, 5.5, and 31 times higher than the average of the other two sampling dates. The sampling period of the abnor-

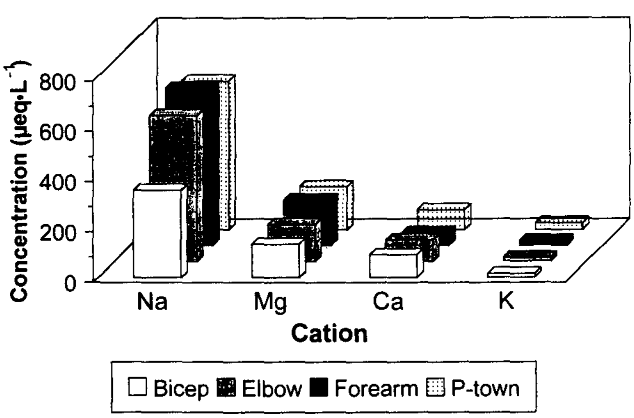

Figure 4.–The mean concentrations of sodium, magnesium, calcium, and potassium in the study lakes by region.

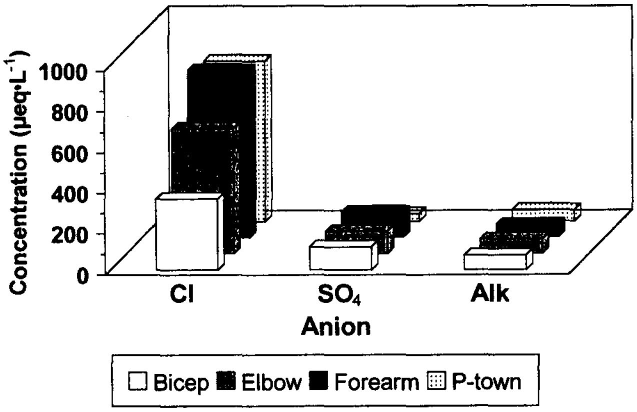

Figure 5.-The mean concentrations of chloride, sulfate, and alkalinity anions in the study lakes by region.

mally high Chl-a concentration was different for each of the three lakes.

Mean and median TP levels for all of the study lakes were 14.2 $\mu g \cdot L^{-1}$ and 10.2 $\mu g \cdot L^{-1}$, respectively. Forty-seven percent of the lakes sampled had TP concentrations less than 10 $\mu g \cdot L^{-1}$, and more than 70% of the lakes had TP concentrations less than 15 $\mu g \cdot L^{-1}$. Sixty-nine percent of the lakes located in the Forearm region had TP levels < 10 $\mu g \cdot L^{-1}$, in contrast to only 42% in the Bicep region and 43% in the Elbow region. All four lakes sampled in Provincetown had TP levels greater than 15 $\mu g \cdot L^{-1}$, including two with concentrations above 50 $\mu g \cdot L^{-1}$.

Mean and median TN concentrations for all of the lakes studied were 250 $\mu g \cdot L^{-1}$ and 237 $\mu g \cdot L^{-1}$, respectively. Mean TN concentrations in the Bicep, Elbow, Forearm, and Provincetown regions were 250 $\mu g \cdot L^{-1}$, 246 $\mu g \cdot L^{-1}$, 173 $\mu g \cdot L^{-1}$, and 567 $\mu g \cdot L^{-1}$. Seven lakes in the Forearm region had TN concentrations less than 150 $\mu g \cdot L^{-1}$, compared to one lake in both the Bicep and Elbow regions, and none in Provincetown. All four lakes in Provincetown had TN values greater than 400 $\mu g \cdot L^{-1}$.

Total phosphorus showed a greater correspondence to chlorophyll-a values than TN did. The r^2 for TP and Chl-a was 0.30, compared to 0.24 for TN and Chl-a. The r^2 for Chl-a and Secchi disk depth was 0.29, and the r^2 for TN versus TP was 0.55. The TN:TP ranged from 7.5 in Great Pond in Provincetown, to 48.3 in Deep Pond in the Bicep region. The mean TN:TP decreased with distance from the canal, with values of 23.5, 21.9, 16.6, and 14.7 for the Bicep, Elbow, Forearm, and Provincetown regions, respectively.

PCA results

The PCA based on both trophic and chemical characteristics showed a clear spatial separation between lakes in the Bicep region and lakes in the Forearm region, with lakes in the Elbow region spanning both areas (Fig. 6). The separation was most highly correlated with the SC, Cl^-, and Na^+ axes, and less along the TP, TN, and alkalinity axes. The lakes in the Provincetown region were generally influenced more by the trophic parameters than lakes in other regions. Many of the lakes in the Forearm region were towards the low or oligotrophic end of each trophic parameter. The PCA scores for the chemical characteristics showed that regional differences among lakes on Cape Cod are characterized more by varying SC, Mg^{2+}, Cl^-, and Na^+ levels, rather than by pH, alkalinity, or Ca^{2+} levels (Fig. 6). There was a large amount of overlap among the four regions when only the trophic characteristics were used, indicating less correlation with these variables.

Discussion

pH and Alkalinity

Enhanced acidity in dry deposition and precipitation from nitric and sulfuric acids have increased the acidity of many lakes in the northeast U.S. (Norton et al. 1981, Del Prete and Schofield 1981, Davis et al. 1983, Husar et al. 1991), in some cases with significant ecological consequences (Gorham and Gordon 1960, Baker and Christensen 1991). Uutala et al. (1994) used paleolimnological methods to demonstrate that fish loss in several Ontario lakes coincided with recent periods of increased acidity. Many Adirondack lakes have also been shown to be especially prone to changes in pH as a result of acid precipitation (Schofield 1976, Pfeiffer and Festa 1980, Cumming et al. 1992). Kingston et al. (1992) reported that increased aluminum concentrations associated with lake acidification

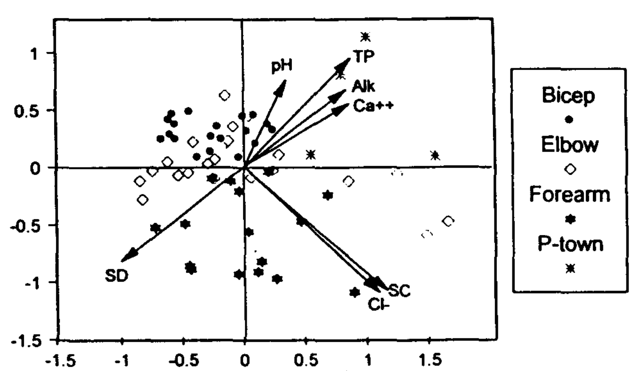

Figure 6.-PCA sample scores along the first two axes based on 13 chemical and physical characteristics. See text for details.

in the Adirondack region have resulted in declines in fish populations, and in some cases, complete loss of fish.

The percentage of acidic lakes with low buffering capacity found in this study was greater than other regions examined in eastern North America. The median alkalinity value for all study lakes on Cape Cod was 23 $\mu eq \cdot L^{-1}$, which is lower than median values in other regions of Massachusetts (Mattson et al. 1992), Connecticut (Canavan and Siver 1994), the Adirondacks (Charles 1985), other areas in the northeast U.S., including the Poconos, southern New England, central New England, and Maine (Brakke et al. 1988), and Ontario (Hall and Smol 1996). Brakke et al. (1988) found that 11% of the lakes in the Adirondack region were estimated to be acidic (alkalinity < 0 $\mu eq \cdot L^{-1}$), which was the highest percentage of acidic lakes in all regions examined in the eastern U.S., excluding areas in Florida. In this study, over three times as many of the lakes sampled on Cape Cod (37%) had alkalinity values less than 0 $\mu eq \cdot L^{-1}$. The percentage of waterbodies with alkalinity values less than 0 $\mu eq \cdot L^{-1}$ was even greater on the outer Cape Cod region. For this reason, special attention should be given to lakes on Cape Cod due to their current acid status and their vulnerability to further acidification. Since there is little documentation of how pH values of Cape Cod lakes have changed in the past, it is not possible to determine at this time if the lakes, especially those on the outer Cape, were historically acidic or if they have significantly declined in pH over the last century. Thus, paleolimnological studies will be vital to our understanding of how these lakes have been effected by enhanced acidity.

One detailed paleolimnological study of a waterbody on the outer Cape Cod region was completed by Winkler (1988). Using siliceous diatom remains to reconstruct lake pH, Winkler (1988) suggested that the pH of Duck Pond in Wellfleet has always been acidic (approximately 5.3 throughout its 12,000 year history). The pH of Duck Pond was 4.6 in the early 1980s (Winkler 1988), and 4.8 in our study. Winkler (1988) showed that although the pH in the pond has dropped in the last 150 years, the pond has had periods of similar pH decline over the last several thousand years. Winkler (1988) further suggested that many Cape lakes may be naturally acidic as a result of acid litter from vegetation consisting largely of conifer forests with ericaceous understories, and soils composed of crystalline and noncalcareous sands.

The major source of buffering in many lakes comes from the weathering of carbonate and bicarbonate rock. The high correlation between calcium concentrations and alkalinity ($r^2 = 0.81$) suggests that alkalinity sources of Cape Cod lakes are associated with calcium-based rock sources. Despite this finding, the overall low alkalinity values indicate that there is very little weathering of the glacial deposits contributing to the alkalinity of Cape Cod lakes.

Other potential alternate sources of alkalinity include sulfate reduction in lake sediments (Giblin et al. 1990), alkalinity generation via alterations to the surrounding watersheds (e.g., residential development) (Siver et al., 1999), and organic acid contributions (Cole 1994). Reduction of sulfate produces alkalinity. If the reduced sulfur is subsequently buried in the lake sediments, the alkalinity generated represents a permanent gain to the waterbody (Giblin et al. 1990). Winkler (1988) and Giblin et al. (1990) suggested that sulfate reduction may be an important source of alkalinity in lakes of Cape Cod. Winkler's (1988) study on Duck Pond in Wellfleet found that sulfate in precipitation greatly exceeded in-lake sulfate concentrations (20 times higher in the precipitation), which could be indirect evidence for sulfate reduction (and net alkalinity generation) in the pond. However, Urban (1994) and Giblin et al. (1990) found that the amount of alkalinity generated by sulfate reduction in lake sediments is not necessarily correlated with the concentration of sulfate in overlying waters. Thus, further study will be needed in order to determine the contribution that sulfate reduction, coupled with long-term burial in the sediments, plays in the buffering of these waterbodies. Organic acids could be significantly contributing to the buffer system in Duck Pond in Provincetown (Fig. 3). Duck Pond (Provincetown) had an abnormally high alkalinity (161 $\mu eq \cdot L^{-1}$) for a lake with a pH of 5.5 and it clearly does not fit the pH:alkalinity pattern observed in the other 59 lakes. In general, much of the alkalinity generation in Cape Cod lakes is thought to stem from weathering of rock since alkalinity concentrations are highly correlated with calcium values, and neither sulfur burial mechanisms nor organic acid buffering contributions are associated with calcium sources.

Dissolved Salts

There was close agreement in the charge balance for the cations and anions measured in the study lakes. Mean cation (Na^+, Ca^{2+}, Mg^{2+}, K^+, and H^+) and anion (CO_3^{2-}, HCO_3^-, Cl^-, and SO_4^{2-}) totals for the major ions were 774 $\mu eq \cdot L^{-1}$ and 746 $\mu eq \cdot L^{-1}$, respectively, and totals of median values were 695 $\mu eq \cdot L^{-1}$ and 684 $\mu eq \cdot L^{-1}$, respectively. The slight difference between cation and anion totals (4% difference for mean values) may be attributed to unquantified organic anions or nitrate anions (e.g., Brakke et al. 1988, Mattson et al. 1992).

Even though the absolute contribution of H^+ ions was greatest in the more acidic lakes in the Forearm region, the relative contribution to the total cation charge was lower than lakes in the Bicep region due to the much higher concentrations of Na^+ ions in waterbodies on the outer Cape. On average, H^+ ions contributed less than 1% of the total cation concentrations, as compared to 67% for the Na^+ ions. Some biological processes, such as uptake mechanisms involving charge-based binding sites, are affected moreso by the relative, and not absolute, abundances of certain ions. Thus, it is possible that the high concentration of Na^+ ions in the acidic lakes on Cape Cod may be acting on biological mechanisms by minimizing the effects of elevated H^+ ion concentrations.

Sodium and Cl^- were the dominant cation and anion species, presumably due to the proximity of the waterbodies to the ocean. Cole (1994) suggested that Cl^- is commonly the third-ranked anion in inland waters, in terms of equivalence, after bicarbonate and sulfate species, which agrees with the findings of Brakke et al. (1988) for lakes in the northeast U.S. However, both Mattson et al. (1992) and Canavan and Siver (1994) found Cl^- to be the dominant anion in many of the lakes in Massachusetts and Connecticut, respectively. In Massachusetts, both road salts (NaCl and $CaCl_2$) and sea spray resulted in elevated Na^+ and Cl^- levels (Mattson et al. 1992). Road salts were also suspected to contribute to Na^+ and Cl^- concentrations in Connecticut lakes (Canavan and Siver 1994). Mattson et al. (1992) showed that population density and mean chloride levels were highly correlated, suggesting that anthropogenic influences (such as road salts and Cl^- from sewage) can alter chloride levels in lakes more than sea spray. While this may be true for many inland lakes in Massachusetts, three lines of evidence suggest that the elevated chloride levels in the Cape lakes is more likely due to the proximity to the ocean. First, there was a geographic gradient of Na^+ and Cl^- levels in waterbodies on Cape Cod, with the lowest concentrations occurring in lakes closest to the Cape Cod Canal, and the highest concentrations occurring in waterbodies farther out on the peninsula. Second, there was an inverse relationship between population density and ionic concentrations. The highest Na^+ and Cl^- levels were found in the Forearm region, which has the lowest population densities since many of the lakes are located within the Cape Cod National Seashore. Third, further supporting evidence that the Na^+ and Cl^- in Cape Cod lakes originates from sea spray is the ratio of Na:Cl in the waterbodies. The mean Na:Cl in this study was 0.89, which is very close to the 0.86 Na:Cl of seawater (Sullivan et al. 1988).

Since Na^+ and Cl^- were the dominant anion and cation, it is not surprising that conductivity was highly correlated with the Na^+ and Cl^- concentrations (r^2=0.81 and 0.93, respectively). Like the concentrations of Na^+ and Cl^-, the conductivity tended to increase with distance out onto the peninsula. Brakke et al. (1988) found the median conductivity in northeast U.S. lakes to be 43 $\mu S \cdot cm^{-1}$, and the median conductivity in southern New England to be 82 $\mu S \cdot cm^{-1}$ (the highest of any region in the Northeast). Thus, mean and median conductivity values found in this study (120 $\mu S \cdot cm^{-1}$ and 101 $\mu S \cdot cm^{-1}$, respectively) were considerably higher than those found in most regions of the northeast U.S.

Weathering of soils is often the primary source of Ca^{2+}, Mg^{2+}, and K^+ ions in many watersheds. In the northeast U.S., Ca^{2+} and Mg^{2+} have often been found to be the dominant cations (Brakke et al. 1988, Canavan and Siver 1994), especially in regions underlain with bedrock consisting of marble. For example, Mattson et al. (1992) reported mean Ca^{2+} concentrations of 1270 $\mu eq \cdot L^{-1}$ in lakes situated in the Stockbridge region of western Massachusetts, and Canavan and Siver (1994) found similar mean concentrations of 1140 $\mu eq \cdot L^{-1}$ in waterbodies located in the Marble Valley region of Connecticut. In contrast, the median concentration of Ca^{2+} in Cape Cod lakes was found to be only 67 $\mu eq \cdot L^{-1}$, similar to the 73 $\mu eq \cdot L^{-1}$ value reported by Mattson et al. (1992). The low mean Ca^{2+} concentrations reported for lakes on Cape Cod is less than half that observed in waterbodies from any other region examined in the northeast U.S. (Brakke et al. 1988, Canavan and Siver 1994, Mattson et al. 1992).

Magnesium concentrations in lakes in the northeast U.S. are often highly correlated with Ca^{2+} concentrations. For instance, studies by Charles (1985) and Canavan and Siver (1994) both reported r^2 values of 0.85 for Mg^{2+} and Ca^{2+} concentrations. In this study these cations were not correlated ($r^2 = 0.15$). Mean and median Mg^{2+} concentrations of lakes on Cape Cod were found to be greater than those in lakes in the Eastern Uplands of Connecticut (Canavan and Siver 1994) and the Berkshire and Central regions of Massachusetts (Mattson et al. 1992). Magnesium concentrations in lakes increased considerably with distance from the Cape Cod Canal, suggesting that sea spray could be a significant source of Mg^{2+}. This hypothesis is further supported by the fact that Mg^{2+} concentrations were highly correlated with Cl^- ($r^2 = 0.61$) and conductivity ($r^2 = 0.71$).

Evidence that sea spray is a significant source of Mg^{2+} is further strengthened by the Mg^{2+}:Ca^{2+} ratio. In 59 of the 60 lakes (with Schoolhouse Lake in Chatham being the exception), the Mg^{2+} levels exceeded the Ca^{2+} levels, a finding that supports the work of Mattson et al. (1992). Mattson et al. (1992) reported that Cape Cod was the only region in Massachusetts where average Mg^{2+} levels exceeded those of Ca^{2+}. Brakke et al. (1988) found that, on average, Ca^{2+} levels exceeded Mg^{2+} levels in all areas in the Northeast by more than 250%. Both increased Mg^{2+} from sea spray and atypically low Ca^{2+} levels most likely contributed to the high Mg^{2+}:Ca^{2+} of Cape Cod lakes. In the PCA analysis the pH, alkalinity, and Ca^{2+} vectors were virtually perpendicular to those for the Na^+, Cl^-, conductivity, and Mg^{2+} suggesting two sets of uncorrelated parameters. The lack of a relation between alkalinity and conductivity-related parameters in the PCA analysis is consistent with the hypothesis that the elevated Cl^-, Na^+, and Mg^{2+} levels are coming from sea spray, while alkalinity and Ca^{2+} are derived primarily from other sources, such as glacial till.

The SO_4^{2-} levels found in this study are consistent with findings reported by both Mattson et al. (1992) and Brakke et al. (1988). Median SO_4^{2-} levels were 115 $\mu eq \cdot L^{-1}$ in both our study and the study by Brakke et al. (1988) of lakes in the northeast U.S., and were similar to the 123 $\mu eq \cdot L^{-1}$ value reported by Mattson et al. (1992) for lakes in Massachusetts. The major source of sulfate to inland lakes is from atmospheric deposition, especially the burning of coal (Husar et al. 1991) and less so from volcanic activity (Cole 1994). While the sulfur deposition stemming from industrial and volcanic sources would most likely be fairly uniform throughout the Cape region, there was some variation in the SO_4^{2-} levels of the lakes sampled. The SO_4^{2-} levels ranged from 20 $\mu eq\, L^{-1}$ in Great Pond in Provincetown, to 198 $\mu eq \cdot L^{-1}$ in Ryder Pond in Wellfleet. Deviations in SO_4^{2-} concentrations among lakes could be the result of differences in evapoconcentration of the lakes (Mattson et al., 1992), varying amounts of SO_4^{2-} entering from sea spray which commonly has sulfate levels two orders of magnitude higher than fresh water, or differential use of sulfate within the lake basin. Interestingly, the lowest SO_4^{2-} concentrations were found in the Provincetown region where the effects of sea spray would be expected to be the greatest. Three of the four Provincetown ponds were just over one meter deep, and were anoxic at one meter, where the water samples were taken. In these three lakes, sulfate is likely being used as an alternate electron acceptor in the absence of oxygen. For this reason, the low sulfate levels in the Provincetown lakes most likely reflect microbial activity rather than low sulfur inputs into the lakes.

Trophic characteristics

As expected, the slow weathering of the sandy soils and the relatively low population densities resulted in lower total phosphorus levels than those typically found elsewhere in southern New England. The median total phosphorus level found in this study (10.2 $\mu g \cdot L^{-1}$) was lower than the median TP value reported by Brakke et al. (1988) in southern New England lakes (14.0 $\mu g \cdot L^{-1}$) and that reported by Canavan and Siver (1994) for lakes in Connecticut (27 $\mu g \cdot L^{-1}$). However, median TP concentrations were slightly greater in Cape Cod lakes than in the Adirondacks, central New England and Maine (Brakke et al. 1988). Based on data from six waterbodies Rohm et al. (1995) prepared frequency distributions of TP concentrations for lakes in the Cape Cod region. Rohm et al. (1995) estimated that more than 50% of the lakes and ponds had total phosphorus concentrations above 20 $\mu g \cdot L^{-1}$. Our results indicate that a larger proportion of the waterbodies on Cape Cod have lower TP concentrations than suggested by Rohm et al. (1995). Part of the difference may be due to the fact that the Cape Cod region as defined by Rohm et al. (1995) included lakes west of the Cape Cod canal on the mainland, whereas our survey included only lakes to the east of the canal.

Except for the lakes situated within the dune deposits in Provincetown, there was little difference in trophic characteristics among lakes in the other three regions examined. Generally the lowest TP, TN, and Chl-*a* concentrations and the highest Secchi disk depths were found in lakes in the Forearm region, although the differences between the Forearm, Elbow, and Bicep regions were slight (Table 3). The PCA scores for the trophic parameters showed that lakes in the Forearm region were generally the most oligotrophic, although there was a significant amount of overlap with waterbodies in the Bicep and Elbow regions. Lakes in the Provincetown region were clearly more eutrophic than lakes in other regions, a fact clearly supported by the PCA results.

Since phosphorus and nitrogen are usually the limiting nutrients in most inland lakes, the N:P ratio can indicate which of the two nutrients is more likely limiting growth in a given system. Studies by Sakamoto (1966) and Downing and McCauley (1992) suggested that nitrogen is likely to be the limiting nutrient in lakes where the N:P ratio is less than 10 and 14, respectively. In contrast, waterbodies with N:P ratios greater than 17 are indicative of P-limitation (Sakamoto 1966). Only 7% and 23% of the lakes on Cape Cod had ratios below 10 and 14, respectively, indicating that most waterbodies were probably not nitrogen limited. Sixty percent of the lakes did have N:P values above 17 indicating phosphorus limitation, with the majority of these lakes being in the Bicep and Elbow regions. The high N:P ratios, coupled with the overall low TP concentrations, support the hypothesis that phosphorus limits primary production in many lakes on Cape Cod.

With the exception of elevated ion levels from salt spray and the four eutrophic lakes in Provincetown, the lakes of Cape Cod are similar in many ways to lakes of the Adirondacks. Lakes in both regions are nutrient poor and predominantly oligotrophic in nature. Our study found Cape Cod lakes to have the same median Chl-a concentration (2.1 $\mu g \cdot L^{-1}$) as a study of 38 Adirondack lakes by Charles (1985). The study by Charles (1985) found median Secchi disk depth readings to be slightly greater in the Adirondacks compared to our study (5.2 meters and 4.4 meters, respectively), but both were considerably greater than median Secchi depth readings found elsewhere in the Northeast by Brakke et al. (1988). None of the regions in Cape Cod were similar in trophic status to any of the regions examined in Connecticut by Canavan and Siver (1994). In general, lakes on Cape Cod had lower concentrations of TP, TN, and Chl-a, deeper Secchi disk depths, and were more oligotrophic than those in Connecticut.

Conclusions

The lakes of Cape Cod are rather unique and different from lakes in other regions in the eastern U.S. They are very acidic, poorly buffered, oligotrophic, and have high sodium, chloride, and magnesium concentrations. Many of the lakes appear to be phosphorus limited. Median calcium levels, among the lowest in the northeast U.S., are highly correlated with alkalinity, suggesting that alternative alkalinity-generating processes, such as sulfate reduction and organic acids, are contributing very little to the overall alkalinity of lakes on Cape Cod.

The majority of acidic lakes are situated on the outer Cape. Lakes located on the outer Cape generally have lower TN and TP concentrations than lakes situated closer to the mainland. Mean conductivity, Mg^{2+}, Cl^-, and Na^+ levels are highest in the Forearm (outer Cape) region, and mean Ca^{2+} levels are highest closer to the mainland.

ACKNOWLEDGMENTS: We would like to thank Anne Lott, Larry Marsicano, Ethan Cash, as well as other student assistants for their help in the field and the laboratory over the last three years. Thanks also to Dr. Anne Giblin and the Ecosystems Center at the Marine Biological Laboratory, and to Mike Reynolds and John Portnoy of the Cape Cod National Seashore. This project was funded with grants from the National Science Foundation (grant #DEB-9615062), the National Institute of Water Resources, and a Mellon Fellowship from the Center for Conservation Biology and Environmental Studies at Connecticut College.

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