*Journal of Paleolimnology* **29:** 179–197, 2003.
© 2003 *Kluwer Academic Publishers. Printed in the Netherlands.*


# Estimating historical in-lake alkalinity generation from sulfate reduction and its relationship to lake chemistry as inferred from algal microfossils

Peter A. Siver[1,*], Richard Ricard[1], Richard Goodwin[1] and Anne E. Giblin[2]
*[1]Botany Department, Connecticut College, New London, CT 06320, USA; [2]Marine Biological Laboratory, The Ecosystem Center, Woods Hole, MA 02543, USA; *Author for correspondence (e-mail: pasiv@conncoll.edu)*

Received 1 September 2001; accepted in revised form 2 September 2002

*Key words:* Acid deposition, Alkalinity generation, Connecticut, Diatoms, Scaled chrysophytes, Southern New England, Sulfate reduction

## Abstract

Sediment cores were used to estimate in-lake alkalinity generation resulting from sulfate reduction relative to inferred changes in lakewater pH and trophic status over the last century in three Connecticut lakes. Despite being situated in geological settings with crystalline bedrock and thin, poorly buffered soils, and being impacted with high rates of acidic precipitation, none of the study lakes have declined in inferred pH based on scaled chrysophyte and diatom remains. In fact, the pH of one of the lakes, Coventry Lake, has significantly increased over the last century. Over the last ~44 to 69 years the amount of sulfur stored in the sediments from each lake increased from ~two to three times resulting in mean rates of alkalinity generation ranging from 78 to 145 meq $m^{-2}$ $yr^{-1}$, significantly higher than the 45 to 48 meq $m^{-2}$ $yr^{-1}$ of hydrogen ions falling directly on the lake surfaces. In-lake alkalinity generation resulting from sulfate reduction has been sufficient to neutralize all of the acid falling directly onto the lake surfaces, as well as between 9% and 25% of the acid deposited onto the surrounding watersheds. Despite the increased importance of in-lake alkalinity generation, our findings support the hypothesis that significant amounts of alkalinity are also being generated in the catchments of the study lakes. The bulk of the increases in stored sulfur in all three lakes were as Fe sulfides and not in the form of organic sulfur, suggesting that the increases were the result of dissimilatory bacterial reduction of sulfate. As a result of the large increases in storage of Fe sulfides the ratio of total iron to chromium reducible sulfur (Fe:CRS) has declined in all cores over time. Despite the overall decline in Fe:CRS in recent sediments, values are still largely above 3 in more recent sediments of two of the lakes. However, values of Fe:CRS have dropped below 1 in surface sediments of Uncas Lake, suggesting that in-lake loading of phosphorus may be responsible for a recent shift in the algal flora towards a slightly more eutrophic condition.

## Introduction

Many lakes and ponds in northeastern North America, especially ones situated in regions with poorly buffered soils, have significantly declined in pH and/or alkalinity over the last century or more, presumably due to acidic deposition (Charles 1991). Much of the evidence for lake acidification has come from paleolimnological investigations that utilized biological remains of organisms in dated sediment cores as inference tools (Birks et al. 1990). For example, paleolimnological studies have verified that groups of waterbodies in the Adirondacks (Cummings et al. 1992), northern New England (Davis et al. 1994), regions of Ontario (Dixit et al. 1992; Hall and Smol 1996) and Quebec (Dixit and Dixit 1989; Racca et al. 2001) have significantly declined in pH over the last ca. 50 to 150 years, most likely due to anthropogenic acid inputs. Evidence collaborating the paleolimnological findings that mark declines in lakewater pH is summarized by Charles (1991). An extensive collection of studies with similar findings, including

many from Europe, are summarized by Battarbee et al. (1999).

Despite the fact that lakes in many regions of the northeast have acidified over the last century, evidence of a similar trend for waterbodies in the State of Connecticut, situated in southern New England, is lacking (Marsicano and Siver 1993; Siver et al. 1999). In a study of 23 lakes in Connecticut utilizing the remains of scaled chrysophytes and diatoms to infer pH, Siver et al. (1999) found that none of the waterbodies had significantly declined in pH over the last century. In fact, Siver et al. (1999) reported that 20% of the lakes had actually significantly increased in pH over the time period examined. These findings were surprising since a significant number of the lakes were situated in the upland regions of the state that are composed largely of highly resistant, crystalline bedrock and thin, poorly buffered soils, and since this region of southern New England has received very acidic deposition with a mean loading rate of 45 meq $[H^+]$ $m^{-2}$ $yr^{-1}$ (Stensland et al. 1986). Siver et al. (1999) concluded that the Connecticut lakes were not acidifying because of alkalinity generation in the watersheds and/or within the lakes themselves.

A number of processes can yield in-lake generation of alkalinity and hence add buffering capacity to waterbodies (Schindler et al. 1986; Giblin et al. 1990). For example, the dissimilatory reduction of sulfate and nitrate in lake sediments can be important sources of alkalinity to overlying waters (Cook et al. 1986; Schindler et al. 1986; Giblin et al. 1990). Giblin et al. (1990) postulated that, since nitrate is largely retained in forested watersheds of New England, then on an historical basis, sulfate reduction has been the more important alkalinity generating process. In addition, historical rates of sulfate reduction can be estimated from sedimentary profiles, while other alkalinity generating reactions, such as dissimilarory nitrate reduction leave no record in the sediments.

Both assimilatory and dissimilatory sulfate reduction generate alkalinity (David and Mitchell 1985; Cook et al. 1986), but the controls are quite different. Assimilatory sulfate reduction is mediated by phytoplankton and bacteria. The net alkalinity gain to a water body is determined by the amount of organic sulfur permanently buried and would be expected to increase as bacterial and primary production increases. Dissimilatory sulfate reduction is carried out by sulfate-reducing bacteria primarily found in anaerobic hypolimnetic waters or sediments (Rudd et al. 1986; Urban 1994). For each sulfate molecule that is reduced two equivalents of alkalinity are produced:

$$2(CH_2O)+SO_4^{2-}\rightarrow 2HCO_3^- + H_2S \qquad (1)$$

The bicarbonate ions represent a permanent gain in alkalinity to the waterbody provided that the sulfide be retained and buried within the sediments, or is lost to the lake in reduced form (e.g., $H_2S$ or particulate form). Thus, when a mole of $H_2SO_4$ is delivered to and dissociates in a waterbody, it yields two equivalents of hydrogen ions and, if the mole of sulfate is reduced to sulfide, two equivalents of bicarbonate ions, resulting in no net change in alkalinity. If, however, the sulfide is oxidized either in the surface of the sediments or within the water column, it will (re)acidify the waterbody:

$$H_2S+2O_2\rightarrow SO_4^{2-}+2\,H^+ \qquad (2)$$

Reduced sulfur can be effectively buried in lake sediments in either inorganic or organic form (Dornblaster et al. 1994). Storage as reduced inorganic sulfur is primarily in the form of iron sulfides (e.g., FeS or $FeS_2$), and is usually the result of sulfate reduction within the sediments (Mitchell et al. 1988). Organic S in lake sediments can originate from allochthonous watershed sources, in-lake plant and bacterial production, or from the incorporation of sulfides from dissimilatory processes into organic compounds within the sediments (Giblin et al. 1990). The controls on the alkalinity gain due to dissimilatory sulfate reduction are still not well understood (see discussion by Giblin et al. (1991), Kling et al. (1991)), but the sulfate concentration in the water column, the oxygen content of bottom waters, and the degree of eutrophication of the water body are all believed to be important.

The amount of permanent alkalinity yielded in a given waterbody through sulfate reduction and subsequent burial of the sulfide in the sediment can be estimated through the analysis of the quantity of sulfide stored in sediment cores (Mitchell et al. 1988; Giblin et al. 1990). Changes in the bulk storage of total sulfur in lake sediments over a known period of time can be used to quantify both the importance of sulfate reduction as a source of alkalinity, and the degree to which this process has changed over time.

A consequence of an increase in the burial of sulfides with iron is a reduction in the pool of available iron oxides to precipitate phosphates from the water column and retain them in the sediment (Kilham 1982; Caraco et al. 1989; Murray 1994). If precipitation and storage as ferrous sulfide was a primary mechanism for the permanent burial of re-

duced sulfide in a lake, then the supply of iron to the lake from the watershed could become a limiting factor. Thus, an increase in the storage of ferrous sulfides in lake sediments relative to the supply of iron to the lake from the watershed could be coupled with an increase in the release of phosphorus from the sediments to the water column. The increased concentration of phosphorus could, in turn, fuel an increase in the primary productivity of the surface waters.

The main purpose of this study was to estimate historical in-lake alkalinity generation resulting from the reduction of sulfate in three Connecticut lakes relative to changes in lakewater pH and trophic status as inferred from algal remains over the last century. We were interested in estimating both the magnitude of this process and the degree to which it has changed over the last century. We were also interested in determining if burial rates appeared to be strongly controlled by trophic status. We used the sediment sulfur accumulation to estimate the quantities of net or permanent alkalinity generated from sulfate reduction relative to the amounts of hydrogen ions impinging the lake surfaces and their surrounding watersheds in order to estimate the amount of acidic deposition being neutralized by the in-lake reduction of sulfate. Lastly, we examined the amount of inorganic sulfur stored in the sediment cores relative to the supply of Fe in order to gain an understanding of the potential pools of Fe in the sediments of each lake available to bind phosphorus.

## Methods

Six cores, two from each study lake, were taken from the deep basins of the lakes with either a Glew gravity corer (Glew 1988) or a piston corer, and sectioned on site with an extruder (Glew 1989) into one-cm (top 30 cm of sediment) or two-cm sections (below 30 cm) (Table 1). The cores from each lake were taken from relatively broad and flat basins at approximately 150 m (Norwich), 200 m (Uncas) and 400 m (Coventry) apart from each other. Sediment was stored in preweighed whirl-pac bags and processed immediately upon return to the laboratory. After wet weight determinations were made, known aliquots from each section were removed, dried at 105°C to a constant weight and used to estimate total dry weight for each section. The dried sediment from each section was homogenized with a mortar and pestle and used for all chemical analyses. Aliquots of the remaining wet sediment were used to prepare samples for all scaled chrysophyte and diatom work. Several sediment sections near the 5 to 6 cm level from each of the two cores from Norwich Pond contained high concentrations of sand grains.

Two estimates of the hydrogen ion loads from precipitation onto the lake and watershed surfaces were used in the study. First, the estimate made by Stensland et al. (1986) for the northeast United States of 45 meq $H^+ m^{-2} yr^{-1}$ was used. Second, a continuous precipitation database assembled by Richard Goodwin between 1983 and 1998 at the Burham Brook Nature Preserve (East Hampton, CT), located only a few km from the Uncas and Norwich watersheds, was also used to estimate hydrogen ion loads. The Goodwin database consists of rainfall and pH estimates from 908 precipitation events. The pH data were converted to hydrogen ion concentrations, weighted by the amount of precipitation and used to estimate annual loads of $H^+$ for each of the 16 years. The pH data was not available for only a very few precipitation events over the 16 year period; in these

*Table 1.* Information concerning the six cores used in this study, including the type of core, year taken, whether it was used for CRS analysis, the point in the core above which the concentration of lead begins to significantly increase, and estimates of the rates of alkalinity generation due to sulfate reduction in recent vs. older (pre- 1900) sediments. Estimates of the portion of alkalinity generation due to sulfate reduction attributed to the CRS fraction are given in parenthesis. See text for details.

| Lake | Type of core | Year cored | CRS analysis? | Section where [lead] increases (cm) | Alkalinity generation ($meq\ m^{-2}\ yr^{-1}$) total (CRS only) | |
|---|---|---|---|---|---|---|
| | | | | | Recent | Pre-1900 |
| Uncas | Gravity | 1996 | No | 11–12 | 146 | 63 |
| Uncas | Gravity | 1998 | Yes | 12–13 | 144 (101) | 58 (18) |
| Norwich | Gravity | 1996 | No | 18–19 | 76 | 40 |
| Norwich | Piston | 1998 | Yes | 12–13 | 80 (56) | 44 (16) |
| Coventry | Gravity | 1991 | No | 17–18 | 110 | 51 |
| Coventry | Piston | 1998 | Yes | 17–18 | 106 (87) | 39 (15) |

few instances the weighted mean pH of all precipitation events for that given year were used in the calculations.

Procedures used for the preparation, identification and quantification of scaled chrysophytes and planktonic diatoms are outlined in Siver and Marsicano (scaled chrysophytes; 1996) and Siver (diatoms; 1999). The weighted averaging-based inference models outlined in Siver et al. (1999) were used to reconstruct pH and trophic score for one core from each lake. Trophic scores are based on a PCA using total phosphorus, total nitrogen, chlorophyll-α and Secchi disk depths as described by Field et al. (1996), except for being multiplied by 100. Scaled chrysophyte remains were used to make inferences for pH and trophic score at a minimum of ten sections for each core. Planktonic diatom remains from sediment representing the surface, 1970, 1934 and 1890 were also used to infer pH. Because inference models for total phosphorus based on planktonic diatoms were not statistically significant for these study lakes, this variable was not reconstructed.

Methods for measurement of sedimentary chemical components were essentially similar to those of Giblin et al. (1990). Total sulfur was measured using a LECO SC-32 sulfur analyzer. Inorganic reduced sulfur (which includes FeS, $FeS_2$ and elemental S and is referred to in this paper as the chromium reducible sulfur, or CRS, fraction) was analyzed using the chromium reduction method of Zhabina and Volkov (1978) as modified by Howarth and Merkel (1984). Although total S was measured on all cores, CRS was analyzed from only one core from each lake. Organic sulfur was calculated as the difference between total S and the CRS fraction. Total iron concentrations were measured using a hot concentrated $HNO_3$ and HCl digest. This extraction removes oxides, pyrite and metals bound by organic matter, but will not fully extract all Fe associated with clays (Fostner and Salomons 1980). Loosely bound lead from the atmosphere was extracted with cold 1.6 N nitric acid and analyzed with a Perkin Elmer 2380 flame atomic absorption spectrophotometer (Ng and Patterson 1982).

In each core analyzed in this study the concentrations of lead estimated from the Ng and Patterson (1982) method significantly increased in the upper portions of the cores, presumably commencing with contamination largely from the burning of gasoline with lead additives (Siver and Wozniak 2001). In a previous study Siver and Wozniak (2001) used cores that were dated with lead-210 to estimate the time period when the lead concentrations began to significantly increase in each of the three lakes included in this study (Table 1). The year estimates obtained by Siver and Wozniak (2001) representing the depths in the cores were the lead concentrations begin to rise were 1952 for Uncas, 1927 for Norwich and 1934 for Coventry. These dates were used to estimate the age of the depth in each core where the lead concentration began to sharply increase.

Estimates of net in-lake alkalinity generation resulting from sulfate reduction on a per unit area and per year basis were made in a similar fashion as outlined in Giblin et al. (1990). Essentially, the total amount of sulfur stored in the sediment layers above the point in the core where the total lead concentration began to increase were summed and divided by the surface area of the core tube and the number of years represented by that section of the core (Table 1). Our estimates are based on the following assumptions. First, the estimates represent net in-lake alkalinity generated only from sulfate reduction and not from other processes such as nitrate, iron or manganese reduction. Second, we assumed that the sulfur in each core, both inorganic and organic fractions, was reduced within the lake and not in the watershed and subsequently transported to the deep basin. Third, we assumed that two equivalents of alkalinity were generated for each equivalent of sulfur stored in the sediments. Thus, we assumed that all organic sulfur was carbon-bonded. Fourth, our estimates do not include any loss of reduced sulfur from the lake as particulate matter or inorganic reduced sulfur. Fifth, we base our estimates for each lake basin on data collected from two cores taken from widely separated sections of the deep basins. Thus, our estimates assume that sulfate reduction and storage, as measured in the deep portions of the lake, are similar across the basin. Consequences of each assumption are discussed below.

Concentrations of alkalinity at 1 m, 5 m (the metalimnion) and 9 m (the hypolimnion) in each study lake were tracked weekly from June, 1999 through early September, 1999. Duplicate samples were taken at each depth with a horizontal van Dorn bottle and the alkalinity estimated using the Gran titration method (Wetzel and Likens 1991).

## Study lakes

Two of the study lakes, Uncas Pond (41° 22′36″N; 72°18′36″W) and Norwich Pond (41° 23′14″N;

72°18′07″W), are located in the Nehantic State Forest situated on the coastal slope of the Eastern Uplands geologic zone in Connecticut (Canavan and Siver 1995). Coventry Lake (41° 46′20″N; 72°19′36″W), also known as Wamgumbaug Lake, is located more inland, in the Town of Coventry, in the Eastern Uplands (Canavan and Siver 1995). The Eastern Uplands region of Connecticut consists of rolling hills and is composed largely of schists, gneiss, some granites and other relatively resistant rocks (Bell 1985). All three waterbodies are drainage lakes, have a similar maximum depth of ca. 12 m, and have mean depths of 6.7 (Uncas), 6.9 (Norwich) and 8.8 m (Coventry). The ratio of watershed:lake surface area is 12.1 and 11.5 for Uncas and Norwich Ponds, resulting in water retention times of 274 days and 329 days, respectively. The watershed:lake surface area is only 5.6 for Coventry Lake resulting in a water retention time of 986 days. The maximum depth of each lake extends over a relatively large portion of the bottom, yielding flat basins.

Over 98% of the watersheds of both Uncas and Norwich ponds are composed of forests and wetlands and have been since at least 1934 (Figure 3) (Field et al. 1996). In contrast, the watershed of Coventry Lake is currently 33% residential lands, 7% open fields and/or agricultural land, and the remainder forests or water features. In 1934 only 4% of the Coventry watershed was residential (Figure 3), but 24% was in agriculture. The majority of the construction of cottages and homes in the Coventry Lake watershed took place between 1934 and 1970 (Field et al. 1996).

Over the last decade alkalinity concentrations in Uncas and Norwich ponds ranged between 90 and 140 $\mu$eq $L^{-1}$, and both lakes had epilimnetic pH values mostly between 6.5 and 7 (Canavan and Siver 1995). Alkalinity and pH estimates in the more developed Coventry Lake have ranged between 320 and 410 $\mu$eq $L^{-1}$ and 7.0 and 7.6, respectively. Alkalinity concentrations in the surface waters of all three lakes were slightly lower during the current study period (see below). Both Uncas and Norwich ponds have low specific conductance values ranging mostly between 30 $\mu$S and 40 $\mu$S. The mean specific conductance of Coventry is 108 $\mu$S, considerably higher than the mean of 63 $\mu$S for waterbodies in the Eastern Uplands (Canavan and Siver 1995). Sulfate concentrations of Uncas and Norwich are very similar, 65–70 $\mu$M, while Conventry has a somewhat higher sulfate concentration of 100 $\mu$M. Uncas and Norwich ponds are best classified as oligotrophic to mesotrophic, and Coventry as mesotrophic to eutrophic. However, due to their morphometry all there ponds are anoxic by mid-summer. Norwich and Conventry are anoxic by mid June, while anoxia in Uncas is delayed until early July. Further information on lake water chemistry or the watersheds is given by Canavan and Siver (1995), Frink and Norvell (1984), respectively. Further information on each lake can also be obtained at http://silicasecchidisk.conncoll.edu.

## Results. Estimates of $H^+$ loads based on a 16-year precipitation database

The Goodwin database consisted of 908 precipitation events covering the 16-year period from 1983 through 1998. The annual total amount of precipitation ranged from 76 cm in 1983 to 147 cm in 1998 with a 16-year mean of 112 cm. Even though the amount of precipitation per event ranged widely from 0.05 cm to 21.6 cm, 60% of the events deposited less than 3 cm (Figure 1A). Approximately 70% of the precipitation events over the 16-year period had a pH between 4.0 and 5.0, with a range from a low of 3.25 (April, 1984) to a high of 7.2 (July, 1991) (Figure 1B).

The yearly loading rates of $H^+$ ions were calculated by summing the numbers of $H^+$ ions in all precipitation events in a given year. Loading rates ranged from 21.5 meq $m^{-2}$ $yr^{-1}$ in 1995 to a high of 125.6 meq $m^{-2}$ $yr^{-1}$ in 1984 (Figure 1C), with a 16-year mean of 48 meq $m^{-2}$ $yr^{-1}$.

## pH reconstructions

The inferred pH values for Uncas and Norwich ponds have remained relatively constant over the last 100 years fluctuating around pH 7 (Figure 2). Based on scaled chrysophyte remains the inferred pH has ranged from 6.8 to 7.2 over the last century in both of these waterbodies and was virtually the same in 1890 as it was in 1996. Scaled chrysophyte reconstructions did indicate a slight, but not significant, decline in the inferred pH of Norwich Pond since 1970. Except for a slightly higher inferred pH value of 7.4 at the surface of Norwich Pond, reconstructions based on diatom remains are in agreement with those based on scaled chrysophytes. In neither lake was a significant decline in pH noted.

In Coventry Lake inferred pH values based on both scaled chrysophytes and diatoms ranged from 7.0 to 7.5 over the time period represented in the core (Figure 2). The inferred pH has, in fact, increased

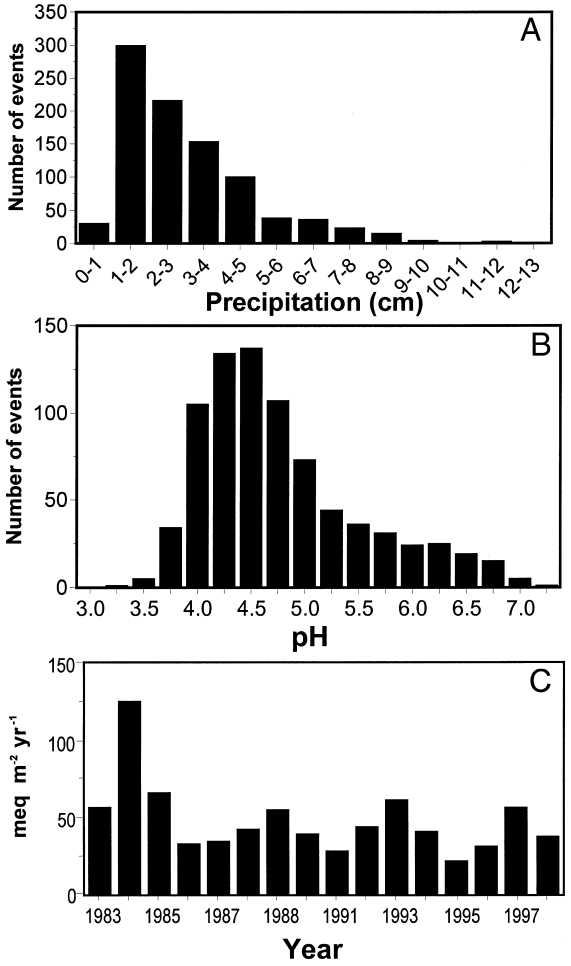


*Figure 1.* Results from the 16-year Goodwin precipitation data base. A) The distribution of precipitation events vs. the amount of precipitation. B) The distribution of precipitation events vs. pH. C) Estimates of the annual loading of $H^+$ from precipitation between 1983 and 1998.

steadily since just prior to the 1934 period to the present day, and the values in the recent sediment layers are significantly higher than those prior to the 1934 period. In all three lakes inferred pH values made from surface sediments are similar to mean pH values measured in the water column.

## Inferred trophic conditions

The inferred trophic scores have not significantly changed in either Uncas or Norwich ponds over the last century (Figure 3). In both of these lakes the inferred trophic scores are indicative of waterbodies in an oligotrophic to early mesotrophic condition. Qualitative changes in the planktonic diatom community in the recent sediment layers of Uncas Pond indicate a trend towards an increase in trophic status. The trophic score significantly increased in Coventry lake at about the 20 cm interval (Figure 3). Trophic scores shifted from −60 in 1890, to 6 in 1934, to 41 in surface sediments, representing a change from an oligotrophic to a late mesotrophic condition.

## Total lead concentrations

The total lead concentrations in the bottom sections of all six cores were relatively constant and mostly contained concentrations of lead near or below 50 μg $g^{-1}$ (Figure 4–6). In all of the cores the concentrations of lead began to increase at more or less well defined points and reached concentrations between 200 μg $g^{-1}$ and 350 μg $g^{-1}$. Using the method outlined in Siver and Wozniak (2001), the point in the core where the lead concentrations began to increase ranged between 12 cm (Uncas core taken in 1996) and 19 cm (Norwich core taken in 1996) (Table 1). Although less evident in the cores from Coventry Lake, lead concentrations have declined in the most recent sediments of all three lakes.

## Total sulfur profiles and estimates of alkalinity generation

In all six sediment cores the concentrations of total sulfur significantly increased, often more than doubling, in recent sediments (Figure 4–6). In the Uncas and Norwich cores, the bottom sections had relatively constant concentrations of total sulfur between 0.1 and 0.25 mM S $g^{-1}$ and increased to maximum concentrations of between approximately 0.4 mM S $g^{-1}$ and 1.0 mM S $g^{-1}$ (Figure 4–6). In both cores from Coventry Lake, sulfur concentrations in the lower sections of cores were mostly below 0.1 mM S $g^{-1}$ and gradually increased to peaks near 0.2 mM S $g^{-1}$ in the upper sections (Figure 6). In all Uncas and Norwich cores the increases in total sulfur commenced at about the same time period that the total lead concentrations began to increase (Figure 4–6). In both Coventry Lake cores, the total sulfur concentrations clearly began to increase prior to the increase in total lead concentration. The effects of the layer of sand grains on the concentrations of both total sulfur

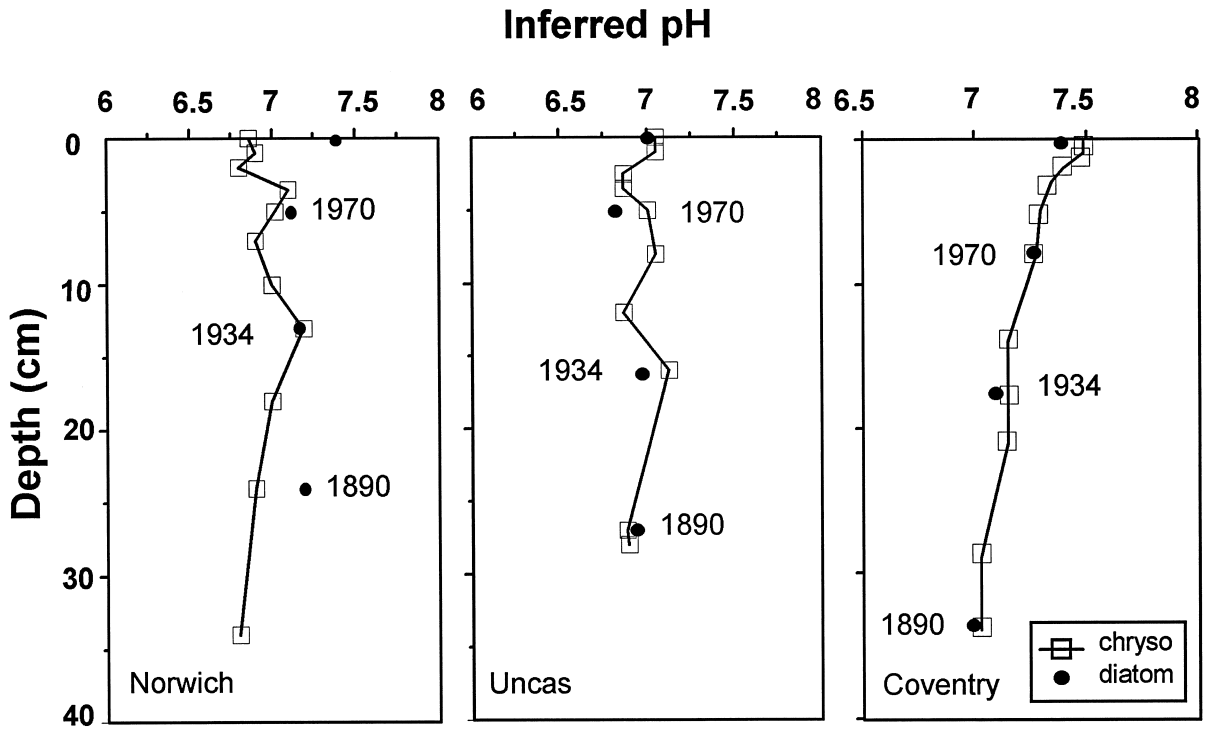


*Figure 2.* Inferred pH values for the three study lakes based on scaled chrysophyte and diatom remains.

and total lead were observed in the Norwich cores (Figure 5).

The total sulfur pools stored in the sediments above the layer determined from the total lead concentrations (marked with a dashed line on Figure 4–6) were estimated for each core and converted to rates of net alkalinity generation. The estimates ranged from a mean of 78 meq $m^{-2}$ $yr^{-1}$ in Norwich, to 108 meq $m^{-2}$ $yr^{-1}$ in Coventry to 145 meq $m^{-2}$ $yr^{-1}$ in Uncas. Estimates of alkalinity generation were similar for both cores from each lake, and no difference was observed between coring methods (e.g., gravity vs. piston cores).

We also calculated the alkalinity generation for the deeper parts of the cores, pre-1900, again using rates of total S burial and assuming a constant sedimentation rate. Rates calculated for pre-1900 sediments were considerably lower than those calculated for rates over the last 50–75 years (Table 1). pre-1900 rates of alkalinity generation were 2.3 fold lower than recent rates in Uncas and in Conventry. Norwich showed a slightly smaller difference with pre-1900 rates about 1.8 fold lower than contemporary rates.

**CRS, organic S and Fe concentrations**

In cores from all three lakes, the concentrations of CRS (i.e., inorganic sulfur component) significantly increased in recent sediments (Figure 7). Below the point in the cores where the lead concentration began to significantly increase, the CRS fraction accounted for a mean of 41%, 46% and 56% of the total sulfur pool in Uncas, Norwich and Coventry, respectively (Figure 7). Above this point the CRS fraction accounted for a mean of 72%, 76% and 82% of the total sulfur in Uncas, Norwich and Coventry, respectively. The large increases in the CRS fraction in recent sediments accounted for the majority of the increase in sulfur storage observed in each lake. In contrast, the organic-S fraction has declined in importance and now accounts for under 30% of the total sulfur pool in sediments representing the last ~50 to 75 years.

Total iron concentrations have increased in the recent sediments of all three lakes (Figure 7). In general, concentrations ranged from between 0.2 mM $g^{-1}$ and 0.4 mM $g^{-1}$ in older sediments and have increased to between 0.6 mM $g^{-1}$ and 0.8 mM $g^{-1}$ in

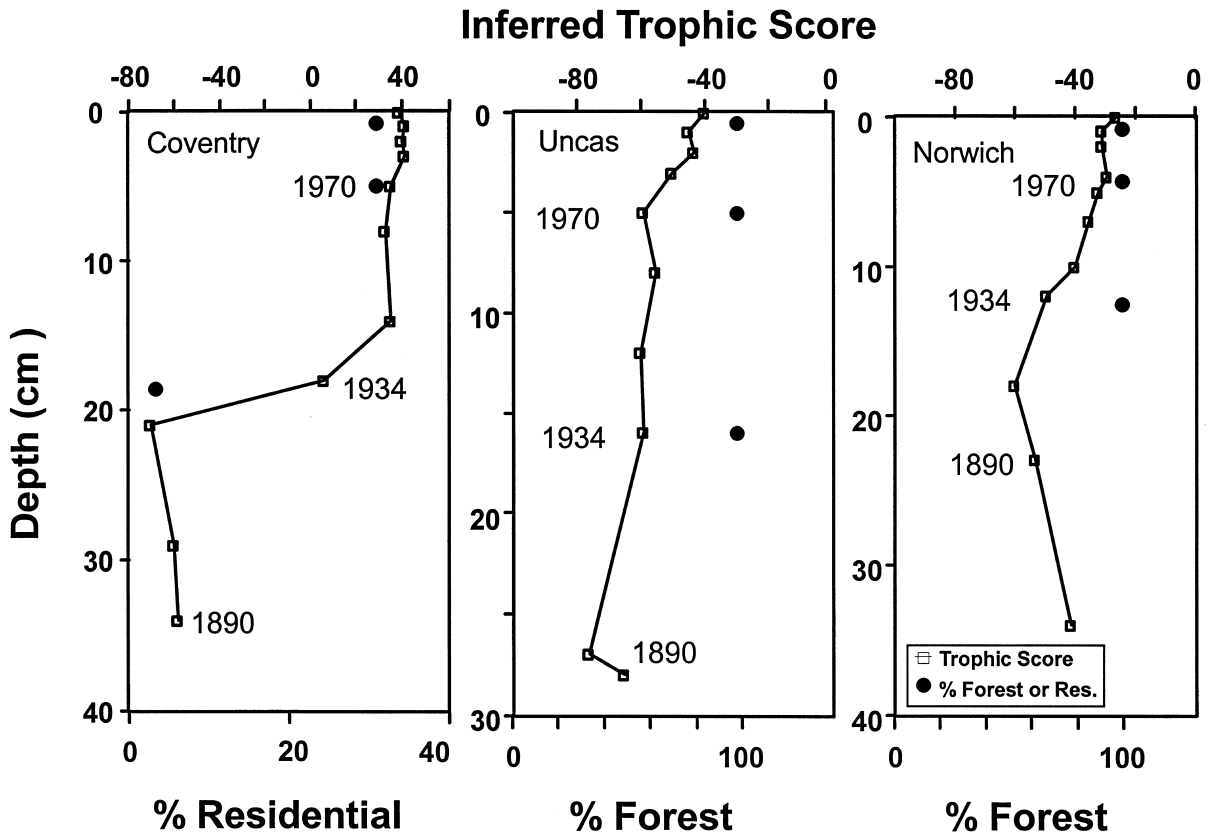


*Figure 3.* Inferred trophic scores based on scaled chrysophyte remains and changes in % cover as forests or residential land in the surrounding watersheds of the three study lakes.

more recent sediments. Despite the increase in total iron, the ratio of total iron to CRS (Fe:CRS) has declined in all cores over time (Figure 7). In Norwich and Coventry the Fe:CRS ratio ranged from 3.5 to 6.5 in older sediments, and has declined only slightly in more recent sediments. The Fe:CRS is more variable within the upper layers of Norwich containing sand grains. The Fe:CRS was lower in Uncas, ranging from between 2.1 and 3.3 in older sediments to values between 0.5 and 1 in the top ten cm of sediment (Figure 7).

### In-lake alkalinity generation

Alkalinity was measured at 1 m, 5 m and 9 m in each of the lakes over the 1999 summer thermal stratification period in order to estimate the amount of alkalinity generation (Figure 8). The 9 m depth was approximately 1 m to 2 m above the surface sediments. The 5 m depth was within the metalimnion of each lake. Thermal stratification had already begun in each lake at the start of sampling in early June and reached maximum development by late July/early August. By late August/early September thermal stratification was beginning to break down and the lakes were loosing heat. Dissolved oxygen concentrations were already below 1 ppm at 9 m in both Norwich and Coventry at the beginning of June and remained below this level thoughout the sampling period. In Uncas the dissolved oxygen concentrations did not fall below 1 ppm until early July, then remainded below this level for the rest of the sampling period.

In all three lakes the alkalinity concentrations at 1 m and 5 m were similar throughout the summer, and concentrations at both depths slowly increased over time (Figure 8). In Uncas and Norwich alkalinity in surface waters increased from about 70 meq $L^{-1}$ in June to 100 meq $L^{-1}$ in late August. In Coventry the alkalinity concentration in surface waters slowly increased from 230 meq $L^{-1}$ to 300 meq $L^{-1}$ over the three month period. Alkalinity levels were consistent-

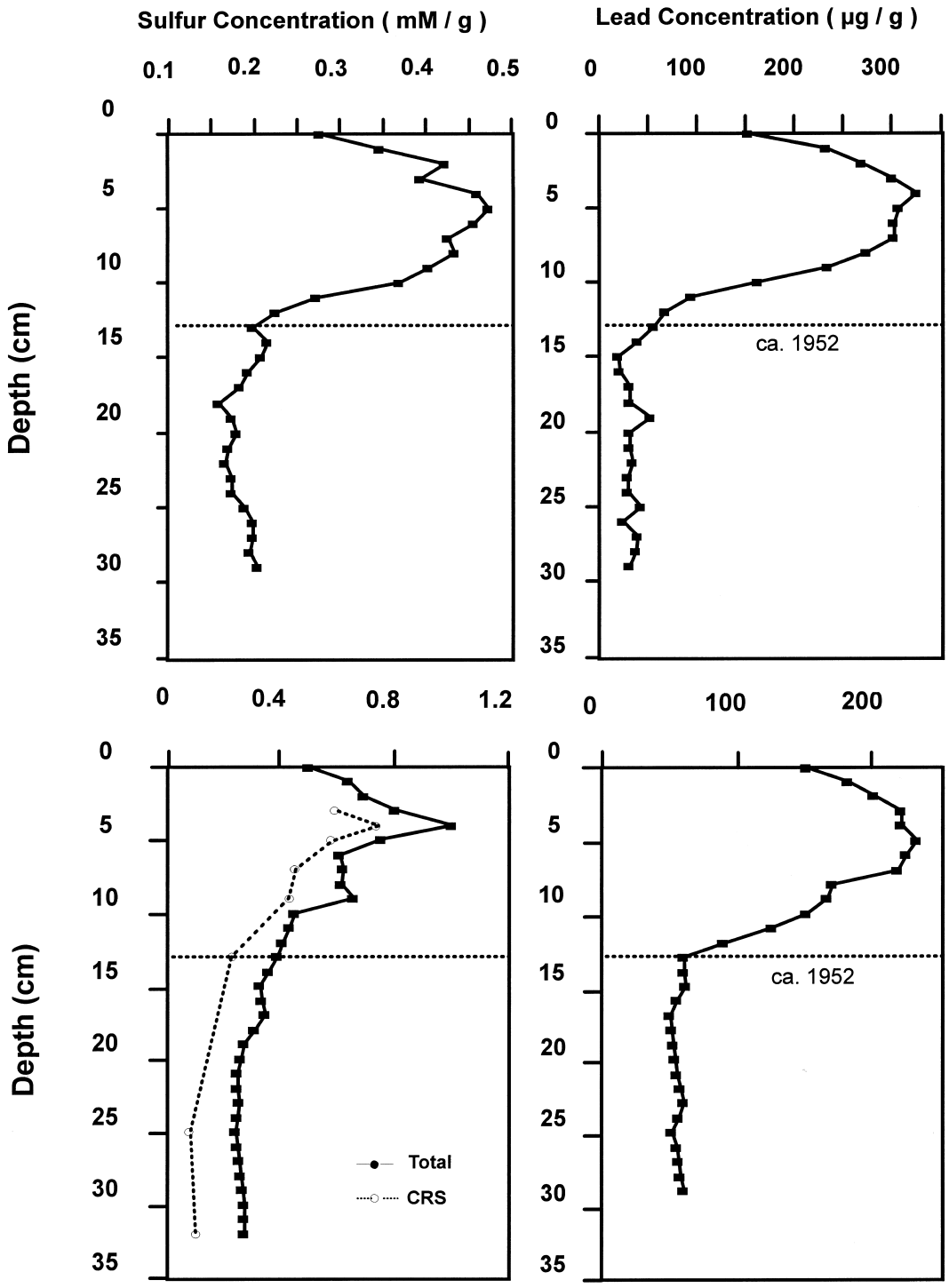


*Figure 4.* Total sulfur, CRS-sulfur and lead concentrations vs. core depth for two gravity cores taken from Uncas Pond. The age of the cores represented by the dashed lines was estimated by the method of Siver and Wozniak (2001).

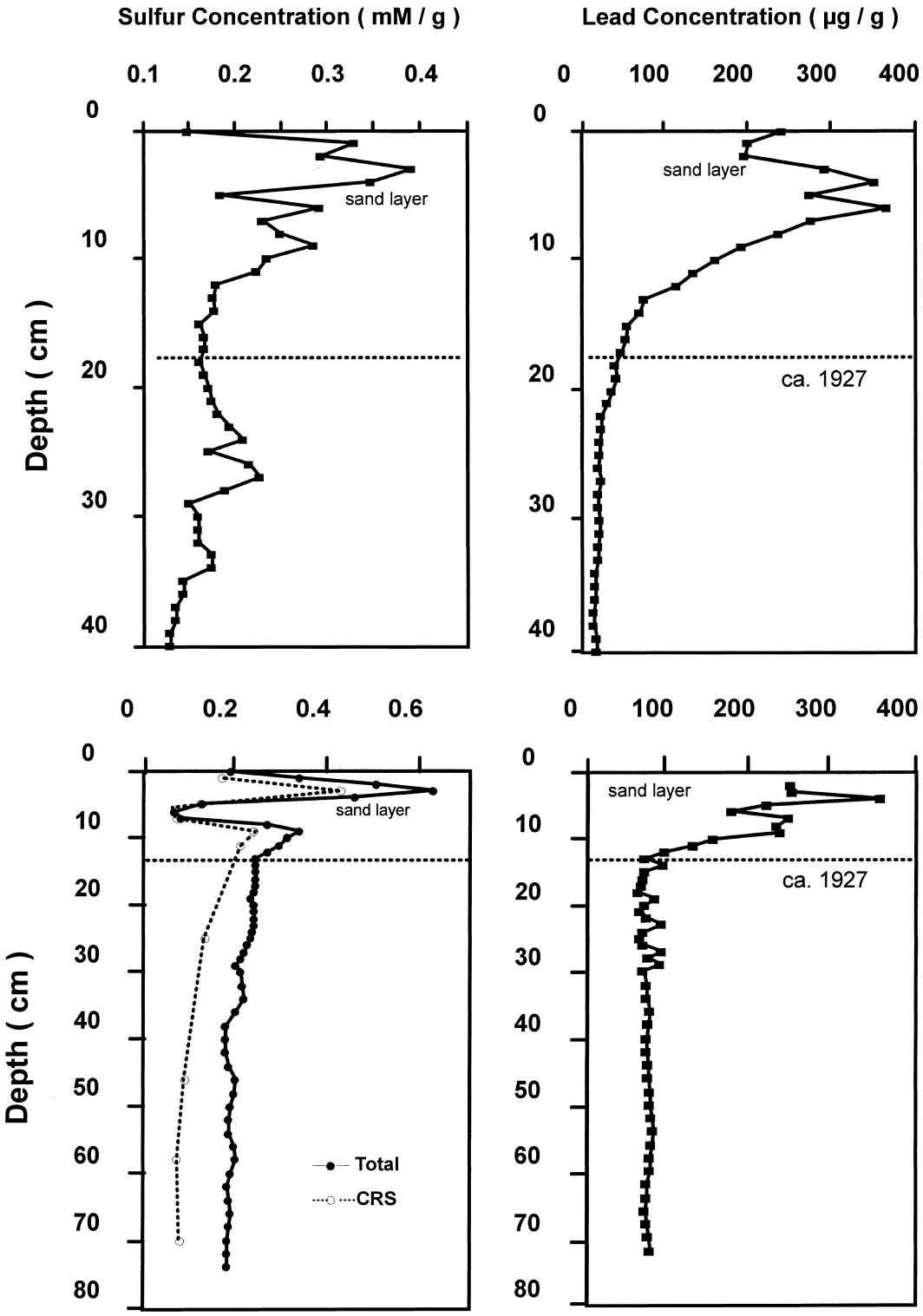


*Figure 5.* Total sulfur, CRS-sulfur and lead concentrations vs. core depth for a gravity core (top panels) and a piston core (bottom panels) from Norwich Pond. The age of the cores represented by the dashed lines was estimated by the method of Siver and Wozniak (2001). The position of a sand layer in each core is noted.

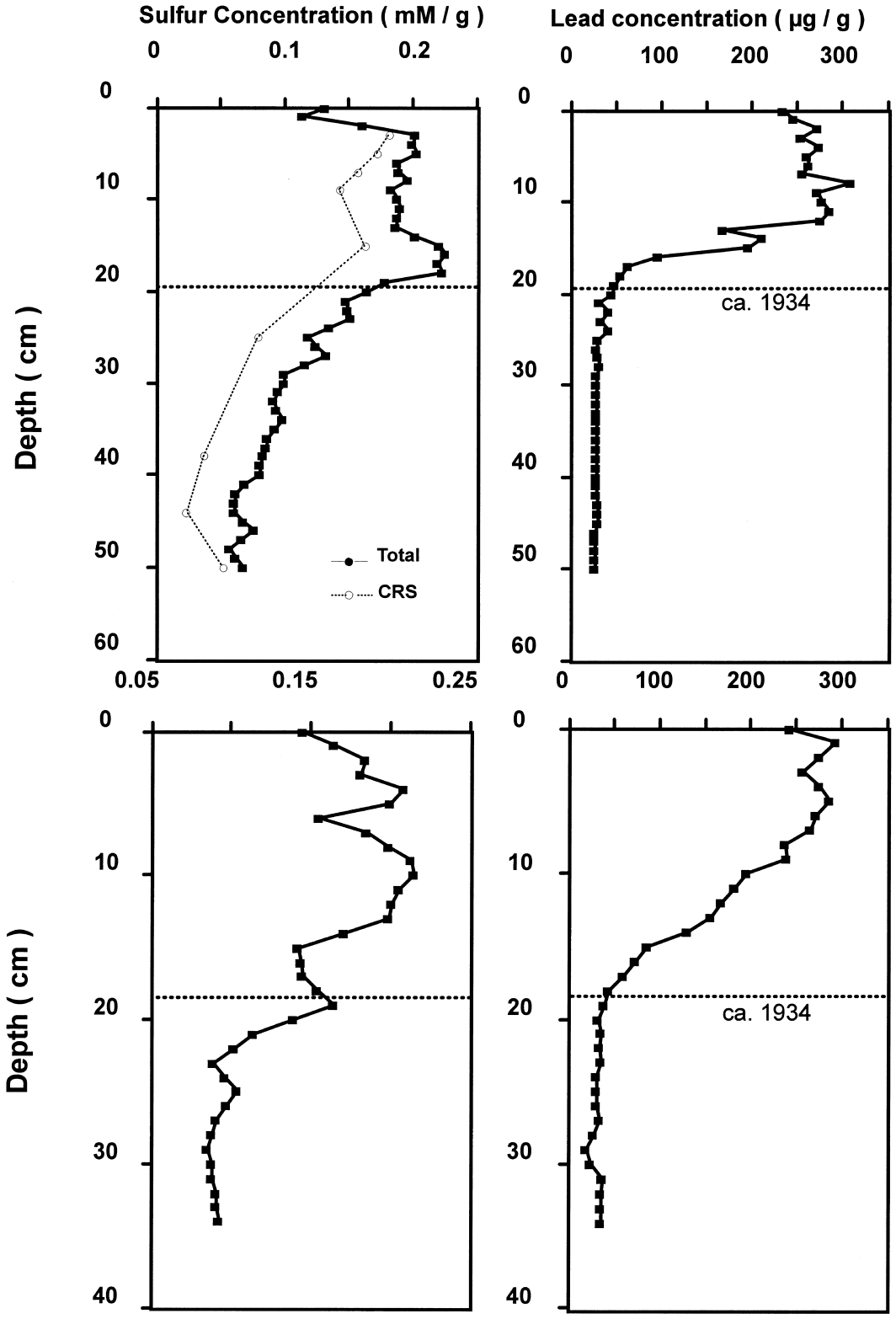


*Figure 6.* Total sulfur, CRS-sulfur and lead concentrations vs. core depth for a piston core (top panels) and a gravity core (bottom panels) from Coventry Lake. The age of the cores represented by the dashed lines was estimated by the method of Siver and Wozniak (2001).

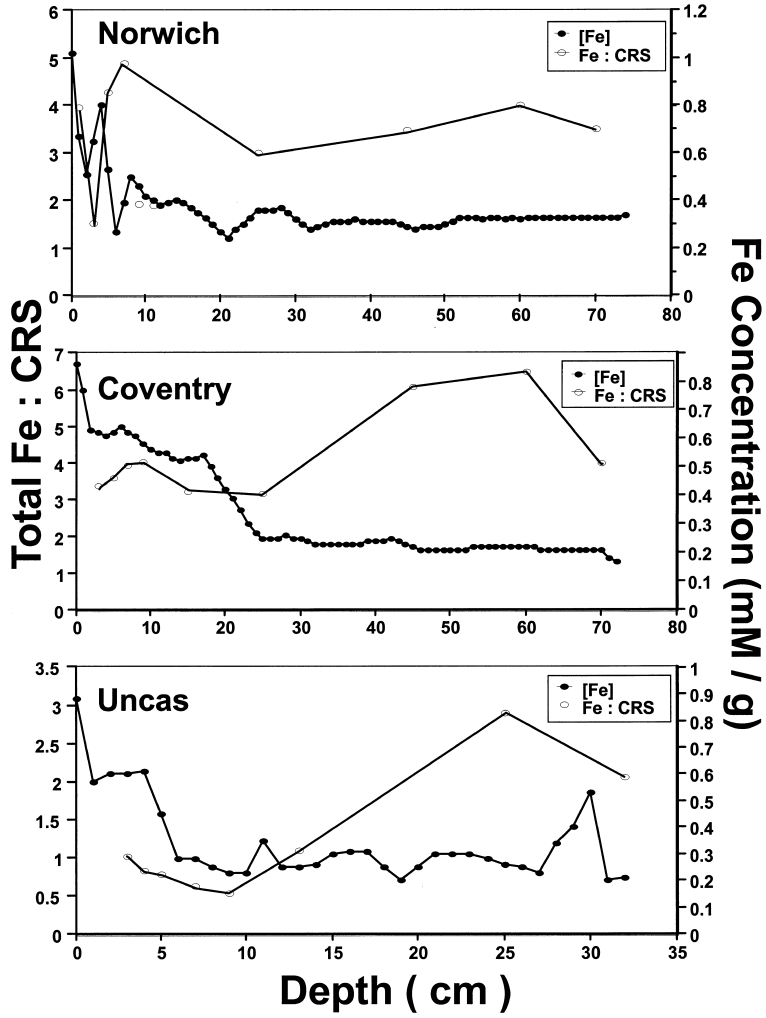


*Figure 7.* The concentration of iron and the total Fe: CRS molar ratio vs. core depth.

ly higher at 9 m than in surface waters and increased significantly over the summer period (Figure 8). In both Norwich and Uncas the increase in alkalinity at 9 m began primarily after mid July, while in Coventry concentrations remained relatively constant until early August. Maximum alkalinity levels of 212, 425, and 694 meq $L^{-1}$ were measured at 9 m in Uncas, Norwich and Coventry, respectively (Figure 8).

## Discussion

There is no question that significant levels of acids have been deposited in the northeastern U.S. over at least the last half century (Husar et al. 1991), and that these acids have contributed to declines in pH and buffering capacities of many aquatic systems (e.g., Charles (1991)). Stensland et al. (1986) reported mean acid deposition rates of 45 meq $m^{-2}$ $yr^{-1}$ for the northeastern US. Based on our 16-year precipitation database, the mean rate of acidic deposition from precipitation in the vicinity of our study lakes was estimated at 48 meq $m^{-2}$ $yr^{-1}$, virtually identical to that reported by Stensland et al. (1986). Despite these high acid deposition rates, and the fact that many Connecticut lakes are situated in watersheds with crystaline bedrock and thin poorly buffered soils, no lakes in the state have been documented to have significantly declined in pH (Marsicano and Siver 1993; Siver et al. 1999). No significant declines in pH were detected in the three lakes included in this study over the last century based on either scaled

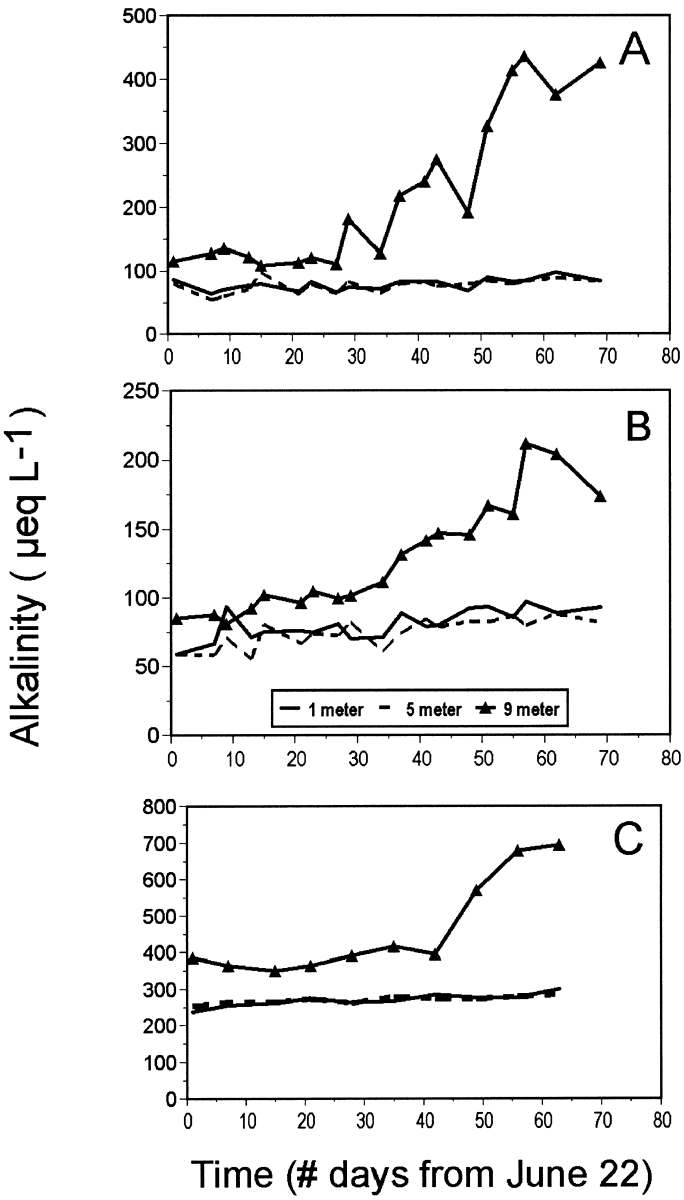


*Figure 8.* Change in alkalinity concentrations at 1 m, 5 m and 9 m depths in Norwich (A), Uncas (B) and Coventry (C) over the summer of 1999. Time is in days from June 22.

chrysophyte or diatom remains. In fact, the pH of Coventry Lake significantly increased during the last century. The pH values inferred from siliceous algal remains for all three lakes, especially Norwich and Coventry, are in good agreement with historical alkalinity data presented by Siver et. al. (1996).

Permanent in-lake generation of alkalinity by reduction of sulfate to sulfide and subsequent removal of the sulfide from the water column through burial in the sediments, loss as $H_2S$ gas, or loss as particulate matter in the outflow, is well documented (Schindler 1986; Schindler et al. 1986; Giblin et al. 1990; Urban 1994). In an earlier work, Siver et al. (1999) suggested that one possible reason why Connecticut lakes had not declined in pH was due to an increase in in-lake alkalinity generation. A primary objective of our current study was to estimate the degree to which sulfate reduction had contributed to in-lake alkalinity generation in our study lakes over the last century. We made these estimates by integrating the concentra-

tions of total sulfur stored in the sediments from each lake over known time periods, a method that has been commonly used in previous works (e.g., Mitchell et al. (1988), Norton et al. (1988), Giblin et al. (1990)). Based on this analysis, mean estimates of in-lake alkalinity generation over the last ~44 to 69 years ranged from 78 to 145 meq $m^{-2}$ $yr^{-1}$ in our lakes, representing rates that are about 2 to 3 times higher than the rate of delivery of hydrogen ions to the lake surfaces as estimated from acid deposition by Stensland et al. (1986) or the Goodwin database. Based on these estimates, and assuming that alkalinity generation estimated from the locations in the basins represented by the cores is similar for the entire lake basin, net in-lake alkalinity generation has been sufficient to neutralize all of the acid falling directly onto the lake surfaces, as well as 16% (Uncas), 9% (Norwich), and 25% (Coventry) of the acid deposited onto the surrounding watersheds.

Our estimates of the contributions of in-lake alkalinity generation to the overall buffering capacities of our study lakes are limited by the assumptions used to make the calculations. Our assumption that all of the sulfur contained in the lake sediments was derived from in-lake processes represents an upper limit to our estimations. There are three major routes by which sulfur becomes part of the total sulfur record (Rudd et al. 1986; Norton et al. 1988; Rudd et al. 1990; Giblin et al. 1990). First, algae and bacteria within the water column can reduce sulfate and assimilate it into organic matter, which can subsequently sink out of the water column and become buried in the sediment. Second, bacterial-based dissimilatory processes can yield sulfide that becomes coupled with either inorganic molecules (e.g., iron) or organic matter in the sediments. Third, allochthonous organic sulfur can be delivered to lake sediments from the watershed. The greater the extent to which sulfur in the lake sediments was derived from allochthonous sources, the more our calculations of in-lake alkalinity represent overestimates. However, because the bulk of the increase in sulfur storage in each core was in inorganic form and not organic sulfur, we believe the increases observed over the last half of the 20th century are largely the result of in-lake processes.

We also made the assumption that each mole of sulfur stored in the sediments represented production of two moles of alkalinity (Norton et al. 1988; Giblin et al. 1990; Urban 1994). This assumption is true for dissimilatory processes where sulfide generation is coupled with formation of inorganic compounds (e.g., iron sulfides), and for both assimilatory and dissimilatory processes where sulfide becomes bonded to carbon (Rudd et al. 1986). However, sulfur that is coupled to organic matter through sulfate ester bonds yields only one equivalent of alkalinity per mole of sulfur (Rudd et al. 1986; Owen and Mitchell 1988). Thus, our calculations would be over estimates by the proportion of the total sulfur pool accounted for by sulfur esters. However, sulfur esters are quite labile and not believed to be an important mechanism for long-term storage of sulfur in lake sediments (Rudd et al. 1986; Cook et al. 1986).

Our calculations of alkalinity generation were derived from sediment cores taken from deep, thermally stratified, and anaerobic sections of the study lakes. An obvious question is whether results based on several cores from the deep basin of a lake are representative of the whole lake? In all likelihood alkalinity generation and subsequent storage of sulfur in aerobic sediments is probably less than in anaerobic sediments (Giblin et al. (1990), Urban (1994) and references therein), which would result in an overestimate on our part if the results were extrapolated to the entire lake basin. However, because the basins of our study lakes are broadly shaped (Frink and Norvell 1984) and since the anaerobic hypolimnetic waters (oxygen concentrations below 1ppm) extend to cover between 48% and 66% of the bottom (Canavan and Siver 1995), we do not believe our calculations of alkalinity generation greatly overestimate those for portion of the lake overlain by hypolimnetic water. If we assume that epilimnetic sediments yielded no alkalinity and removed them from the calculations, in-lake alkalinity generation in hypolimnetic sediments has still been sufficient to neutralize acids that have been deposited directly onto the lake surfaces.

The date at which lead concentrations were found by Siver and Wozniak (2001) to have begun to increase in Uncas Pond was 1952, approximately 20 years later than other waterbodies in the region. As discussed by Siver and Wozniak (2001) it is unclear whether this 20 year difference is real or an error in the lead-210 dating of the Uncas core. If indeed the points in the Uncas cores where lead significantly increased were estimated to be 20 years earlier (e.g., 1932 instead of 1952), then our mean estimate of alkalinity generation in this lake would be 103 meq $m^{-2}$ $yr^{-1}$ which is more in line with estimates for Norwich and Coventry.

In several respects our calculations most likely underestimate the total amount of in-lake alkalinity

generation. First, our estimates do not include loss of sulfide as $H_2S$ gas. Although the rate of loss of $H_2S$ in our lakes is unknown, Rudd et al. (1990) reported this mechanism to be of minor importance. Second, our estimates do not include loss of sulfide in particulate form (e.g., algal biomass) through the outflow (Giblin et al. 1990). Third, our calculations are based solely on sulfur reduction and do not account for alkalinity generation through other processes such as denitrification or dissilimilatory nitrate reduction and reduction of other metals, such as manganese and iron, in surface sediments (Rudd et al. 1990; Urban 1994). If we assume the mean rates of alkalinity production from sulfate reduction estimated in our study were for 1999 and compare this estimate to the net increase in alkalinity actually measured in the hypolimnia of the study lakes at the end of summer thermal stratification, sulfate reduction accounted for nearly all in-lake alkalinity in Uncas and ~70% in both Norwich and Coventry.

Our data supports the fact that in-lake alkalinity generation from sulfate reduction is of importance in our study lakes, that it has significantly increased over the last ~44 to 69 years and that this process generates alkalinity ranging between ~1.5 and 3 times the level of hydrogen ions estimated to impact the lakes directly from precipitation. Based on these estimates, a significant amount of the acidic deposition impacting the watersheds of lakes in our region with small watershed:lake surface area ratios (WA:SA) could also be neutralized. However, as the WA:SA ratio increases, the percentage of the acidic deposition impacting the watershed capable of being neutralized by in-lake alkalinity formation declines. Other sources of alkalinity, presumably generated from watershed-based processes, would additionally be needed to prevent lakes in our region with large WA:SA ratios from acidifying.

Canavan and Siver (1995) provided surface water alkalinity measurements for each of the study lakes that were made over a period of three to five years in the 1990's. If we assume that the alkalinity generated from sulfate reduction was evenly distributed throughout the water column, and adjust the values for water retention time, it accounts for 9%, 11% and 14% of the alkalinity measured by Canavan and Siver (1995) for the surface waters of Norwich, Coventry and Uncas, respectively. Thus, although the rates of in-lake alkalinity production are high in our study lakes compared to many regions examined in North America (Baker et al. 1991), these data also support the hypothesis that significant amounts of alkalinity are being generated in the catchments of our study lakes.

Siver et al. (1999) further suggested that shifts in land use in surrounding watersheds, especially from forests to residential lands, would yield new sources of alkalinity to the lakes and that such a change in land use was at least partially responsible for the lack of a decline in pH in Connecticut lakes. Conversion of forests to residential lands may indeed be responsible for the increase in pH observed in Coventry Lake. In fact, Field et al. (1996) reported that 33% of the Coventry Lake watershed is residential land and that most of the building occurred between ca.1934 and 1970 when the pH significantly increased. Since both Uncas and Norwich are situated in watersheds that have remained over 99% forested since 1934, they lack the same potential sources of alkalinity from residential land development that would be experienced by Coventry Lake. Despite the lack of residential land in the watersheds of Uncas and Norwich ponds, Ricard (2000) found the concentrations of alkalinity in tributaries draining forests and wetland regions in both catchments to most often measure between 80–90% of in-lake surface concentrations, indicating significant watershed-based alkalinity production from these forested catchments.

Our mean estimates of in-lake alkalinity produced by sulfate reduction of 78 to 145 meq $m^{-2}$ $yr^{-1}$ are high compared to other lakes examined in northern New England (Mitchell et al. 1988; Giblin et al. 1990; Kahl et al. 1991), Quebec (Carignan and Tessier 1988), and the upper midwest (Mitchell et al. 1988; Cook and Jager 1991), are similar to estimates made for some seepage ponds on Cape Cod (Giblin et al. 1990) and many ponds examined in the Adirondacks (Mitchell et al. 1988), but are on the low end of measurements made for clearwater recharge lakes in Florida (Pollman and Canfield 1991). For example, using the same methodology and making essentially the same assumptions as we did, Giblin et al. (1990) reported rates ranging between 10 and 68 meq $m^{-2}$ $yr^{-1}$ for northern New England drainage lakes, and 43 to 159 meq $m^{-2}$ $yr^{-1}$ for Cape Cod seepage lakes. A very similar range of rates to those reported by Giblin et al. (1990), between 12 and 53 meq $m^{-2}$ $yr^{-1}$, were also observed by Mitchell et al. (1988) for northern New England lakes. In another study utilizing the amounts of sulfur stored in dated sediment cores from the hypolimnion, Norton et al. (1988) found that alkalinity production from sulfate reduction only ac-

counted for a mean of 5 $\mu g\ L^{-1}$ in poorly buffered lakes in Vermont and Maine. Carignan and Tessier (1988) reported a rate of 60 meq $m^{-2}\ yr^{-1}$ for a lake in Quebec, while estimates ranging from 96 to 303 meq $m^{-2}\ yr^{-1}$ were measured by Perry et al. (1986) for Florida lakes. The ponds we examined have relatively high sulfate concentrations in their overlying water and anoxic hypolimnia which probably contribute to their high rates of sulfur storage.

The relative importance of organic vs. inorganic sulfur has been found to vary widely in freshwater lakes. The majority of both allochthonous-derived sulfur and in-lake algal-derived sulfur is largely organic in nature, whereas the reduction of sulfate by bacteria could yield either organic or inorganic sulfur products. Nriagu and Soon (1985), Rudd et al. (1986, 1990) concluded that the bulk of sulfur in their study lakes was stored as organic S. Burial as organic S has been demonstrated for oligotrophic (Mitchell et al. 1988; David and Mitchell 1985) as well as eutrophic lakes (King and Klug 1982). Burial of sulfur as inorganic sulfides was found as the primary mechanism for long-term storage in lakes in Quebec (Carignan and Tessier 1988), Wisconsin (Brezonik et al. 1987) and New England (Giblin et al. 1990). Although it remains unclear why in some lakes sulfides are buried predominately in an inorganic form, but in others as organic compounds, factors such as anoxic condition (Dornblaster et al. 1994), and turnover dynamics (Kling et al. 1991) appear to be quite important. All three ponds in this study have anoxic hypoliminon for the majority of the summer which would tend to help preserve inorganic reduced forms.

In our lakes the absolute amount of sulfur stored in the organic fraction was either relatively constant over time or declined in more recent sediments. Thus, since the overall amounts of stored sulfur increased in the upper portions of the cores, the majority of the increase was as inorganic sulfur and the inorganic fraction accounted for between 72% and 82% of the total S in the more recent sediments. As noted above, we believe that the bulk of the increase in stored sulfur was the result of dissimilatory reduction of sulfate by bacteria, and not derived from algal or allochthonous sources.

Increases in the storage of sulfur in lake sediments attributed to stimulation of bacterial dissimilatory processes may be linked to an increased delivery of sulfate and/or organic substrates to the sediments from overlying waters, a decline in sulfide oxidation by bacteria in the sediments, or a combination of these factors (Giblin et al. 1990, 1991; Stauffer 1991). It is safe to assume that these three ponds have all experienced an increase in sulfate concentrations over their history due to increased atmospheric deposition (Husar 1986), although the exact magnitude of the increase for this area is not known. Increases in sulfate concentrations have been shown to increase the sulfur content of sediments in experimental lakes (Cook and Schindler 1983), and sulfur storage in sediment has been correlated with sulfate concentrations in natural systems (Norton et al. 1988; Mitchell et al. 1988). Changes in sulfate concentrations may be largely responsible for the increases in sulfur storage we observed in these three ponds.

Surprisingly, we did not observe an affect of trophic status in controlling sulfur storage in these three ponds. We only observed significant changes in trophic status in Coventry Pond, yet the historical changes in sulfur storage we observed in Coventry were no greater than those we observed in Uncas and only somewhat greater than we observed in Norwich, where there was no large change in trophic status. On an absolute basis, we also did not find a relationship between trophic status and recent rates of sulfur burial between these three ponds. One possible explanation, is that the very recent changes in trophic status that Uncas and Norwich may have experienced in the last decade or so, which are not evident in the micro-fossil record, may have still affected the sulfur profiles. However, we believe this is quite unlikely. Although sulfate can diffuse into the sediments and become fixed below the sediment-water interface, the depth of penetration is only a few mm to cm (discussed in Giblin et al. (1990)). While we cannot discount some very recent changes in rates of sulfur storage due to an increase in trophic status over the last decade, the affect would not have caused the large increase in sulfur storage that is evident over the top 10–20 cm as observed in these ponds. Hence, we conclude that changes in sulfate concentrations in the overlying water, rather than changes in trophic status, controlled the long-term burial of sulfur in these systems. This result was somewhat unexpected and may have been strongly influenced by the low oxygen status of the hypolimnia in all the ponds, regardless of trophic status, during summer.

It is well documented that increased storage of sulfur in lake sediments can result in a parallel release of phosphorus to the water column, and a subsequent increase in the eutrophication of the waterbody (Caraco et al. 1989; Urban 1994; Murray 1994;

Olsson et al. 1997). Caraco et al. (1989) proposed that in-lake loading of P from anoxic sediments would increase as more of the available iron became sequestered as FeS. The correlation between the accumulation of FeS in sediments and the release of P into overlying waters was clearly demonstrated by Murray (1994) in Crystal Lake, Connecticut. In a hypertrophic lake in southern Sweden, Olsson et al. (1997) similarly reported that release of P from the sediments occurred in parallel with increased FeS formation, and contributed further to the eutrophication of the lake.

The question arises as to whether the increased storage of iron sulfides in our study lakes has caused a similar increase in the in-lake loading of phosphorus. This is especially of interest in Uncas and Norwich because Siver et al. (1999) noted that, although a significant increase in the trophic status of each of these waterbodies was not inferred from algal remains, a number of more eutrophic taxa of scaled chrysophytes and diatoms were found in the surface sediments, especially in Uncas Lake, perhaps signalling the start of a decline in the trophic conditions of both lakes. It was unclear why more eutrophic taxa were appearing in the recent sediments of Uncas and Norwich, since both lakes were situated in watersheds that have remained heavily forested over the last ~60 years (Field et al. 1996). Siver et al. (1999) concluded that factors other than land-use changes, such as in-lake loading of nutrients or changes in food-web dynamics, may have caused the changes.

Based on geochemical results from this study an argument supporting an increased release of P from the sediments into the water column can be made for Uncas Pond. Given a constant rate of supply of iron to the sediments, the more sulfur that becomes stored as iron sulfide compounds, the less iron there is available to bind with and sequester P in the sediments. If we assume that all iron in the sediments of a lake was bound as either FeS or $FeS_2$ the molar ratio of iron to inorganic iron-bound-S (e.g., the CRS fraction in our study) would be 1 or 0.5, respectively. Progressively more iron would be available to bind P as the ratio of Fe:CRS increased above 1. In both Norwich and Coventry, Fe:CRS ratios were mostly above 3 in recent sediments indicating a significant pool of iron available for binding P. However, in the top of the core from Uncas, the Fe:CRS ratio dropped below 1 and reached a low of only 0.5, indicating that little, if any, iron was available for binding P. This evidence suggests that an increase in the in-lake loading of P, correlated with the increased storage of sulfur as iron sulfides, is possibly operating in Uncas, but not in Norwich or Coventry. Changes in the concentrations of total phosphorus in the hypolimnion of Uncas over the last two decades may further support this hypothesis. Frink and Norvell (1984) reported total phosphorus concentrations of 15 $\mu g\ L^{-1}$ in the bottom waters of Uncas in July, 1980. In July, 1993 (Canavan and Siver 1995) and in the late summer periods of subsequent years (unpubl. data) total phosphorus levels of 49 $\mu g\ L^{-1}$ or greater have been consistently observed.

In conclusion, the amount of sulfur stored in the sediments of the study lakes has substantially increased over the last ~44 to 69 years. Because the increase in sulfur has been primarily as inorganic Fe sulfide compounds, and not as organic sulfur, we believe it was primarily the result of an increase in dissimilatory bacterial reduction of sulfur. The amount of permanent in-lake alkalinity generated from the reduction of sulfur in these lakes has been sufficient to buffer the loading of hydrogen ions from precipitation falling directly onto the lakes as well as for a portion impacting each watershed. However, in each study lake the increased alkalinity generated from sulfate reduction within the lake has not been sufficient to account for the levels of acidic deposition impacting the whole watershed, nor to account for current lake water alkalinity concentrations. Presumably, alkalinity generated from watershed-based processes accounts for the differences. Lastly, it is likely that over the recent past the release of phosphorus from the sediments of Uncas Pond has increased due to a decline in the concentration of Fe oxides available for binding phosphorus.

**Acknowledgements**

We would like to thank staff and students from the Freshwater Ecology Laboratory at Connecticut College for assistance in the field, Kathy Regan (MBL) for help with geochemical analysis, and three anonymous reviewers for many helpful comments. This study was funded, in part, by NSF grants #DEB-9306587 and #DEB-9615062, assistance from the Environmental Studies Mellon Fund at Connecticut College and a Lucy B. Lehmann Fellowship (MBL) to P.A.S.

## References


Baker L.A., Eilers J.M., Cook R.B., Kaufmann P.R. and Herlihy A.T. 1991. Interregional comparisons of surface water chemistry and biogeochemical processes. In: Charles D.F. (ed.), Acidic Deposition and Aquatic Ecosystems. Springer-Verlag, NY, pp. 567–615.

Battarbee R.W., Charles D.F., Dixit S.S. and Renberg I. 1999. Diatoms as indicators of surface water acidity. In: Stoermer E.F. and Smol J.P. (eds), The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge Univ. Press, N.Y., pp. 85–127.

Bell M. 1985. The Face of Connecticut: People, Geology, and the Land. State Geologic and Natural History Survey of Connecticut, Hartford, CT, 196 pp.

Birks H.J.B., Line J.M., Juggins S., Stevenson A.C. and Ter Braak C.J.F. 1990. Diatoms and pH reconstruction. Phil. Trans. R. Soc. Lond. Ser. B 327: 263–278.

Brezonik P.L, Baker L.A. and Perry T.E. 1987. Mechanisms of alkalinity generation in acid-sensitive soft water lakes. In: Sources and Fates of Aquatic Pollutants. Am. Chem. Soc., pp. 229–260.

Canavan R.W. IV and Siver P.A. 1995. Connecticut Lakes: A Study of the Chemical and Physical Properties of Fifty-six Connecticut Lakes. Connecticut College Arboretum, New London, 299 pp.

Caraco N.F., Cole J.J. and Likens G.E. 1989. Evidence for sulfate-controlled phosphorus release from sediments of aquatic systems. Nature 341: 158–160.

Carignan R. and Tessier A. 1988. The co-diagensis of sulfur and iron in acid lake sediments of southwestern Quebec. Geochim. Cosmochim. Acta. 52: 1179–1188.

Charles D.F. (ed.) 1991. Acidic Deposition and Aquatic Ecosystems. Springer-Verlag, NY, 747 pp.

Cook R.B., Kelly C.A., Schindler D.W. and Turner M.A. 1986. Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. Limnol. Oceanogr. 31: 134–148.

Cook R.B. and Jager H.I. 1991. Upper midwest. In: Charles D.F. (ed.), Acidic Deposition and Aquatic Ecosystems. Springer-Verlag, NY, pp. 421–467.

Cook R.B. and Schindler D.W. 1983. The biogeochemistry of sulfur in an experimentally acidified lake. Ecol. Bull. 35: 115–127.

Cummings B.F., Smol J.P. and Birks H.B.J. 1992. Scaled chrysophytes (Chrysophyceae and Synurophyceae) from Adirondack drainage lakes and their relationship to environmental variables. J. Phycol. 28: 162–178.

David M.B. and Mitchell M.J. 1985. Sulfur constituents and cycling in waters, seston, and sediments of an oligotrophic lake. Limnol. Oceanogr. 30: 1196–1207.

Davis R.B., Anderson D.S, Norton S.A. and Whiting M.C. 1994. Acidity of twelve northern New England (U.S.A.) lakes in recent centuries. J. Paleolim. 12: 103–154.

Dixit A.S. and Dixit S.S. 1989. Surface sediment chrysophytes from 35 Quebec lakes and their usefulness in reconstructing lakewater pH. Can. J. Bot. 67: 2071–2076.

Dixit S.S., Dixit A.S. and Smol J.P. 1992. Long-term trends in lake water pH and metal concentrations inferred from diatoms and chrysophytes in three lakes near Sudbury, Ontario. Can. J. Fish. Aquat. Sci. 49: 17–24.

Dornblaster M., Giblin A.E., Fry B. and Peterson B.J. 1994. Effects of sulfate concentration in the overlying water on sulfate reduction and sulfur storage in lake sediments. Biogeochemistry 24: 129–144.

Field C.K., Siver P.A. and Lott A.M. 1996. Estimating the effects of changing land use patterns on Connecticut lakes. J. Environ. Qual. 25: 325–333.

Fostner U. and Salmons A. 1980. Trace metal analysis on polluted sediments. Environ. Technol. Lett. 1: 494–505.

Frink C.R. and Norvell W.A. 1984. Chemical and Physical Properties of Connecticut Lakes. The Connecticut Agricultural Experiment Station Bulletin no. 817, 27 p + appendices.

Giblin A.E., Likens G.E., White D. and Howarth R.W. 1990. Sulfur storage and alkalinity generation in New England lake sediments. Limnol. Oceanogr. 35: 852–869.

Giblin A.E., Likens G.E. and Howarth R.W. 1991. A reply to the comment by Stauffer. Limnol. Oceanogr. 36: 1265–1271.

Glew J.R. 1988. A new trigger mechanism for sediment samplers. J. Paleolim. 2: 241–243.

Glew J.R. 1989. A portable extruding device for close interval sectioning of unconsolidated core samples. J. Paleolim. 1: 235–239.

Hall R.I. and Smol J.P. 1996. Paleolimnological assessment of long-term water-quality changes in south-central Ontario lakes affected by cottage development and acidification. Can. J. Fish. Aquat. Sci. 53: 1–17.

Howarth R.W. and Merkel S. 1984. Pyrite formation and the measurement of sulfate reduction in salt marsh sediments. Limnol. Oceanogr. 29: 598–608.

Husar R.B. 1986. Emissions of sulfur dioxide and nitrogen oxides and trends for eastern North America. In: Acid Deposition: Long-term trends. NAS, pp. 48–92.

Husar R.B., Sullivan T.J. and Charles D.F. 1991. Historical trends in atmospheric sulfur deposition and methods for assessing long-term trends in surface water chemistry. In: Charles D.F. (ed.), Acidic Deposition and Aquatic Ecosystems. Springer-Verlag, NY, pp. 65–83.

Kahl J.S., Norton S.A., Cronan C.S., Fernandez I.J., Bacon L.C. and Haines T.A. 1991. Maine. In: Charles D.F. (ed.), Acidic Deposition and Aquatic Ecosystems. Springer-Verlag, NY, pp. 203–237.

Kilham P. 1982. Acid precipitation: Its role in the alkalization of a lake in Michigan. Limnol. Oceanogr. 27: 856–867.

King G.M. and Klug M.J. 1982. Sulfhydrolase activity in sediments of Wintergreen Lake, Kalamazoo County, Michingan. Appl. Envir. Microbiol. 39: 950–956.

Kling G.W., Giblin A.E., Fry B. and Peterson B.J. 1991. The role of seasonal turnover in lake alkalinity dynamics. Limnol. Oceanogr. 36: 106–122.

Marsicano L.J. and Siver P.A. 1993. A paleolimnological assessment of lake acidification in five Connecticut lakes. J. Paleolim. 9: 209–221.

Mitchell M.J., Schindler S.C., Owen J.S. and Norton S.A. 1988. Comparison of sulfur concentrations within lake sediment profiles. Hydrobiologia 157: 219–229.

Murray T.E. 1994. Iron, sulfur, and phosphorus interactions in a softwater lake, PhD, Univ. of Connecticut, Storrs, 113 pp.

Ng A. and Patterson C. 1982. Changes in lead and barium with time in California offshore basin sediments. Geochim. Cosmochi. Acta 48: 2307–2321.

Norton S.A., Mitchell M.J., Kakl J.S. and Brewer G.F. 1988. In-lake alkalinity generation by sulfate reduction: A paleolimnological assessment. Water, Air Soil Poll. 39: 33–45.

Nriagu J.O. and Soon Y.K. 1985. Distribution and isotopic composition of sulfur in lake sediments of northern Ontario. Geochim. Cosmochim. Acta 49: 823–834.

Olsson S., Régnell J., Persson A. and Sandgren P. 1997. Sediment-chemistry response to land-use change and pollutant loading in a hypertrophic lake, southern Sweden. J. Paleolim. 17: 275–294.

Owen J.S. and Mitchell M.J. 1988. Sulfur biogeochemistry of an acidic lake in the Adirondack region of New York. In: Rao S. (ed.), Acid Stress and Aquatic Microbial Interactions. CRC, pp. 59–68.

Perry T.E., Pollman C.D. and Brezonik P.L. 1986. Buffering capacity of softwater lake sediments in Florida. In: Isom B.G., Dennis S.D. and Bates J.M. (eds), Impact of Acid Rain and Deposition on Aquatic Biological Systems. Amer. Soc. for Testing and Materials, Philadelphia, PA. ASTM STP 928., pp. 67–83.

Pollman C.D. and Canfield D.E. Jr. 1991. Florida. In: Charles D.F. (ed.), Acidic Deposition and Aquatic Ecosystems. Springer-Verlag, NY, pp. 367–417.

Racca J.M.J., Philibert A., Racca R. and Prairie Y.T. 2001. A comparison between diatom-based pH inference models using artificial neural networks (ANN), weighted averaging (WA) and weighted averaging partial least squares (WA-PLS) regressions. J. Paleolim. 26: 411–422.

Ricard R.P. 2000. Factors controlling the neutralization of acids in three Connecticut lakes, Honor's thesis, Connecticut College, New London, CT 50 pp.

Rudd J.W.M., Kelly C.A. and Furutani A. 1986. The role of sulfur reduction in long term accumulation of organic and inorganic S in lake sediments. Limnol. Oceanogr. 31: 1281–1292.

Rudd J.W.M., Kelly C.A., Schindler D.W. and Turner M.A. 1990. A comparison of the acidification efficiencies of nitric and sulfuric acids by two whole-lake addition experiments. Limnol. Oceanogr. 35: 663–679.

Schindler D.W. 1986. The significance of in-lake production of alkalinity. Water, Air Soil Poll. 30: 921–944.

Schindler D.W., Turner M.A., Stainton M.P. and Linsey G.A. 1986. Natural sources of acid neutralizing capacity in low alkalinity lakes of the Precambrian shield. Science 232: 844–847.

Siver P.A. 1999. Development of paleolimnological inference models for pH, total nitrogen and specific conductivity based on planktonic diatoms. J. Paleolim. 21: 45–59.

Siver P.A. and Marsicano L.J. 1996. Inferring lake trophic status using scaled chrysophytes. Beih. Nova Hedwigia 114: 233–246.

Siver P.A., Canavan R.W. IV, Field C.K., Marsicano L.J. and Lott A.M. 1996. Historical changes in Connecticut lakes over a 55-year period. J. Environ. Qual. 25: 334–345.

Siver P.A., Lott A.M., Cash E., Moss J. and Marsicano L.J. 1999. Century changes in Connecticut, U.S.A., lakes as inferred from siliceous algal remains and their relatioships to land-use change. Limnology and Oceanography 44: 1928–1935.

Siver P.A. and Wozniak J. 2001. The distribution of lead in Connecticut lakes. J. Paleolim. 26: 1–10.

Stauffer R.E. 1991. A comment on ''Sulfur storage and alkalinity generation in New England lake sediments (Giblin et al.)''. Limnol. Oceanogr. 36: 1263–1265.

Stensland G.J., Whelpdale D.M. and Oehlert G. 1986. Precipitation chemistry. In: Committee on Monitoring and Assessment of Trends in Acid Deposition. Acid Deposition: Long Term Trends. National Academy Press, Washington, DC. 506 pp.

Urban N.R. 1994. Retention of sulfur in lake sediments. In: Baker L.A. (ed.), Environmental Chemistry of Lakes and Reservoirs. Advances in Chemistry Series 237. Amer. Chem. Soc., Washington D.C., pp. 323–369.

Wetzel R.G. and Likens G.E. 1991. Limnological Analyses. Springer-Verlag, New York, NY, pp. 323–369.

Zhabina N.N. and Volkov I.I. 1978. A quick method of determination of various sulfur compounds in sea sediments and rocks. In: Krumbein W.E. (ed.), Environmental Biogeochemistry and Geomicrobiology: Methods, Metals and Assessment. Ann Arbor Sci., pp. 735–745.