

## Preliminary Analysis of the Hydrologic and Geochemical Controls on Acid-Neutralizing Capacity in Two Acidic Seepage Lakes in Florida

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In late 1988, parallel studies of Lake Five-O (pH 5.14) in the Florida panhandle and Lake Barco (pH 4.50) in north central Florida were initiated to develop hydrologic and major ion budgets of these lakes as part of an overall effort to improve understanding of the hydrologic, depositional, and biogeochemical factors that control acid-neutralizing capacity (ANC) in seepage lakes. Preliminary findings from these studies indicate that earlier perceptions of lake hydrology and mechanisms of ANC regulation in Florida seepage lakes may have to be revised. The traditional perspective of seepage lakes in the Florida panhandle views these systems as dominated by precipitation inputs and that ANC regulation is due largely to in-lake processes. Our results for Lake Five-O show modest to steep hydraulic gradients almost entirely around the lake. In addition, the horizontal hydraulic conductivity of the surficial aquifer is high (8–74 m day<sup>-1</sup>), indicating that large quantities of groundwater flow into Lake Five-O. Calculations of net groundwater flow from hydrologic budgets also indicate that groundwater may comprise at least 38 to 46% of the total inflow. For Lake Barco, net flow estimates of the minimum groundwater inflow range from 5 to 14% of total inflow. Enrichment factor and ion flux calculations for Lake Five-O and Lake Barco indicate that terrestrial as well as in-lake processes contribute significantly to ANC regulation. The extent that terrestrial processes contribute to ANC generation is directly related to the magnitude of groundwater inflow as well as the degree of ion enrichment or depletion that occurs in the surficial aquifer. Net ANC generation in both study lakes was dominated by anion retention (NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>). Where previous studies concluded that in-lake reduction was the primary sink for SO<sub>4</sub><sup>2-</sup>, our preliminary calculations show that adsorption of SO<sub>4</sub><sup>2-</sup> within the watershed is perhaps twice as important as in-lake reduction as a source of ANC. Net base cation enrichment in both lakes was negligible.

### INTRODUCTION

Seepage lakes, by virtue of having no surface inlets or outlets, receive essentially all their hydrologic income from precipitation falling directly on the lake surface or from groundwater inflow (inseepage). Because precipitation is such an important component of their hydrologic budgets, seepage lakes are gaining increasing attention regarding their sensitivity to acidic deposition (Eilers *et al.*, 1983; Baker *et al.*, 1988a; Henriksen and Brakke, 1988; Pollman and Canfield, 1991). Results from the U.S. Environmental Protection Agency's (EPA) Eastern Lakes Survey (ELS) indicate that nearly 60% of the acidic lakes in the eastern United States (defined as lakes with acid-neutralizing capacity or ANC  $\leq 0$   $\mu\text{eq L}^{-1}$ ) are seepage lakes [Brakke *et al.*, 1987]. In Florida, where more acidic lakes are found than in any other region in the country [Linthurst *et al.*, 1986], 84% of the acidic lakes are seepage lakes [Pollman and Canfield, 1991]. Nearly half of these acidic lakes are clearwater lakes where the acidity is attributable to strong acids, notably H<sub>2</sub>SO<sub>4</sub> [Pollman and Canfield, 1991]. Paleolimnological evidence indicates that some seepage lakes in Florida have become more acidic since about 1950, although the mechanisms accounting for such change (hydrologic and/or atmospheric) are unclear [Sweets *et al.*, 1990]. Moreover, although the factors that

regulate ANC are fairly well known, the quantitative importance of individual factors is uncertain, and the impact of perturbations of any of these components on the chemistry of clearwater seepage lakes cannot be assessed [Goldstein *et al.*, 1985].

In late 1988, two parallel, 4-year studies were begun of the hydrologic and chemical dynamics of two clearwater seepage lakes: Lake Five-O (pH = 5.14, ANC = -4.0  $\mu\text{eq L}^{-1}$ ) in the Florida panhandle; and Lake Barco (pH = 4.50, ANC = -31.3  $\mu\text{eq L}^{-1}$ ) in north central Florida (Figure 1). These studies focus on the relative importance of two geochemical processes that currently are poorly understood: (1) the terrestrial contribution of ANC via groundwater inflow to acidic seepage lakes and (2) the contribution of in-lake processes to ANC, particularly through anion (NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) assimilation and reduction. Results from both lake studies are being integrated as part of the Hydrology and Acidity of Seepage Lakes (HASL) study to improve our understanding at the regional level of the hydrologic and depositional factors that control ANC in seepage lakes. Although lake and precipitation chemistry data exist for numerous lake basins in Florida, the Lake Five-O and Lake Barco studies are the first in Florida to define groundwater flow patterns and geochemistry in the aquifers surrounding acidic seepage lakes.

The purpose of this paper is to present findings from the first year of study on the chemistry and hydrology of each basin and to present the results of a preliminary analysis of the relative importance of terrestrial and in-lake processes in regulating ANC. Because a more accurate quantification of groundwater fluxes is several years from completion, this preliminary analysis relies upon initial estimates of the relative magnitude of groundwater flow to each lake, i.e., the fraction of the total inflow to the lake contributed by

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Paper number 91WR01435.  
0043-1397/91/91WR-01435\$05.00

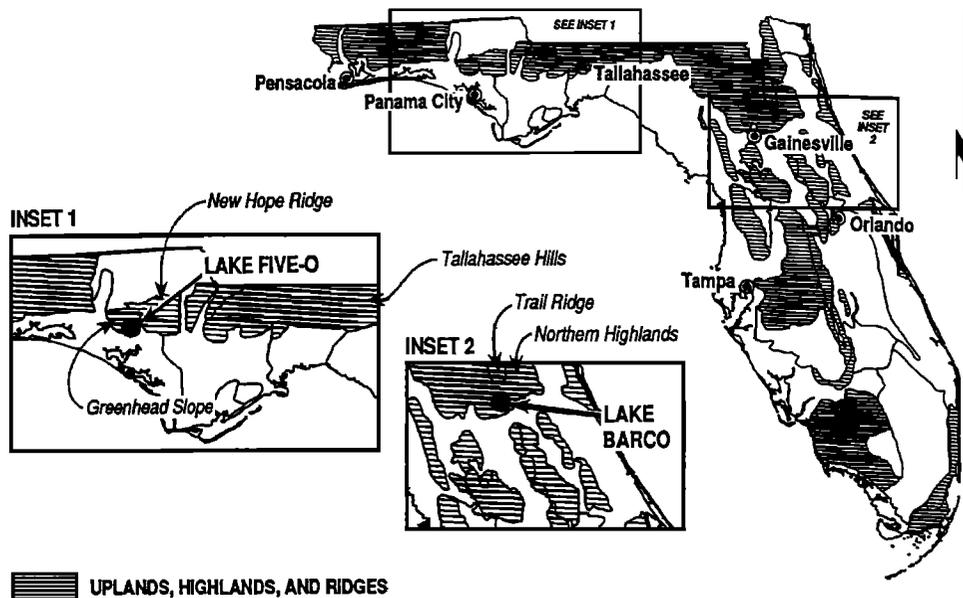


Fig. 1. Site map showing location of Lake Five-O (panhandle) and Lake Barco (north central Florida) in relation to major physiographic regions of Florida.

groundwater. These estimates are based upon the hydrogeology and groundwater flow patterns in the aquifers surrounding each lake and on net groundwater flow calculated from preliminary hydrologic budgets for each lake. Potential errors in the net groundwater flow estimates are discussed. Estimates of steady state groundwater inflow and leakage for each lake also are derived using a geochemical tracer approach [cf. Stauffer, 1985]. Because (1) the chemistry of seepage lakes at any point in time integrates the effects of atmospheric deposition received over the previous several years and (2) the intent of this paper is to focus on long-term mechanisms contributing to ANC production, we have adopted a steady state approach using averaged lakewater chemistry, long-term depositional data, and long-term hydrologic data to calculate enrichment factors.

#### STUDY AREA

##### *Lake Five-O*

Lake Five-O is in the Florida panhandle approximately 30 km north of Panama City in the Greenhead Slope physiographic region (Figure 1). This area is underlain by mantled karst and is characterized by irregular sandhills and numerous doline-type seepage lakes [Schmidt and Clark, 1980]. The Lake Five-O watershed is part of a relict marine terrace lying between 21 and 52 m above mean sea level (MSL). Surficial soils in the region are deeply weathered, acidic typic quartzipsamments. Primary weatherable minerals in the Pliocene to Holocene aged sands are largely absent, although iron staining of subsurface sands is common.

The unconfined surficial aquifer occurs in unconsolidated and very permeable quartz sands that average about 18 m thick on the plateau surrounding Lake Five-O [Andrews *et al.*, 1990]. It is underlain by the Jackson Bluff Formation, an intermediate confining unit separating the surficial aquifer from the upper Floridan aquifer. The Jackson Bluff Formation consists of calcareous, sandy clay to clayey sand with biogenic deposits of phosphate [Andrews *et al.*, 1990]. The

Floridan aquifer system is a massive series of limestones and dolomites that underlie virtually all of Florida [Heath and Conover, 1981].

Lake Five-O is a deep depression surrounded by otherwise flat terrain that currently is used to grow timber. The watershed was logged to the periphery of the lake basin (approximately 50 m from the shoreline) in spring 1968 before the start of the study and was replanted with sand pine in fall 1988. The climate is subtropical and humid. Annual precipitation at Panama City averaged 168 cm from 1968 through 1987 [Andrews *et al.*, 1990].

The surface area of Lake Five-O is 11.2 ha, and the lake has an average depth of 9.8 m (at stage 14.61 m MSL). Maximum depth is nearly 15 m. Unlike many Florida lakes (yet typical of other lakes in the New Hope Ridge/Greenhead Slope area; cf. Canfield *et al.* [1983]), Lake Five-O is sufficiently deep to undergo stable thermal stratification during the summer.

##### *Lake Barco*

Lake Barco is within the Katherine Ordway Preserve near the southern toe of the Trail Ridge physiographic region in north central Florida (Figure 1). Lake Barco lies in sandhill karst. Lakes in the region largely originate from dissolution of the underlying limestone, followed by piping of mantle sediments into extended networks of solution channels within the bedrock. Collapse and sinkhole formation ultimately ensue such that karst features (depressions and lakes) are formed entirely within the surficial deposits and usually none of the calcareous bedrock is exposed [Arrington and Lindquist, 1987].

Surficial deposits in the Lake Barco watershed are post-Miocene in age and consist primarily of undifferentiated sands with variable amounts of silt and clay. Soils are acidic typic quartzipsamments, with extremely low cation-exchange capacities (CEC) [Volk and Byers, 1983]. The surficial deposits range in thickness from about 30 m along

the crests of the sandhills to about 15 m near Lake Barco. They are underlain by the Hawthorn Formation, which confines or partially confines the underlying upper Floridan aquifer. The Hawthorn Formation is extremely variable, consisting of differing quantities of clay and clayey sands, quartz sands, carbonate and dolomite deposits, and phosphatic granules [Scott and McGill, 1981; Scott, 1983]. Both Lake Five-O and Lake Barco lie in regions of recharge to the Floridan aquifer system [Aucott, 1988].

Surface area of Lake Barco is 11.7 ha, and the average depth is 4.8 m. Maximum depth is approximately 6.7 m. Lake Barco does not stratify stably and remains isothermal throughout the year.

## METHODS

### Overview

Data collection and analysis for both lakes are structured toward developing independent estimates of all components to the hydrologic and major ion budgets for each lake. For seepage lakes that receive negligible amounts of overland flow the water budget is simply

$$\Delta V \pm \xi_{\Delta V} = P \pm \xi_P - E \pm \xi_E + Q_i \pm \xi_{Q_i} - Q_o \pm \xi_{Q_o} \quad (1)$$

where  $\Delta V$  is the change in lake storage or volume ( $m^3$ ) for the period of interest,  $P$  is the total volume of precipitation received by the lake ( $m^3$ ),  $E$  is evaporation from the lake surface ( $m^3$ ),  $Q_i$  is groundwater inflow to the lake ( $m^3$ ),  $Q_o$  is groundwater outflow from the lake (leakage,  $m^3$ ), and  $\xi_i$  represents the error ( $m^3$ ) inherent in measuring term  $i$ .

Mechanisms of ANC generation or production can be evaluated by developing budgets for all the major ions contributing to ANC [e.g., Baker et al., 1986; Lin et al. 1987]. In acidic, clearwater lakes (e.g., dissolved organic carbon  $\leq 2 \text{ mgL}^{-1}$ ), organic acid anion contributions to ANC are minor and ANC may be defined as

$$[\text{ANC}] = [\text{HCO}_3^-] - [\text{H}^+] \quad (2)$$

Electroneutrality requires that the sum of cations is equivalent to the sum of anions:

$$[\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+] + [\text{Al}^{3+}] + [\text{Mn}^{2+}] + [\text{H}^+] = [\text{Cl}^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCO}_3^-] \quad (3)$$

From (2) and (3), changes in [ANC] can be expressed as

$$\Delta[\text{ANC}] = \Delta[C_B] + \Delta[\text{NH}_4^+] + \Delta[\text{Al}^{3+}] + \Delta[\text{Mn}^{2+}] - \Delta[\text{Cl}^-] - \Delta[\text{SO}_4^{2-}] - \Delta[\text{NO}_3^-] \quad (4)$$

where  $[C_B]$  is the sum of base cations ( $[\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+]$ ).

One fundamental objective of the hydrologic budget analysis is to evaluate the effects of residual measurement error,  $\xi_{\text{res}}$ , on the chemical budgets [cf. LaBaugh, 1985]. For lakes that receive small quantities of groundwater inflow the residual error may exceed estimated inputs [cf. Tacconi, 1988].

### Hydrologic Budget

Groundwater interactions with Lake Five-O and Lake Barco were interpreted from the distribution hydraulic head in the aquifers surrounding each lake. A total of 53 observation wells, including four groups of nested wells, have been installed around Lake Five-O to measure the horizontal and vertical head gradients around the lake (Figure 2). Forty-two of the Lake Five-O wells were completed in the surficial aquifer to map the elevation of the water table, and two wells were completed in the upper Floridan aquifer [Andrews et al., 1990]. The observation well network around Lake Barco includes a total of 43 wells: 20 wells finished within the surficial aquifer and three groups of nested wells finished at various depths within the surficial aquifer, the intermediate confining unit, and the upper Floridan aquifer. Six midlake wells also were jetted into the surficial aquifer below the lake bottom in Lake Barco following methods described by Lee et al. [1991]. At both sites, wells generally were constructed with 5.1-cm (2-inch) diameter polyvinyl chloride (PVC) casing with 1.7 m or less of PVC well screen. Well elevations at both lakes were surveyed from benchmark elevations to the nearest 0.01 foot MSL. Biweekly (Barco) and monthly (Five-O) synoptic measurements of groundwater elevations began in October and November 1988 for Lake Barco and Lake Five-O, respectively.

Rainfall was measured continuously onsite at each lake with recording tipping bucket and Belfort weighing bucket rain gages. (The use of brand, firm, or trade names in this article is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.) Measurements began at Lake Barco on April 29, 1989. Prior to this date, daily precipitation measured at the Florida Acid Deposition Monitoring Program (FADMP) site in Gainesville was used to estimate precipitation at the site. For Lake Five-O the onsite precipitation record began March 1, 1989, and daily precipitation measured at the FADMP site in Caryville was used to extend the record prior to this date. Lake stage also was measured continuously at both lakes with recording stage gages; lake volumes were determined from bathymetric data recorded to the nearest 0.3-m (1-foot) contour interval.

Lake evaporation losses for this paper were estimated from monthly average pan evaporation measured in Milton (130 km from Lake Five-O) for the period 1962 to 1987 and Gainesville (33 km from Lake Barco) for the period 1953 to 1987 [National Oceanic and Atmospheric Administration, 1953-1987]. Monthly pan-to-lake coefficients were used to adjust monthly pan evaporation to lake evaporation. These coefficients were derived from energy budget evaporation estimates for Lake Lucerne, Florida, and measured pan evaporation from a National Weather Service-type climate station also operated on-site (T. M. Lee, and A. Swancar, unpublished manuscript, 1990). Lake Lucerne, which is a seepage lake on the Central Ridge about 185 km south of Lake Barco, is very similar in size and physical setting to Lake Barco [Lee et al., 1991]. It currently is the only lake in Florida for which energy budget evaporation data are available.

For this analysis the monthly net groundwater flux to each lake was calculated for a 14-month period. Net groundwater flux ( $Q_{\text{net}}$ ;  $Q_{\text{net}} = Q_i - Q_o$ ) was solved as a residual term from the hydrologic budget equation and thus includes the

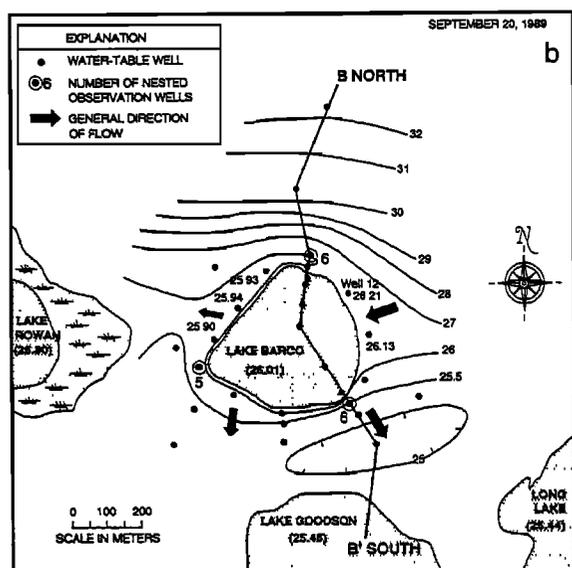
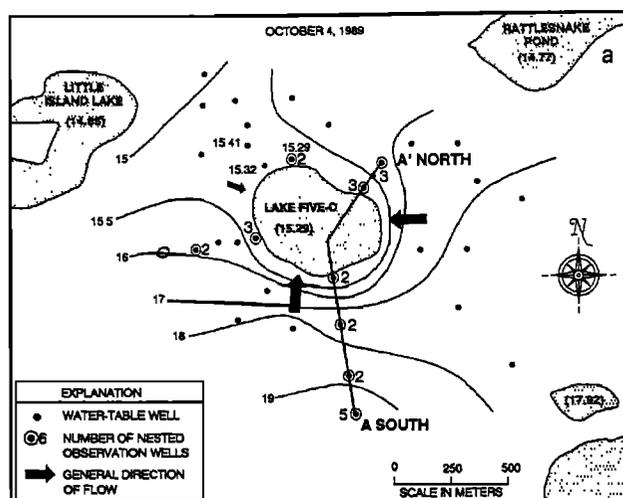


Fig. 2. Water table elevation contours (feet above mean sea level) in the vicinities of (a) Lake Five-O (October 4, 1989) and (b) Lake Barco (September 20, 1989). Also shown on figure are transect lines (A-A', Lake Five-O; B-B', Lake Barco) used to show vertical head gradients in Figure 3. Head measurements from selected wells are included in Figure 2b to illustrate the slight hydrologic depression along the northwestern and northern margins of Lake Barco as well as the inflow gradient along the northeastern margin.

cumulative errors of measurement of the other budget terms [equation (1)]. The error in measured budget terms equals the confidence limits or standard deviation around the measured value. The cumulative error in  $Q_{net}$  then is calculated from the variance of the total error in the measured components [Ramette, 1981; LaBaugh, 1985]:

$$\xi_{net} = \sqrt{\xi_P^2 + \xi_E^2 + \xi_{\Delta V}^2} \quad (5)$$

Confidence limits for the hydrologic budget were estimated by multiplying the individual measured terms for the budget by percentage errors derived from the literature for the appropriate measurement technique. This approach assumes that the measurement of each term is independent of the

other terms and that no intercorrelations (or covariances) exist between measurement errors [Winter, 1981; LaBaugh and Winter, 1984].

### Chemical Budget

Evaluation of sources and sinks of major ions consisted of monitoring several different pathways: atmospheric inputs, groundwater inflow, and in-lake processing. Wet-only atmospheric deposition was measured onsite at each lake with an Aerochemetrics 301 wet/dry collector. Weekly samples were analyzed for specific conductance, pH,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and  $NO_3^-$  by Environmental Science and Engineering, Inc., in Gainesville, Florida. Rainfall mass, pH, and specific conductance also were measured onsite. Dry deposition was estimated based on wet/dry deposition ratios derived by Baker [1991] for Florida from dry bucket (base cations and  $Cl^-$ ) and ambient aerosol (S and N species) measurements conducted as part of FADMP.

Groundwater and lakewater samples were collected every 6 weeks from each lake basin and analyzed for  $SiO_2$ , dissolved organic carbon (DOC), dissolved inorganic carbon (DIC),  $F^-$ , and total dissolved Fe, Al, and Mn in addition to the suite of physical and chemical characteristics measured for precipitation. Five or six surficial aquifer wells were sampled routinely and synoptic surveys of about 20 wells at each lake were conducted semiannually. Lake samples were collected 1.5 m below the lake surface with a peristaltic pump. During periods when Lake Five-O was thermally stratified a second sample was collected below the thermocline, approximately 2 m from the lake bottom. Groundwater was sampled using a peristaltic pump where the depth to the water table permitted. At Lake Five-O this depth was too great for some wells, and they were sampled using Teflon-lined bailers dedicated to the study. Groundwater samples were collected after withdrawing at least 3 times the standing water volume in the well, and after the specific conductance of the collected groundwater had stabilized to within  $1 \mu S \text{ cm}^{-1}$ . Groundwater samples collected at Lake Five-O were filtered in the laboratory (0.2- $\mu m$  Nuclepore membrane filter) to minimize contamination caused by handling the samples in the field. Almost all Lake Barco groundwater samples were sampled by peristaltic pump, and filtration (0.2- $\mu m$  Nuclepore membrane filter) was performed in the field using in-line filters.

### Analytical

Analytical protocols (sampling, preservation, and analysis) followed analytical and quality assurance/quality control guidelines for dilute surface waters [U.S. Environmental Protection Agency (EPA), 1987; Drouse et al., 1986]. ANC was measured by Gran titration [U.S. EPA, 1987]. Anions were measured by micromembrane suppressed ion chromatography (IC) and major cations were measured by inductively coupled argon plasma emission spectroscopy (ICP, species:  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$ ) and atomic absorption spectrophotometry (AAS; species:  $K^+$ ).  $NH_4^+$  was measured colorimetrically using an automated phenate method, and pH was measured using an Orion Ross electrode. Carbon species were measured by infrared detection after conversion to the inorganic form. Al was measured by AAS with graphite furnace, and Fe and Mn were measured by

ICP.  $\text{SiO}_2$  was measured colorimetrically by the automated molybdate blue method, and  $\text{F}^-$  was measured by ion selective electrode.

## RESULTS

### Hydrology

The distribution of hydraulic head in the surrounding aquifers can be used to develop a preliminary interpretation of the groundwater flow patterns around Lakes Five-O and Barco. The areal head distribution around each lake is defined by the elevation of the water table in the surrounding surficial aquifer. The vertical head distribution in each basin is defined by the head in wells completed at different depths between the water table and the upper Floridan aquifer.

At Lake Five-O the groundwater flow pattern and high hydraulic conductivities in the surficial aquifer ( $8\text{--}74 \text{ m d}^{-1}$ ) imply large quantities of groundwater inflow [Andrews *et al.*, 1990]. Elevational gradients in the water table for October 4, 1989, were toward the lake around its entire perimeter, indicating a centripetal pattern of groundwater flow toward the lake (Figure 2a). Gradients were steepest around the southern half of the lake and relatively flat to the northwest. This flow pattern was consistent during the first year of the study. Cross-sectional flow patterns indicate further that Lake Five-O receives large quantities of groundwater inflow. At the southern edge of the lake, Lake Five-O intercepts groundwater inflow from most of the entire thickness of the surficial aquifer (Figure 3a). To the north of the lake, however, the lower head gradients toward the lake reduce the flow intercepted by the lakebed. Whether inflow or downward leakage occurs along the gradual ledge in the lake bottom on the north side of Lake Five-O cannot be determined.

The vertical head distribution around Lake Five-O and the large quantities of inflow likely to be received by Lake Five-O imply that the lake also loses considerable amounts of water through leakage to the adjacent and underlying aquifers in addition to evaporative losses. Much of this leakage loss appears focused in the deepest part of the lake where contact between the lake bottom and intermediate confining unit is inferred. Seismic reflection profiles show evidence of subsidence in the intermediate confining unit beneath the lake [Andrews *et al.*, 1990]. These collapse features can enhance the vertical hydraulic connection between the lake, the intervening collapsed materials, and the transmissive Upper Floridan aquifer [Lee *et al.*, 1991].

For Lake Barco, leakage predominates over groundwater inflow. In general, groundwater inflow from the surficial aquifer enters one end of the lake (the northern perimeter) and leakage losses occur along the other end (the southern perimeter). Water-table gradients for September 20, 1989 (Figure 2b) generally are representative of conditions observed for the first 9 months of the study. Shallow groundwater flow within the northern half of the Lake Barco basin is toward the lake (Figure 2b). However, actual inflow is constrained to the northeastern side of the lake. As indicated by water table elevations below lake stage, some localized outflow, rather than inflow, occurs along the northern and northwestern margins of the lake. Inflow gradients toward Lake Barco were probably below normal during this period of the study, as rainfall and therefore recharge to the surficial

aquifer were well below normal. Steep water table gradients away from Lake Barco occur along the southern and, in particular, the southeastern margins of the lake (Figure 2b). Overall, the pattern of groundwater flow is away from Lake Barco and toward three nearby lakes, which all lie at lower altitudes.

The vertical head distribution along a cross section through Lake Barco more clearly illustrates the pattern of groundwater outflow occurring from both the apparent inflow as well as the outflow sides of the lake (see transect line in Figure 2b). Groundwater inflow that moves laterally toward the lake from the northern half of the basin is not intercepted by the lakebed along transect B-B'. Instead, this flow bypasses beneath the lake where it is augmented by leakage through the lake bottom (Figure 3b). Compared to the outflow side, vertical head values are always higher on the apparent inflow side of Lake Barco, causing lateral groundwater flow underneath the lake. Groundwater inflow occurs along the northeast margin for approximately 12% of the total circumference of the lake. Vertical head gradients in this area near Lake Barco have not been measured, and the depth to which inflow may occur along the lake bottom cannot be inferred.

Lower limits of the groundwater inflow and leakage from each lake were estimated from net flow calculations and the probable errors in  $Q_{\text{net}}$  (Table 1). Although this analysis does not yield the absolute magnitude of groundwater flow, it can be used to estimate lower limits of  $Q_i$  and  $Q_o$ . For intervals where  $Q_{\text{net}}$  is positive, groundwater inflow exceeds leakage, and  $Q_{\text{net}}$  defines the minimum groundwater inflow over the interval. Likewise, when  $Q_{\text{net}}$  is negative, it defines the minimum leakage. This analysis is sensitive to the period of record used. Because precipitation at Lake Barco was considerably below normal during the study period (88 cm over 402 days compared to the 30-year average of 134 cm), long-term net  $Q_i$  is probably underestimated by this method; conversely, because precipitation at Lake Five-O was somewhat above normal (176 cm over 342 days), long-term net  $Q_i$  is probably overestimated.

Error in  $Q_{\text{net}}$  is the aggregate of errors inherent in estimating  $P$ ,  $E$ , and  $\Delta V$  (equation (5)). Error in monthly  $P$  and  $\Delta V$  terms for both lakes was assumed to be  $\pm 10$  and  $\pm 5\%$ , respectively [Winter, 1981]. The error in monthly evaporation estimates is not known but is assumed to be  $\pm 20\%$ . Monthly pan-to-lake coefficients can deviate significantly from the annual pan-evaporation coefficient for a lake due to monthly variations in climate and stored heat in the lake. For example, monthly pan-evaporation coefficients derived from energy-budget analyses for two lakes in humid areas of the eastern United States, Lake Lucerne, Florida (T. M. Lee, and A. Swancar, unpublished manuscript, 1990), and Pretty Lake, Indiana [Ficke, 1971], deviated from the commonly used annual pan-evaporation coefficient of 0.7 [Linsley *et al.*, 1975] by  $-28$  to  $+34\%$ . The use of monthly pan-evaporation coefficients derived for Lake Lucerne is believed to be superior to using an annual average pan-evaporation coefficient and should significantly reduce the uncertainty in our monthly estimates of evaporative losses from Lakes Five-O and Barco.

For both lakes, errors attributed to  $P$ ,  $E$ , and  $\Delta V$  are too small to account for all the monthly  $Q_{\text{net}}$  values, and significant groundwater seepage is indicated (Table 1). Except for November and June, the error in monthly  $Q_{\text{net}}$  at

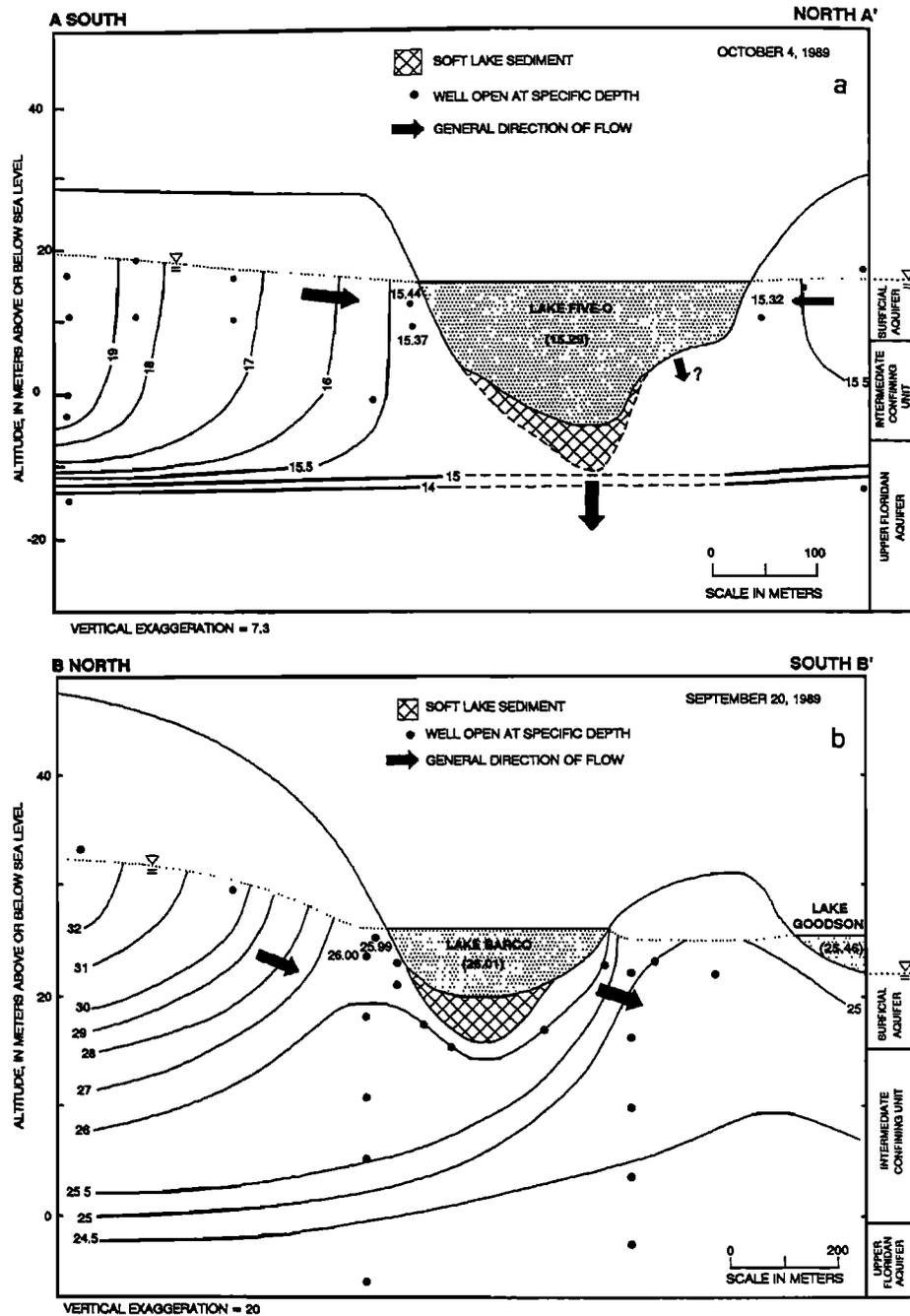


Fig. 3. Vertical distribution of hydraulic head (in feet) showing generalized flow at (a) Lake Five-O (October 4, 1989) and (b) Lake Barco (September 20, 1989). Cross-sectional lines shown in Figure 2. Head measurements from selected wells are included in Figure 3b to illustrate the slight hydrologic depression along the immediate, northern periphery of Lake Barco.

Lake Five-O generally is much smaller than  $Q_{net}$  itself. In November and June, the aggregated error exceeds  $Q_{net}$ , and we cannot clearly define whether net flow actually occurred and in what direction it occurred. Potential errors comprise a higher percentage of  $Q_{net}$  for Lake Barco, yet exceed  $Q_{net}$  only for 2 months (December and February; Table 1). Net flow calculations indicate that at least 38 to 46% of the total inflow to Lake Five-O was from groundwater inflow. For Lake Barco, net  $Q_i$  was substantially smaller, ranging from 5 to 14% of the total inflow between September 1988 and November 1989 (Table 1). Although the differences in net  $Q_i$

estimates as a result of errors were nearly identical for both lakes (8 to 9%), because of the smaller magnitude of net  $Q_i$ , potential errors produce a nearly threefold range in net  $Q_i$  for Lake Barco, whereas the relative difference in estimates of net  $Q_i$  in Lake Five-O is only 21%.

The importance of groundwater to Lake Five-O's hydrologic budget also is shown by directly comparing cumulative precipitation to changes in lake stage (Figure 4). When lake stage increases more rapidly than cumulative precipitation (or increases in the absence of additional rainfall), that portion of the hydrograph clearly defines net inflow. Such

TABLE 1a. Net Flow Hydrologic Budget Analysis for Lake Five-O

Date	Precipitation	Evaporation	Lake Volume	$\Delta V$	Net Flow	Residual Error	$Q_{net} + RE^*$	$Q_{net} - RE^*$
July 19, 1988			1,059,400					
Aug. 19, 1988	15,900	13,900	1,072,400	13,000	11,000	3300	14,300	7700
Sept. 19, 1988	38,800	14,300	1,103,000	30,600	6100	5100	11,200	1000
Oct. 19, 1988	9000	12,000	1,140,200	37,200	40,200	3200	43,400	37,000
Nov. 19, 1988	4900	8400	1,137,600	-2600	900	1800	2700	900
Dec. 20, 1988	3,400	5,500	1,118,200	-19,400	-17,300	=500	-15,800	-18,800
Jan. 20, 1989	8200	4600	1,094,700	-23,500	-27,100	1700	-25,400	-28,800
Feb. 20, 1989	1800	4800	1,062,700	-32,000	-29,000	1900	-27,100	-30,900
March 20, 1989	9000	7200	1,036,000	-26,700	-28,500	2200	-36,300	-30,700
April 20, 1989	27,100	14,000	1,036,400	400	-12,700	3900	-8800	-16,600
May 20, 1989	5900	16,000	1,019,100	-17,300	-7200	3400	-3800	-10,600
June 20, 1989	51,000	15,500	1,059,100	40,000	6300	10,800	-1800	
July 20, 1989	36,500	14,400	1,148,400	89,300	67,200	6400	73,600	60,800
Aug. 20, 1989	18,400	14,000	1,189,200	40,800	36,400	3900	40,300	32,500
Totals	229,900	144,600		129,800	44,500	44,600	89,100	-100
Net $Q_i$					166,300		196,400	139,000
Net $Q_o$					-121,800		107,300	-139,100
Net $Q_i$ , %					42		46	38

\* RE is residual error.

Net flow defined as  $\Delta V - (P - E)$ . All flows in  $m^3$ . Net flow >0 defines net  $Q_i$ ; net flow <0 defines net  $Q_o$ .

was the case from May 29 through August 26, 1989, when stage in Lake Five-O increased at a rate faster than supported by direct precipitation (Figure 4a). By the end of August 1989, stage in Lake Five-O had increased 0.58 m beyond total precipitation for the period (0.93 m). Excluding both evaporation and leakage during this period, the increase in stage that is unsupported by direct precipitation to Lake Five-O equates to a minimum of 38% inflow from groundwater. Precipitation at Lake Barco was subnormal for the same period, and stage in the lake has declined steadily since the study began (Figure 4b).

Precipitation Chemistry

Wet deposition chemistry analyses are available for Lake Barco from July through early December 1989 and for Lake

Five-O from May through November 1989. Volume-weighted mean pH of wet deposition was 4.50 and 4.62 for Lake Barco and Lake Five-O, respectively, which is similar to wet-only measurements made in Gainesville (56 km from Lake Barco; pH = 4.60) and Caryville (41 km from Lake Five-O; pH = 4.66) between 1983 and 1988 as part of FADMP (E. Edgerton, personal communication, 1990).

Dry/wet deposition ratios for major ions developed by Baker [1991] were applied in conjunction with the 1983-1988 volume-weighted mean (VWM) wet concentrations to estimate VWM total concentrations at the Gainesville and Caryville FADMP sites (Figure 5).  $H^+$  was calculated as the difference between the sum of the strong acid anions [ $C_A$ ] and [ $C_B$ ] + [ $NH_4^+$ ]. One potentially significant difference between site-specific measurements made at Lake Five-O

TABLE 1b. Net Flow Hydrologic Budget Analysis for Lake Barco

Date	Precipitation	Evaporation	Lake Volume	$\Delta V$	Net Flow	Residual Error	$Q_{net} + RE^*$	$Q_{net} - RE^*$
Sept. 29, 1988			616,300					
Oct. 17, 1988	3700	7300	616,800	500	4100	1500	5600	2600
Nov. 10, 1988	6300	8200	619,900	3100	5000	1800	6800	3200
Dec. 15, 1988	12,800	8200	625,100	5200	600	2100	2700	-1500
Jan. 26, 1989	4600	7900	618,900	-6200	-2900	1700	-1200	-4600
Feb. 20, 1989	0	4900	614,800	-4,100	800	1000	1800	-200
March 20, 1989	6300	8100	602,000	-12,800	-10,000	2000	-8000	-12,000
April 20, 1989	4000	17,000	584,200	-17,800	-4800	3500	-1300	-8300
May 20, 1989	3000	19,200	556,500	-27,700	-11,500	4100	-7400	-15,600
June 20, 1989	10,800	17,500	536,900	-19,600	-12,900	3800	-9100	-16,700
July 20, 1989	13,100	15,200	521,800	-15,100	-13,000	3400	-9600	-16,400
Aug. 20, 1989	15,500	14,700	508,800	-13,000	-13,800	3400	-10,400	-17,200
Sept. 20, 1989	14,500	15,200	500,800	-8000	-7300	3400	-3900	-10,700
Oct. 20, 1989	7100	12,300	484,700	-16,100	-10,900	2700	-8200	-13,600
Nov. 5, 1989	300	5200	473,400	-11,300	-6400	1200	-5200	-7600
Totals	102,000	161,900		-142,900	-83,000	35,600	-47,400	-118,600
Net $Q_i$					10,500		16,900	5800
Net $Q_o$					-83,500		64,300	124,400
Net $Q_i$ , %					9		14	5

\* RE is residual error.

Net Flow defined as  $\Delta V - (P - E)$ . All flow in  $m^3$ . Net flow >0 defines net  $Q_i$ ; net flow <0 defines net  $Q_o$ .

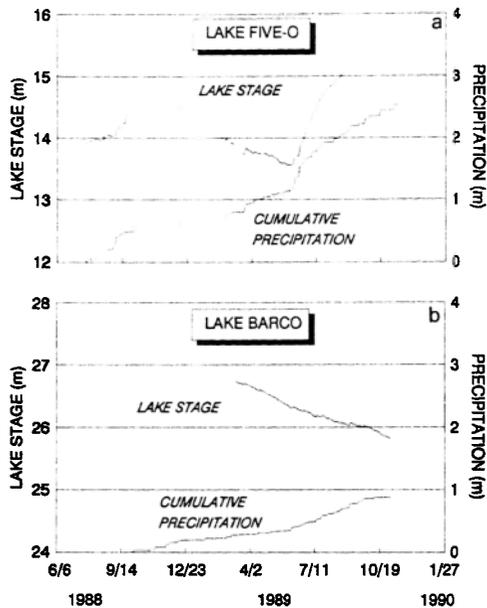


Fig. 4. Cumulative precipitation and lake stages in (a) Lake Five-O and (b) Lake Barco. Start date for cumulative precipitation coincides with the first point in time lake stage was measured.

and long-term FADMP measurements made at Caryville concerns  $\text{Cl}^-$  and  $\text{Na}^+$  measurements; by virtue of being closer to the Gulf of Mexico (30 km compared to 59 km for Caryville), VWM wet concentrations of these two ions are nearly 50% higher at Lake Five-O. However, the period of record available to date at Lake Five-O is only about 7 months, and the significance of these differences can be evaluated fully only when a longer record of precipitation chemistry at Lake Five-O has been developed.

#### Lake Chemistry

Routine monitoring of lakewater chemistry in Lake Five-O began in late January 1989 and in Lake Barco in May 1989. Bimonthly lakewater chemistry measurements for both lakes also are available from June 1988 through April 1989 [Pollman *et al.*, 1990]. Average chemistry for both lakes is summarized in Figure 5. Typical of other seepage lakes in the Panhandle and the Greenhead Slope/New Hope Ridge regions, the chemistry of Lake Five-O is extremely dilute (mean conductivity =  $16.0 \mu\text{S cm}^{-1}$ ; cf. Kanciruk *et al.* [1986] and Linthurst *et al.* [1986]). Overall ion chemistry is heavily influenced by marine aerosols, with  $\text{Cl}^-$  and  $\text{Na}^+$  the dominant anion and cation.  $[\text{Cl}^-]$  averages  $91 \mu\text{eq L}^{-1}$ , of which  $68 \mu\text{eq L}^{-1}$  are derived from marine aerosols (using  $\text{Cl}^-$  to define marine inputs of base cations).  $\text{SO}_4^{2-}$  concentrations averaged  $44 \mu\text{eq L}^{-1}$ .

Characteristic of many lakes in north central Florida, the overall ionic strength of Lake Barco is more concentrated than that in Panhandle seepage lakes. To a large degree, these differences appear related to higher rates of evaporative concentration in north central Florida compared to the Panhandle [Pollman and Canfield, 1991]. As in Lake Five-O, the effect of marine aerosols on Lake Barco's chemistry is profound (Figure 5).  $\text{SO}_4^{2-}$  concentrations were similar to  $\text{Cl}^-$  concentrations, averaging about  $140 \mu\text{eq L}^{-1}$ .  $\text{Cl}^-$  concentrations in Lake Barco averaged  $230 \mu\text{eq L}^{-1}$ , which

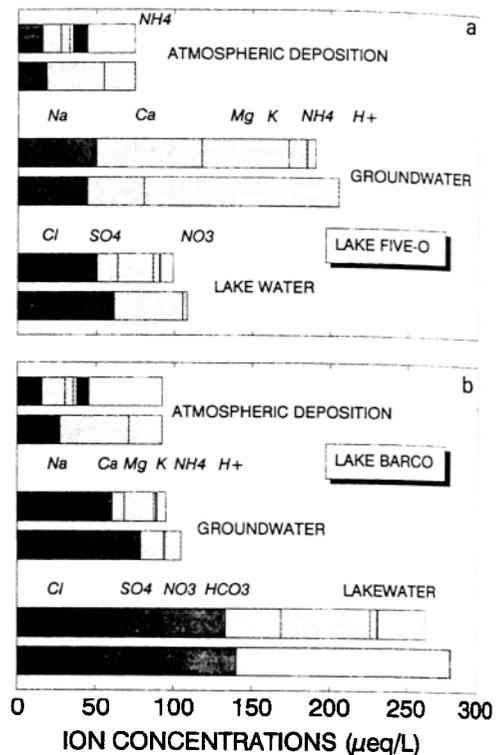


Fig. 5. Ion bar charts of long term total (wet and dry) precipitation, shallow groundwater, and lakewater chemistry for (a) Lake Five-O (Well 4) and (b) Lake Barco (WTB-12). Wet precipitation chemistry from 1983–1988 for Caryville (Figure 5a) and Gainesville (Figure 5b) (E. Edgerton, personal communication, 1990), lakewater chemistry from June 1988 through November 1989, and groundwater chemistry from February 1989 through November 1989.

is more than twice as the average concentration in Lake Five-O. Approximately  $156 \mu\text{eq L}^{-1}$  of the base cations are derived from marine aerosols. DOC in Lake Barco is even lower than that in Lake Five-O, averaging  $0.59 \text{ mg L}^{-1}$ .

Seasonal dynamics of major ions in acidic seepage lakes in Florida are not well understood. The only previous effort to conduct continuous, long-term monitoring was by Baker [1984], who studied McCloud Lake near Lake Barco between 1980 and 1982. Baker's results showed that lakewater constituents derived primarily from precipitation, namely,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ , varied with changes in lake volume as lake volume increased, concentrations of these constituents declined. A similar type response is observed in Lake Barco (Figure 6b).  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations increased by about 20 to  $30 \mu\text{eq L}^{-1}$  as stage in Lake Barco fell from September 1988 through November 1989. As mentioned previously, north central Florida experienced a drought during this period, and the volume in Lake Barco declined by 23%. Similar, consistent changes in base cations (other than  $\text{Na}^+$ ),  $\text{H}^+$ , and ANC are not as evident (Figure 7b). Ion concentrations in Lake Five-O were much more stable, in part because such extreme drought conditions were not observed in the Panhandle (Figures 7a and 8a). In addition, the mean depth of Lake Five-O is approximately twice that of Lake Barco; thus there is more ionic "inertia" to overcome in order to produce the same changes in concentration that were observed in Lake Barco.

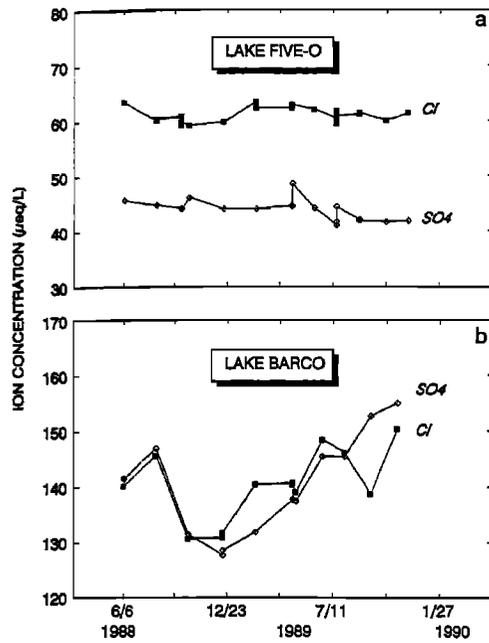


Fig. 6.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations ( $\mu\text{eq L}^{-1}$ ) in (a) Lake Five-O and (b) Lake Barco from June 1988 through November 1989. Plots include data collected from both lakes from June 1988 through April 1989 by Pollman et al. [1990].

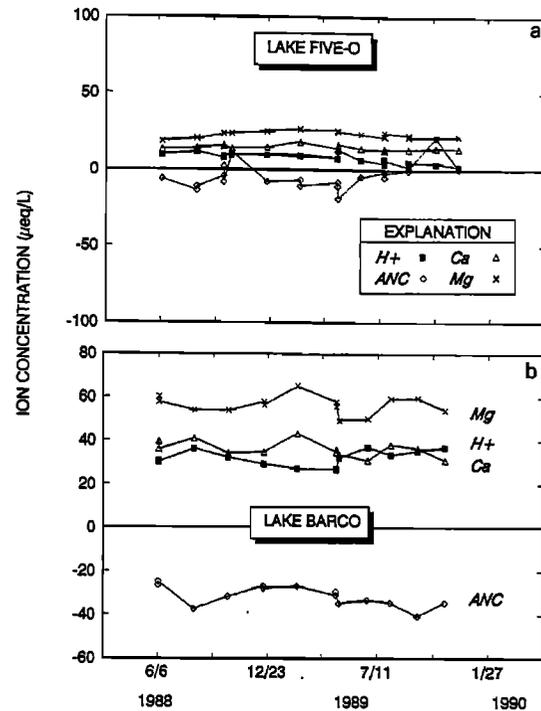


Fig. 7.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ , and ANC concentrations ( $\mu\text{eq L}^{-1}$ ) in (a) Lake Five-O and (b) Lake Barco from June 1988 through November 1989. Plots include data collected from both lakes from June 1988 through April 1989 by Pollman et al. [1990].

Groundwater Chemistry

Concentrations of shallow groundwater at both lakes were surprisingly dilute. Specific conductance at inflow wells averaged  $28.2 \mu\text{S cm}^{-1}$  for Lake Five-O (Wells 4, 5, 6.1, 7, 15, and 18) and  $14.2 \mu\text{S cm}^{-1}$  for Lake Barco (Well WTB-12). Inflow wells were selected on the basis of water table elevations in conjunction with  $\text{Cl}^-$  concentrations; proximal, upgradient wells with  $[\text{Cl}^-]$   $10 \mu\text{eq L}^{-1}$  or more lower than lakewater concentrations were considered representative inflow wells (Figures 2 and 8). At Lake Five-O the thickness of the unsaturated zone where the suite of inflow wells were sited is typically more than 7 m; for Well WTB-12 in Lake Barco, the depth to the water table is about 2.9 m. Consistent with low CEC and low base saturation in the surficial soils, base cation concentrations are low and ANC concentrations are less than  $10 \mu\text{eq L}^{-1}$ . Al and Fe mobilization was not significant and concentrations averaged less than 15 and  $10 \mu\text{eq L}^{-1}$ , respectively.  $C_B$  concentrations were higher in the Lake Five-O inflow wells, presumably because of the longer vertical distance traveled by percolating precipitation or, as is more likely, because of base cations released subsequent to logging of the watershed (Normann and Likens, 1979).

The low concentrations of  $C_B$  and ANC observed in the Lake Barco inflow well are not consistent with earlier measurements of Baker [1984] of the chemistry of in-seepage to McCloud Lake. Baker measured total base cation concentrations ( $C_B = 198 \mu\text{eq L}^{-1}$ ) in in-seepage (using in situ seepage meters) that were approximately  $100 \mu\text{eq L}^{-1}$  higher than those measured in Well WTB-12 ( $C_B = 89 \mu\text{eq L}^{-1}$ ), although  $\text{H}^+$  ( $1.1$  compared to  $5.0 \mu\text{eq L}^{-1}$ ) and strong acid anion concentrations ( $83 \mu\text{eq L}^{-1}$  compared to  $93.3 \mu\text{eq L}^{-1}$ ) were rather similar in both groundwaters. The differences in measured  $C_B$  between the two neighboring

lakes may reflect in part an analytical artifact in Baker's  $\text{Ca}^{2+}$  measurements. The computed cation:anion balance for our measurements of Well WTB-12 agrees within 10% (i.e.,  $[\text{C}_B] + [\text{H}^+] + [\text{NH}_4^+] \approx [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{HCO}_3^-]$ ). Although Baker did not measure ANC (and, indirectly,  $\text{HCO}_3^-$ ), we can calculate an approximate value for  $\text{HCO}_3^-$  based on pH and an assumed value for the partial pressure of  $\text{CO}_2$  that the sample was in equilibrium with at the time of analysis [Stumm and Morgan, 1981]. Laboratory pH was conducted on samples exposed to the atmosphere (E. Edgerton, personal communication, 1990), and  $P_{\text{CO}_2}$  was assumed to range from 1 to 10 times the atmospheric partial pressure. Using this approach, the cation:anion ratio for Baker's data ranges from 1.5 to 2.3, which equates to a cation excess ranging from 57 to  $111 \mu\text{eq L}^{-1}$ . Much of that excess may be due to overestimation of  $\text{Ca}^{2+}$ , which averaged  $92 \mu\text{eq L}^{-1}$  for McCloud Lake in-seepage compared to only  $9 \mu\text{eq L}^{-1}$  in Lake Barco shallow well water. (When we compare average  $\text{Ca}^{2+}$  concentrations reported by Baker [1984] for McCloud lake itself with recent data collected as part of the PIRLA project and by Pollman et al. [1990] using ELS sampling and analytical protocols, similar differences appear. For example, Baker reports  $\text{Ca}^{2+}$  concentrations ranging from 63 to  $118 \mu\text{eq L}^{-1}$  in 1981–1982 compared to concentrations ranging from 35 to  $45 \mu\text{eq L}^{-1}$  for 1985 ( $n = 2$ ) and 1988–1989 ( $n = 2$ ). Ratios of  $\text{Ca}^{2+}:\text{Cl}^-$  also are high in comparison ( $0.22$ – $0.79$  compared to  $0.23$ – $0.27$ ) and, because  $\text{Cl}^-$  concentrations across the studies are rather similar, suggest possible positive bias with  $\text{Ca}^{2+}$  concentrations reported by Baker.) Since surficial sands in both watersheds are very similar (highly weathered typical quartzipsamments), it seems unlikely that one watershed would have a significant source of  $\text{Ca}^{2+}$  and the other would not.

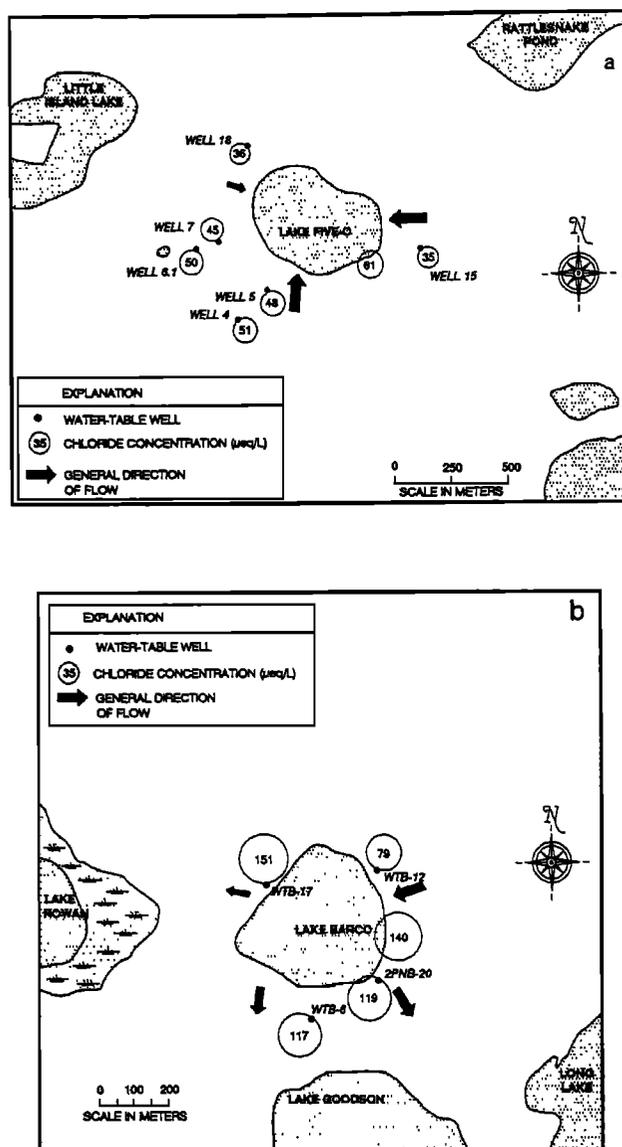


Fig. 8. Location of wells used to define inflow shallow groundwater chemistry. Inflow wells were selected on the basis of head gradients (Figure 2) and  $\text{Cl}^-$  concentrations in groundwater compared to lakewater. Lower panel shows both inflow (WTB-12) and outflow (WTB-17, WTB-6, and 2 PNB-20) wells for Lake Barco.

$\text{NO}_3^-$  concentrations were rather high in Lake Five-O shallow groundwater (average concentration =  $125 \mu\text{eq L}^{-1}$ ), whereas  $\text{NO}_3^-$  is virtually absent from Lake Barco shallow groundwater ( $0.6 \mu\text{eq L}^{-1}$  at Well WTB-12). Compared to Lake Barco,  $\text{NO}_3^-$  concentrations in McCloud Lake in seepage also are elevated, although the concentrations are still considerably lower ( $2.1 - 8.7 \mu\text{eq L}^{-1}$ ) [Baker, 1984] than those in Lake Five-O. High  $\text{NO}_3^-$  concentrations were a consistent feature of other shallow water table wells at Lake Five-O and in all likelihood reflect initial devegetation and reduced vegetative uptake of nutrients similar to patterns observed in Hubbard Brook following clear cutting [Bormann and Likens, 1979].  $\text{NH}_4^+$  concentrations at both watersheds are virtually nil ( $<1 \mu\text{eq L}^{-1}$ ). Although the reasons for such differences between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  depletion in the shallow groundwater at Lake Five-O are unclear,  $\text{NH}_4^+$  is readily adsorbed by soils and can be nitrified in

acidic soils to  $\text{NO}_3^-$ , while  $\text{NO}_3^-$  is highly mobile and is readily leached [de Haan and Zwerman, 1978].

#### Enrichment Factor Calculations

Enrichment factors, in which measured concentrations in lakewater are compared to concentrations predicted from atmospheric deposition, have been used recently to infer the extent and mechanisms of ANC generation in both drainage and seepage lakes [e.g., Baker et al., 1986, 1988a; Pollman and Canfield, 1991; Lin et al., 1987; Lee and Schnoor, 1988]. Enrichment factor calculations typically use a geochemical tracer to normalize for changes in lakewater concentration due to evaporative concentration. Most often this tracer is  $\text{Cl}^-$  [Lin et al., 1987; Baker et al., 1988a; Pollman and Canfield, 1991] because of its generally conservative geochemical behavior [Feth, 1981]. The surficial, unconsolidated deposits are highly weathered and leached and, for watersheds that are not disturbed by fertilizing and other cultural inputs, there are no apparent sources of  $\text{Cl}^-$  other than atmospheric deposition.

Ion enrichment or depletion was calculated by using ratios of  $\text{Cl}^-$  in lakewater to total deposition to predict lakewater concentrations for a particular constituent,  $i$ , as a function of atmospheric loadings:

$$[i]_{\text{exp}} = [i]_d \times [\text{Cl}^-]_{\text{lw}} / [\text{Cl}^-]_d \quad (6)$$

where  $[i]_{\text{exp}}$  is the expected or predicted lakewater concentration and  $[i]_d$  is the VWM concentration in precipitation of constituent  $i$ ;  $[\text{Cl}^-]_{\text{lw}}$  and  $[\text{Cl}^-]_d$  are the concentrations of  $\text{Cl}^-$  in lakewater and precipitation, respectively. The enrichment factor (EF) then is simply the ratio of the observed to the expected lakewater concentration, and the magnitude of ion reaction is the difference between  $[i]_{\text{lw}}$  and  $[i]_{\text{exp}}$ . Enrichment factors can be calculated in a similar manner for groundwater.

Separation of ANC production into shallow groundwater and in-lake components was based on estimated groundwater inflows derived from  $\text{Cl}^-$  balances. The assumption that  $\text{Cl}^-$  is conservative can be used to advantage in conjunction with the hydrologic mass balance to solve explicitly for  $Q_i$  and  $Q_o$  [cf. Stauffer, 1985]. Assuming conservative behavior, the mass balance equation for  $\text{Cl}^-$  is

$$\Delta S_{\text{Cl}} = L_{\text{Cl}} \times A + Q_i \times [\text{Cl}^-]_{\text{gw}} - Q_o \times [\text{Cl}^-]_{\text{lw}} \quad (7)$$

where  $S_{\text{Cl}}$  is the mass of  $\text{Cl}^-$  stored in the lake (meq).  $L_{\text{Cl}}$  is the areal atmospheric loading rate of  $\text{Cl}^-$  to the lake ( $\text{meq m}^{-2} \text{yr}^{-1}$ ),  $A$  is the lake surface area ( $\text{m}^2$ ), and  $[\text{Cl}^-]_{\text{gw}}$  is the concentration of  $\text{Cl}^-$  in groundwater inflow. Under steady state conditions, (1) and (7) represent two equations and two unknowns,  $Q_i$  and  $Q_o$ , which can be solved explicitly.

Steady-state values for  $Q_i$  and  $Q_o$  for both lakes were calculated as follows. Long-term deposition at Gainesville (1983–1988) was used to estimate atmospheric inputs for Lake Barco. Because  $\text{Cl}^-$  deposition appears to be significantly higher at Lake Five-O than at Caryville, VWM concentrations measured onsite were used to estimate atmospheric inputs at Lake Five-O. Concentrations measured at inflow wells (Figure 8) were used to estimate  $[\text{Cl}^-]_{\text{gw}}$ . Resultant steady state  $Q_i$  estimates equate to 43 and 13% of total inflow to Lake Five-O and Lake Barco, which agree

TABLE 2a. Enrichment Factor Calculations for Lake Five-O

Ion	Groundwater	Precipitation Loading	Lake Water	EF <sub>gw</sub>	EF <sub>lw</sub>	ANC Flux	
						Groundwater	In-Lake
Ca <sup>2+</sup>	67.8	16.8	17.3	3.81	0.70	56.9	-68.2
Mg <sup>2+</sup>	55.8	10.7	23.1	4.90	1.45	50.6	-39.9
Na <sup>+</sup>	50.1	32.4	49.9	1.46	1.04	17.9	-14.9
K <sup>+</sup>	11.1	3.5	3.8	2.95	0.72	8.4	-10.5
C <sub>B</sub>	184.8	63.5	94.0	2.74	1.00	133.8	-133.5
NH <sub>4</sub> <sup>+</sup>	0.6	17.8	0.8	0.03	0.03	-20.8	-17.3
NO <sub>3</sub> <sup>-</sup>	124.5	30.9	2.8	3.80	0.06	-104.5	168.5
SO <sub>4</sub> <sup>2-</sup>	36.9	70.2	44.1	0.49	0.42	42.9	46.4
Cl <sup>-</sup>	44.0	41.4	61.3	1.00	1.00	0.0	0.0
ANC*	-19.9	-61.3	-13.3				
Σ ANC flux						51.5	64.0

\*ANC calculated as C<sub>B</sub> + NH<sub>4</sub><sup>+</sup> - C<sub>A</sub>.

Lake Five-O atmospheric deposition estimates are derived from on-site measurements, while Lake Barco atmospheric deposition estimates are derived from Gainesville data from 1983-1988. Evaporation losses used in calculation of Q<sub>i</sub> assume pan-evaporation coefficient of 0.75 (T. M. Lee and A. Swancar, unpublished manuscript, 1990). Groundwater EF calculations based on chemistry measured for inflow wells 4, 5, 6.1, 7, 15, and 18 (Lake Five-O) and WTB-12 (Lake Barco). (Q<sub>i</sub> and Q<sub>o</sub> estimates used to calculate ANC fluxes are based on coupled Cl<sup>-</sup> and water balance (see text), Estimates for steady state Q<sub>i</sub> are 43% and 13% of total inflow for Lake Five-O and Lake Barco, respectively. Groundwater and lakewater concentrations in μeq L<sup>-1</sup>; precipitation loadings and flux estimates are in meq m<sup>-2</sup> yr<sup>-1</sup>; EF values are dimensionless.

reasonably well with estimates of net Q<sub>i</sub> of 42 and 9% for 1988-1989 (Table 1).

One disadvantage to the use of Cl<sup>-</sup> as a geochemical tracer to define Q relates to the strength of the signal. The robustness of the tracer as an estimator of Q is directly related to the difference between groundwater and lakewater concentrations of the tracer. When this difference (ΔCl<sup>-</sup>) is not large (as is the case for Lake Five-O), small changes in ΔCl<sup>-</sup> translate to rather large changes in Q<sub>i</sub>. This approach also is sensitive to errors in estimated deposition as well as errors in precipitation and evaporation.

Previous EF analyses by Baker et al. [1988a] and Pollman and Carfield [1991] indicated that anion retention (SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) dominates ANC production in "undisturbed" Florida seepage lakes. Our calculation for Lake Five-O and Lake Barco support that basic conclusion. Overall EF values for C<sub>B</sub> show virtually no net base cation enrichment in either Lake Five-O or Lake Barco (EF<sub>lw</sub> in Table 2), although the enrichment of individual base cations varies significantly. Mg<sup>2+</sup> is enriched by about 45% in both lakes, while Ca<sup>2+</sup> and K<sup>+</sup> both show net depletion. Na<sup>+</sup> enrichment is marginal (4 to 15%) and not significant relative to analytical

uncertainty and uncertainty in wet and dry deposition estimates [cf. Baker et al., 1988a]. NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were almost wholly depleted in both lakes, with estimated losses of 94 to 99% for NO<sub>3</sub><sup>-</sup> and 97 to 99% for NH<sub>4</sub><sup>+</sup>. SO<sub>4</sub><sup>2-</sup> retention was less efficient, with 50% (Lake Barco) to 58% (Lake Five-O) of SO<sub>4</sub><sup>2-</sup> inputs consumed.

Steady state ANC fluxes associated with ion enrichment and depletion in a seepage lake can be calculated as the product of Q<sub>o</sub> and the magnitude of ion reaction (expressed as meq m<sup>-3</sup>) normalized to lake area. Thus the overall flux of ANC due to a particular ion reaction is

$$ANC\ Flux_{lw,i} = [Q_o \times ([i]_{exp,lw} - [i]_{lw})] / A \quad (8)$$

The ion reaction component of (8) implicitly includes contributions from both terrestrial and in-lake processes. Note that base cation enrichment and acid anion depletion contribute to ANC production, whereas base cation depletion and acid anion enrichment contribute to ANC consumption (equation (4)).

In a similar manner, contributions of groundwater inflow to ANC fluxes to the lake are

TABLE 2b. Enrichment Factor Calculations for Lake Barco

Ion	Groundwater	Precipitation Loading	Lake Water	EF <sub>gw</sub>	EF <sub>lw</sub>	ANC Flux	
						Groundwater	In-Lake
Ca <sup>2+</sup>	8.5	19.9	36.2	0.13	0.31	-11.1	-11.3
Mg <sup>2+</sup>	18.6	6.8	56.6	0.84	1.43	-0.7	5.5
Na <sup>+</sup>	60.2	20.0	133.2	0.92	1.15	-1.0	5.8
K <sup>+</sup>	1.3	2.7	4.3	0.15	0.28	-1.5	-1.7
C <sub>B</sub>	88.7	49.4	230.2	0.55	0.80	-14.3	-1.7
NH <sub>4</sub> <sup>+</sup>	0.8	11.2	0.9	0.02	0.01	-7.0	-11.1
NO <sub>3</sub> <sup>-</sup>	0.6	27.7	0.7	0.01	0.00	17.6	27.6
SO <sub>4</sub> <sup>2-</sup>	14.7	48.5	140.1	0.09	0.50	28.2	11.8
Cl <sup>-</sup>	79.0	24.2	140.3	1.00	1.00	0.0	0.0
ANC	-4.9	-39.8	-49.9				
Σ ANC flux						24.5	26.6

See footnotes of Table 2a.

TABLE 3. Sensitivity Analysis of ANC Flux Calculations (Table 2) to Variations in Evaporation and Dry Deposition Estimates

Sensitivity Variable and Percent Change	$Q_i$ , %	Terrestrial			In-Lake		
		$C_B$	$SO_4^{2-}$	$NO_3^-$	$C_B$	$SO_4^{2-}$	$NO_3^-$
<i>Evaporation Sensitivity Analysis</i>							
Lake Five-O							
-20%*	18	39	13	-31	-39	42	70
+20%	57	228	73	-178	-228	51	267
Lake Barco							
-20%*	0	0	0	0	-19	47	53
+20%	37	-56	110	69	22	25	-28
<i>Dry Deposition Sensitivity Analysis</i>							
Lake Five-O							
+50%†	50	169	62	-133	-179	58	219
-50%	35	96	26	-75	-88	34	118
Lake Barco							
+50%†	16	-22	39	25	-5	14	34
-50%	9	-8	18	11	2	9	21

\*Pan coefficient.

†Variation in dry deposition.

All flux estimates in  $\text{meq m}^{-2} \text{ yr}^{-1}$ .

$$\text{ANC Flux}_{gw} = [Q_i \times ([i]_{\text{exp},gw} - [i]_{gw})]/A \quad (9)$$

The component of ion enrichment due solely to in-lake processes can be calculated as the difference between the overall lakewater ANC flux and the groundwater contribution to ion reaction:

$$\text{ANC Flux}_{\text{in-lake}} = [Q_o \times ([i]_{\text{exp},lw} - [i]_{lw}) - Q_i \times ([i]_{\text{exp},gw} - [i]_{gw})]/A \quad (10)$$

In Lake Five-O shallow groundwater the ANC flux due to  $C_B$  enrichment was approximately  $134 \text{ meq m}^{-2} \text{ yr}^{-1}$ . The largest components of this flux resulted from enrichment of  $\text{Ca}^{2+}$  ( $57 \text{ meq m}^{-2} \text{ yr}^{-1}$ ) and  $\text{Mg}^{2+}$  ( $51 \text{ meq m}^{-2} \text{ yr}^{-1}$ ). Though enrichment for  $\text{Na}^+$  was appreciable (46%), its contributions to the ANC flux were comparatively small.  $\text{NO}_3^-$  was greatly enriched (380%) and was a source of acidity ( $105 \text{ meq m}^{-2} \text{ yr}^{-1}$ ), apparently as a result of recent logging.  $\text{SO}_4^{2-}$  retention contributed one third as much to the groundwater flux of ANC as  $C_B$  enrichment. Adsorption isotherms conducted for Lake Five-O soils suggest that terrestrial retention of  $\text{SO}_4^{2-}$  occurs through specific anion adsorption, presumably onto iron sesquioxides [cf. *Rajan*, 1978].

In Lake Barco, net depletion of  $C_B$  was observed in shallow groundwater.  $\text{Na}^+$  essentially was conserved, while  $\text{Ca}^{2+}$  and  $\text{K}^+$  were highly depleted (Table 2).  $\text{SO}_4^{2-}$  retention was the major source of ANC supplied by shallow groundwater ( $28 \text{ meq m}^{-2} \text{ yr}^{-1}$ ).  $\text{NO}_3^-$  retention provided another  $18 \text{ meq m}^{-2} \text{ yr}^{-1}$ , while  $\text{NH}_4^+$  retention contributed about  $7 \text{ meq m}^{-2} \text{ yr}^{-1}$  production of acidity.

In-lake ANC generation in both lakes centers around  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  retention.  $\text{NO}_3^-$  retention was dominant, contributing about  $170 \text{ meq m}^{-2} \text{ yr}^{-1}$  to ANC production in Lake Five-O and  $28 \text{ meq m}^{-2} \text{ yr}^{-1}$  in Lake Barco, while  $\text{SO}_4^{2-}$  retention provided another  $46 \text{ meq m}^{-2} \text{ yr}^{-1}$  in Lake Five-O and  $12 \text{ meq m}^{-2} \text{ yr}^{-1}$  in Lake Barco. Studies by *Perry et al.* [1986] on other Florida softwater lake sediments indicate that dissimilatory  $\text{SO}_4^{2-}$  reduction is the primary removal mechanism for  $\text{SO}_4^{2-}$  diffusing across the sediment-water interface.

One difficulty with our present calculations of ANC fluxes for Lake Five-O is that large in-lake sinks of base cations ( $134 \text{ meq m}^{-2} \text{ yr}^{-1}$ ) must be inferred to account for virtually no net enrichment of  $C_B$  in the water column. Otherwise, Lake Five-O would have appreciably higher concentrations of  $C_B$  than currently observed. In addition, and consistent with our definition of ANC as the difference between  $C_B$  and  $C_A$ , lakewater concentrations of ANC also would be higher because the large influx of groundwater to Lake Five-O carries with it high concentrations of  $\text{NO}_3^-$  that ultimately become a source of ANC as  $\text{NO}_3^-$  is consumed by algal uptake and denitrification. Two phenomena possibly can account for the base cation and  $\text{NO}_3^-$  anomalies. First, and most likely, is that the watershed and the lake are not at steady state and that the lake is experiencing a pulse of cations and  $\text{NO}_3^-$  flushing through the watershed as a result of logging [cf. *Bormann and Likens*, 1979]. Alternatively, sedimentation of seston may be a sink for base cations. For example, *Baker et al.* [1988b] estimated basinwide gross sedimentation rates totaling  $31 \text{ meq m}^{-2} \text{ yr}^{-1}$  for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  in Little Rock Lake, Wisconsin. However, net incorporation of base cations into the sediments will be only a fraction of the gross sedimentation rate as particulate organic matter is mineralized and nutrients are recycled [e.g., *Armstrong et al.*, 1987]. Gross particulate sedimentation in Lake Five-O during summer 1989 was  $151 \text{ g m}^{-2} \text{ yr}^{-1}$ , which is almost identical to rates measured in Little Rock Lake ( $155 \text{ g m}^{-2} \text{ yr}^{-1}$ ) [*Baker et al.*, 1988b]. Thus it seems rather unlikely that in-lake sinks can account for all the inferred losses of  $C_B$ .

Sensitivity analyses were conducted to evaluate the effects of uncertainty in estimating evaporation and dry deposition on terrestrial and in-lake ANC flux estimates for  $C_B$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  (Table 3). Pan evaporation was varied by  $\pm 20\%$ , and because of its inherently large uncertainty, dry deposition was varied by  $\pm 50\%$ .

Variations in pan-evaporation coefficient estimates primarily affected flux estimates for  $\text{SO}_4^{2-}$  and  $C_B$ . Increasing the pan-evaporation coefficient by 20% not only increases estimates of evaporative loss but increases estimates for  $Q_i$  as

well. As a result, even larger in-lake losses of  $C_B$  are calculated for Lake Five-O. For Lake Barco the high estimate of pan evaporation indicates that virtually all  $\text{SO}_4^{2-}$  losses are terrestrial, and no in-lake reduction of  $\text{SO}_4^{2-}$  occurs. Some in-lake mobilization of  $C_B$  is predicted for Lake Barco to compensate for the predicted increase of groundwater depleted in  $C_B$  flowing into the lake. Decreasing the pan-evaporation coefficient by 20% indicates no groundwater inflow to Lake Barco occurs, which would be the case if Lake Barco was mounded above the adjacent groundwater table. However, hydraulic head measurements in the basin clearly demonstrate the occurrence of groundwater inflow, and because  $\text{SO}_4^{2-}$  is depleted in shallow groundwater as well, terrestrial retention of  $\text{SO}_4^{2-}$  clearly contributes ANC to Lake Barco.

Estimates of terrestrial contributions of  $\text{SO}_4^{2-}$  losses to ANC fluxes in both lakes also were sensitive to changes in assumed dry deposition. This sensitivity primarily reflected the effect of variations in dry deposition on calculated  $Q_i$  derived from (1) and (7); estimates of  $Q_i$  increased under the high dry deposition scenario as a direct consequence of the higher deposition rate of  $\text{Cl}^-$ . Actual EF values for individual ions were only marginally influenced by changes in assumed dry deposition because changes in dry deposition were applied simultaneously to all ions. For  $\text{SO}_4^{2-}$ , higher estimates of  $Q_i$  produced higher rates of ANC flux associated with terrestrial retention of  $\text{SO}_4^{2-}$ . Terrestrial  $\text{SO}_4^{2-}$  loss estimates ranged from 26 to 62  $\text{meq m}^{-2} \text{yr}^{-1}$  for Lake Five-O and from 18 to 39  $\text{meq m}^{-2} \text{yr}^{-1}$  for Lake Barco.

Reducing dry deposition by 50% elevates in-lake  $\text{SO}_4^{2-}$  reduction in Lake Five-O to a somewhat more important process compared to terrestrial retention. Estimates of in-lake  $C_B$  and  $\text{NO}_3^-$  fluxes for Lake Five-O also were sensitive to changes in dry deposition estimates (about 90 to 100  $\text{meq m}^{-2} \text{yr}^{-1}$  respectively). In contrast, the magnitude of changes effected by varying dry deposition on estimated in-lake fluxes of  $C_B$  and  $\text{NO}_3^-$  in Lake Barco was less sensitive (7  $\text{meq m}^{-2} \text{yr}^{-1}$  for both parameters) because of (1) the smaller rates of groundwater inflow to and leakage from the lake and (2) the lower concentrations of  $C_B$  and  $\text{NO}_3^-$  in Lake Barco groundwater.

## DISCUSSION

Because consumption of  $\text{SO}_4^{2-}$  is less efficient than  $\text{NO}_3^-$  consumption, the ability to process and remove atmospheric inputs of  $\text{SO}_4^{2-}$  has been regarded as the critical component to ANC regulation in softwater Florida seepage lakes [Baker et al., 1988a]. Our results for Lake Five-O and Lake Barco indicate that terrestrial retention of  $\text{SO}_4^{2-}$  can be at least as important as in-lake retention. Nearly half of the total  $\text{SO}_4^{2-}$  removed from Lake Five-O and its contributing watershed is retained within the soils. In Lake Barco, terrestrial retention of  $\text{SO}_4^{2-}$  is approximately twice the magnitude of in-lake  $\text{SO}_4^{2-}$  reduction. These results are qualitatively consistent with results from the National Streamwater Survey (NSS), which indicate that terrestrial retention of  $\text{SO}_4^{2-}$  is significant in dilute, acidic, clearwater streams in northern Florida [Kaufman et al., 1988]. When all other ion contributions to ANC production are considered, terrestrial and in-lake contributions were equally important in Lake Barco. The same also can be said for Lake Five-O, assuming that steady state conditions apply (Table 2). However, Lake Five-O in all

likelihood is not at steady state, and  $C_B$  and ANC should rise in the lake as  $C_B$  and  $\text{NO}_3^-$  continue to flush into the lake.

Because of their extremely dilute chemistry seepage lakes in the Florida panhandle have been regarded as particularly sensitive to acidic deposition [Baker et al., 1988a; Pollman and Canfield, 1991]. In-lake processes rather than base cation supply from terrestrial weathering and ion exchange were believed to control ANC in softwater, acidic seepage lakes in Florida [Baker et al., 1988a; Pollman and Canfield, 1991]. According to this conceptual model, because  $\text{SO}_4^{2-}$  reduction does not completely remove  $\text{SO}_4^{2-}$  from lakewater, seepage lakes would be sensitive to changes in  $\text{SO}_4^{2-}$  deposition. This perception of sensitivity was predicated on two relatively untested assumptions regarding groundwater chemistry and inflow rates. The first was derived from studies of in-seepage at McCloud Lake [Baker, 1984] that indicated shallow groundwater carried appreciable quantities of base cations and ANC. Because (1) the soils in the McCloud Lake watershed (typic quartzipsamment) were typical of soils in Florida highlands, and (2) McCloud Lake itself is quite acidic (pH 4.65) and is similar to other clearwater, acidic lakes in north central Florida, the chemistry of in-seepage at McCloud Lake was believed a reasonable paradigm for in-seepage for other north central Florida lakes [e.g., Baker and Brezonik, 1988].

The second assumption relating to perceived sensitivity follows directly from the notion that in-seepage contains appreciable quantities of  $C_B$  and ANC. If the first assumption is true, then lakes that receive large fluxes of groundwater inflow also should have concentrations of ANC appreciably  $>0$ . However, because lakes in the panhandle have (1) low conductivities (median conductivity = 17.7  $\mu\text{S cm}^{-1}$ ), (2) low  $C_B$  (median  $C_B = 104 \mu\text{eq L}^{-1}$ ), and (3) low ANC (median ANC = -23.7  $\mu\text{eq L}^{-1}$ ) [Kanciruk et al., 1986; C. D. Pollman, unpublished data, 1991], it seemed highly unlikely that seepage lakes in the Florida panhandle received anything more than very small quantities of groundwater. Baker et al. [1988a] further supported this view by analyzing long-term trends in monthly precipitation and evaporation, concluding that groundwater contributed about 1% to total hydrologic inputs for seepage lakes in the Florida panhandle and about 11% for seepage lakes in north central Florida.

Preliminary results from this study challenge this conventional view of Florida panhandle lakes and their inherent sensitivity to acidic deposition from several perspectives. First, our results indicate that panhandle lakes may receive much more groundwater inflow than previously believed. Second, terrestrial contributions to ANC production, particularly through  $\text{SO}_4^{2-}$  retention, may be as important or more important than in-lake processes. Finally, the contribution of base cation enrichment to ANC production in shallow groundwater may be overstated. This particularly appears to be true for Lake Barco, where EF calculations indicate that some net depletion of  $C_B$  may occur (Table 2). For Lake Five-O, base cation enrichment may indeed be important; however, a fundamental difficulty is presented reconciling apparently large inputs of  $C_B$  beyond that supplied by precipitation with overall EF calculations from this study and others [Baker et al., 1988a; Pollman and Canfield, 1991] that show  $C_B$  enrichment in acidic seepage lakes is marginal.

For Lake Barco our preliminary results are consistent with other estimates of seepage inflow rates for lakes in north central Florida [Baker, 1984; Baker and Brezonik,

1988]. However, our estimates of groundwater inflow for Lake Barco are relatively sensitive to errors in estimates of precipitation and evaporation (Table 1), which, in turn, underscores the need to independently quantify each component of the hydrologic budget and the associated error of measurement so that reliable estimates of groundwater and ion inputs can be developed. Relatively extreme climatic conditions observed at both lakes (drought at Lake Barco and above-average precipitation at Lake Five-O) during this investigation imposed short-term (months) perturbations on the long-term hydrologic regime characteristic of these lakes. These potential errors and climatic effects are particularly important considerations when predicting how changes in  $\text{SO}_4^{2-}$  deposition will affect lakewater ANC. Within the range of estimated steady state inflows derived from  $\text{Cl}^-$  balances, estimates of in-lake  $\text{SO}_4^{2-}$  reduction range from 9 to 58 meq  $\text{m}^{-2} \text{yr}^{-1}$ , and terrestrial ANC inputs from  $\text{SO}_4^{2-}$  retention range from >0 to 110 meq  $\text{m}^{-2} \text{yr}^{-1}$  (Table 3). Although these calculations demonstrate the considerable uncertainty inherent in our current estimates, our results qualitatively indicate that terrestrial retention of  $\text{SO}_4^{2-}$  is important for some seepage lakes in north central Florida.

#### CONCLUSIONS

Preliminary results from hydrologic and ion budget studies of Lake Five-O and Lake Barco indicate that some seepage lakes in the Florida panhandle receive more groundwater inflow than previously believed. Net groundwater flow ( $Q_{\text{net}}$ ), which was calculated as the residual term in monthly hydrologic budgets for each lake, was used to estimate net  $Q_i$  (inflow) and  $Q_o$  (outflow). Estimates of net  $Q_i$  for Lake Five-O were relatively insensitive to potential errors in precipitation and evaporation, ranging from 38 to 46% of total inflow. Net  $Q_i$  estimates for Lake Barco, which experienced a drought during the period of study, were much more sensitive to precipitation and evaporation errors. Net  $Q_i$  estimates for Lake Barco ranged from 5 to 14% of total inflow. High rates of  $Q_i$  in Lake Five-O also were confirmed by changes in lake stage over a 3-month period in which lake stage increased by more than 150% of the cumulative precipitation for the same period. Hydrologic gradients around Lake Five-O indicate that inflow occurs around most of the lake perimeter. Inflow is more restricted in Lake Barco, with inflow from the surficial aquifer entering the lake from the northeast and leakage losses to the surficial aquifer occurring along the southern perimeter.

Enrichment factor and ion flux calculations for Lakes Five-O and Barco indicate that terrestrial processes participate more actively in ANC regulation of acidic seepage lakes than previously believed. The extent that terrestrial processes contribute to ANC generation is directly related to the magnitude of  $Q_i$  as well as the degree of ion enrichment or depletion that occurs in the watershed soils. Net ANC generation in both study lakes was dominated by anion retention ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ). Where previous studies concluded that in-lake reduction was the primary sink for  $\text{SO}_4^{2-}$ , our preliminary calculations for both Lake Five-O and Lake Barco show that retention of  $\text{SO}_4^{2-}$  within watershed soils is perhaps twice as important as in-lake reduction.

*Acknowledgments.* Much of the early impetus for this project came from extended conversations between the senior author and J.

M. Eilers of E&S Environmental Chemistry on the nature of Florida seepage lake chemistry. C. Watkins (Florida Department of Environmental Regulation (FDER)) performed the initial site reconnaissance to locate a lake in the Florida Panhandle suitable for this study. The authors also gratefully acknowledge the efforts of J. Collins (U.S. Geological Survey [USGS]) for continued, diligent field support. M. Fisher and D. A. Graetz (University of Florida) provided field and analytical support for measuring porewater chemistry. S. F. Baird (KBN Engineering and Applied Sciences, Inc. (KBN)) assisted in data reduction and analyses, and H. Prentice (Environmental Science and Engineering, Inc. (ESE)) was responsible for precipitation, lake, and groundwater chemical analyses. The authors also thank L. A. Baker, R. A. Goldstein, J. J. Jansen, J. LaBaugh, G. O. Layman, J. Turk, and C. Watkins for critical comments on an earlier version of this manuscript. Finally, we wish to thank the Rosewood Timber Company and its forest manager, George H. Eubank, for granting us access to Lake Five-O and the Katherine C. Ordway Preserve Management Advisory Board for granting us access to Lake Barco. This work is supported by grants and cooperative efforts from the following agencies: U.S. Environmental Protection Agency (EPA), U.S. Geological Survey (USGS), Florida Electric Power Coordinating Group (FCG), Electric Power Research Institute (EPRI), Southern Company Services (SCS), and the Florida Department of Environmental Regulation (FDER). The Lake Barco study is funded jointly by USGS and FDER; the Lake Five-O study is funded jointly by FCG, USGS, EPRI, SCS, and EPA as part of the Hydrology and Acidity of Seepage Lakes Study (HASL).

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(Received July 25, 1990;  
revised May 17, 1991;  
accepted May 29, 1991.)