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Front Cover: Close-up view of a patch-reef coral head in Grahams Harbor, north of Dump Reef. As shown here, Caribbean shallow-water reefs have declined since the mid-1980s and are now largely overgrown by fleshy green macroalgae and a variety of encrusting organisms. See Curran et al., "Shallow-water reefs in transition," this volume, p. 13. Photograph by Ron Lewis.

Back Cover: Dr. A. Conrad Neumann, University of North Carolina, Chapel Hill, NC, Keynote Speaker for the 11th Symposium and author of "Cement loading: A carbonate retrospective," this volume, p. xii. Photograph by Mark Boardman.

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A GEOCHEMICAL COMPARISON OF THE SURFACE AND SEDIMENT PORE WATERS OF SPITTAL POND AND WARWICK POND, BERMUDA

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ABSTRACT

The groundwater of Bermuda, like that of most small oceanic islands, consists of both seawater and fresh rainwater. Fresh groundwater exists in lenses in the center of the island, and groundwater salinity grades outward towards the edges of the island to seawater concentrations. The ponds of Bermuda may be thought of as "outcrops" of the groundwater.

Spittal Pond is a marine pond located on the southeastern coast of Bermuda. It has two relatively deep basins (~60-80 cm) separated by a ridge that nearly reaches the water surface. Warwick Pond is a single basin of uniform depth (~20 cm) and is the only naturally occurring freshwater pond on Bermuda. We believe that Spittal Pond and Warwick Pond represent near end members of the spectrum of groundwater salinities in Bermuda and have conducted a geochemical comparison of their surface and sediment pore water.

Our study of Spittal and Warwick Ponds involved field and laboratory analysis of surface and sediment pore-water chemistry. Pond waters were sampled at the surface and at depth (near the sediment-water interface). We measured temperature, pH, and conductivity in the field and collected samples for quantitative analysis of alkalinity and major cation and anion concentrations. Analyses indicate that both ponds are vertically well-mixed, and that Spittal Pond is saline while Warwick Pond is brackish. Data also indicate that while the chemistry of Warwick Pond is nearly uniform, the water in the northeastern and southwestern basins of Spittal Pond show significantly different chemistries.

Eleven sediment cores (150-400 cm long) were extracted from the ponds. We sampled four of the cores at 10-cm intervals and determined water content of the sediments and major ion concentrations of the pore water. Water content ranged from 80% for the surface sediments to 40% for the basal clays and, in general, decreased with depth. Profiles of cations and anions show trends that can be explained by diffusive and advective transport of water through the sediments.

INTRODUCTION

The islands of Bermuda are situated in the western North Atlantic Ocean (32°N, 64°W) approximately 1000 km east of Cape Hatteras, NC. The islands sit upon a volcanic seamount and are composed of carbonate bioclastic eolianite interbedded with paleosols (Vacher et al., 1995). Spittal Pond is located in Smith's Parish on the southeastern coast of the island. Warwick Pond is southwest of Spittal Pond in Warwick Parish and is further inland (about 0.8 km from the coast) than Spittal Pond (Figure 1).

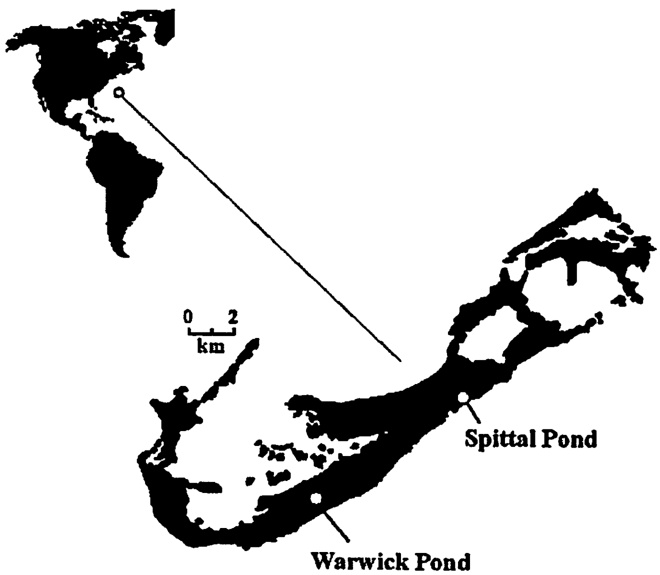

Figure 1. Location of Bermuda and Warwick and Spittal Ponds.

Spittal Pond is a marine pond, and Warwick Pond is the only naturally occurring freshwater pond on Bermuda. We believe that Spittal Pond and Warwick Pond represent the range of the geochemical conditions of Bermuda's ponds.

The purposes of this study were to document and compare the inorganic geochemistry of these two ponds and to understand their hydrologic environments. This study provides a much-needed foundation for future studies on the island including the calibration of hydrogeologic models and environmental geochemical studies.

The Hydrogeology of Bermuda

Because fresh rainwater is less dense than seawater, the groundwater of oceanic islands exists in freshwater lenses (see Figure 2). Vacher and Rowe (1997) indicate the presence of five freshwater lenses in Bermuda; the general location of these lenses is shown in Figure 3. If we consider the ponds to be "outcrops" of the groundwater, contours of groundwater salinity around these lenses of fresh groundwater place Spittal Pond at 10-25% seawater and Warwick Pond at 3-10% seawater (Vacher, 1974).

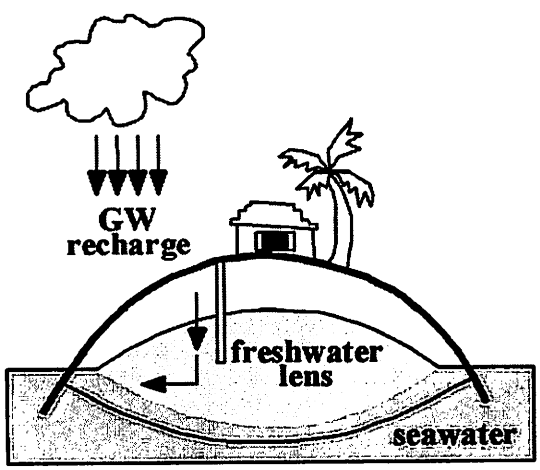

Figure 2. The structure of a freshwater lens.

Figure 3. The general locations of the freshwater lenses of Bermuda.

Site Descriptions

Spittal Pond (Figure 4) is an inter-dunal pond located in Smith's Parish. It lies within a nature preserve and sanctuary that was developed between 1954 and 1976 (Thomas and Wassmann, 1992). The pond is ~500 meters long and is ~38 cm deep. A ridge at the western end of the northeast basin separates the pond into two distinct basins (Jenks, 1970). The northeast basin is relatively shallow and of relatively constant depth (~45 cm); the southwest basin is deeper and shows more range in depth (~45-75 cm) (Figure 5). There are approximately 23 cm of unconsolidated organic sediment below the sediment-water interface.

The salinity of Spittal Pond ranges from 6.5 to 42.5 ‰. Breaching of the lowlands by ocean waves during major storms and hurricanes has been documented (Department of Agriculture and Fisheries, 1969) and it is thought that changes in the pond's salinity are dictated by salt-water incursions during storms (increasing the salinity of the pond), interception of fresh rainwater during wet weather (decreasing the salinity), and evaporation (increasing the salinity).

Warwick Pond (Figure 6) is ~300 meters long and is of a constant depth of ~20 cm from the water surface to the sediment-water interface (Figure 7). There are nearly 2 meters of uncon-

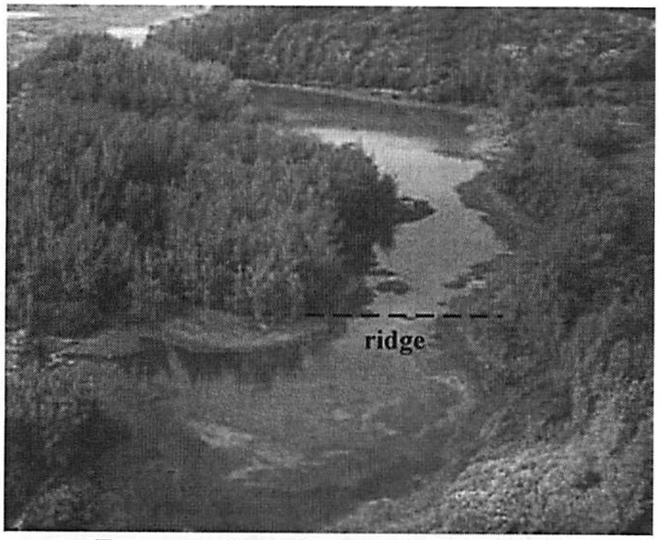

Figure 4. Spittal Pond (looking SW).

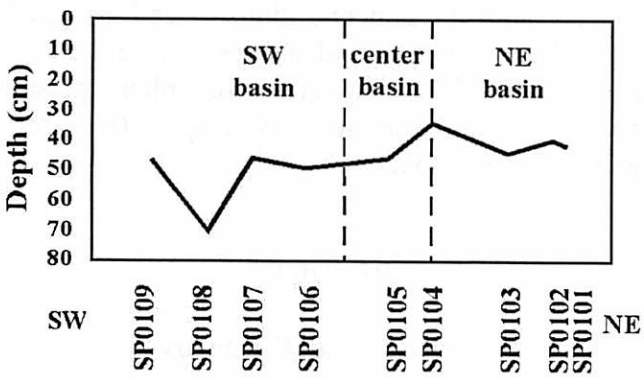

Figure 5. Depth profile for Spittal Pond.

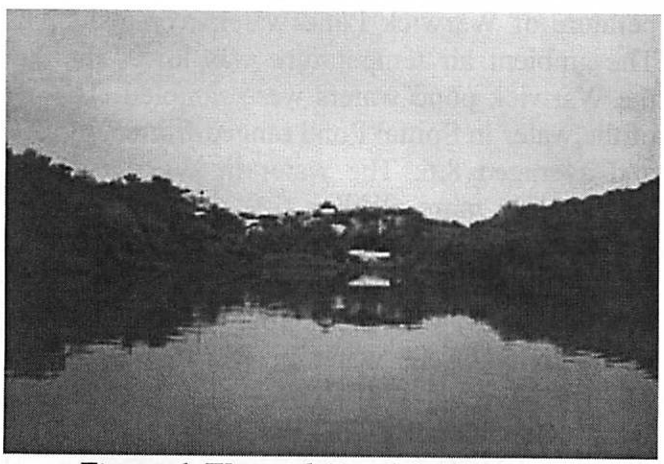

Figure 6. Warwick Pond (looking SW).

solidated organic sediment below the sediment-water interface.

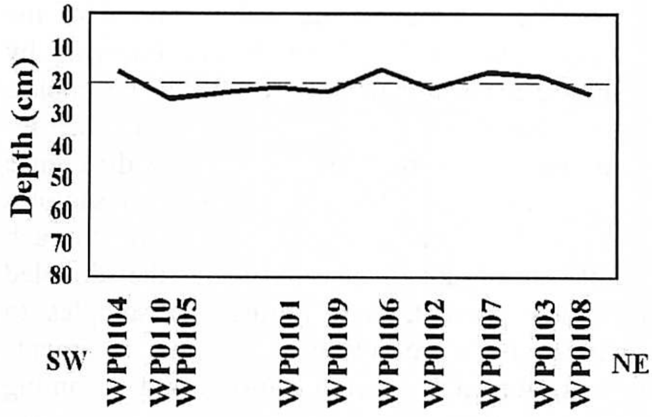

Figure 7. Depth profile for Warwick Pond

METHODS

Collection of Surface Water Samples

We collected surface water samples from 9 sites along the axis of Spittal Pond and from 10 sites in Warwick Pond in June of 2001; the locations of the sampling sites are shown in Figure 8. At each site, water samples were collected from the surface and at depth (at the sediment-water interface) in acid-washed Nalgene LDPE bottles rinsed twice with the pond water at each sample site. The samples were brought back to the Bermuda Aquarium and eventually back to the mainland for analysis.

Core Retrieval and Processing

We recovered 5 vibracores of sediment from Spittal Pond and 6 vibracores of sediment from Warwick Pond following standard vibracoring practices (Hoyt and Demarest, 1981). The locations of the cores used in this study (three from Spittal Pond and one from Warwick Pond) are shown in Figure 8. In most cases we cored into the eolianite bedrock and were, in these cases, assured that we had retrieved a core that represented the full sediment column. We cut the cores into 1 meter lengths and took them to the Bermuda Aquarium where they were split, photographed, and logged (see Tackaberry et al., 2004). We divided each of the cores into 10-cm interval samples, bagged them, stored them in coolers, and brought them back to the mainland for analysis.

We determined the water content of the sediments for each of the 10-cm intervals by weighing a portion of each of the wet samples, drying these samples overnight at 110° C, re-weighing the samples, and taking the difference between the two weights. We prepared samples for cation and anion analysis by adding to each sample an aliquot of distilled water that doubled the water content, centrifuging the samples to separate the pore water from the sediments (Cohen, personal communication), and decanting our pore water samples from the centrifuge tubes.

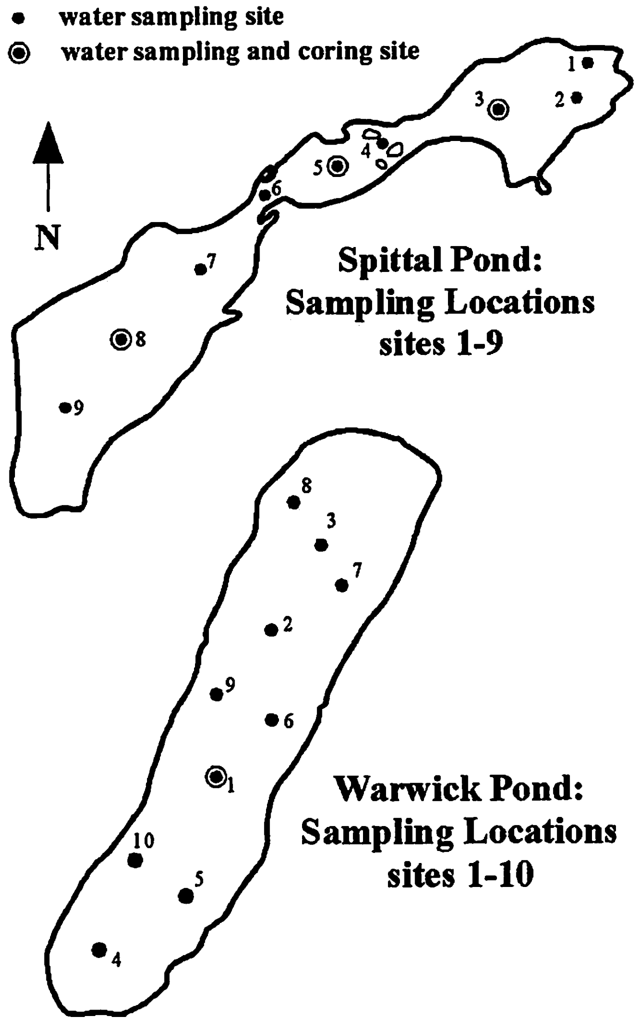

Figure 8. Location of sampling sites (note that the diagrams are not shown at the same scale: Warwick Pond is approximately half the size of Spittal Pond).

Chemical Analyses

We measured and recorded the temperature, pH, and conductivity of both the surface water samples and the water samples collected at depth (at the sediment-water interface). Temperature and pH were measured using an Oakton® pH 6 Acorn Series meter, which was calibrated with 4.01 and 7.00 standard pH buffers prior to each use in the field. Conductivity was measured using an Oakton® CON 5 Acorn Series meter calibrated with 447 and 1413 μS standard solutions. We ran alkalinity titrations with a 0.02N HCl solution on the same day that the samples were collected and calculated HCO_3^- from these titrations.

All of the surface and pore-water samples were filtered through 0.45 mm glass filters, and we measured the concentrations of cations (Ca^{+2}, Mg^{+2}, Na^+, and K^+) and anions (Cl^- and SO_4^{-2}) using ICP-AES (inductively-coupled plasma atomic emission spectroscopy) and IC (ion chromatography), respectively.

RESULTS

Surface Water Chemistry

The temperature of the water in both ponds was 25-30° C (Figure 9). The temperature of Spittal Pond water averaged 29° C. The temperature of Warwick Pond water averaged 27°C. The ambient air temperature was lower the day the Warwick pond waters were sampled. The pH of the water in Spittal Pond ranged from 6.5 to 9.0 and averaged 8.6. The water in Warwick Pond was slightly more alkaline (~9.2), and the pH of the water was essentially constant across the pond (Figure 9). The conductivity of the water in Spittal Pond (~20 μS) was nearly four times that of the conductivity of the water in Warwick Pond (~5 μS).

Concentrations of Ca^{+2}, Mg^{+2}, Na^+, K^+, Cl, SO_4^{-2}, and HCO_3^- are all higher in the waters of Spittal Pond than in Warwick Pond (Figures 10, 11). Most of the ion concentrations in Warwick

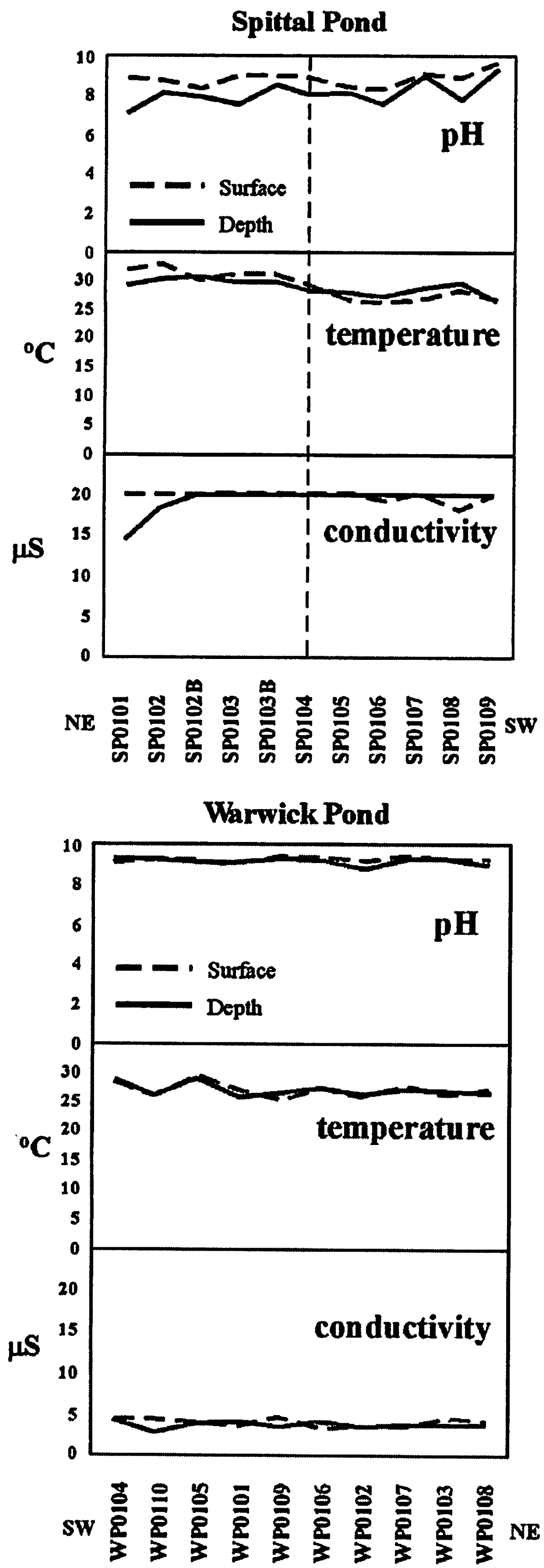

Figure 9. The measured pH, temperature, and conductivity in Spittal and Warwick Ponds.

Pond are nearly constant both across the pond and with depth (but note Ca^{+2} and HCO_3^-). In Spittal Pond, all of the ion concentrations are markedly higher in the northeast basin than in the southwest basin (Figures 10 and 11).

Sediment and Pore Water Analyses

Sediment type and water contents of the cores pulled from the center basin of Spittal Pond (site 5 in Figure 8) and from Warwick Pond (site 1 in Figure 8) are shown in Figures 12 and 13, respectively. The log from Spittal Pond is representative of the types of sediments in the pond, but the stratigraphy of the sediments is difficult to correlate (see Tackaberry et al., 2004).

The top 40 cm of the Spittal Pond core consists of dark brown, "soupy" (unconsolidated) sediment. Below that layer is ~150 cm of gelatinous sapric peat (very reminiscent of tomato aspic). Underlying this highly decomposed sapric peat is a layer of fibrous hemic peat and underlying the hemic peat are two distinct layers of clay: one gray and suitable for throwing on a potter's wheel, the other brown and slightly siltier than the gray clay. The sediment core from Warwick Pond has four units of sapric, gelatinous peat. Water content in each of the peat layers was high in both cores (~60-80%). The water contents in the clays found in Spittal Pond were markedly lower than those of the peat and averaged 40%.

Major cation concentrations in the pore-water samples from the cores are shown in Figure 14. The pore waters in the sediments of Spittal Pond approach seawater concentrations and in some cases (notably Ca^{+2} and Mg^{+2} in the hemic peat and clays) exceed those of normal seawater. Potassium concentrations are also high in the pore waters of the basal clays. The cation concentrations in the pore waters in the sediments of Warwick Pond are all much lower than seawater, and the ion profiles are generally unremarkable.

DISCUSSION

Concentrations of Ca^{+2}, Mg^{+2}, Na^+ and K^+ in Spittal Pond are high in the northeast basin

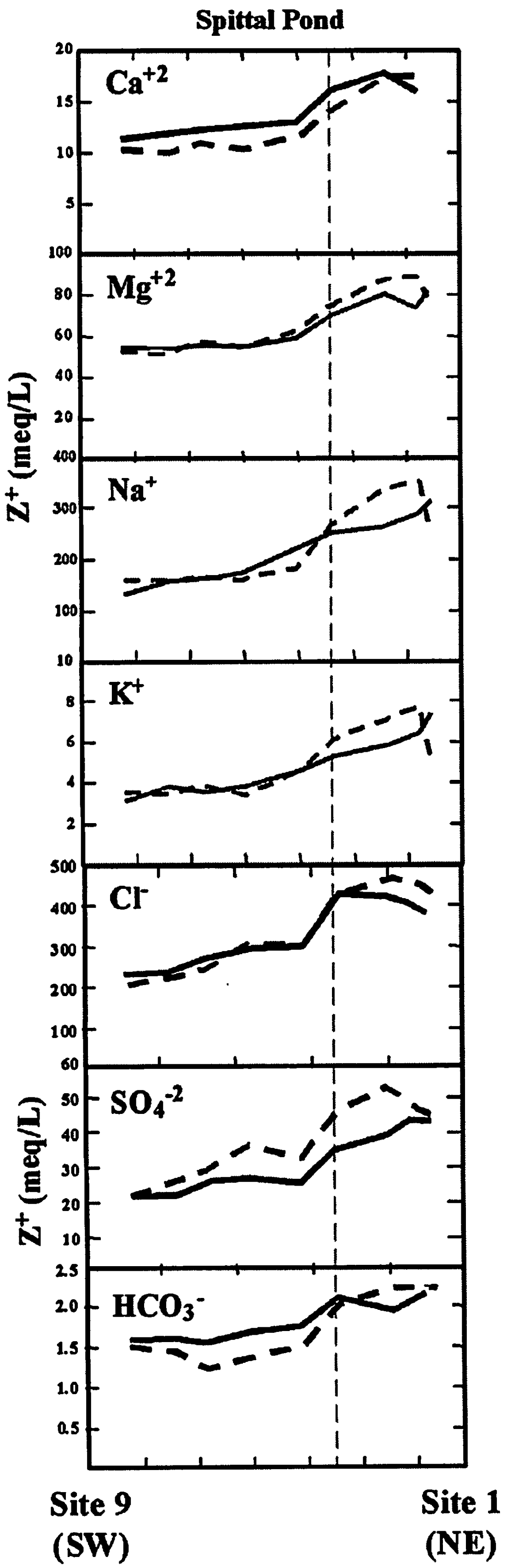

Figure 10 . The measured ion concentrations in Spittal Pond.

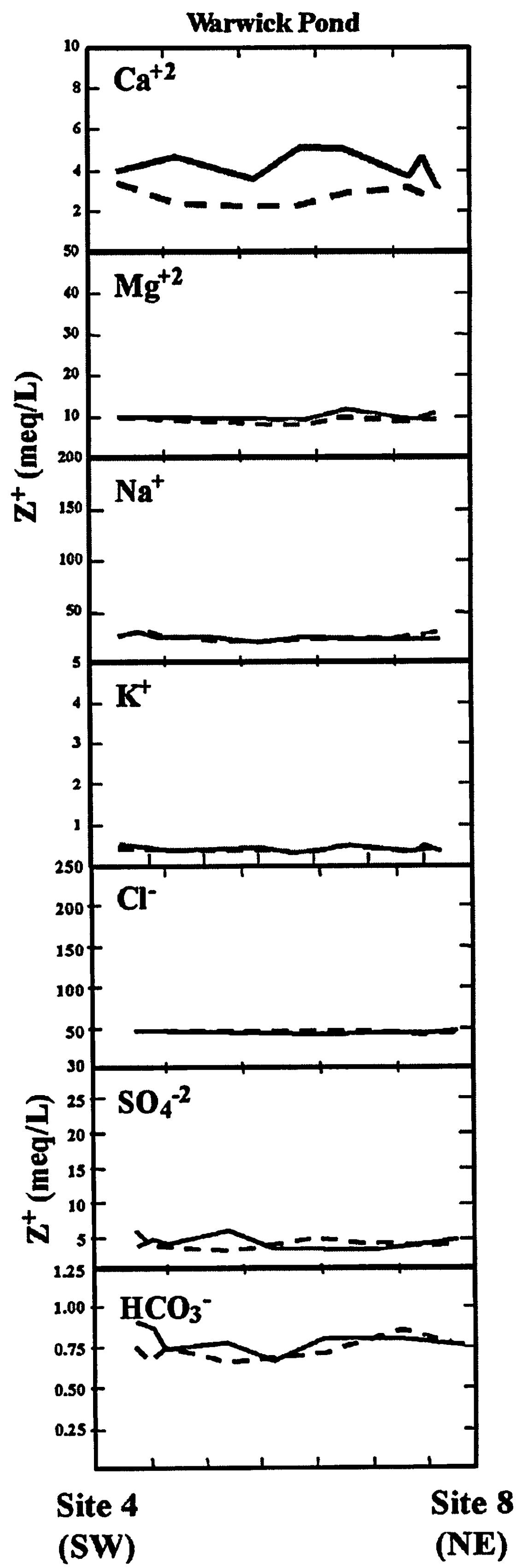

Figure 11. The measured ion concentrations in Warwick Pond.

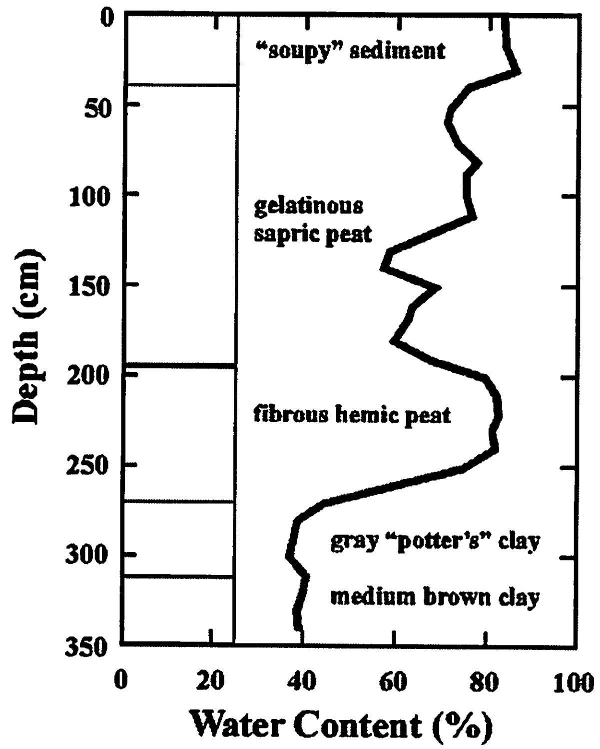

Figure 12. Core log showing sediment type and water content of core taken from center basin of Spittal Pond (see Figure 8 for location of core).

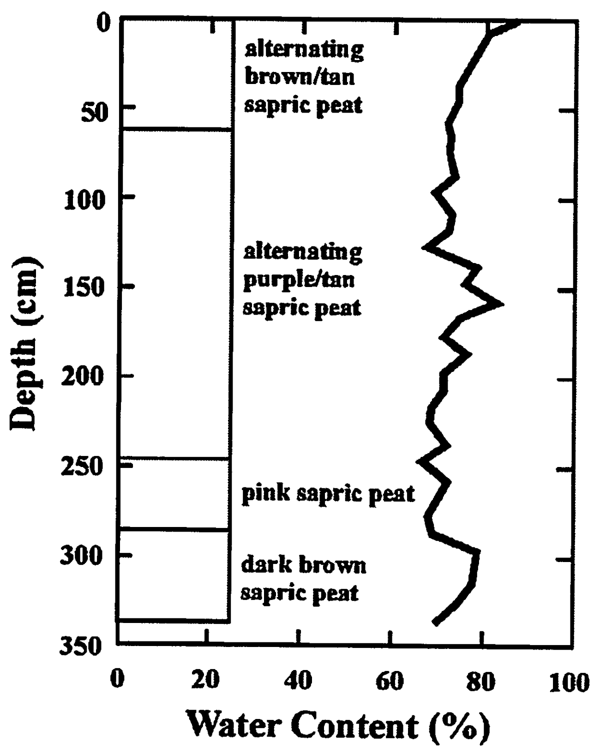

Figure 13. Core log showing sediment type and water content of core taken from Warwick Pond (see Figure 8 for location of core).

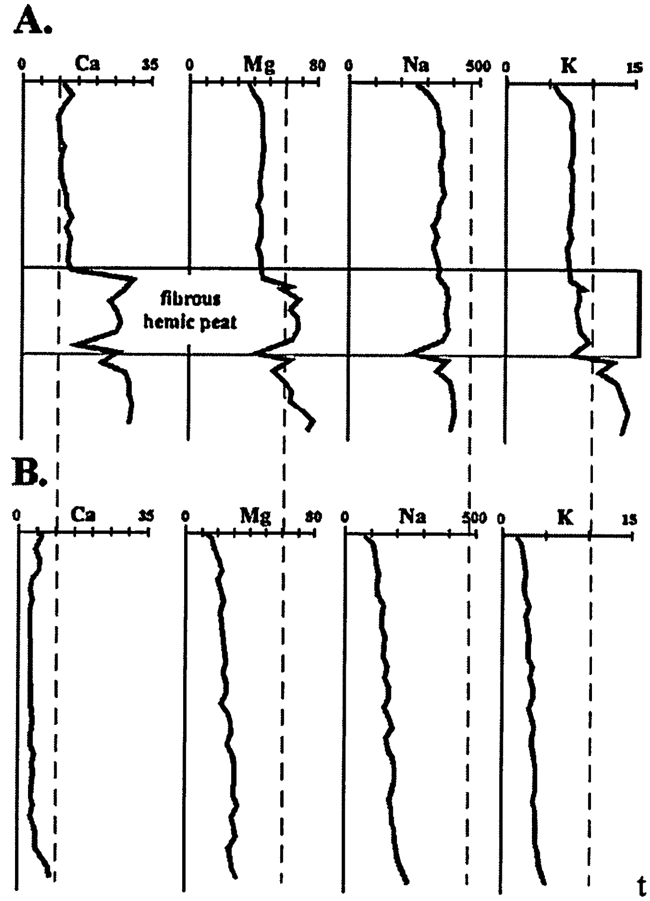

Figure 14. Cation concentrations (in mmol/L) for (A) the core pulled from Spittal Pond and (B) the core pulled from Warwick Pond. Dashed lines indicate seawater concentrations.

(approximately a 3:1 mix of seawater and freshwater concentrations) and decrease across the pond to the southwest basin (where the concentrations are approximately a 2:1 mix of seawater and freshwater). It appears that the ridge in the center of the basin acts as a barrier to mixing, keeping the basins hydraulically separate. The larger ratio of seawater to freshwater in the northeast basin can be explained by storm wash into the basin, which is very close to the southern shore of the island, or possibly (but less likely) by differential evaporation. Warwick Pond has very low concentrations of all ions but is still brackish. Elevated Ca^{+2} concentrations at depth indicate the influx of groundwater.

Cation and anion concentrations are normalized to seawater concentrations and are plotted below as functions of Na^{+} and Cl^{-} concentrations (Figures 15, 16). Also shown on these plots (as a solid line) is a seawater dilution line. The ion concentrations in Spittal Pond lie between 29% and 79% seawater concentration. Excess calcium in Spittal Pond surface water can be explained by the dissolution of limestone bedrock. The concentrations of Ca^{+2} in Spittal Pond are in equilibrium with limestone at pH = 7.7 and a PCO_2 of 10^{-3} bar. The elevated calcium ion concentrations in the surface water of Spittal Pond provide evidence that there is a groundwater contribution to the pond. The magnesium concentration of the surface waters was also higher than the seawater dilution curve. The source of the excess magnesium is more problematic. It may be due to systematic analytical error, but could also be due to the presence of Mg in the bedrock since both ponds sit on the Paget Formation which is composed of Mg-calcite and aragonite rather than calcite. Potassium concentrations fall on the seawater dilution curve, indicating that the potassium in the pond waters is derived from seawater. Bicarbonate concentrations are elevated, as would be expected with a contribution of groundwater that is in equilibrium with limestone, and sulfate concentrations fall around the seawater dilution curve, indicating that they are also seawater derived.

Ion concentrations are much lower in Warwick Pond and lie between 5% and 9% seawater concentration. The same patterns exist: calcium and bicarbonate ion concentrations are elevated with respect to seawater, magnesium is slightly elevated, and both potassium and sulfate show seawater signatures.

The differences in the ion concentration signatures of the two ponds suggest different hydrologic processes are operating in the two ponds. In Spittal Pond, the surface water appears to have both groundwater and seawater signatures. This is most likely due to the fact that Spittal Pond lies so near the ocean and not near one of Bermuda's freshwater lenses. As a result, Spittal Pond, as an outcrop of the groundwater, is more saline than Warwick Pond because of its location on the island. However, there also appears to be a large contribution of storm washover to the surface waters of Spittal Pond, at least at the time of this study. This hypothesis is supported by the presence of the ridge between the basins in Spittal Pond which effectively separates the pond into two distinct basins and by the elevated ion concentrations in the northeast basin with respect to the southeast basin. We cannot comment on whether storms generally wash seawater into the northeast basin rather than into the southeast basin; both basins appear to be within "striking distance." The presence of storm-disturbed sediments in the sediment cores from the southeast basin suggests that there has been storm washover into this basin. The geochemical data we collected suggest that both basins are subject to storm washover depending on the direction of the winds. We envision that Spittal Pond is a very hydrologically dynamic environment.

The chemistry of the pore waters in the sediments of Spittal Pond indicates that diffusion has erased any differences in water chemistry at the time of deposition of the sapric peat. The elevated calcium concentrations indicate that there is significant advection of groundwater through the hemic peat layer. Magnesium concentrations are also elevated in the hemic peat; we have no explanation for these elevated concentrations, but the fact that the magnesium profile parallels the calcium profile indicates that they are source-related. Elevated potassium concentrations in the basal clays of Spittal Pond suggest ion exchange is occurring.

Warwick Pond, in contrast, appears to be a very quiescent environment. The seawater signature is what would be expected given the position of the pond on the island. Warwick Pond lies near a 10% salinity contour on maps of the groundwater salinity of Bermuda (Vacher and Rowe, 1997). The elevated calcium and bicarbonate concentrations indicate that the chemistry is governed by calcite dissolution, and that there is a large groundwater contribution to the pond. The chemistry of the pore waters in the sediments of Warwick Pond appears to be uninteresting and is probably governed by diffusion processes.

SUMMARY AND CONCLUSIONS

In summary, Spittal Pond appears to have two distinct basins that are, at least to some extent, hydraulically separate. At the time of this study, the pond was chemically compartmented.

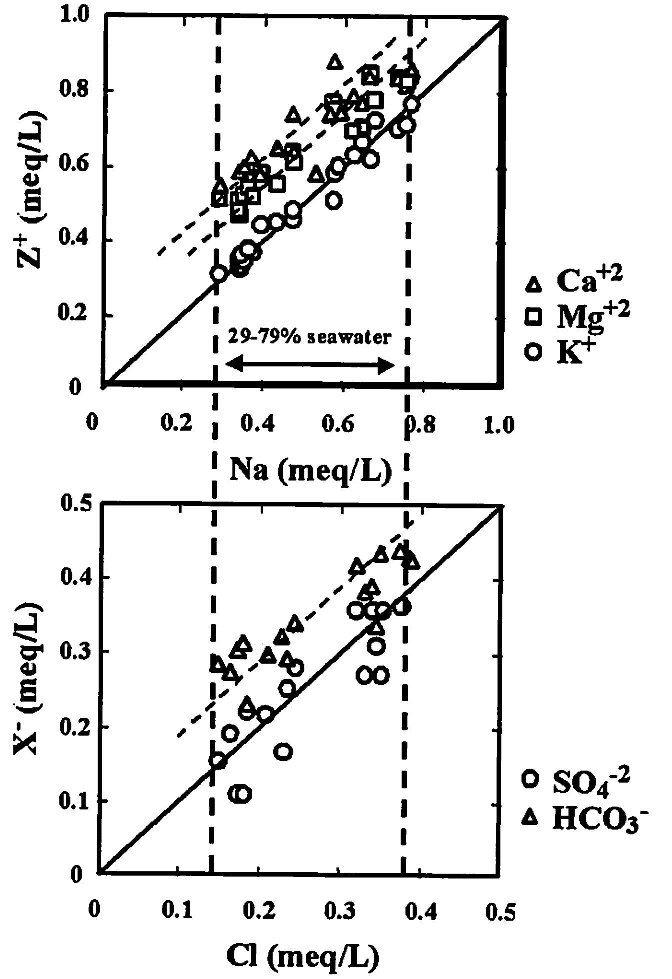

Figure 15. Ion concentrations in Spittal Pond normalized to sodium and chloride ion concentrations.

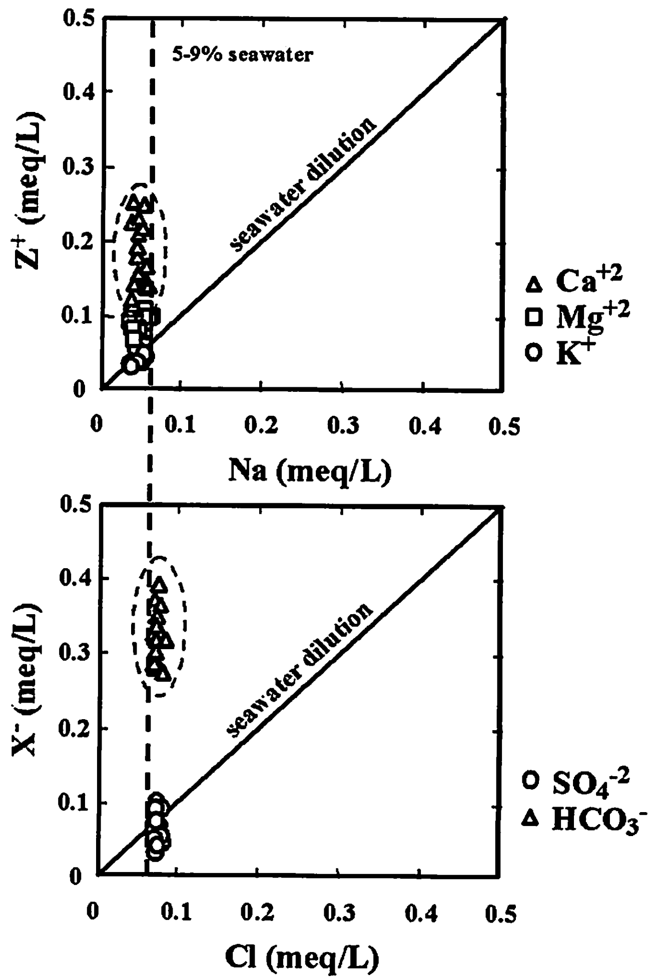

Figure 16. Ion concentrations in Warwick Pond normalized to sodium and chloride ion concentrations.

While it is groundwater-fed (as suggested by elevated calcium and bicarbonate ion concentrations), it is also subject to storm washover. Elevated ion concentrations in the northeast basin suggest most recent washover of the sea into that pond from that direction. In contrast, Warwick Pond appears rather uninteresting both chemically and hydrologically. The water in the pond appears to be entirely derived from rainwater and groundwater. The pond is of uniform depth and the surface water is chemically well-mixed.

Our initial hypothesis, that Spittal Pond and Warwick Pond represent near end members of the groundwater salinity spectrum of Bermuda, is supported by our study. What may also be true is that we have captured end members of the relative dynamics of the pond environments of Bermuda, with Spittal Pond representing the most dynamic and Warwick the most quiescent.

ACKNOWLEDGMENTS

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Chemistry at Colby College for their assistance in the ICP-AES and IC analyses.

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