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The water chemistry of Carolina bays: A regional survey

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With 4 figures and 6 tables in the text

Abstract

The water chemistry of 49 Carolina bays (including 5 bay lakes) was determined along two transects extending from the extreme upper coastal plain to the coast. Bays were selected to represent different coastal plain marine terraces and different vegetation communities. Waters were quite soft (median Ca = 1.69 mg/l) and acidic (median pH = 4.6). Dissolved organic carbon (DOC) averaged 17.2 mg/l and represented 38 % of the total anions. Although a low solute (1.07 meq/l), ombrotrophic condition predominated, the Carolina bays exhibited high interbay variation. A gradation from mixed mineral weathering and precipitation to chemical dominance by precipitation was evident. This gradation was attributed to geologic differences within and between remnant coastal terraces and, perhaps, to successional wetland paludification. Surficial groundwater had a significant influence on bay water chemistry; in one Carolina lake, the influence of deep groundwater was apparent. A bay ordination constructed from canonical discriminant function analysis of chemistry data corresponded well to plant community classifications.

Introduction

Shallow, isolated wetlands have diverse water chemistry. Water chemistry can vary from extremely dilute, acidic conditions in dystrophic bogs to hyperalkaline conditions in wetlands of arid climates (Schalles 1989 a). Groundwater-fed wetlands may also exhibit pronounced surface chemistry variation within a single landscape (LaBaugh et al. 1987, Schalles 1989 b). Differing groundwater sources, the proportions of groundwater and atmospheric inputs, hydrologic residence times, and the degree of evaporative concentration are major variables influencing the variation in surface water chemistry among wetlands within a landscape. Further, marine versus continental sources may strongly influence the atmospheric loadings and resultant chemistries of ombrotrophic wetlands (Gorham et al. 1985).

Carolina bay wetlands are shallow, elliptical depressions with a striking parallel alignment of the major axes in a northwest to southeast direction

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(Prouty 1952). Communities within these depressions differ according to hydroperiod and related degrees of fire frequencies and peat accrual (Wharton 1978, Sharitz & Gibbons 1982). Larger, deeper sites contain lakes (Frey 1949). However, the majority of bays have wetland vegetation ranging from marshes to shrub-bog pocosins to hardwood- or cypress-dominated swamp forests. Water chemistries of Carolina bays are typically very soft and acidic (Schalles 1989 b), and biological production is low to moderate (Tilly 1973, Sharitz & Gibbons 1982, Schalles & Shure 1989).

Although Carolina bays are the only abundant lentic systems of natural origins on the coastal plains of North Carolina, South Carolina and most of Georgia, the few studies that included water chemistry of Carolina bays (Frey 1949, Tilly 1973, Schalles 1989 b) were incomplete treatments of the ionic characteristics of these waters. Further, the water chemistry of these abundant habitats has never been examined on a regional scale (Sharitz & Gibbons 1982). The primary objectives of this study were: (1) to characterize the chemistry of bay waters, including the major inorganic ions and dissolved organic carbon (DOC), and (2) to gain some insight regarding factors controlling bay water chemistry, i.e. geographic position on the coastal plain, groundwater geochemistry, and vegetative state.

Materials and methods

Study region

The coastal plain region of North and South Carolina contains the greatest densities of Carolina bays. Bays commonly occur on flat interfluves with sandy, well-weathered soils. Thom (1970) recognized two less common types in northeastern South Carolina: in stabilized dune fields and, rarely, at contact zones between fluvial terraces. In the present study region, bay elevations range from several meters near the coast to approximately 180 to 215 m on the extreme upper coastal plain and adjacent Piedmont province.

Large parts of the coastal plain are broad depositional marine terraces of Quaternary-age occurring in belts roughly parallel to former shorelines (Murray 1961). The oldest and most elevated deposit landform, the Citronelle, is well dissected and dates to the early Quaternary. Lower elevation terraces are flatter and represent a younger sequence of bar and lagoon shoreline features separated by weak scarp slopes (Doering 1960).

The climate is humid and sub-tropical along the South Carolina coast and becomes slightly more temperate and dry inland. Mean annual precipitation of the study region ranges from 120 mm in the upper coastal plain to 130 mm along the coast (NOAA 1987). Mean annual temperature for the area is approximately 16.5 °C (range: 7.0 °C in January to 26.5 °C in July). The growing season averages 200 days on the upper coastal plain and 270 days near the coast.

Bay and bay lake selection

National High Altitude Photography (NHAP 1:58,000 scale, U.S. Geological Survey) color infrared imagery taken from 1981 to 1983 and topographic maps

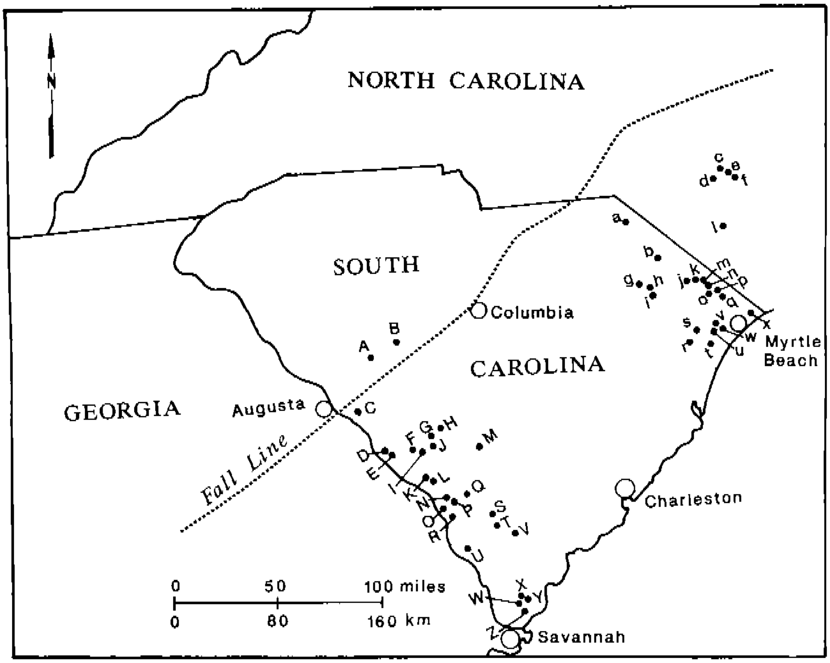

Fig. 1. The location of Carolina bays sampled. Bays along the Savannah transect are designated with capital letters. Bay lakes (c, d, e, f and l) and bays along the Myrtle Beach transect are noted with small letters.

(1:24,000 scale, U.S. Geological Survey) were used to identify candidate Carolina bays for sampling. Bays were selected which had standing water during the period of the overflights (January to May). When a bay was located, the presence of water and the lack of significant human disturbance within the bay were used as criteria for final selection.

The bays were selected along two transects. Both transects were located within the area of greatest bay density on the Atlantic coastal plain (Sharitz & Gibbons 1982). One transect extended from above the Fall Line along the Savannah River to the coast. The second ran along the South Carolina-North Carolina border and ended near Myrtle Beach (Fig. 1). The transects were selected because they provided significant numbers of bays within a variety of coastal terraces. Further, the work of Thom (1970) with Carolina bays in the lower portion of the Myrtle Beach transect (Horry and Marion counties) and the work of Schalles et al. (1989 b) in bays of the upper portion of the Savannah transect provided useful background descriptions. An attempt was made to select bays such that a uniform distribution of bays along each transect and a variety of vegetation/hydrology types were obtained. The following vegetation/hydrology types were defined: bay lake, marsh with pond, mixed marsh/swamp forest, pine forest, cypress swamp forest, hardwood swamp forest, and pocosin.

Twenty-five Carolina bays along the Savannah transect and 20 bays along the Myrtle Beach transect were sampled. Five bay lakes described by Frey (1949) were also sampled.

Table 1. General description of the Carolina bays and bay lakes.

Bay	Common name	County	Underlying geology	Elevation* (m AMSL)	Vegetation/Hydrology class	Level of disturbance of surrounding land	Peat depth (cm)
A		Edgefield	Pre-Cretaceous	195	Marsh with Pond	Clear cutting near bay	9
B		Saluda	Pre-Cretaceous	215	Marsh with Pond	Orchard near bay	<1
C	Mathis Lake	Aiken	Citronelle	158	Marsh with Pond	Fields draining to bay	15
D		Aiken	Fluvial terrace	59	Hardwood Swamp	None	22
E	Matlock Bay	Aiken	Fluvial terrace	59	Hardwood Swamp	Fields near bay	39
F	Flamingo Bay	Aiken	Citronelle	105	Marsh with Pond	None	14
G	Sisters Lake	Barnwell	Citronelle	115	Marsh with Pond	Pasture near bay	9
H		Barnwell	Citronelle	112	Pine Forest	None	11
I	Diversity Bay	Aiken	Citronelle	112	Mixed Marsh/Swamp	None	24
J	Thunder Bay	Barnwell	Citronelle	69	Marsh with Pond	None	11
K	Lake Echee	Allendale	Citronelle/Fluvial Terrace?	46	Marsh with Pond	Pasture near bay	16
L		Allendale	Citronelle/Fluvial Terrace?	46	Marsh with Pond	None	<1
M		Allendale	Sunderland Terrace	16	Cypress Swamp	None	22
N		Allendale	Citronelle	69	Hardwood Swamp	None	138
O		Allendale	Citronelle	18	Mixed Marsh/Swamp	None	16
P		Allendale	Sunderland Terrace	62	Cypress Swamp	None	16
Q		Allendale	Sunderland Terrace	59	Marsh with Pond	None	30
R		Allendale	Sunderland Terrace	66	Marsh with Pond	None	57
S		Hampton	Wicomico Terrace	33	Mixed Marsh/Swamp	None	>200
T		Hampton	Wicomico Terrace	34	Hardwood Swamp	None	108
U		Hampton	Wicomico Terrace	39	Cypress Swamp	None	29
V		Hampton	Wicomico Terrace	7	Pine Forest	None	18
W		Beaufort	Pamlico Terrace	7	Hardwood Swamp	Fields of young pine near bay	10
X		Beaufort	Pamlico Terrace	7	Mixed Marsh/Swamp	Fields near bay	16
Z		Beaufort	Pamlico Terrace	7	Mixed Marsh/Swamp	None	36

Table 1. Continued.

Bay	Common name	County	Underlying geology	Elevation* (m AMSL)	Vegetation/Hydrology class	Level of disturbance of surrounding land	Peat depth (cm)
a		Marlboro	Sunderland Terrace		Mixed Marsh/Swamp	None	23
b		Dillon	Sunderland Terrace		Pine Forest	None	18
c	Jones Lake	Bladen	Sunderland Terrace	23	Bay Lake	None, Protected State Park	<1
d	Bay Tree Lake	Bladen	Sunderland Terrace	25	Bay Lake	None, Residential	<1
e	White Lake	Bladen	Sunderland Terrace	22	Bay Lake	None, Residential/Commercial	<1
f	Singletary Lake	Bladen	Sunderland Terrace	20	Bay Lake	None	<1
g		Dillon	Sunderland Terrace	18	Hardwood Swamp	Logging near bay	98
h		Marion	Wicomico Terrace	39	Hardwood	None	19
i	Pee Dee Islands Bay	Marion	Wicomico Terrace	13	Pocosin**	None	61
j	Fox Bay	Marion	Wicomico Terrace	26	Hardwood Swamp	Fields near bay	13
k	Noel Bay	Marion	Wicomico Terrace	46	Pocosin	None	11
l	Lake Waccamaw	Columbus	Sunderland Terrace	16	Bay Lake	None, Residential	<1
m		Horry	Wicomico Terrace	20	Hardwood Swamp	None	43
n		Horry	Wicomico Terrace	20	Marsh with Pond	None	22
o		Horry	Wicomico Terrace	33	Pocosin	Fields near bay	33
p		Horry	Penholaway Terrace	33	Hardwood Swamp	Construction near bay	8
q		Horry	Penholaway Terrace	36	Pocosin	None	15
r		Horry	Talbot Terrace	3	Hardwood Swamp	None	40
s		Horry	Talbot Terrace	4	Pocosin	None	41
t		Horry	Talbot Terrace	4	Pocosin	None	24
u		Horry	Talbot Terrace	3	Pocosin	None	18
v		Horry	Talbot Terrace	3	Cypress Swamp	None	15
w		Horry	Talbot Terrace	3	Pocosin	None	16
x		Horry	Pamlico Terrace	13	Pocosin	Logging near bay	180

* Meters above mean sea level. ** Broadleaved evergreen shrub bog/pond pine communities.

Field work and sampling

Bays were sampled between January 4, 1988 and January 16, 1988. Several physical characteristics were noted at each bay. A map was drawn indicating gross land use around the bay, extent of vegetative cover, vegetation type and approximate location of sample sites within the bay. Fig. 1 and Table 1 summarize the locations and general characteristics of the 49 bays and bay lakes from which acceptable water samples were obtained.

Four sampling locations were chosen to determine the level of variation within each bay. At each location, water temperature and peat depth (using a 2 m long, 0.64 cm diameter stainless steel rod) were measured. Although considerable effort was made to sample peat depth at representative locations in the bays, the imprecision of this technique rendered the measurements semi-quantitative in nature. Water temperatures ranged from 0 to 13 °C. Water samples were collected by hand from 2 to 10 cm below the surface using cleaned plastic bottles (total alkalinity, specific conductance, major anions, major cations), or chromic acid-washed, glass bottles (dissolved organic carbon or DOC). Each bottle was rinsed five times with sample water before final collection. Major cation samples were acidified with Ultrex nitric acid immediately after collection. The samples were transported on ice and stored in a 4 °C refrigerator until further laboratory processing. A duplicate set of samples at one of the locations was taken for analytical quality control (QC) at every third bay.

Water chemistry

Total alkalinity (potentiometric titration, APHA 1980) and pH (Orion Research Microprocessor Ionalyzer 1901, Orion 8130 Ross combination pH electrode) were determined within 24 h of collection. Infrequently, a sample was held for as much as 48 h prior to analysis. Similar studies of bog waters (GORHAM et al. 1985), which included a field versus laboratory pH comparison, suggested that laboratory measurements were adequate for our purposes. However, as pH was not analyzed immediately in the field, the pH values should be considered indicators of general conditions, not measurements of high analytical accuracy.

Specific conductance was measured with a Sybron PM-70CB conductivity bridge and a Fisher cell (cell constant = 0.105 cm). Sodium, K, Ca, and Mg were measured by flame atomic absorption spectrophotometry (Hitachi 180-80A Atomic Absorption Spectrophotometer with Zeeman background correction). Total reactive Fe and Mn were determined with a Perkin-Elmer Model 370 atomic absorption spectrophotometer.

Samples used in Cl and SO_4 analyses were passed through a 0.45 μm membrane filter and then a Sepak reverse phase column. Sulfate and Cl concentrations were determined using a Dionex 4020i ion chromatograph with a conductivity detector and a HPIC-AS4A separator column (0.424 g/l sodium carbonate; 0.126 g/l sodium bicarbonate eluant). Dissolved silica was measured by the Heteropoly Blue Method using Hach Co. (Loveland, CO) reagents and a Bausch and Lomb Spec-20 (700 nm).

All DOC samples were filtered with a Type A/E glass fiber filter (Gelman Sciences, Inc.; 1.6 μm particle retention) previously ashed for 5 hours at 500 °C. Samples in glass bottles (one per bay or two per QC bay) were then analyzed using the standard persulfate oxidation procedure (MENZEL & VACARRO 1964) (OI Corporation Model 5240 Ampoule Analyzing Unit; Model 3300 Infrared Gas Analyzer). Another filtered aliquot from this bottle was used to determine the optical absorbance at 360 nm using a 10 cm quartz cell and a Beckman DU-70 spectrophotometer. A standard curve of DOC versus absorbance was then constructed from the samples taken from the glass bottle. Absorbances (360 nm) of the samples taken in plastic bottles from the three other locations within each bay were then converted to DOC concentrations using this standard curve. The relation between DOC and ABS_{360} was linear with the exception of data from bays t, k and i (middle of the Myrtle Beach transect, Fig. 1). All three bays had pocosin vegetation. These outliers, which were apparently above the linear range of the calibration curve and associated with very high DOC concentrations, were omitted from the final regression model. The resultant regression line (mg C/l = $9.85*ABS_{360} + 1.79$, n = 46, $r^2 = 0.86$) had no apparent pattern to the associated residuals. Although this method was internally consistent, our regression results were quite different from those of LEWIS & TYBURCZY (1974) and LEWIS & CANFIELD (1977). Therefore, direct application of such regression equations without internal validation and calibration, as suggested by these authors, is not recommended.

Analytical quality control (QC)

The duplicate samples from QC sites were combined later in a large container and then divided into two aliquots. One aliquot was used for the routine analysis and the second was spiked with a known concentration of analyte for calculation of spike recovery.

U.S. Environmental Protection Agency quality control samples for pH, specific conductance, anions and cations were also determined to be well within the acceptable range (95 % confidence interval). Analysts lacked knowledge of the acceptable range for the quality control standards for each variable.

Results and discussion

Analytical results and statistical characterization

Ionic balance was estimated using the milliequivalents of Ca^{+2}, Mg^{+2}, Na^+, K^+, H^+, HCO_3^-, Cl^-, SO_4^{-2} and DOC. The naturally-occurring, polycarboxylic acids were included in the calculations using a charge estimate of 0.0055 mM/g DOM (PERDUE et al. 1984 a, 1984 b). The DOC concentrations were then used to calculate the mMoles of charge contributed by the DOM in bay waters assuming DOM (mg/l) = 2*DOC (mg/l) (BECK et al. 1974). The average sums of cations and anions in Carolina bay waters were 0.547 meq/l and 0.524 meq/l, respectively (Table 2). Sodium dominated the cation pool (38.6 %), followed by Ca (20.6 %) and Mg (20.6 %). Three anions were codominant: DOC (37.6 %), SO_4 (25.4 %) and Cl (34.1 %). The mean (± SD) percentage ionic imbalance for the bay water analyses was −0.7 ± 5.7 %, indicating good ionic characterization of these soft waters.

The thirteen variables examined had skewed distributions. Consequently, the median, range, and lower and upper quartiles were used to describe central tendencies and associated dispersions (Table 3). In subsequent univariate and multivariate statistical analyses, log transformations were applied to normalize these data. The average relative standard deviations (RSD) for the "within

Table 2. Average concentrations by weight (mg/l) and equivalence (meq/l) and the percent equivalence for major cations and anions in 49 Carolina bay wetlands and lakes.

Variable	mg/l	meq/l	% meq
Ca^{++}	2.45	0.122	20.6
Mg^{++}	1.36	0.112	20.6
Na^{+}	4.73	0.206	38.6
K^{+}	1.98	0.051	8.1
H^{+}	0.056	0.056	12.1
ΣCations		0.547	100
Cl^{-}	5.89	0.166	34.1
SO_4^{--}	7.41	0.155	25.4
HCO_3^{-}	1.31	0.012	2.9
DOC	17.11	0.191	37.6
ΣAnions		0.524	100

bay" replicates and the mean spike recoveries for QC samples indicated that the sampling and analytical scheme was adequate for characterizing the water chemistry for each bay. Variance between bays (nested ANOVA) accounted for 76 to 94 % of the total variance (Table 3). Sodium (21 %) and Cl (24 %) had the greatest "within bay" variances, and K (6 %) and SO_4 (6 %) had the least. These results suggested that the sampling structure was adequate to effectively define water chemistry variation between bays.

Most of the variable pairings lacked significant correlation ($\alpha = 0.05$). Bivariate plots of all variables indicated that the majority of the structure in these data was contained in nine variables: pH, DOC, Cl, SO_4, HCO_3, SiO_2, Na, Mg and Ca. The strong correlations between these variables were summarized with Kendall Tau Beta coefficients (Table 4). Not unexpectedly, there were strong concordances between Na/Cl, as well as Mg/Ca/SO_4/SiO_2. These relationships reflected a common marine atmospheric source of Na and Cl, and related geologic origins of Ca, Mg, SiO_2 and, perhaps, SO_4. There were also positive correlations between pH and Ca/HCO_3 and a negative correlation between pH and DOC. Although no significant correlation existed between pH and SO_4 ($\alpha = 0.05$) when all of the bays were used in the computations, there was a significant, negative correlation between these two variables for the Savannah transect bays ($r = -0.3067$, $p = 0.032$, $n = 25$). Peat depth, which ranged from 0 to >200 cm (Table 1), had significant, positive correlations with DOC, Fe, and SiO_2, and negative correlations with K, HCO_3, and pH (Table 4).

General chemical patterns

Water chemistry values of the surveyed Carolina bays and bay lakes generally fell within the range of values found in other softwater, acidic systems in-

Table 3. Summary of Carolina bay and bay lake chemistry and associated measures of analytical quality (n = 49).

Variable	Units	Median	Range	Q_1 & Q_3*	ANOVA (%) Within	ANOVA (%) Between	RSD**	Mean spike recovery (%)
Sp. Concl.	μmhos/cm	76	29 – 177	47 – 96	13	87	10	100
pH		4.6	3.4 – 6.7	4.1 – 5.3	8	92	3	NA
Ca	mg/l	1.69	0.16 – 11.75	0.76 – 3.30	9	91	20	94
Mg	mg/l	1.12	0.36 – 3.53	0.85 – 1.71	10	90	12	109
Na	mg/l	4.05	1.06 – 14.19	2.69 – 5.77	21	79	13	102
K	mg/l	0.86	0.27 – 16.22	0.42 – 1.73	6	94	16	105
T.Alk	mg/l as $CaCO_3$	<0.1	<0.1 – 11.4	<0.1 – 1.8	12	88	20	102
SO_4	mg/l as SO_4	3.9	0.2 – 23.9	1.2 – 13.1	6	94	23	98
Cl	mg/l	6.0	3.4 – 9.9	4.7 – 6.6	24	76	8	90
DOC	mg C/l	17.2	2.1 – 70.0	8.0 – 25.6	6	94	12	100***
SiO_2	mg/l SiO_2	3.6	0.1 – 21.8	1.7 – 6.8	8	92	29	107
Fe	mg/l	0.22	0.01 – 2.42	0.07 – 0.43	9	91	32	91
Mn	mg/l	0.05	<0.01 – 2.47	0.03 – 0.14	11	89	25	85

* First quartile & Third quartile.

** The median relative standard deviation of the entire sampling-analysis process, i.e., variation between values for the 4 samples taken at different locations within each bay. Median of 49 sites.

*** DOC by combustion.

Table 4. Kendall Tau Beta correlation coefficients ($n = 49$) (upper matrix), probability values (P that $r = 0$, lower matrix) and transect median values for water quality.

r P(r = 0)	K	Na	Cl	Mg	Ca	SO_4	HCO_3	DOC	pH	Mn	Fe	SiO_2	Cond.	Peat (cm)	Savannah transect median
K		.208	.238	.220	.389	.112	.308	−.116	.399	.449	.032	.014	.039	−.278	1.10
Na	.0354		.619	.317	.286	.281	.006	−.177	.062	.095	−.057	.181	.366	−.019	4.5
Cl	.0162	.0001		.254	.279	.179	.103	−.088	.134	.077	.109	.229	.305	.075	6.2
Mg	.0261	.0013	.0099		.452	.497	−.014	−.022	−.008	.185	−.132	.311	.461	−.050	1.03
Ca	.0001	.0038	.0048	<.0001		.312	.264	−.082	.343	.414	.026	.280	.174	−.071	2.11
SO_4	.2552	.0044	.0689	<.0001	.0016		−.138	−.126	−.166	.089	−.375	.336	.590	−.176	2.2
HCO_3	.0045	.9536	.3415	.8996	.0148	.2036		−.287	.742	.241	.079	−.086	−.203	−.243	0.7
DOC	.2410	.0730	.3746	.9862	.4079	.2020	.0081		−.338	−.208	.293	.090	.111	.254	14.3
pH	.0001	.5291	.1732	.9382	.0005	.0928	.0001	.0006		.395	.099	−.061	−.314	−.210	5.2
Mn	<.0001	.3386	.4378	.0614	<.0001	.3654	.0262	.0347	.0001		.036	.175	−.054	−.070	0.11
Fe	.7497	.5635	.2698	.1315	.7893	.0001	.4666	.0029	.3173	.7173		.062	−.197	.286	0.26
SiO_2	.8903	.0675	.0204	.0017	.0047	.0007	.4260	.3607	.5404	.0771	.5290		.252	.261	1.40
Cond.	.6917	.0002	.0020	<.0001	.0786	<.0001	.0610	.2625	.0015	.5871	.0465	.0107		−.026	57
Peat (cm)	.0054	.8492	.4522	.6163	.4786	.0780	.0266	.0111	.0358	.4840	.0042	.0093	.7955		16
Myrtle Beach transect median	0.65	3.8	5.6	1.26	0.94	5.3	<0.1	22.7	4.2	0.03	0.16	3.5	76	18	

Table 5. Comparison of Carolina bay water chemistry with those of other softwater, acid systems including those of the Southeastern U.S. (#'s 1-6).

Site	Sp. cond. (μmhos/cm)	pH	Dissolved constituents (mg/l)									Reference
			SiO_2	DOC	Ca	Mg	Na	K	Cl	SO_4	HCO_3	
1. Carolina bays (South Carolina, USA)	36	4.3		16	1.3	0.6	1.4	0.6				Schalles (1989b)
2. Shallow groundwater (South Carolina, USA)	40	5.6	4.1		2.2	0.4	2.9	1.0	3.3	1.7	9.8	Cahill (1982)
3. Satilla River (Georgia, USA)		4.6	6.6	23	1.3	0.7	3.7	1.0	6.1	0.7	2.6	Beck et al. (1974)
4. Cypress Dome (Florida, USA)	60	4.5	4.2	40	2.9	1.4	4.9	0.3	8.2	2.6	2.2	Dierberg & Brezonik (1984)
5. Okefenokee Swamp (Georgia, USA)	43	3.9	2.4	40	0.7	0.5	3.1	0.2	5.9			Cohen et al. (1984)
6. Croatan Low Pocosin (North Carolina, USA)		3.7		45	0.1	0.5	2.9	0.6	5.0	2.6		Gorham et al. (1985)
7. Great Dismal Swamp (Virginia, USA)	107	4.3	4.7		4.5	1.3	6.6	2.3	10.3	13.6	2.0	Lichtler & Walker (1979)
8. Perched bogs (Minnesota, USA)	51	3.6	2.7		2.4	1.4	0.6	1.3	0.7	4.6	0	Boelter & Verry (1977)
9. Maritime bogs (Canada)		4.1		27	0.4	0.7	4.8	0.2	8.1	1.1		Gorham et al. (1985)
10. Maritime bogs (Ireland)		4.2		26	1.4	1.9	13.6	0.9	24.0	4.0		Gorham et al. (1985)
11. Continental bogs (Canada, USA)		4.0		32	0.7	0.3	0.2	0.2	0.2	0.7		Gorham et al. (1985)
12. Gorelyy Mohk Bog (USSR)	41	4.0	1.3	41	1.9	0.5	0.8	0.2	2.0	3.1	1.4	Yefimov & Yefimova (1973)
13. Bogs & poor fens (Scandinavia)		4.0		32	1.1	0.4	1.7	0.4	1.6	4.2	0	Sjörs (1961)
14. Tasek Bera (Malaysia)	14	5.2	2.4		0.4	0.3	1.1	0.5	1.9	3.2	1.8	Ikusima et al. (1982)
Carolina bays (median values, n = 49 sites)	76	4.6	3.6	17	1.7	1.1	4.1	0.9	6.0	3.9	< 0.1	(This study)

cluding those on the southeastern Atlantic coastal plain (Table 5). Calcium and HCO_3 concentrations were extremely low in waters of the bays and bay lakes, reflecting an ombrotrophic status for these wetlands and an associated, highly weathered geology. Shallow groundwater on the coastal plain can be quite dilute (Table 5, zones 1 and 2 of CAHILL 1982); consequently, groundwater inputs may chemically resemble atmospheric inputs to Carolina bays. Overall, specific conductance and cation concentrations were higher than those encountered in previous studies of Carolina bays in Aiken and Barnwell counties, SC (1974 to 1980, upper portion of the Savannah transect) (Table 5, see SCHALLES 1989 b). These differences could relate to a closer average distance to the Atlantic Ocean of bays in this study and stronger marine, atmospheric influence. Compared to those reported in the earlier Carolina bay studies, Na concentrations had the greatest increase of the cations. Waters of the Dismal Swamp in southeastern Virginia, and Canadian and Irish maritime bogs (Table 5) were also close to the ocean and had comparatively higher Na values. The mid-1980s were drier than the late 1970s in the South Carolina coastal plain region, and higher solute concentrations in Carolina bays of the present study could also reflect greater evaporative concentration (SCHALLES 1989 b) or substrate oxidation and consequent acid production, which mobilized metals to the dissolved pool (GORHAM 1961).

"Excess" SO_4 (GORHAM et al. 1985) was estimated by assuming that all Cl was derived from marine sources and a seawater SO_4 : Cl molar ratio (0.105). The average bay SO_4 : Cl ratio was 1.01, which suggested considerable enrichment from other sources. Excess SO_4 concentrations were particularly high in nine bays (D, E, L, M, T, V, W, g and j; range 17—22 mg/l SO_4) and four bay lakes (c, d, e, and f; range 12—19 mg/l SO_4). Groundwater enrichment and microbial oxidation and cycling could account for much of the excess SO_4 and interbay differences. However, GORHAM et al. (1985) concluded that excess SO_4 in bog waters is often correlated with anthropogenic additions. These workers also noted high excess SO_4 in a pocosin site in North Carolina.

Carolina bay and bay lake DOC concentrations were lower and pH slightly higher than values from other softwater, dystrophic wetlands (Table 5). A general inverse relationship between pH and DOC concentration was apparent in Table 4. The influence upon pH by organic acids has been well documented for bog waters (HEMOND 1980, GORHAM et al. 1985, KEREKES et al. 1986). Sulfate could also contribute to the influence upon bog water pH (GORHAM et al. 1985, KEREKES et al. 1986). The inverse relationship between SO_4 and pH in bays of the Savannah transect suggested a contribution of SO_4 to pH control in a subset of the bay waters examined in this study.

Manganese had the most variable geographic pattern of the measured variables. Sixteen Carolina bays had Mn concentrations greater than 0.10 mg/l. Ten of the sixteen bays, including five of six bays exceeding 0.30 mg Mn/l in their waters, were located on the Citronelle feature of the Savannah transect. SCHALLES (1989 b) also noted relatively high Mn concentrations in a number of bays in this same region. In contrast, waters from twenty of the twenty-four bays and bay lakes on the Myrtle Beach transect had Mn concentrations less than 0.10 mg/l, and none had concentrations above 0.15 mg/l. Other surface waters of the coastal plain region also have low Mn concentrations (SCHALLES 1989 b). Some sedimentary rocks contain significant amounts of Mn; oxides and hydroxides are the most common forms of Mn in soil and rock (FAUST & ALY 1981). The three ions with strongest correlations to Mn (Ca, Mg, and SO_4) likely have predominately geological origins, and suggest a geological origin for most of the Mn in bay waters.

Median SiO_2 concentrations were low and varied widely between bays (Table 3). This variability could reflect variations in coastal plain groundwater (CAHILL 1982) which result from different contact times of water and silicate minerals and from proportional differences in atmospheric versus groundwater loading. Most of the SiO_2 in coastal plain water likely originates from the weathering of quartz sand and alumino-silicate clays (DIERBERG & BREZONIK 1984). Low concentrations and seasonal availability of SiO_2 in acidic southeastern wetlands are also influenced by biological activity. Amorphous silica from phytoliths, diatom frustules, and sponge spicules was the dominant ash component in peats from the Okefenokee Swamp (ANDREJO & COHEN 1984), and suggest significant biogeochemical cycling in dystrophic wetlands. In a Florida cypress dome, SiO_2 concentrations were higher in the winter (4—6 mg/l as Si) than in the spring or summer growing period ($<$ 1.0 mg/l as Si) (DIERBERG & BREZONIK 1984). The present survey was conducted in early January during the period of lowest biological activity.

Bay comparisons and regional patterns

The absence of statistical correlations for many variable pairs and relatively high variation between bays suggested a general lack of clear, dominant factors controlling all aspects of the water chemistry of Carolina bays. However, examination of the geology surrounding the bay wetlands and lakes revealed several additional patterns.

The bays from the Myrtle Beach transect had higher median concentrations of SO_4 and DOC, and lower median pH than those of the Savannah transect (Table 4). Median Ca and total alkalinity were generally higher in bays from the Savannah transect than those of the Myrtle Beach transect. Trivariate plots of cations (Fig. 2) suggested a clear trend in the Savannah transect bays from a predominance of the monovalent cations to partial Ca dominance. The bays surveyed by SCHALLES (1989 b) on the upper reaches of the Savannah transect displayed cation proportions and variability similar to the Savannah

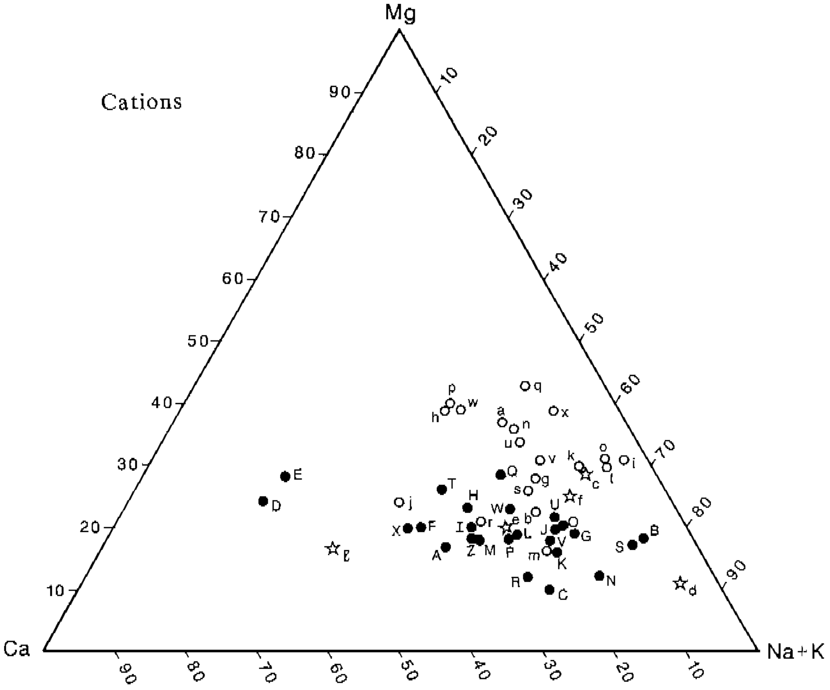

Fig. 2. Trivariate plot of the relative proportions of Na + K, Ca and Mg in Carolina bay waters. Capital and small letters correspond to bays and bay lakes as shown in Fig. 1.

transect bays in this study. In contrast to this trend, bays from the Myrtle Beach transect had no distinct pattern and proportionately more Mg than those of the Savannah transect. The less distinct trend noted for the Myrtle Beach transect bays was deemed a product of the more complex geology associated with fluvial terraces and younger, remnant island and estuarine features (see Colquhoun 1969, Thom 1970). The Myrtle Beach bays had very low proportions of HCO_3 relative to SO_4 or Cl (Fig. 3). In comparison, bays from the Savannah transect tended to have higher proportions of HCO_3 than those of the Myrtle Beach transect.

Several trends existed between water chemistry and geological features underlying the bays. For example, bays D and E of the Savannah transect were outliers relative to the elevated proportions of Ca (Fig. 2) and had elevated concentrations of SO_4 (Fig. 3). These two bays were situated on the Savannah River fluvial terrace and, consequently, overlaid material derived from the Piedmont as well as the coastal plains. Two Savannah transect bays (L and M) on the seaward edge of the Citronelle (formerly classified as high terrace) had elevated concentrations of Ca (5.26 and 5.62 mg/l), Mg (1.90 and 2.67 mg/l), and SO_4 (17.3 and 20.3 mg/l as SO_4). These bays were located near the north-

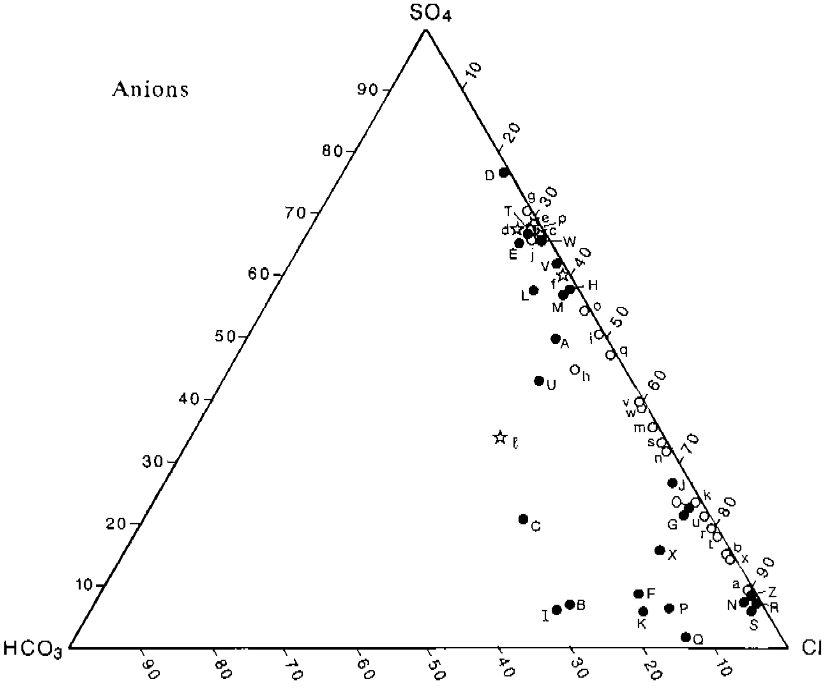

Fig. 3. Trivariate plot of the relative proportions of Cl, HCO_3 and SO_4 in Carolina bay waters. Capital and small letters correspond to bays and bay lakes as shown in Fig. 1.

west margin of the lower coastal terraces where extensive limestone deposits occur (SIPLE 1967).

Other general trends were noted for the bays and bay lakes. The bays from the Wicomico Terrace (Table 1) clustered into two distinct groups relative to the proportions of major cations in their waters (Fig. 2). The pocosin bays from this terrace occurred in sandy regions, which included a relic barrier island. Their chemistry was dominated by the monovalent cations. Other bays, associated with the back barrier areas of the terrace or with river terraces, tended to have waters with higher proportions of Ca and Mg than those of the pocosins. All but two bays (bays v and x) on the most recent terraces (Talbot and Pamlico, Table 1) on the Myrtle Beach transect were classified as pocosin and had average to moderately low concentrations of Ca (1.19—2.47 mg/l), Mg (0.68—1.31 mg/l) and SO_4 (1.6—3.6 mg/l as SO_4) and slightly higher concentrations of DOC (21.2—55.9 mg C/l) than bays further inland along this transect.

FREY (1949) provided the first limnological accounts of the remarkable set of bay lakes in southeastern North Carolina, and the results of the present study largely parallel his earlier findings. White Lake (bay e), which is fed by a large artesian aquifer (FREY 1949, WELLS & BOYCE 1953), had higher Ca (3.4

versus 0.6—0.8 mg/l) and Mg (1.6 versus 0.8—1.1 mg/l) concentrations compared to three nearby bay lakes (bays c, d and f). White Lake had lower DOC concentrations (2.1 versus 4.0—5.5 mg C/l), apparently as a result of a higher groundwater flushing rate (Wells & Boyce 1953) and an absence of peripheral bog drainage into the lake (Frey 1949). Lake Waccamaw (bay e) is geographically separated from the other North Carolina bay lakes. In the present study, Lake Waccamaw had relatively high concentrations of Ca (6.2 mg/l), HCO_3 (7.4 mg/l as $CaCO_3$), and pH (6.68), characteristics attributable to a calcareous Miocene formation that outcrops along its shore (Frey 1949).

Overall, pH values measured in the present study were generally lower than those reported by Frey (6.68 versus 7.0, 4.43 versus 4.9, 3.86 versus 4.5, 4.49 versus 4.4, and 3.90 versus 4.3 for Waccamaw, White, Singletary, Black, and Jones Lakes, respectively). Subsequent to Frey's work, highly colored bog drainage was diverted from Black Lake and the lake was renamed Bay Tree Lake as part of a resort home development project. As a consequence, the lake could have experienced reduced DOC and organic acidity. Except for those of Waccamaw Lake water, total alkalinity concentrations in bay lake waters were below the detection limit ($<$ 0.1 mg/l as $CaCO_3$). Using methyl orange indicator, Frey (1949) measured total alkalinity values of 1.6 to 3.0 mg/l as $CaCO_3$ in these same lakes. Further, SO_4 concentrations measured in the present study were approximately 250 % higher than those measured by Frey (1949). It is possible that the measurements separated by 40 years reflect increased lake acidity; however, methodological differences could have contributed to the observed differences (Gorham & Detenbeck 1986). Further investigation of these poorly buffered systems is necessary.

Vegetation/hydrology

To understand better the variables contributing most to differences between bays, canonical discriminant analysis (SAS 1986) was applied, using individual bays as "groups", and replicate samples within each bay as "cases". The first three discriminant functions accounted for 64.8 % of the total variance when 11 functions were extracted. These discriminant functions had high eigenvalues and cannonical correlations (Table 6). Dissolved organic carbon and K concentrations dominated the first axis, and their function coefficients had different signs (Table 6), and result in sites with high DOC concentrations clustering to the right and sites with high concentrations of K clustering to the left along the first ordination axis (Fig. 4). Potassium and DOC concentrations had the greatest amount of the total variation between bays (Table 3) and had the poorest correlations with the other variables. Sulfate, pH and K were the strongest discriminators in the second function. Perhaps surprisingly, based on their geographic variability and geologic

Table 6. Summary of first three discriminant functions computed from Canonical Discriminant Analysis (SAS, 1986) of eleven water chemistry variables. Log_{10} transformations were applied to all variables. Standardized coefficients for those variables with the highest weightings in the first three functions are given. The strongest discriminator for each axis is indicated by an asterisk.

	Canonical variables		
	I	II	III
Eigenvalues	51.0	38.7	27.1
Canonical correlation	0.991	0.987	0.982
Proportion of variance explained by function	0.286	0.213	0.149
Variable	Standardized coefficients for canonical variables		
Log DOC	4.22*	0.19	1.83
Log K	−2.73	2.22	2.48*
Log Mn	−1.23	−0.04	1.17
Log SiO_2	1.22	0.22	1.72
Log SO_4	0.36	4.05*	−0.08
Log pH	−0.06	−2.20	1.35
Log Ca	0.03	−0.70	−0.25
Log Mg	−0.04	−0.05	0.13

sources, Ca and Mg were poor discriminators. The bay lakes (bays c, d, e, f and l) were scattered through the left side of the ordination, with White Lake and Lake Waccamaw separated by almost 20 standard deviation units (Fig. 4). Certain chemical patterns appeared to be correlated with the dominant vegetation types. Vegetation classifications (Table 1) were used to label group means in the canonical discriminant analysis ordination (Fig. 4). Pocosin bays, with their distinctive evergreen and deciduous shrub vegetation (Christensen et al. 1981) and their distinctive water chemistry were clustered on the upper, right side of the ordination and had little overlap with the other types. The pocosins had relatively high DOC and low K concentrations, characteristics associated with vegetation influences on surface chemistry. The sclerophyllous leaves of many pocosin evergreen and deciduous shrubs have high concentrations of aromatic compounds (Christensen et al. 1981) and function as a rich source of DOC. These secondary plant compounds could have contributed to some of the major deviations noted in the regression analysis of the DOC concentration and absorbance data. The stagnant, ombrotrophic hydrology and consequent low calcium carbonate levels of pocosin waters could foster long residence times for DOC. The low K concentrations in pocosins could indicate active nutrient cycling despite the season. Potassium appears to be a sensitive indicator of vegetation status in southeastern wetlands, with elevated concentrations in the non-growing season or following drought conditions or plant

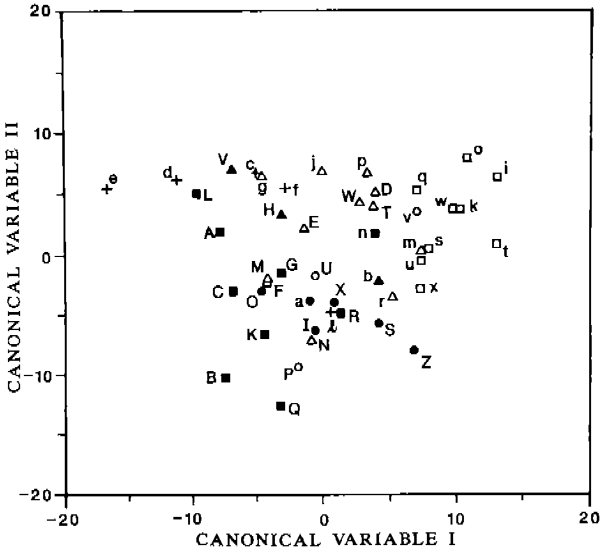

Fig. 4. Ordination of the Carolinan bays along the first and second discriminant functions (+ = bay lake, ■ = marsh with pond, ● = mixed marsh/swamp forest, ▲ = pine forest, ○ = cypress swamp forest, △ = hardwood swamp forest, and □ = pocosin).

damage (Bosserman 1984, Schalles 1989 b). In the ordination (Fig. 4), marsh wetland habitats were located on the left and lower left and swamp forest habitats had positions generally intermediate to the marsh and pocosin positions. Most hardwood swamp forest sites were clustered in the upper center of the ordination distribution. In earlier bay surveys, Schalles (1989 b) found higher specific conductance and DOC levels in swamp forest sites compared to marsh sites. Overall, the ordination scheme and habitat could reflect a gradation from the more minerotrophic, groundwater supplied lakes, swamps and marshes to the more ombrotrophic, hydrologically isolated conditions (Daniel 1981) and active vegetative dominance of the pocosin shrub bog habitats. Schwintzer & Tomberlin (1982) applied principal components analysis (PCA) to water chemistry of shallow groundwaters in northern Michigan wetlands. They also achieved good separations by vegetation type (bog, forested swamp and fen) and concluded that an ombrotrophic to minerotrophic gradient and differences in detrital decay products were the most important chemical factors explaining their plant community groupings in the ordination.

Summary of general trends

It was clear from the Carolina bay waters examined in this survey that surficial groundwater has a strong influence on bay water chemistry. In the case of one bay lake (White Lake or bay e), there was also evidence of deeper groundwater influence. Many of the bays with a significant excess of SO_4 were outside the original envelope of water chemistry derived by Gibbs (1970). Clearly, these deviations and the correlations between SO_4, Mg, Ca, and Si were associated with the chemical leaching of the coastal plains soils (Beck et al. 1974).

Paludification and associated peat accrual (Sjors 1950, Gorham et al. 1985) could produce the observed gradation from mixed mineral weathering/precipitation to precipitation dominated chemistry in bays. Gorham and others (see Moore & Bellamy 1974) observed that the accrual of peat during a transition from fen to bog was accompanied by a distinct change in water chemistry. As peat accumulated, the flux of groundwater was reduced and an epiphenomenal transition in water chemistry toward precipitation dominance occurred. Such a process could be occurring in Carolina bays examined in the present study. As the peat depth increased, the pH, HCO_3, and Ca decreased and DOC concentration increased (Table 4). Based on the water chemistry, the accumulation of peat in bays appeared to inhibit surficial groundwater influx similar to the inhibition noted for bogs (Gorham et al. 1985), and, perhaps, further influenced bay water chemistry by cation exchange.

Although the trends noted for Carolina bays were consistent with a paludification mechanism, there is an alternate explanation. Bays with the thinnest peat deposits are generally believed to be on the upper coastal plain (Frey 1950, Schalles & Shure 1989). Surveyed Carolina bays on the Citronelle (Coharie terrace bays, as described in Frey 1950) did have the thinnest peat deposits, and several of the bays on the Wicomico and Talbot terraces had the thickest peat deposits. It could be argued that water chemistry was determined by position on the coastal plain and peat depth was simply correlated with location on the coastal plain. The influence of the underlying geology on surficial groundwater contributions to bay water chemistry, as discussed above, would support this mechanism. Correlations between peat depth and water chemistry variables were rather weak, although approximately half of them were significant (Table 4). Further, the general trend in mixed mineral weathering/precipitation to precipitation dominance noted for the study bays was similar but less extreme than that of several rivers of the southeastern United States coastal plain (Beck et al. 1974). Rivers in the upper coastal plain had significant rock weathering influence, but those of the lower coastal plains (flatwoods) were precipitation dominated. Unfortunately, it is impossible to reject either mechanism (paludification versus variation in groundwater chemistry) for explaining the relationships noted between peat depth and water chemistry with the information collected in this survey.

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