GEOCHEMISTRY OF SURFACE AND PORE WATER AT USGS CORING SITES IN WETLANDS OF SOUTH FLORIDA: 1994 AND 1995

by

William H. Orem[1] , Harry E. Lerch[1] , and Peter Rawlik[2]
[1] U.S. Geological Survey, 956 National Center, Reston, VA 20192
[2] South Florida Water Management District, 3301 Gun Club Road, West Palm Beach., FL 33416-4680

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Abstract

In this report, we present preliminary data on surface and pore water geochemistry from 22 sites in south Florida sampled during 1994 and 1995. These results are part of a larger study designed to evaluate the role of biogeochemical processes in sediments in the cycling of carbon, nitrogen, phosphorus, and sulfur in the south Florida ecosystem. The data are briefly discussed in regard to regional trends in the concentrations of chemical species, and general diagenetic processes in sediments. These results are part of a larger study designed to evaluate the role of biogeochemical processes in sediments in the cycling of carbon, nitrogen, phosphorus, and sulfur in the south Florida ecosystem. These elements play a crucial role in regulating organic sedimentation, nutrient dynamics, redox conditions, and the biogeochemistry of mercury in the threatened wetlands of south Florida.

Pore water samples for chemical analyis were obtained using a piston corer/squeezer designed to avoid compression of the sediment and avoid oxidation and contamination of the pore water samples. Results show distinct regional trends in both surface water and pore water geochemistry. Most chemical species in surface and pore water show peak concentrations in Water Conservation Area 2A, with diminishing concentrations to the south and west into Water Conservation Area 3A, and Everglades National Park. The largest differences observed were for phosphate and sulfide, with concentrations in pore waters in Water Conservation Area 2A up to 500x higher than concentrations observed in freshwater marsh areas of Water Conservation Area 3A and Everglades National Park. Sites near the Hillsboro Canal in Water Conservation Area 2A are heavily contaminated with both phosphorus and sulfur. Pore water profiles for dissolved reactive phosphate suggest that recycling of phosphorus at these contaminated sites occurs primarily in the upper 20 cm of sediment. High levels of sulfide in pore water in Water Conservation Area 2A may inhibit mercury methylation here. At sites in Water Conservation Area 3A south of Alligator Alley, sulfide levels are much lower and sulfate reduction in the sediments here may be conducive to methyl mercury formation. Concentration versus depth profiles of biogeochemically important chemical species in pore water at most sites are smoth curves amenable to modelling using standard diagenetic equations. This should allow prediction of rates of biogeochemical processes in these sediments for incorporation in ecosystem models..

Introduction

The south Florida wetlands ecosystem is an environment of great size and diversity, covering an area of over 28,000 km^2 or about 450 km north to south and 100 km east to west at its maximum extent (Light and Dineen, 1994). The ecosystem encompasses a variety of wetland habitats, including the Kissimmee River system, Lake Okeechobee, freshwater marshes south of Lake Okeechobee (the Everglades), Big Cypress Swamp, mangrove swamps along the coast, and Florida Bay (Davis and Ogden, 1994). These diverse habitats are interconnected by the flow of fresh water from one part of the ecosystem to another, and provide a unique home for an abundance of wildlife, some of which are found nowhere else.

South Florida wetlands are currently in crisis due to the combined effects of urbanization, agriculture, and nearly 100 years of water management. Critical problems include: (1) contamination of freshwater marshes and Florida Bay with phosphorus (P) and other elements, resulting in changes in the native flora and possible secondary effects on native fauna (Koch and Reddy, 1992; Craft and Richardson, 1993; Davis 1994), (2) changes in the natural hydrologic flow of the region, resulting in the subsidence of organic soils, fires in the freshwater marshes, and diminished freshwater flow to Florida Bay (Light and Dineen, 1994; McIvor et al. 1994), (3) contamination of fish and other wildlife with mercury (Hg) at levels high enough to pose a potential threat to human health (Lambou et al., 1991; and Delfino et al., 1993), (4) large decreases in wildlife populations, especially those of wading birds (Robertson and Frederick, 1994), and (5) extensive algal blooms, hypersaline conditions, seagrass dieoff, and diminishing productivity of fisheries in Florida Bay (Boesch et al., 1993).

In response to these problems, the U.S. Geological Survey has established a Critical Ecosystems Program for south Florida to examine geologic, hydrologic, geochemical, and biological framework of this ecosystem, establish the important processes contributing to its degradation, and assist land and water managers in efforts to "restore" the ecosystem. Restoration within the context of south Florida implies finding solutions to allow the equitable coexistance of agriculture, urban areas, fisheries, and wildlife habitat. In this report we present initial chemical analyses of surface and pore waters that are part of a study designed to describe the biogeochemical cycling of elements in sediments from south Florida wetlands.

Biogeochemical processes in sediments play an important but little understood role in many of the problems facing south Florida wetlands. For example, biogeochemical processes in sediments are central to nutrient recycling and the ultimate fate of excess nutrients entering the Everglades from agricultural runoff. Sediments likely also play an important role in the geochemistry of mercury, as sulfate reduction in sediments is thought to be the principal mechanism in the conversion of dissolved mercury to methyl mercury, a neurotoxin and bioaccumulated form of mercury. Sediments also contain a record of past environmental conditions in the south Florida ecosystem. An understanding of past conditions is essential for any effort to restore this wetlands ecosystem to a pristine state.

For many decades geochemists have studied the chemistry of pore water (the water present in the pore spaces of sediments) to attempt to understand biogeochemical processes occurring in sediments (Berner, 1971 and 1980). The enrichment or depletion of various chemical species in pore water can indicate the nature of ongoing biogeochemical processes in the sediments; processes that are not readily apparent from studies of the solid phase geochemistry. Pore water chemical data also provides the basis for quantitative estimates of the rates of biogeochemical processes occurring in the sediments (Berner, 1980).

In this report we present surface water and pore water data from a number of sites in south Florida wetlands, including sites in the Water Conservation Areas (WCA), Everglades National Park (ENP), and Big Cypress National Preserve (BC). We present herein a brief overview of spatial trends in the data, and a description of the probable biogeochemical processes producing the observed trends. Future reports will emphasize a more quantitative approach, including modelling of the data and estimation of the rates of biogeochemical reactions. In addition to analyses of surface and pore waters, geochemical analyses of solid phase sediments were also conducted at each of the study sites detailed here. Results of these solid phase studies will be presented in future reports.

Study Area

Coring sites for pore water studies were chosen based on the objectives of this project and on the recommendations of federal and state land and water management agencies located in south Florida. Wherever possible, sites already established by other agencies (state and federal) were

sampled in order to maximize interagency comparison of data. Our sites (Table 1 and Fig. 1) comprise a general north-south transect in the eastern Everglades, including sites in WCA 1A (Loxahatchee National Wildlife Refuge), 2A, 3A, and 3B, and Everglades National Park. Separate cores for studies of peat geochemistry were also obtained at all of these sites (reports in preparation). Surface water samples were collected prior to any coring in clean polyethylene bottles. Additional surface water samples were collected at 10 other sites (mostly in Big Cypress National Preserve) where pore water was not collected (Table 1 and Fig. 1). Bottles were rinsed several times with surface water, and a sample was collected by submerging the capped bottle to about 30 cm above the peat surface, slowly opening the bottle, and completely filling and recapping it underwater.

In WCA 1A, cores for pore water studies were collected at two locations along a transect established by the Environmental Protection Agency (a site near the Hillsboro Canal and a site in the center of area 1A). Cores in WCA 2A were collected at South Florida Water Management District (SFWMD) "Threshold Study Sites", including phosphorus-impacted areas near the Hillsboro Canal dominated by cattails, ***Typha sp.*** (sites E1 and F1), and a site near the center of WCA 2A with little phosphorus contamination and dominated by sawgrass, ***Cladium jamaicense*** (site U3). In WCA 3A we selected three coring sites for pore water studies, one at the northern edge that is frequently dry at the surface (hydrostation #3), a location in the center of area 3A south of Alligator Alley dominated by sawgrass (hydrostation #15), and a site at the southern extreme of area 3B just north of the Tamiami Trail also dominated by sawgrass and with a marl layer in the peat profile (site TT). Sites cored in Everglades National Park included Grossmans Hammock in the northeastern area of the park where short sawgrass in thin peat overlies karstic limestone bedrock, Pa-Hay-Okee Lookout at the eastern edge of the Shark River Slough with dominant sawgrass vegetation, and a site along Taylor Creek with brackish water and short red mangrove trees, ***Rhizophora mangle***.

Coring and Pore Water Extraction

Pore water samples were obtained by coring and subsequent squeezing of the core using a specially designed stationary piston coring device and squeezing apparatus (Fig. 2). A detailed

Table 1. Sample identification, location, sampling date, and general description of study sites in south Florida, 1994-1995.

FIG. 1 ID[1]	FIELD ID	LAT.	LONG.	SAMPLES	DATE	GENERAL COMMENTS
I. Water Conservation Area 1A (Loxahatchee NWR)						
1. 1A-1	42195P1	26°28.782'N	80°26.565'W	SW,PW,SD	4/21/95	EPA transect site 1; @0.2 km east of Hillsboro Canal; Typhia/Pistia marsh
2. 1A-5	42095C1	26°28.842'N	80°25.809'W	SW,SD	4/20/95	EPA transect site 5; @0.5 km east of Hillsboro Canal; tall/thick sawgrass marsh
3. 1A-7	42195P2	26°28.873'N	80°24.931'W	SW,PW,SD	4/21/95	EPA transect site 7; near center of Area 1A @ 2.9 km east of Hillsboro Canal; sawgrass/water lily marsh
II. Water Conservation Area 2A						
4. 2A-E1	3194P1	26°21.09'N	80°21.20'W	SW,PW,SD	3/1/94	SFWMD site E1; @1.9 km south of Hillsboro Canal; Typha marsh
5. 2A-U3	3194P2	26°17.27'N	80°25.01'W	SW,PW,SD	3/1/94	SFWMD site U3; Center of Area 2A @9.8 km south/southwest of Hillsboro Canal; sawgrass and water lily marsh
6. 2A-U3	42595P1	26°17.25'N	80°24.68'W	SW,PW,SD	4/25/95	SFWMD site U3 (same as above but about 0.3 km east)
7. 2A-F1	42695P1	26°21.58'N	80°22.23'W	SW,PW,SD	4/26/95	SFWMD site F1; @1.9 km south of Hillsboro Canal; Typha marsh
8. 2A-E2	3194A1	26°20.52'N	80°21.16'W	SW,SD	3/1/94	SFWMD site E2; @2.7 km south of Hillsboro Canal; Typha marsh with some sawgrass
9. 2A-F3	3194A2	26°19.79'N	80°23.29'W	SW,SD	3/1/94	SFWMD site F3; @5.6 km south/southwest of Hillsboro Canal; sawgrass marsh with some Typha
II. Water Conservation Area 3A						
10. 3A-TT	22794P1	25°45.720'N	80°30.460'W	SW,PW,SD	2/27/94	Site just north of picnic area off route 41 (Tamiami Trail); sawgrass marsh
11. 3A-15	42795P1	25°58.455'N	80°40.127'W	SW,PW,SD	4/27/95	Site in the center of WCA 3A south of Alligator Alley; sawgrass/water lily marsh
12. 3A-3	42795P2	26°16.173'N	80°36.812'W	SW,PW,SD	4/27/95	Site in the center of WCA 3A north of Alligator Alley; sawgrass marsh, often drys out

Table 1 (continued).

IV. Everglades National Park						
13. ENP-PHO	22694P1	25°25.968'N	80°46.452'W	SW,PW,SD	2/26/94	Pa-Hay-Okee Lookout site; eastern edge of Shark River Slough; sawgrass marsh
14. ENP-GH	3694P1	25°37.134'N	80°34.968'W	SW,PW,SD	3/6/94	Site on south side of Grossmans Hammock; short/thin sawgrass marsh
15. ENP-C111	42395C2	25°19.117'N	80°31.517'W	SW,SD	4/23/95	Site just east of ENP and 0.5 km south of dog leg in the C111 canal; disturbed area with some sawgrass, mostly dry
16. ENP-TC1	42395C1	25°11.773'N	80°38.216'W	SW,SD	4/23/95	Site at east end of first lake up Taylor Creek; dwarf red mangrove swamp
17. ENP-TC2	42395P1	25°12.339'N	80°38.641'W	SW,PW,SD	4/23/95	Site at north end of third lake up Taylor Creek; dwarf red mangrove swamp
V. Big Cypress National Preserve						
18. BC-1	3394W1	26°02.851'N	81°21.683'W	SW	3/3/94	Sample collected from canal adjacent to route 29 in Deep Lake
19. BC-2	3394CY3	26°01.539'N	81°15.845'W	SW,SD	3/3/94	Sample collected on west side of Turner River Road (route 839) just north of route 841 intersection; dwarf cypress swamp
20. BC-3	3394CY2	26°01.467'N	81°15.936'W	SW,SD	3/3/94	Sample collected on west side of Turner River Road (route 839) just north of route 841 intersection; mature cypress dome
21. BC-4	3394CY1	25°57.790'N	81°21.413'W	SW,SD	3/3/94	Sample collected on south side of Wagonwheel Road (route 837) about midway between routes 29 and 841 (Birdon Road); sawgrass marsh
22. BC-5	3594CY1	25°52.116'N	80°54.816'W	SW,SD	3/5/94	Sample collected on north side of Jet Port Road to Dade-Collier Training Airport; dwarf cypress and sawgrass
23. BC-6	3594CY4	25°18.300'N	80°34.416'W	SW,SD	3/5/94	Sample collected on south side of Loop Road (route 94), about 2 mi. west of Pinecrest; mature cypress strand

1 - Sample identifications as shown in Fig. 1
2 - SW = surface water, PW = pore water, SD = sediment (cores, and auger samples)

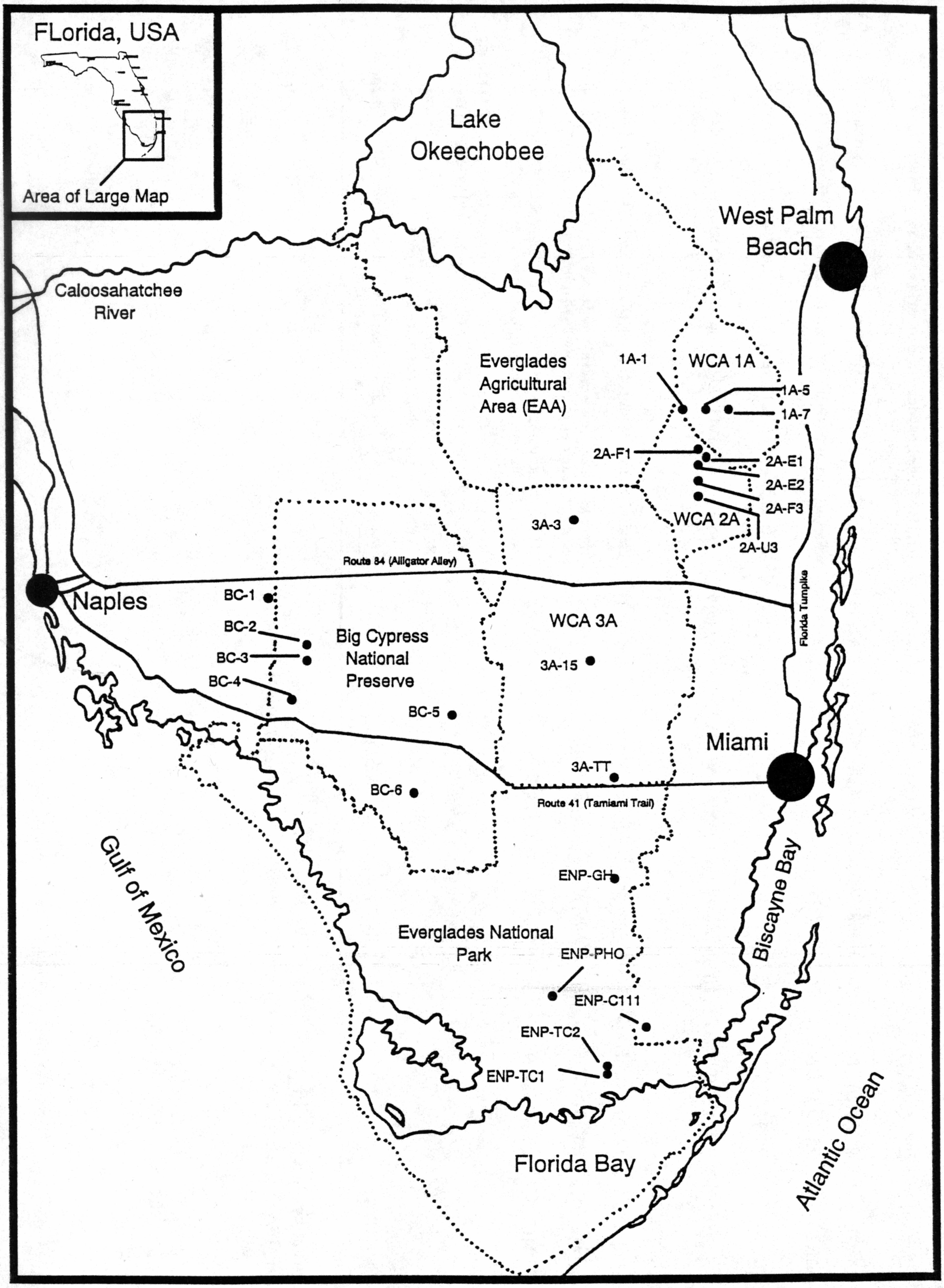


Figure 1. Map of south Florida showing the sampling locations in the Water Conservation Areas (WCA 1A, 2A, and 3A), Everglades National Park (ENP), and Big Cypress National Preserve (BC) during 1994 and 1995.

description of the coring and squeezing apparatus is presented elsewhere (Orem and Lerch 1997). The squeezing device is a modified version of that developed by Jahnke (1988). The advantages of this approach for pore water extraction in wetland sediments containing rooted aquatic macrophytes are discussed by Howes et al. (1985). Piston cores were taken using a monopod, an acrylic core tube, a PVC piston with a pair of o-rings, an aluminum cutter with cutting teeth, and a set of iron handles (Fig. 2A). The core tube has a series of holes at 2 cm intervals tapped for a 1/4-28 thread, which act as exit ports for pore water from different depths during squeezing. The holes are sealed during coring with 1/4-28 roundhead nylon screws and small o-rings.

In the Everglades we chose coring sites where the peat surface appeared undisturbed, and the vegetation was not so thick as to impede access. Airplane cable attached to the piston was fed through the core tube, the piston was tapped into the core tube with a rubber mallet, and the cutter was screwed onto the end of the core tube. The airplane cable was then attached to the monopod, and the iron handles were clamped around the core tube at a convenient height. A core was obtained by first twisting and pushing the core barrel with the handles to allow the serrated edge of the cutter to slice through any surface mat of rootlets and plant debris. Once through the root mat the core barrel easily penetrated into the peat while the piston remained stationary at the peat surface. We generally used core barrels of 4, 3, and 2 feet in length. Once the core barrel was emplaced in the peat to the desired depth, the cable was removed from the monopod pole and wrapped tightly around the handles to prevent the piston from slipping during recovery of the core. The core was then lifted from the peat with the handles (some effort required), and the bottom was capped and taped. The eye bolt and cable unit was usually removed from the piston at this point by unscrewing it with a wrench. Every attempt was made to keep the core as vertical as possible during return to base for pore water extraction. Cores for geochemical analyses of the peat were obtained in an identical manner.

Squeezing of the core for pore water extraction was begun as soon as possible after return to an appropriate base (boat launch area, motel parking lot, laboratory, etc.). The cutter and cap on the end of the core tube were removed and the core tube was placed into the squeezer support and secured with aluminum clamps (Fig. 2B). A squeezing piston with two o-rings was tapped into the bottom of the core barrel with a rubber mallet, and a push piston (no o-rings) attached to a threaded steel rod was screwed up until it made contact with the squeezing piston. The core was raised with

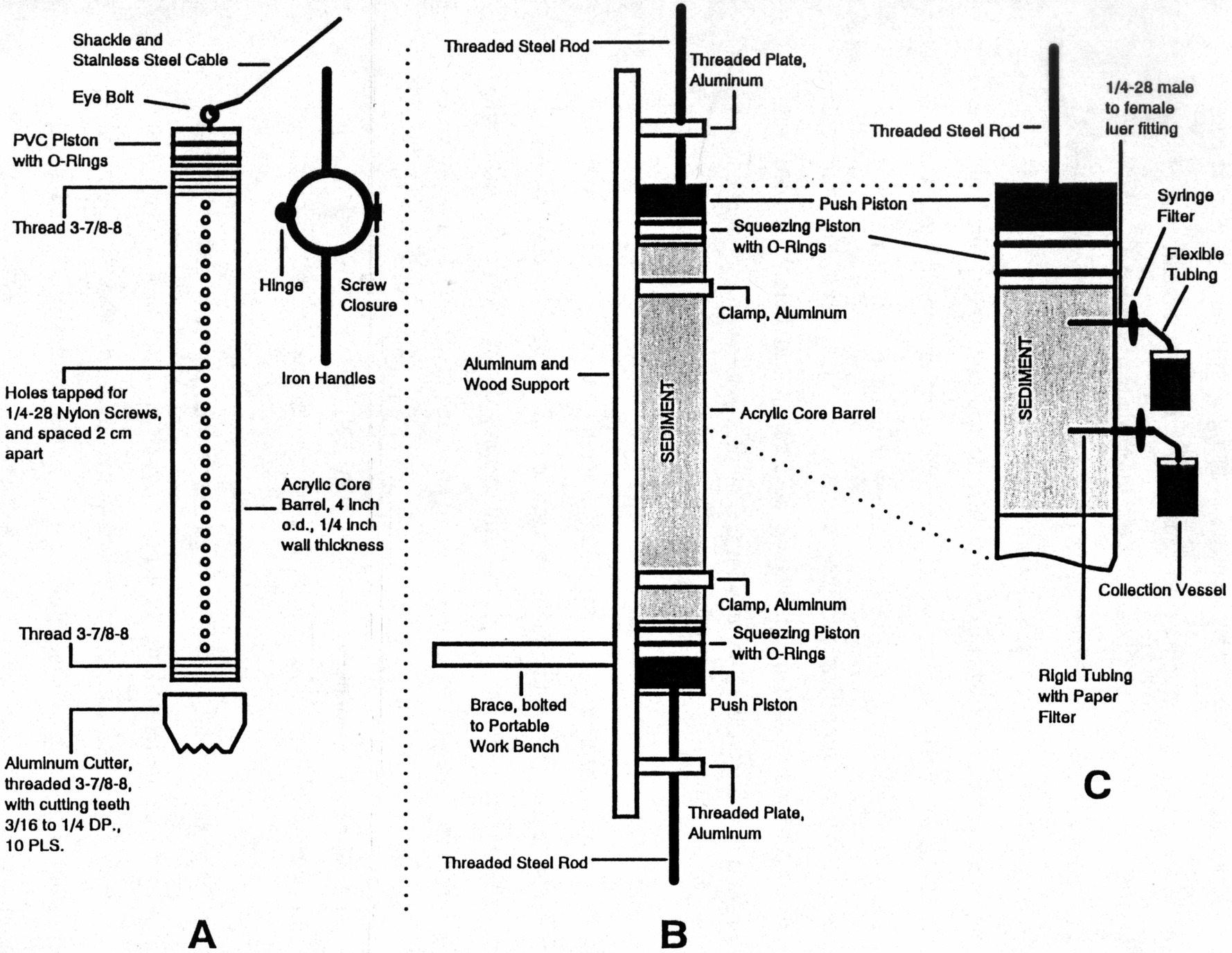


Figure 2. Diagram of sediment piston coring device and pore water squeezer. The coring device (A) consists of a plexiglas core barrel, alumninum cutter, polyethylene piston, and iron handles. During coring, the piston is attached to a monopod (not shown) with steel cable. Pore water is obtained from a core by attaching the core barrel to a support, adding a second piston, and gradually compressing the core using threaded steel rods and threaded plates attached to the support (B). Pore water from various depth intervals exits the core through holes in the side of the core barrel, passes through a syringe filter, and is collected in appropriate vessels (C). See text and Orem and Lerch (1997) for more details.

the bottom piston by turning the lower threaded rod arrangement with a socket wrench until the core was in the desired position relative to the sampling ports on the side of the core barrel. A sampling port above the sediment surface was opened by removing the roundhead nylon screw to allow excess overlying water to escape during the positioning of the core, then reclosed. Sufficient overlying water is left above the sediment core so that no air is trapped below the upper squeezing piston. Next, An upper push piston attached to a threaded rod was screwed down until it abutted the top squeezing piston (the latter already in place from the coring operation). The nylon screws were removed from the sampling ports at the depth intervals to be sampled and were replaced with 1/4-28 male to female luer fittings. The luer fittings contained a tightly-rolled quarter piece of 5.5 cm diameter Whatman filter paper as a pre-filter. One end of the fitting was attached to a piece of rigid plastic tubing 2-3 cm in length (Fig. 2C). The rigid tubing extends into the center of the peat matrix to minimize the chance of sampling water that flows along the inner wall of the core tube (Jahnke, 1988). Syringe filters (Gelman 25 mm, 0.45 μm ion chromatography Acrodisc) were locked onto the luer fittings and sampling containers were attached to the syringe filters with a small piece of flexible tubing (Fig. 2C). We used disposable plastic syringes for collection of samples for dissolved gases and pH, and small plastic bottles with plastic fittings pushed through the lids for collection of pore water for other dissolved constituents (nutrients, anions, cations, and dissolved organic carbon). All plastic fittings, tubing, and containers used in the pore water extraction were soaked overnight in 10% HCl and thoroughly rinsed with deionized/distilled water prior to use.

Pore water began to flow from the sampling ports into the collection vessels as the steel rods from the top and bottom were alternately advanced, squeezing the peat and forcing the pore water out the sampling ports. After the initiation of flow, only the bottom threaded rod and piston was turned, avoiding potential problems of excessive compression of the surface sediment and smearing of the pore water profile at the surface (Jahnke, 1988). The pressure on the core was maintained by continuing to screw down the bottom threaded rod and piston about every 10-15 min or when the pore water flow seemed to diminish significantly. Squeezing continued for 2-5 hours, depending on the quantity of pore water desired and the characteristics of the peat. Aliquots of pore water for immediate analysis of volatile dissolved constituents (e.g. dissolved sulfide, pH, alkalinity) were collected as soon as sufficient sample was available. Syringe filters were normally changed once or twice during the course of squeezing to maintain proper flow. This was done by reducing pressure

on the core barrel (e.g. slightly retracting the threaded rod and piston), and quickly replacing the filter. Occasionally, some depth intervals would produce "dry holes" or little pore water recovery for no apparent reason, possibly due to blockage of the rigid plastic tubing in the peat. Typical yields of pore water (excluding "dry holes") ranged from 20 to 60 ml for each interval. Peat cores were compressed by 4-11 cm by squeezing. Squeezing was terminated simply by retracting the threaded rod and piston and removing the sample containers, syringe filters, and luer fittings. The core tube was removed from the squeezer, the nylon screws and washers were replaced in the pore water sampling ports, and the core was extruded. After cleaning, the core tube was ready to be used again.

Analytical Methods

Filtered pore water samples collected from the squeezer were distributed into various containers for analysis. Titration alkalinity, pH, and H_2S were determined immediately after collection. Pore water for pH and H_2S was collected in disposable plastic syringes to minimize degassing and oxidation by contact with the atmosphere. Pore water for titration alkalinity was transferred to clean polyethylene bottles, titrated with 0.1 M HCl to a fixed pH between 3.5 and 2.8, and finally acidified with 0.1 ml of concentrated Ultrex HNO_3. This same sample was then stored for later analysis of major cations (Na, K, Ca, Mg, Sr). Pore water for reactive phosphate and ammonium was stored frozen on dry ice in clean plastic bottles for 1 to 5 days before analysis in the field. Pore water samples for analysis of anions by ion chromatography (F, Cl, Br, SO_4^{2-}) were transferred to clean plastic bottles, and 0.1 M zinc zcetate (0.1 ml per 1.0 ml sample) was added to precipitate sulfide and avoid artifacts from oxidation to sulfate during storage. Pore water for DOC analysis was transferred to clean plastic bottles or glass tubes, and the samples for DOC and anions analysis were stored frozen on dry ice until return to laboratory facilities.

Surface waters were first subsampled with a disposable plastic syringe for analysis of pH and H_2S, then filtered (0.4 μm Nuclepore filters) using a plastic Millipore filtering apparatus and a hand pump. Distribution, storage and analysis of surface water samples was otherwise the same as for pore waters.

Polyethylene bottles for titration alkalinity and storage of water samples for metals analysis were cleaned by soaking overnight in 10% ultrex HNO_3 followed by thorough washing with

Table 2. Analytical methods and precision for pore water and surface water sample analysis.

COMPONENT	TECHNIQUE	ANALYTICAL PRECISION[1]	REFERENCE
pH	Electrode	± 0.1 pH units	EPA, 1983
Titration Alkalinity	Titration	± 0.08 meq/l	Strickland and Parsons, 1973
ΣH_2S	Specific Ion Electrode	± 5% RSD	Baumann, 1974
Reactive Phosphate	Colorimetric	± 2% RSD	EPA, 1983 Strickland and Parsons, 1973
Ammonium	Colorimetric	± 2% RSD	EPA, 1983 Strickland and Parsons, 1973
Anions (Cl^-,F^-,Br^-,NO_{3-},SO_4^{2-})	Ion Chromatography	± 3% RSD	Pyen et al., 1986
Cations (Na^+,K^+,Ca^{2+},Mg^{2+},Sr^{2+})	ICP Atomic Emission Spectroscopy	± 3% RSD	Lichte et al., 1987
Dissolved Organic Carbon	Wet Chemical Oxidation and UV Iradiation with Nondispersive IR Detection of CO_2	± 4% RSD	Orem and Hatcher, 1987

1 - RSD = relative standard deviation

deionized/distilled water. Glass tubes for storage of water samples for DOC analysis were washed with 10% HCl, rinsed with deionized/distilled water, and baked overnight at 450° C. Plasticware used in the collection and filtration of surface water samples, and plastic bottles for storage of nutrient, anion, and DOC water samples were soaked overnight in 10% HCl followed by thorough rinsing in deionized/distilled water. Deionized/distilled water blanks were run through the entire filtration, handling, and storage scheme used for the samples. No significant contamination was observed for any of the analyses reported here, indicating that the cleaning and handling approach used for the surface and pore water samples was adequate.

The analytical procedures used and their precision (reported as % relative standard deviation except for pH and titration alkalinity) are shown in Table 2. In the field we used a Brinkman fiber optic probe spectrophotometer for the phosphate and ammonium analyses, and an Orion portable pH/mv meter and Orion electrodes for the pH, titration alkalinity, and H_2S analyses. The DOC analyses were performed at USGS laboratories in Reston, VA using an O.I. Corporation model 700 TOC analyzer. Ion Chromatography analyses for anions and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses for metals were conducted at USGS laboratories in Denver, CO. Trade names used are for descriptive purposes only and do not constitute endorsement of products by the U.S. Geological Survey.

Results and Discussion

Trends in surface water geochemistry

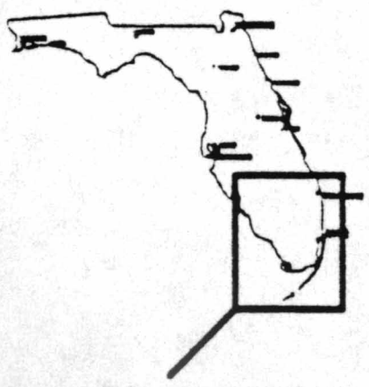
Surface water concentrations of dissolved chemical species at selected sites in south Florida during March 1994 and April 1995 are shown in Figs. 3A to 3F. It is important to understand that the analyses reported here represent mere snapshots of the regional surface water geochemistry. Concentrations of chemical species at a site could show large temporal variability compared to the values reported here. Closely timed, synoptic sampling of surface waters, such as that carried out by the SFWMD, is necessary to thoroughly document temporal trends in surface water geochemistry. Nevertheless, trends reported here are generally consistent with more extensive databases of surface water chemistry from south Florida wetlands.

pH and alkalinity - Surface water pH values (Fig. 3A) ranged from slightly acidic values in

WCA 1A (6.6 to 6.9) to slightly basic values elsewhere (7.1 to 7.8). The slightly acidic conditions in WCA 1A likely reflect the dominance of rainfall to freshwater input in this area, and the acidity of the Loxahatchee peat comprising the substrate in WCA 1A. Titration alkalinity values (Fig. 3A) ranged from 0.2 to 8.6 meq/l, with the lowest alkalinities observed in WCA 1A (0.2 to 1.6 meq/l) and the highest in WCA 2A (5.1 to 8.6 meq/l). Relatively low alkalinities were also generally observed in surface waters from Big Cypress Preserve, with most values around 2.0 to 2.2 meq/l. Titration alkalinity in most natural waters largely represents a measure of total dissolved carbonate species (primarily HCO_3^- at the pH values reported here) in the water. Processes controlling total dissolved carbonate species concentrations include dissolution or precipitation of carbonates, and heterotrophic respiratory activity. The relatively high levels of alkalinity in WCA 2A compared to other sites may reflect higher rates of respiration. The high nutrient load into WCA 2A from canal discharge supports high rates of primary production and high heterotrophic activity (respiration). This is in contrast to more oligotrophic wetland areas in WCA 1A and ENP. Titration alkalinities at a site in the center of WCA 2A dominated by sawgrass (2A-U3) were only marginally lower than sites near the Hillsboro Canal dominated by cattail (Sites 2A-E1 and 2A-F1). The exceptionally low alkalinities in surface waters from WCA 1A reflect the dominance of rainwater input to this wetland area. Low alkalinities in Big Cypress Preserve likely reflect both low heterotrophic activity in this oligotrophic environment, and low carbonate content of the quartz sand sediments.

Dissolved organic carbon - Concentrations of dissolved organic carbon (DOC) in surface waters (Fig. 3B) ranged from 6.2 to 48.2 ppm C. DOC concentrations were highest in WCA 2A and showed a general trend of decreasing values to the south and west. The high levels of DOC in WCA 2A is consistent with a pattern of high concentrations for most dissolved chemical species in surface water from WCA 2A. The high concentrations of DOC in WCA 2A likely result from decomposition of organic debris from the artificially elevated biomass produced in response to input of excess nutrients. Note that the sites in the center of WCA 2A (2A-U3) dominated by sawgrass have about the same surface water DOC values as sites near the Hillsboro Canal dominated by cattail (2A-E1 and 2A-F1). This may reflect thorough mixing of DOC in surface

FLorida, USA



Area of Large Map

Lake Okeechobee

West Palm Beach

Caloosahatchee River

Everglades Agricultural Area (EAA)

6.8|1.2

WCA 1

6.9|1.6

6.6|0.2

7.2|7.3

7.6|8.6

7.6|8.6

7.6|7.1

7.3|6.0

WCA 2A

7.6|6.6 (3/94)

7.7|5.1 (4/95)

Route 84 (Alligator Alley)

Florida Turnpike

Naples

7.6|4.1

7.3|2.2

7.1|2.0

Big Cypress National Preserve

WCA 3A

7.3|3.4

7.4|2.2

7.6|2.0

Miami

7.8|2.4

7.3|2.2

Route 41 (Tamiami Trail)

Gulf of Mexico

7.8|4.7

Biscayne Bay

Everglades National Park

7.3|2.4

ND

7.7|3.3

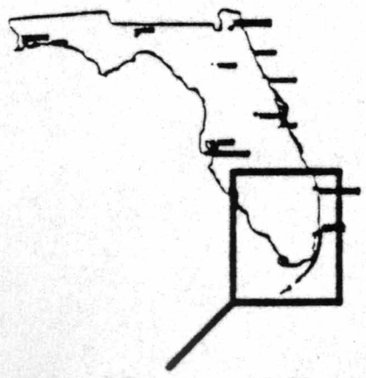
7.50|4.1

Florida Bay

Atlantic Ocean

Fig. 3A.
Surface Water
pH | Titration Alkalinity (meq/l)

FLorida, USA



Area of Large Map

Lake Okeechobee

West Palm Beach

Caloosahatchee River

Everglades Agricultural Area (EAA)

20.6

WCA 1

29.7

24.2

41.7

43.4

45.6

48.2

28.6

WCA 2A

42.4 (3/94)

47.6 (4/95)

Route 84 (Alligator Alley)

Florida Turnpike

Naples

10.9

11.6

7.9

Big Cypress National Preserve

WCA 3A

19.1

6.2

14.5

Miami

19.1

8.7

Route 41 (Tamiami Trail)

10.9

Gulf of Mexico

Everglades National Park

Biscayne Bay

9.6

15.5

7.4

10.8

Florida Bay

Atlantic Ocean

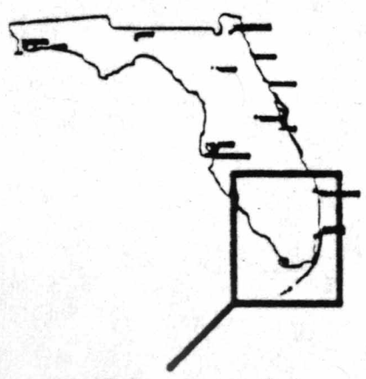
Fig. 3B.
Surface Water
Dissolved Organic Carbon (mg/l C)

water from WCA 2A. The relatively high DOC concentrations in WCA 1A are surprising considering the low concentrations of most other dissolved chemical species here. The efficient production of dissolved organic acids from the Loxahatchee peat in WCA 1A, which also produces the slightly acidic conditions, may contribute to the higher than expected DOC concentrations.

Nutrients - Concentrations of dissolved reactive phosphate (DRP) and ammonium in marsh surface waters (Fig. 3C) were much more variable than for most other dissolved chemical species. DRP concentrations ranged from 146 to <0.9 µg/l over all our sampling sites, with most areas higher than the 8 to 10 µg/l background level expected for pristine areas. High DRP concentrations were observed in WCA 2A, as anticipated. Note the high degree of variability of DRP concentrations in WCA 2A. Sites sampled in 1994 in WCA 2A range from 22.8 to 31.3 µg/l, while samples collected in 1995 ranged from 110 to 114 µg/l. No significant differences in surface water DRP concentrations were observed along the nutrient gradient in WCA 2A (sites 2A-E1 and 2A-F1 near the Hillsboro Canal to site 2A-U3 in the center of WCA 2A). It is likely that our sampling occurred after a period of lower canal water discharge to the marsh in 1994, and after a period of higher canal water discharge in 1995. This result emphasizes the importance of high periodicity of surface water sampling, especially for evaluating nutrient input to the marshes. An unexpected result in the surface water DRP data is the high concentrations at the two most northerly sites in Big Cypress Preserve BC-1 and BC-2, 129 and 146 µg/l, respectively. This result could be anomalous, but deserves further attention. Exceptionally low surface water DRP concentrations were observed in the rainfall-dominated and relatively pristine WCA 1A, and in the tidal Taylor Creek area in the far southeast of ENP.

Ammonium concentrations in surface waters range over two orders of magnitude from 227 to <3 µg/l (Fig. 3C). No general regional trends were observed in the ammonium data, probably reflecting the multiple sources of ammonium to surface waters (e.g. canal discharge, nitrogen fixation by periphyton, and rainfall). The highest concentration by far (227 µg/l) was observed in WCA 2A at site 2A-F1 near the Hillsboro Canal. Other sites in WCA 2A, however, had much lower concentrations, particularly samples collected in 1994. Moderate levels of ammonium were observed in rainfall-dominated WCA 1A (15 to 39 µg/l), with the highest concentration at the center of WCA 1A. Low to moderate ammonium concentrations were observed at sites in WCA 3A and ENP.

FLorida, USA



Area of Large Map

Lake Okeechobee

West Palm Beach

Caloosahatchee River

Everglades Agricultural Area (EAA)

1.0|17.3

WCA 1

<0.9|15.4

<0.9|39.1

114|227

22.8|<3.0

22.7|<3.0

31.3|<3.0

WCA 2A

13.3|28.1

22.8|5.0 (3/94)

110|17.8 (4/95)

Route 84 (Alligator Alley)

Naples

129|<0.2

WCA 3A

146|ND

10.2|ND

Big Cypress National Preserve

7.6|11.5

33.5|ND

14.4|ND

Miami

22.8|<3.0

31.4|ND

Route 41 (Tamiami Trail)

Gulf of Mexico

9.5|10.8

Biscayne Bay

Everglades National Park

22.8|10.8

29.9|52.9

<0.9|15.0

<0.9|17.3

Florida Bay

Atlantic Ocean

Fig. 3C.
Surface Water
Phosphate | Ammonium (ug/l)

Major anions - Concentrations of chloride, fluoride, and sulfate in surface waters (Fig. 3D) followed the general regional pattern of highest values in WCA 2A, and lower concentrations in WCA 1A and to the south in WCA 3A and ENP (excluding the brackish water sites in the far southeast along Taylor Creek, ENP-TC1 and ENP-TC2). Chloride concentrations ranged from 152 to 22 mg/l in the freshwater areas of the Everglades. The highest values were observed at the two sites near the Hillsboro Canal in WCA 2A (E1 and F1), and the lowest value was observed in the center of rainfall dominated WCA 1A. Chloride concentrations in the center of WCA 2A ranged from 64 to 97 mg/l, somewhat lower than sites near the Hillsboro Canal and similar to concentrations in the portion of WCA 3A north of Alligator Alley. Chloride concentrations in the freshwater areas of ENP ranged from 42 to 66 mg/l.

Fluoride concentrations ranged from 0.60 to 0.06 mg/l, with the highest concentrations at sites along the Hillsboro Canal in WCA 2A (E1 and F1), and at a disturbed site in the far southeast along the C111 canal (ENP-C111). In WCA 1A, 3A and in the freshwater areas of ENP fluoride concentrations ranged from 0.06 to 0.16 mg/l. Fluoride concentrations in the center of WCA 2A were quite variable, ranging from 0.09 to 0.41 mg/l. The poor sensitivity of the fluoride data from the brackish water Taylor Creek sites (ENP-TC1 and ENP-TC2) reflects interference in the fluoride measurement from a large chloride peak using ion chromatography.

Sulfate concentrations in the freshwater Everglades ranged from 55 to 0.5 mg/l. The highest sulfate concentrations were observed in WCA 2A. Sites near the Hillsboro Canal in WCA 2A (E1 and F1) and in the center of WCA 2A (U3) had similar concentrations in 1994 and 1995, indicating that sulfate from canal discharge can penetrate into the center of marsh areas. Sulfate concentrations outside of WCA 2A are much lower and do not exceed 2 mg/l in WCA 3A south of Alligator Alley and freshwater areas of ENP. Sulfate concentrations in WCA 1A appear to be somewhat elevated, except in the center of the marsh (1A-7).

Major Cations - Concentrations of major cations in surface waters are shown in Figs. 3E (Na and K) and 3F (Ca, Mg, and Sr). Transition metal cations in these waters were generally below the detection limits of ICP-AES (Lichte et al. 1987). Concentrations of sodium ranged from 9 to 138 ppm in the freshwater marshes. Again, the highest concentrations were observed in WCA 2A, with gradually lower concentrations to the south into ENP (except at the brackish water Taylor Creek sites ENP-TC1 and ENP-TC2) and to the west into Big Cypress Preserve. Sodium concentrations

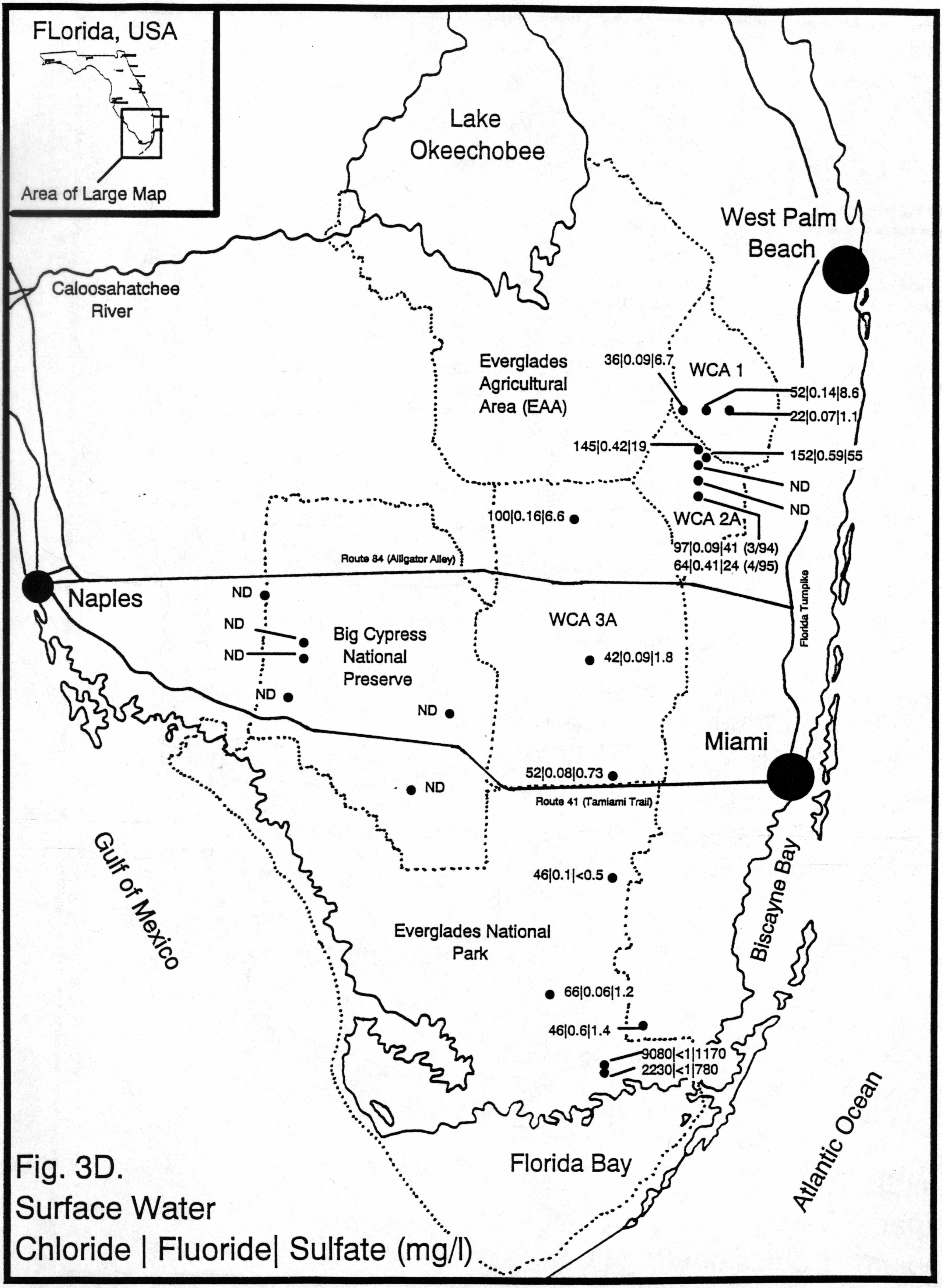


Fig. 3D.
Surface Water
Chloride | Fluoride| Sulfate (mg/l)

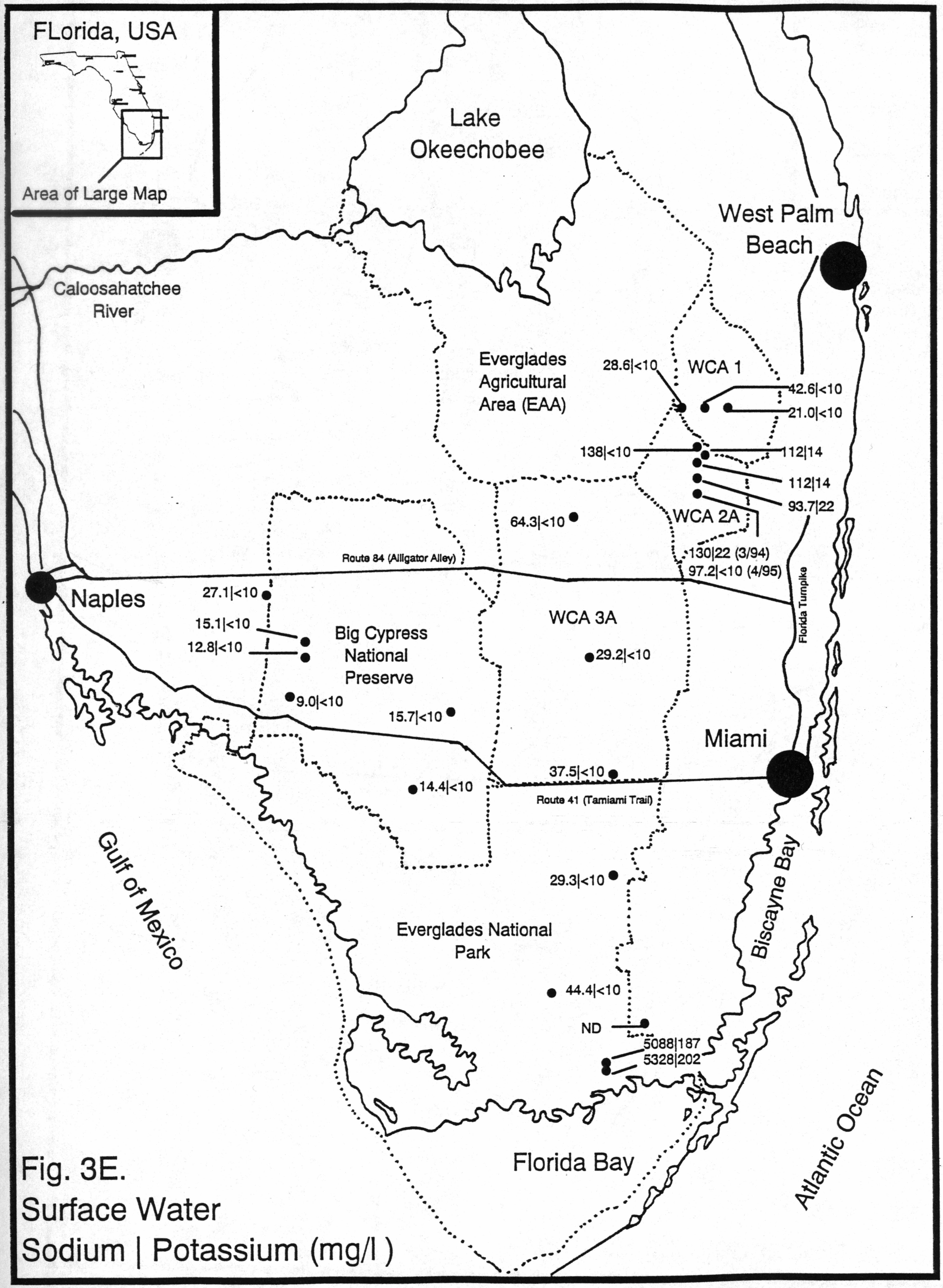
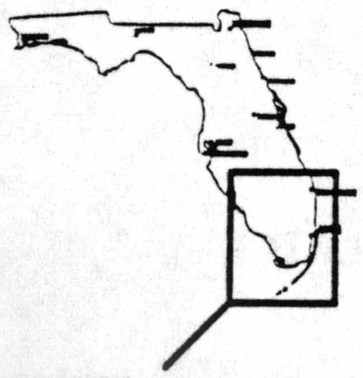


Fig. 3E.
Surface Water
Sodium | Potassium (mg/l)

FLorida, USA



Area of Large Map

Lake Okeechobee

West Palm Beach

Caloosahatchee River

27.6|8.9|0.70

Everglades Agricultural Area (EAA)

19.4|6.4|0.52

WCA 1

10.6|4.2|0.24

95.2|36.9|2.84

74.3|29.0|2.2

74.1|28.7|2.2

59.1|21.1|1.6

WCA 2A

93.0|17.3|1.09

Route 84 (Alligator Alley)

79.0|31.4|2.4 (3/94)

47.8|26.7|1.8 (4/95)

Florida Turnpike

Naples

80.6|7.6|0.24

44.6|3.7|0.12

37.9|4.8|<0.10

Big Cypress National Preserve

43.4|3.4|<0.10

WCA 3A

62.1|9.6|0.62

45.9|2.5|0.18

Miami

49.5|8.8|0.53

45.5|3.2|0.31

Route 41 (Tamiami Trail)

93.0|5.0|0.68

Gulf of Mexico

Everglades National Park

52.9|6.0|0.54

ND

229\614|3.72

235|635|3.96

Biscayne Bay

Florida Bay

Atlantic Ocean

Fig. 3F.
Surface Water
Calcium | Magnesium | Strontium (mg/ll)

in WCA 1A were moderate to low compared to other areas. Potassium concentrations ranged from <10 to 22 ppm in WCA 2A, and were below the detection limit of 10 ppm elsewhere in the freshwater areas of the Everglades.

Concentrations of calcium in the freshwater Everglades (Fig. 3F) ranged from 10.6 to 95.2 ppm. Somewhat higher concentrations were observed in WCA 2A than elsewhere, but high concentrations were also found at sites in WCA 3A (3A-3), ENP (ENP-GH), and Big Cypress (BC-1). Calcium concentrations were notably lower in WCA 1A, with concentrations ranging from 10.6 to 27.6 ppm. Concentrations of calcium in surface waters are likely controlled by processes such as canal discharge, calcium uptake by periphyton, ion exchange onto peat surfaces, incorporation in calcium oxalate during peat decomposition, and dissolution of marl. Concentrations of magnesium ranged from 2.5 to 36.9 ppm, with highest concentrations in WCA 2A and gradually lower concentrations to the south (WCA 3A and ENP) and west (Big Cypress Preserve). Magnesium concentrations were also low in WCA 1A. Strontium concentrations ranged from <0.1 to 2.8 ppm, and generally followed the same regional distribution pattern as magnesium.

Pore water geochemistry

Concentrations of dissolved chemical species in pore water from 12 cores collected at different sites in south Florida during 1994 and 1995 are presented in Tables 3 and 4, and Figures 4A to 4L. In the figures, pore water profiles are arranged with sites in the north (WCA 1A) in the upper left hand corner of the figures, and sites in the south (ENP) in the lower right hand corner. No pore water samples were collected from Big Cypress Preserve in 1994 or 1995 due to the high sand content of the organic soils there. Data points plotted in the figures at a depth = 0 are surface water concentrations.

pH and alkalinity - Values of pH in pore waters typically ranged from 6.5 to 8.0, with slightly more acidic conditions (as low as 5.8) at site 1A-7 located in the center of rainfall-dominated WCA 1A (Table 3 and Fig. 4A). Vertical profiles of pH in many of the cores exhibited an initial decrease in pH from the surface water to the near-surface pore waters, followed by a gradual increase or levelling of pH values below this. The initial decline in pH likely reflects accumulation of protolytic chemical species (e.g. dissolved organic acids, protonated carbonate species, and hydrogen sulfide) in pore waters of near-surface peats where bacterial activity and decomposition

Table 3. Surface water and pore water values for pH, titration alaklinity (T.A.), dissolved organic carbon (DOC), sulfide (ΣH_2S), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), ammonium (NH_4^+), nitrate (NO_3^-), chloride (Cl^-), fluoride (F^-), and bromide (Br^-) in USGS 1994 and 1995 cores from selected sites in south Florida. Surface water samples are indicated by depth 0 cm.

CORE #	DEPTH (cm)	pH	T.A. (meq/l)	DOC (mg/l)	ΣH_2S (µg/l)	SO_4^{2-} (mg/l)	PO_4^{3-} (µg/l)	NH_4^+ (µg/l)	NO_3^- (mg/l)	Cl^- (mg/l)	F^- (mg/l)	Br^- (mg/l)
I. Water Conservation Area 1A (Loxahatchee NWR)												
1.GP42195P1	0	6.8	1.2	20.4	<0.01	6.7	1.0	17.3	<0.5	36	0.09	---
1A - 1	2	6.6	5.8	53.4	11.3	0.86	20.9	202	<0.5	136	0.41	---
	6	6.6	6.9	53.0	186	1.3	61.7	189	<0.5	114	0.45	---
	10	6.5	---	---	49.6	---	74.1	---	---	---	---	---
	17	6.6	---	77.8	0.32	---	76.0	---	---	---	---	---
	27	6.8	10.9	76.4	39.3	1.3	31.3	34.1	<0.5	255	0.43	---
	37	6.7	10.7	72.8	<0.01	0.65	26.6	47.4	<0.5	282	0.33	0.86
	47	6.7	10.3	66.6	<0.01	0.85	19.0	106	<0.5	253	0.38	0.81
	57	6.6	9.8	67.2	<0.01	0.56	11.4	161	<0.5	187	0.41	0.60
	67	6.7	---	62.0	0.01	---	5.7	225	---	---	---	---
	77	6.2	---	---	---	---	---	---	---	---	---	---
2.GP42195P2	0	6.6	---	25.1	<0.01	1.1	<0.9	39.1	<0.5	22	0.07	---
1A - 7	4	---	---	59.7	---	---	---	---	---	---	---	---
	9	5.8	---	40.0	---	---	5.7	---	---	---	---	---
	14	6.1	---	42.3	---	---	5.7	---	---	---	---	---
	19	6.2	---	34.3	---	---	<0.9	1340	---	---	---	---
	24	6.2	---	35.2	---	---	<0.9	---	---	---	---	---
	29	6.2	---	---	---	---	---	---	---	---	---	---
	39	6.1	---	---	---	---	---	---	---	---	---	---
	49	6.0	---	46.2	---	---	---	---	---	---	---	---
	59	6.2	---	31.4	---	---	<0.9	---	---	---	---	---
	75	6.1		---	---	---	---	---	---	---	---	---

Table 3. Continued.

CORE #	DEPTH (cm)	pH	T.A.	DOC	ΣH_2S	SO_4^{2-}	PO_4^{3-}	NH_4^+	NO_3^-	Cl^-	F^-	Br^-
II. Water Conservation Area 2A												
3.GP3194P1	0	7.6	8.6	43.4	---	55	22.8	<3.0	<0.5	152	0.59	0.45
2A - E1	2	7.8	10.6	99.8	---	2.5	1380	194	<0.5	208	0.50	0.64
	9	7.7	11.6	110	---	0.6	837	159	<0.5	186	1.30	0.59
	14	7.3	9.6	75.7	---	1.0	258	54.8	<0.5	186	0.63	0.63
	24	7.4	9.8	77.4	---	0.7	76.9	4.15	<0.5	195	0.46	0.60
	34	7.3	9.6	58.4	---	0.5	63.6	18.0	<0.5	234	0.53	0.66
	44	7.6	9.6	52.6	---	<0.5	74.1	49.2	<0.5	171	0.41	0.48
	54	7.2	10.5	59.7	---	2.0	36.1	21.1	<0.5	312	0.44	0.85
	64	7.2	11.4	65.3	---	2.3	58.9	33.6	<0.5	264	0.32	0.81
4.GP3194P2	0	7.6	6.6	33.7	---	41	22.8	5.0	<0.5	97	0.09	0.22
2A - U3	2	7.1	9.5	135	---	63	144	349	<0.5	208	0.39	0.43
	7	7.4	9.6	59.1	---	49	31.3	312	<0.5	226	0.53	0.56
	12	7.4	9.5	49.9	---	43	67.4	344	<0.5	211	0.45	0.61
	17	7.3	9.5	66.2	---	30	208	266	<0.5	235	0.52	0.79
	27	7.2	10.6	78.4	---	9.9	22.8	146	<0.5	249	0.50	0.90
	42	7.2	11.0	127	---	2.0	81.7	194	<0.5	203	0.41	0.66
	52	---	---	---	---	1.4	26.6	298	<0.5	315	0.23	0.90
	62	---	---	---	---	---	29.4	---	---	---	---	---
5.GP42595P1	0	7.7	5.1	47.9	0.01	24	110	17.8	<0.5	64	0.41	<0.20
2A - U3	2	6.9	8.1	45.4	1520	14	41.8	1780	<0.5	218	0.48	0.77
	6	6.8	8.5	53.9	1780	5.8	52.2	1790	<0.5	174	0.35	0.58
	10	6.7	9.3	52.2	1200	3.9	78.8	2350	<0.5	194	0.32	0.65
	14	6.7	---	53.0	1030	---	78.8	2537	---	---	---	---
	21	6.7	8.9	60.2	406	1.3	53.2	2320	<0.5	163	0.45	0.54

Table 3. Continued.

CORE #	DEPTH (cm)	pH	T.A. (meq/l)	DOC (mg/l)	ΣH_2S (µg/l)	SO_4^{2-} (mg/l)	PO_4^{3-} (µg/l)	NH_4^+ (µg/l)	NO_3^- (mg/l)	Cl^- (mg/l)	F^- (mg/l)	Br^- (mg/l)
5.GP42595P1	26	6.8	---	---	42.5	---	---	---	---	---	---	---
2A - U3	36	6.7	8.9	65.9	16.7	<0.5	44.6	2230	<0.5	222	0.45	0.73
	41	6.7	8.2	91.6	9.69	<0.5	33.2	1645	<0.5	141	0.37	0.42
	51	6.6	9.2	59.7	26.6	<0.5	43.7	1640	<0.5	212	0.29	0.54
	61	6.9	9.0	54.3	14.3	<0.5	19.9	1120	<0.5	178	0.45	0.52
	71	6.7	8.8	---	1.00	<0.5	35.1	1560	<0.5	254	0.47	0.69
6.GP42695P1	0	7.2	7.3	41.4	117	19	114	227	<0.5	145	0.42	0.49
2A - F1	3	6.6	17.6	---	53.7	7	2720	2950	<0.5	393	0.78	1.5
	7	6.6	18.6	44.8	39.3	2.7	2210	3560	<0.5	124	0.69	0.48
	11	7.0	21.1	144	36.4	6.2	2540	2860	<0.5	402	0.70	1.7
	15	6.7	20.4	116	36.4	5.9	2510	2990	<0.5	528	0.93	2.1
	20	6.7	20.8	153	33.6	6.1	1990	2430	<0.5	404	0.72	1.7
	25	6.8	21.5	150	31.1	1.4	1740	2320	<0.5	264	0.66	0.94
	30	6.8	---	---	31.1	---	1360	---	---	---	---	---
	40	6.7	21.8	152	31.1	3.5	764	1620	<0.5	714	0.93	2.6
	50	6.8	21.7	158	33.6	1.7	736	1430	<0.5	585	0.88	1.9
	60	6.9	---	---	28.8	---	864	---	---	---	---	---
	70	6.9	---	---	28.8	---	---	---	---	---	---	---
III. Water Conservation Area 3A												
7.GP22794P1	0	7.8	2.4	19.1	---	0.73	22.8	<3.0	<0.5	52	0.08	---
3A - TT	6	---	---	35.2	---	<0.5	14.2	208	<0.5	54	0.66	---
	11	---	---	---	---	<0.5	31.3	---	2.4	45	0.61	---
	21	---	---	---	---	<0.5	22.8	225	<0.5	51	0.13	---
	31	---	---	---	---	<0.5	22.8	---	<0.5	46	0.15	---
	41	---	---	---	---	---	43.7	---	---	---	---	---

Table 3. Continued.

CORE #	DEPTH (cm)	pH	T.A. (meq/l)	DOC (mg/l)	ΣH_2S (µg/l)	SO_4^{2-} (mg/l)	PO_4^{3-} (µg/l)	NH_4^+ (µg/l)	NO_3^- (mg/l)	CL^- (mg/l)	F^- (mg/l)	Br^- (mg/l)
7.GP22794P1	51	---	---	21.4	---	<0.5	19.0	409	<0.5	46	0.10	---
3A - TT	90	7.6	4.2	26.1	---	0.73	36.1	28.9	<0.5	52	0.14	---
8.GP42795P1	0	7.3	3.4	19.1	0.18	1.8	7.6	11.5	<0.5	42	0.09	---
3A - 15	2	6.5	4.1	33.4	<0.01	1.1	30.4	1100	<0.5	61	0.14	---
	6	6.4	3.8	25.6	<0.01	<0.5	19.9	723	<0.5	62	0.12	---
	10	6.4	5.0	---	0.01	<0.5	24.7	778	<0.5	53	0.13	---
	14	6.5	5.4	25.6	0.01	<0.5	24.7	924	<0.5	60	0.12	---
	18	6.6	5.8	---	0.13	<0.5	19.9	934	<0.5	63	0.13	---
	25	6.7	6.1	25.7	2.37	<0.5	19.9	955	<0.5	52	0.14	---
	30	6.6	6.1	26.9	4.22	<0.5	17.1	847	<0.5	53	0.15	---
	40	6.7	6.8	23.8	0.10	<0.5	17.1	1360	<0.5	43	0.20	---
	50	6.6	7.6	27.6	1.78	<0.5	39.9	1510	<0.5	55	0.16	---
	60	6.7	7.7	25.1	0.03	<0.5	19.9	1740	<0.5	51	0.14	---
	70	6.7	8.3	24.1	0.18	<0.5	19.9	1810	<0.5	48	0.14	---
9.GP42795P2	0	7.3	6.0	28.6	0.04	6.6	13.3	28.1	<0.5	100	0.16	<0.20
3A - 3	5	6.3	6.7	---	0.01	2.2	15.2	188	<0.5	115	0.25	0.48
	10	---	8.8	---	---	---	0.95	119	---	---	---	---
	15	6.6	9.6	37.4	<0.01	<0.5	0.95	75.2	<0.5	147	0.51	0.75
	20	6.6	9.5	26.0	0.10	<0.5	0.95	77.0	<0.5	139	0.36	0.87
IV. Everglades National Park												
10.GP22694P1	0	7.3	2.4	9.6	---	1.2	22.8	10.8	<0.5	66	0.06	---
ENP - PHO	5	---	---	---	---	<0.5	24.7	---	<0.5	59	0.66	---
	12	---	---	---	---	<0.5	121	---	<0.5	54	0.61	---
	22	---	---	---	---	<0.5	20.9	409	<0.5	54	0.13	---

Table 3. Continued.

CORE #	DEPTH (cm)	pH	T.A. (mg/l)	DOC (mg/l)	ΣH_2S (µg/l)	SO_4^{2-} (mg/l)	PO_4^{3-} (µg/l)	NH_4^+ (µg/l)	NO_3^- (mg/l)	Cl^- (mg/l)	F^- (mg/l)	Br^- (mg/l)
10.GP22694P1	32	---	---	---	---	---	55.1	---	---	---	---	---
ENP - PHO	110	7.3	4.6	8.5	---	<0.5	9.5	81.4	<0.5	51	0.06	---
11.GP3694P1	0	7.8	4.7	10.9	---	<0.5	9.5	10.8	<0.5	46	0.10	<0.20
ENP - GH	1	7.9	---	30.2	---	1.0	20.9	408	<0.5	46	0.65	<0.20
	5	7.5	---	25.5	---	<0.5	9.5	408	<0.5	44	0.46	<0.20
	10	7.2	4.7	12.4	---	<0.5	12.3	409	<0.5	46	0.14	<0.20
	15	7.3	4.0	12.7	---	<0.5	9.5	393	<0.5	47	0.14	<0.20
	25	7.5	---	---	---	<0.5	19.0	410	<0.5	50	0.14	<0.20
	35	7.8	---	---	---	---	57.0	---	---	---	---	---
	41	---	6.2	---	---	<0.5	11.4	379	<0.5	42	0.10	<0.20
12.GP42395P1	0	7.7	3.3	7.4	<0.01	1170	<0.9	15.0	<0.5	9080	<1	---
ENP - TC2	3	6.6	6.1	28.1	7210	862	36.1	1240	<0.5	7980	<1	---
	7	6.6	7.6	31.0	18300	640	129	1990	<0.5	9270	<1	---
	11	---	---	---	---	---	---	---	---	---	---	---
	15	6.6	15.4	139	58900	508	270	993	<0.5	9260	<1	---
	22	6.7	---	100	54500	699	320	1220	<0.5	8290	<1	---
	32	6.6	19.2	152	80400	1010	274	587	<0.5	11700	<1	---
	42	6.6	19.5	153	80400	1240	291	344	<0.5	12000	<1	---
	52	6.6	---	33.7	94000	---	115	---	---	---	---	---
	62	6.5	19.4	33.5	102000	1960	314	629	<0.5	19300	<1	---
	72	6.6	---	46.1	102000	---	267	---	---	---	---	---

Table 4. Contentrations (mg/l) of Na, K, Ca, Mg, Fe, Sr, and Si in surface water and pore water from 1994 and 1995 USGS cores at selected sites in south Florida. Surface water samples are indicated by the 0 cm depth interval.

CORE #	DEPTH (cm)	Na	K	Ca	Mg	Fe	Sr	Si
I. Water Conservation Area 1A (Loxahatchee NWR)								
1.GP42195P1	0	28.6	<10	19.4	6.4	<0.1	0.52	<1.0
1A - 1	2	98.7	<10	70.3	24.5	<0.1	2.13	<1.0
	6	127	<10	91.0	33.1	<0.1	2.76	<1.0
	27	185	13.5	119	45.4	<0.1	3.82	<1.0
	37	185	<10	111	44.2	<0.1	3.55	<1.0
	47	121	<10	68.3	25.4	<0.1	2.22	<1.0
	57	204	<10	115	44.4	<0.1	3.78	<1.0
2.GP42195P2	No Data							
1A - 7	No Data							
II. Water Conservation Area 2A								
3.GP3194P1	0	112	14	74.3	29.0	<0.1	2.2	<1.0
2A - E1	2	140	13	107	34.3	0.11	2.8	<1.0
	9	165	16	136	37.6	0.18	3.4	<1.0
	14	156	<10	111	30.2	<0.1	2.6	<1.0
	24	166	<10	113	30.2	<0.1	2.6	<1.0
	34	165	<10	110	29.5	<0.1	2.5	<1.0
	44	175	<10	120	31.2	<0.1	2.5	<1.0
	54	179	<10	126	32.3	<0.1	2.6	<1.0
	64	128	<10	96.4	23.5	<0.1	1.8	<1.0

Table 4. Continued.

CORE #	DEPTH (cm)	Na	K	Ca	Mg	Fe	Sr	Si
4.GP3194P2	0	130	22	79.0	31.4	<0.1	2.4	<1.0
2A - U3	2	147	14	86.8	36.0	<0.1	2.6	<1.0
	7	179	15	101	43.0	<0.1	3.1	<1.0
	12	128	11	70.0	30.9	<0.1	2.2	<1.0
	17	168	13	90.1	37.2	<0.1	2.5	<1.0
	27	194	19	104	37.1	<0.1	2.4	<1.0
	42	207	12	114	33.8	<0.1	2.2	<1.0
5.GP42595P1	0	97.2	<10	47.8	26.7	<0.1	1.75	<1.0
2A - U3	2	151	17.5	107	41.1	<0.1	3.38	<1.0
	6	150	12.5	107	41.8	<0.1	3.38	<1.0
	10	152	<10	102	41.0	<0.1	3.12	<1.0
	21	180	<10	110	40.8	<0.1	3.12	<1.0
	36	124	<10	74.5	23.0	0.18	1.75	<1.0
	41	180	<10	116	34.1	0.32	2.70	<1.0
	51	174	<10	116	31.6	0.74	2.47	1.23
	61	181	<10	124	32.6	1.23	2.47	1.23
	71	180	<10	126	31.1	1.17	2.47	<1.0
6.GP42695P1	0	138	<10	95.2	36.9	<0.1	2.84	1.23
2A - F1	3	307	<10	201	66.5	<0.1	5.07	1.33
	7	357	<10	219	73.2	<0.1	5.60	2.73
	11	374	<10	224	76.4	<0.1	5.72	4.40

Table 4. Continued.

CORE #	DEPTH (cm)	Na	K	Ca	Mg	Fe	Sr	Si
6.GP42695P1	15	300	<10	176	63.4	<0.1	4.73	2.87
2A - F1	20	327	<10	183	65.1	<0.1	4.87	2.87
	25	460	<10	260	89.2	<0.1	6.60	4.40
	40	480	<10	265	93.7	<0.1	6.82	4.35
	50	391	<10	216	77.1	<0.1	5.73	4.30
III. Water Conservation Area 3A								
7.GP22794P1	0	37.5	<10	49.5	8.8	<0.1	0.53	<1.0
3A - TT	90	36.8	<10	74.0	8.7	<0.1	0.49	<1.0
8.GP42795P1	0	29.2	<10	62.1	9.6	0.28	0.62	<1.0
3A - 15	2	40.2	<10	74.9	9.8	0.13	0.73	<1.0
	6	40.5	<10	73.8	9.2	<0.10	0.69	<1.0
	10	39.1	<10	87.7	9.6	0.42	0.77	<1.0
	14	41.2	<10	96.8	10.0	0.94	0.86	<1.0
	18	42.4	<10	106	10.3	1.3	0.98	<1.0
	25	41.8	<10	101	9.6	2.3	0.98	<1.0
	30	41.5	<10	112	11.2	2.1	1.11	<1.0
	40	33.7	<10	105	7.9	1.6	1.08	<1.0
	50	38.3	<10	145	10.5	2.3	1.52	<1.0
	60	36.4	<10	152	11.1	1.4	1.62	<1.0
	70	28.8	<10	131	9.4	1.5	1.40	<1.0

Table 4. Continued.

CORE #	DEPTH (cm)	Na	K	Ca	Mg	Fe	Sr	Si
9.GP42795P2	0	64.3	<10	93.0	17.3	<0.1	1.09	<1.0
3A - 3	5	74.5	<10	127	18.4	0.14	1.32	<1.0
	10	79.7	<10	168	24.0	<0.1	1.68	<1.0
	15	72.0	<10	158	21.5	<0.1	1.62	<1.0
	20	59.5	<10	134	18.5	<0.1	1.38	<1.0
IV. Everglades National Park								
10.GP22694P1	0	44.4	<10	52.9	6.0	<0.1	0.54	<1.0
ENP - PHO	110	30.8	40	82.2	5.2	<0.1	0.58	<1.0
11.GP3694P1	0	29.3	<10	93.0	5.0	<0.1	0.68	<1.0
ENP - GH	10	31.8	<10	101	5.3	0.84	0.78	<1.0
	15	31.3	<10	94.2	5.1	1.00	0.77	<1.0
	41	29.4	<10	120	7.0	<0.1	0.96	<1.0
12.GP42395P1	0	5088	187	229	614	<0.1	3.72	<1.0
ENP - TC2	3	4524	155	259	532	<0.1	3.72	<1.0
	7	3046	97.4	175	381	<0.1	2.59	<1.0
	15	4453	148	204	547	<0.1	3.20	<1.0
	32	6027	198	260	741	<0.1	4.10	<1.0
	42	7858	277	324	940	<0.1	5.47	<1.0
	62	9842	328	400	1151	<0.1	6.16	<1.0

Fig. 4A

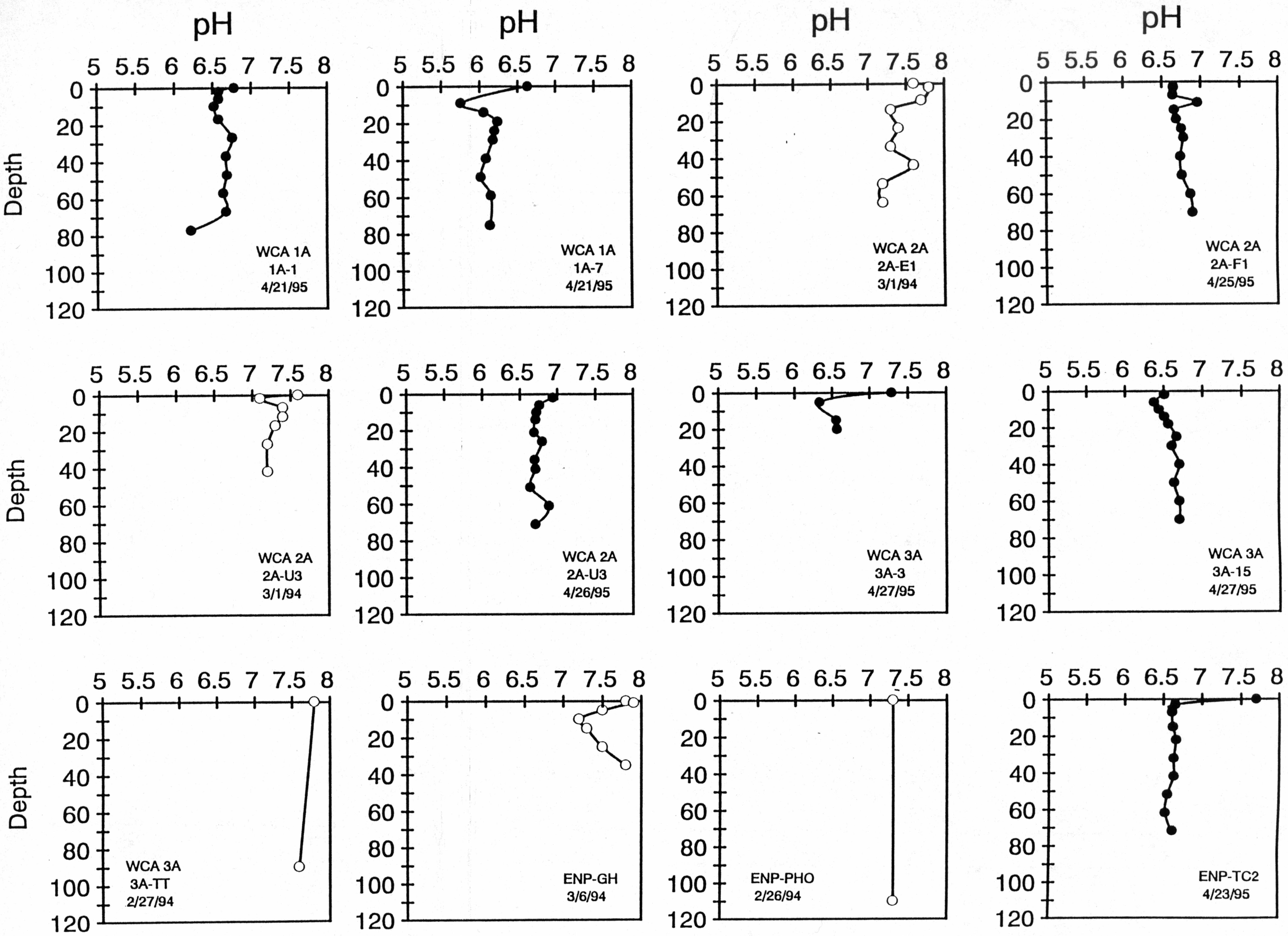

pH
5 5.5 6 6.5 7 7.5 8
Depth
0
20
40
60
80
100
120
WCA 1A
1A-1
4/21/95
WCA 1A
1A-7
4/21/95
WCA 2A
2A-E1
3/1/94
WCA 2A
2A-F1
4/25/95
WCA 2A
2A-U3
3/1/94
WCA 2A
2A-U3
4/26/95
WCA 3A
3A-3
4/27/95
WCA 3A
3A-15
4/27/95
WCA 3A
3A-TT
2/27/94
ENP-GH
3/6/94
ENP-PHO
2/26/94
ENP-TC2
4/23/95

Fig. 4B

Titration Alkalinity (meq/l)

Depth (cm)

WCA 1A
1A-1
4/21/95

No Data

WCA 1A
1A-7
4/21/95

WCA 2A
2A-E1
3/1/94

WCA 2A
2A-F1
4/25/95

WCA 2A
2A-U3
3/1/94

WCA 2A
2A-U3
4/26/95

WCA 3A
3A-3
4/27/95

WCA 3A
3A-15
4/27/95

WCA 3A
3A-TT
2/27/94

ENP-GH
3/6/94

ENP-PHO
2/26/94

ENP-TC2
4/23/95

of organic matter are expected to be highest.

Titration alkalinity values in pore waters ranged from 4 to 22 meq/l (Table 3 and Fig. 4B). Higher titration alkalinities were observed at sites in WCA 2A compared to sites in WCA 3A and freshwater areas of ENP. This likely reflects higher heterotrophic activity and production of dissolved carbonate species in sediments at sites in eutrophic WCA 2A compared to other areas. Within WCA 2A, sites in the heavily nutrient-impacted cattail areas near the Hillsboro Canal (2A-E1 and 2A-F1) have somewhat higher pore water titration alkalinities compared to a sawgrass-dominated site near the center of WCA 2A (2A-U3). A cattail-dominated site near the Hillsboro Canal in WCA 1A (1A-1) also had relatively high alkalinities (up to 12 meq/l), as did a brackish water site in ENP along Taylor Creek (ENP-TC2). Vertical profiles for titration alkalinity typically exhibited gradual increases with depth to some maximum values (10-22 meq/l in WCA 2A, 4-10 meq/l in WCA 3A, and 4-7 meq/l in freshwater areas of ENP), and a levelling-off to constant or slightly decreasing values below the maximum.

Dissolved organic carbon - Concentrations of dissolved organic carbon (DOC) in pore waters (Table 3 and Fig. 4C) ranged from 12 to 160 ppm C (1 to 13 mmoles/l). Note that this concentration range is similar in magnitude to that for titration alkalinity (4 to 22 meq/l), indicating that cycling of DOC is a very important mechanism for carbon transport between reservoirs in the Everglades. Generally higher concentrations of DOC were observed in pore water at sites in WCA 2A (40-160 ppm C), especially at site F1 near the Hillsboro Canal compared to sites in other areas. High concentrations of DOC (up to 153 ppm C) were also observed in pore water from the brackish water site in ENP along Taylor Creek (ENP-TC2). At sites in WCA 3A and in the freshwater areas of ENP DOC concentrations in pore water did not exceed 40 ppm C, consistent with previous studies from this area (Orem et al., 1987). DOC concentrations in pore water from WCA 1A generally ranged from 40-80 ppm C, with generally higher concentrations at the site near the Hillsboro Canal (1A-1). Profiles of DOC concentration versus depth in pore water were somewhat variable, but often exhibited increasing concentration with depth to some maximum value, and then constant to decreasing concentrations below the maximum. In most cores the maximum concentration of DOC was attained at a depth of 20 cm or less that corresponds to the zone of freshest organic matter and highest bacterial activity. Several cores (e.g. 1A-7 and 2A-U3) appeared to exhibit multiple DOC maxima downcore.

Fig. 4C

Dissolved Organic Carbon (mg/l C)

Sulfide and sulfate - Concentrations of sulfide and sulfate in pore water from our series of sites are shown in Table 3 and Figs. 4D and 4E, respectively. In natural waters, sulfate is the major oxidized form of sulfur and sulfide is the major reduced form (usually present as HS^- at circumneutral pH values). Concentrations of these two forms of sulfur in wetlands are regulated by several different processes: (1) sulfate input from runoff and precipitation, (2) sulfate reduction under anoxic conditions in sediments, (3) oxidation of sulfide to sulfate after diffusion back into oxic surface waters, (4) reaction of sulfide with sedimentary and dissolved organic matter to form organic sulfur compounds, and (5) the reaction of sulfide with dissolved metals to form insoluble metal sulfide phases in sediments.

Dissolved sulfide concentrations (Fig. 4D) vary by more than 5 orders of magnitude in pore waters from sites sampled in 1995 (sulfide was not measured during 1994), from nearly 2,000 µg/l to below the detection limit of about 0.01 µg/l. The highest sulfide concentrations were observed in WCA 2A. At a cattail-dominated site near the Hillsboro Canal in WCA 2A (2A-F1) sulfide concentrations were actually higher in the surface water (@125 µg/l) than in the pore water (25 to 50 µg/l), suggesting rapid rates of sulfate reduction near the sediment/water interface, and/or rapid diffusion of sulfide into the surface water here. At depth in this core, sulfide concentrations reached an asymptotic value of about 25 µg/l down to the bottom of the core (@75 cm). In contrast, the site near the center of WCA 2A (2A-U3) exhibited very low surface water sulfide concentration (0.01 µg/l), a dramatic increase to a peak sulfide concentration of 1780 µg/l at a depth of 6 cm, and then a decline to concentrations < 20 µg/l below 60 cm. In WCA 1A, a site near the Hillsboro Canal (1A-1) also had relatively high sulfide concentrations, with near-surface pore water values approaching 200 µg/l. In the center of WCA 1A (site 1A-7), however, sulfide in pore water was below the detection limit throughout the core (<0.01 µg/l). Sulfide concentrations were also generally low (but detectable) at both sites in WCA 3A (3A-3 and 3A-15). At the brackish water mangrove site along Taylor Creek in ENP (ENP-TC2) sulfide levels gradually increased with depth to values near 100 µg/l.

Vertical profiles of dissolved sulfate in pore water from our series of sites in south Florida are shown in Fig. 4E. At most sites, sulfate concentrations show an exponential decrease with depth, reflecting bacterially-mediated reduction of sulfate to sulfide. Surface water sulfate concentrations were highest at sites in WCA 2A (2A-F1, 2A-E1, and 2A-U3), ranging from 20 to 60 mg/l.

Fig. 4D

Sulfide (ug/l)

Depth

WCA 1A
1A-1
4/21/95

WCA 1A
1A-7
4/21/95

No Data

WCA 2A
2A-E1
3/1/94

WCA 2A
2A-F1
4/25/95

No Data

WCA 2A
2A-U3
3/1/94

WCA 2A
2A-U3
4/26/95

No Data

WCA 3A
3A-3
4/27/95

WCA 3A
3A-15
4/27/95

No Data

WCA 3A
3A-TT
2/27/94

No Data

ENP-GH
3/6/94

No Data

ENP-PHO
2/26/94

ENP-TC2
4/23/95

Fig. 4E

Sulfate (mg/l)

Inspection of the profiles at sites 2A-U3 and 2A-F1 suggests that rates of sulfate reduction are higher at the latter site. This may reflect differences in the organic matter composition of the sediments, mostly sawgrass at 2A-U3 and mostly cattails at 2A-F1, with cattail detritus perhaps being more easily degraded under anaerobic conditions (Davis 1991). The sulfate profile at 2A-F1 shows an interesting pattern with depth; an initial exponential decrease with depth followed by a slight increase in sulfate concentration in the 10 to 20 cm range. This may reflect pumping of oxygen into the root zone by cattails at this site, resulting in some oxidation of sulfide or peat organic sulfur to sulfate. Cattails may be more efficient at moving oxygen into their roots and thus at aerating the surrounding sediments, compared to sawgrass (Grace 1988; Koch and Rawlik 1993; Davis 1994), with cattails having large internal air spaces for oxygen and employing pressurized bulk flow ventilation, and sawgrass using much slower diffusive gas exchange (Chanton et al. 1993). There is also some indication of this effect at a cattail site near the Hillsboro Canal in WCA 1A (1A-1). South of WCA 2A (in WCA 3A and ENP) sulfate concentrations in surface waters are significantly lower (7 mg/l at 3A-3, 2 mg/l at 3A-15, and about 1 mg/l at freshwater marsh sites in ENP), but vertical profiles of sulfate concentration still show evidence of sulfate reduction. At the brackish water site in ENP (ENP-TC2), sulfate concentrations decrease exponentially with depth to about 20 cm, but than sharply increase. This reflects intrusion of denser/saltier seawater from Florida Bay underlying a fresher lens of water flowing down Taylor Creek.

Nutrients - Concentrations of reactive phosphate and ammonium in pore waters are presented in Table 3 and Figs. 4F and 4G, respectively. Reactive phosphate concentrations in pore waters range from <0.9 µg/l to nearly 3,000 µg/l. The highest concentrations of reactive phosphate were observed in pore water from the sites nearest the canal in WCA 2A (2A-F1 and 2A-E1), with peak values in the near-surface pore water of 1,000 to 3,000 µg/l. Phosphate concentrations at the central marsh site in WCA 2A (2A-U3) are about 10 times lower (peak values of 100 to 200 µg/l) than those at the sites nearest to the canal. This is consistent with the phosphate gradient observed in solid phase sediments in WCA 2A, which shows much higher concentrations at the canal sites (Koch and Reddy, 1992). The lowest reactive phosphate concentrations in pore water that we observed were from the center marsh site in WCA 1A (1A-7), with a peak concentration of only about 6 µg/l. This site is rainfall-dominated and likely receives little or no canal discharge water. In contrast, the site in WCA 1A near the Hillsboro Canal (1A-1), which likely receives some canal

Fig. 4F

Reactive Phosphate (ug/l)

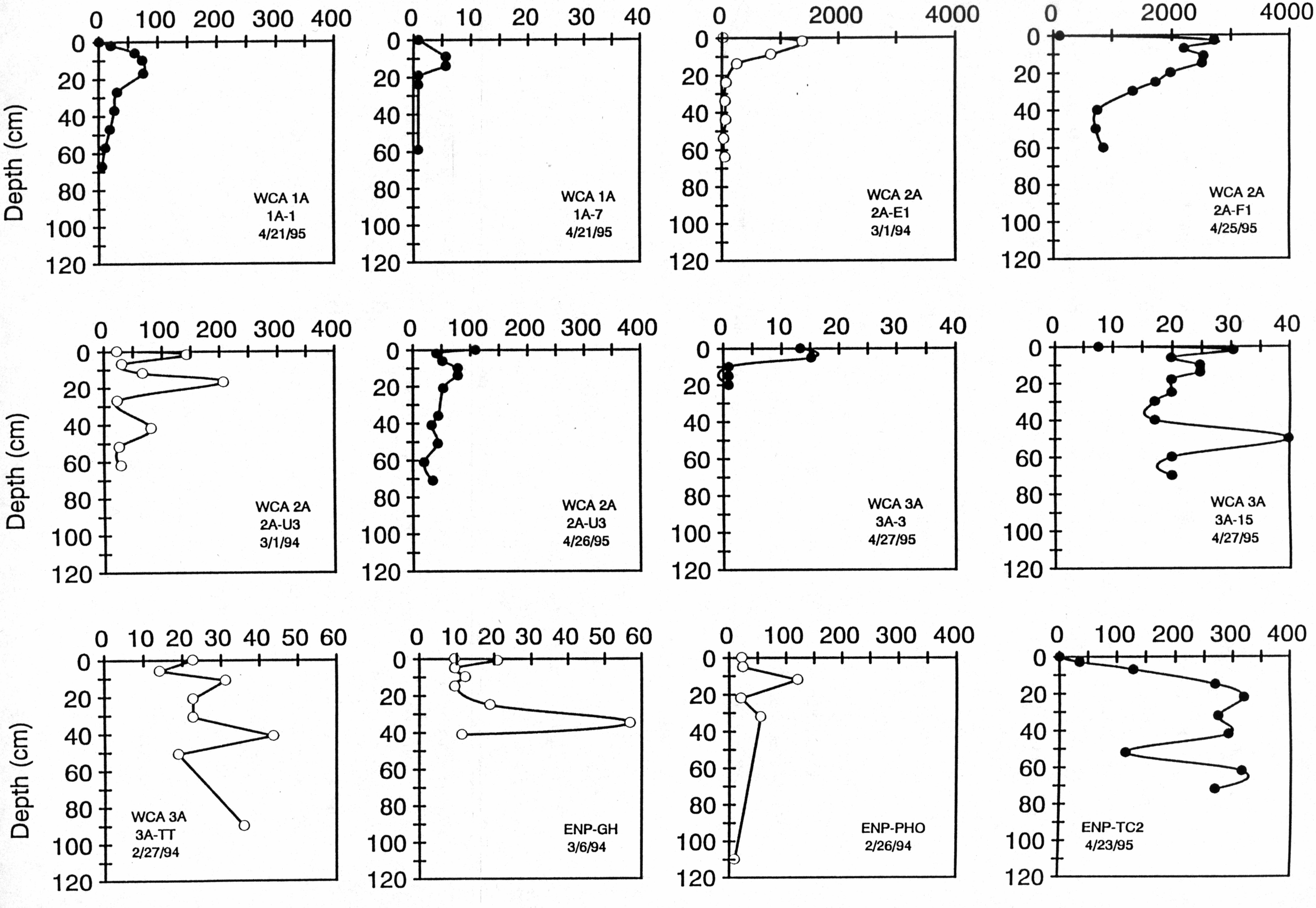
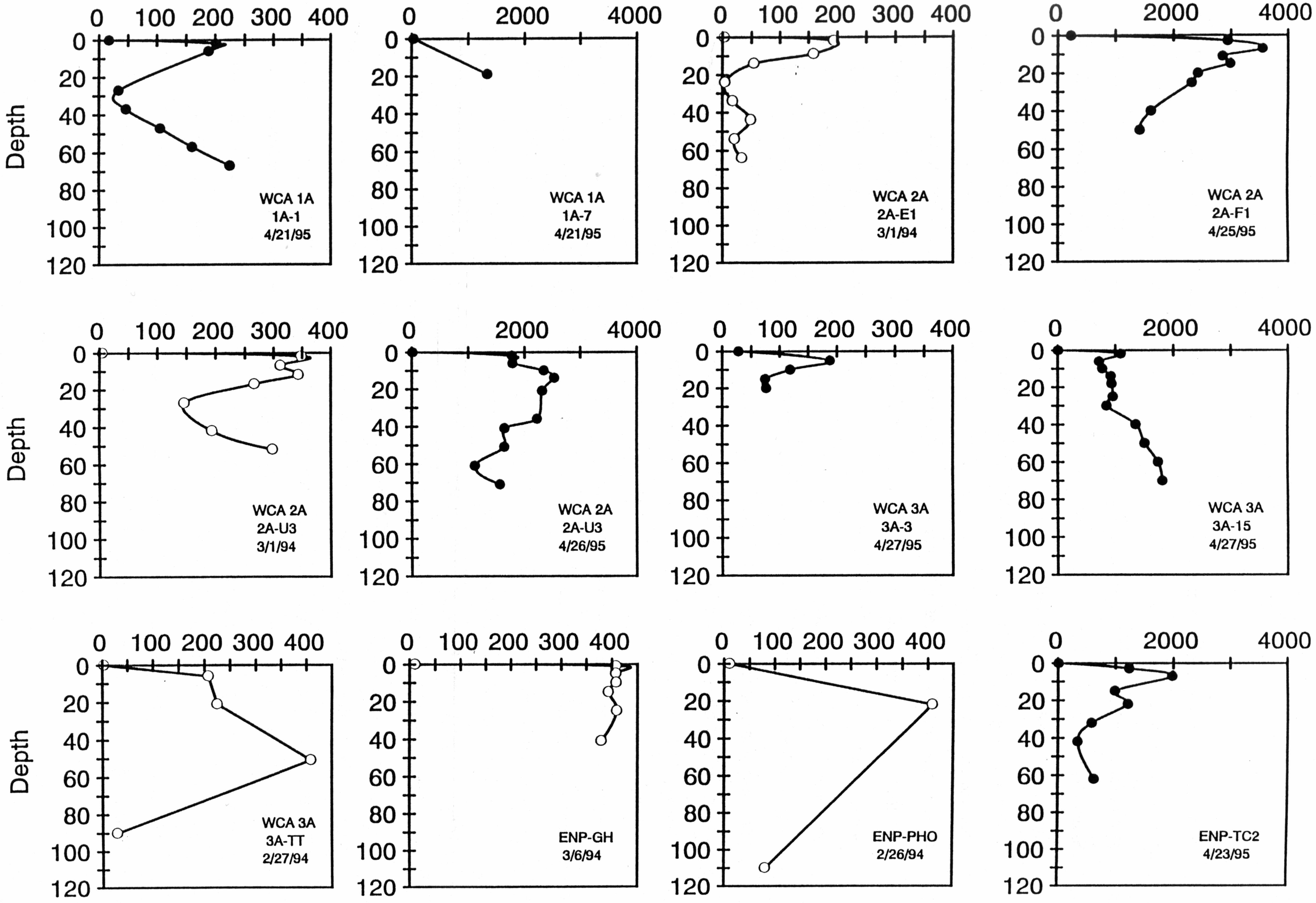


Fig. 4G

Ammonium (ug/l)



seepage, has peak phosphate concentrations about 10x higher. Peak phosphate concentrations in pore water from the freshwater marshes of WCA 3A and ENP were generally less than 60 µg/l, except for a peak value of about 120 µg/l at the Pa-Hay-Okee Lookout site near the eastern edge of Shark River Slough. The mangrove site in Taylor Creek (ENP-TC2) had peak phosphate concentrations of about 350 µg/l.

Many of the profiles of phosphate concentration in pore waters versus depth (Fig. 4F) are characterized by a large concentration gradient from surface water values to much higher near-surface pore water concentrations. Peak concentrations of phosphate in pore waters usually occur in the upper 20 cm. Below the peak value, phosphate concentrations gradually decrease. This pattern is consistent with a zone of maximal microbial activity, organic biodegradation, and recycling of phosphorus (sedimentary organic phosphorus to inorganic dissolved phosphate) within the near-surface sediments. Several profiles, however, deviate from this general vertical pattern, exhibiting phosphate maxima at depths well below 20 cm (3A-15, ENP-TT, and ENP-GH). Such patterns which deviate from the norm may reflect local anomalies in substarte characteristics, microbial community structure in the sediments, or the DRP concentration of groundwater infiltrating the sediments.

Ammonium concentrations in pore waters (Fig. 4G) range from about 4 µg/l to 3,600 µg/l. At most sites, ammonium concentrations in pore waters are in the 100 to 400 µg/l range. Very high ammonium concentrations (1,000 to 3,600 µg/l) were observed in pore water at sites F1 and U3 in WCA 2A during 1995 sampling. During 1994 sampling, however, ammonium concentrations at sites U3 and E1 (near F1) were approximately 10x lower. Thus, ammonium concentrations appear to exhibit a marked temporal variability. Temporal studies of pore water geochemistry at selected sites (including F1 and U3 in WCA 2A) are currently underway and will be discussed in future reports. Other sites with peak ammonium concentrations exceeding 1,000 µg/l include 1A-7, 3A-15, and ENP-TC2. The 1A-7 and 3A-15 sites are considered to be relatively "pristine", with little discharge from canal water draining agricultural areas. Thus, high ammonium concentrations in pore waters are not only associated with areas contaminated by canal runoff. Nitrogen fixation by periphyton in surface waters (Browder et al. 1994), and subsequent microbial recycling of organic N from periphyton detritus in sediments may also produce high ammonium concentrations in pore waters. Excluding the brackish water Taylor Creek site (ENP-TC2), sites in and near ENP had

ammonium concentrations in pore water generally in the range of 100 to 400 µg/l. Vertical profiles of ammonium in pore water had somewhat different characteristics at each site, but often exhibited a sharp initial increase to a maximum concentration in the near-surface pore water, followed by a gradual decrease to somewhat lower concentrations at depth.

Chloride, fluoride, and bromide - Concentrations of major anions in pore water (chloride, fluoride, and bromide) are presented in Table 3 and Figs. 4H and 4I. In general, concentrations of these anions in pore water are somewhat higher than in surface water. This could be due to evaporative concentration of pore water during dry periods. Alternatively, higher concentrations of anions in pore water could reflect equilibrium with salts or mineral phases in the peat, or upwelling of higher ionic strength groundwater. The range of concentrations of these anions in pore waters from the freshwater marshes are about 40-700 mg/l for chloride, 0.1-1.3 mg/l for fluoride, and <0.2-2.6 mg/l for bromide. Overall, Chloride, fluoride, and bromide concentrations in pore waters were somewhat higher at sites in WCA 2A compared to areas in WCA 3A and ENP (excluding the brackish water site ENP-TC2). This likely reflects influx of excess anions into WCA 2A from canal discharge. Concentrations of chloride are also higher at the site near the Hillsboro Canal in WCA 1A (1A-1), compared to sites in WCA 3A and ENP. This may be due to some seepage of water from the canal at this site. Very high chloride concentrations at the ENP-TC2 site reflect brackish water conditions. Note the change to higher chloride concentrations in pore water below 25 cm at the ENP-TC2 site. This is consistent with the sulfate data and reflects the presence of fresher (lower density) water in the surface sediments and saltier Florida Bay water in deeper sediments.

Major cations - Concentrations of major cations in pore water (sodium, potassium, calcium, magnesium, and strontium) are presented in Table 4 and Figs. 4J, 4K, and 4L. The pore water geochemistry of cations at these sites follows a pattern similar to that observed for the major anions (chloride, fluoride, and bromide): (1) generally higher concentrations in pore water compared to surface water, (2) highest concentrations at sites in WCA 2A, and the near-canal site in WCA 1A (1A-1) compared to sites in WCA 3A and ENP (Ca is an exception to this pattern), and (3) fresher water overlying saltier water in sediments at the mangrove site along Taylor Creek (ENP-TC2). Note that the shapes of the profiles for sodium, calcium, magnesium, and strontium are similar at individual sites, suggesting similar controls on pore water concentrations. Potassium concentrations are generally at the detection limit (10 ppm) by the analytical method used here (ICP-AES), and

Fig. 4H

Chloride (mg/l)

Fig. 4l

Fluoride (•) and Bromide (▲) (mg/l)

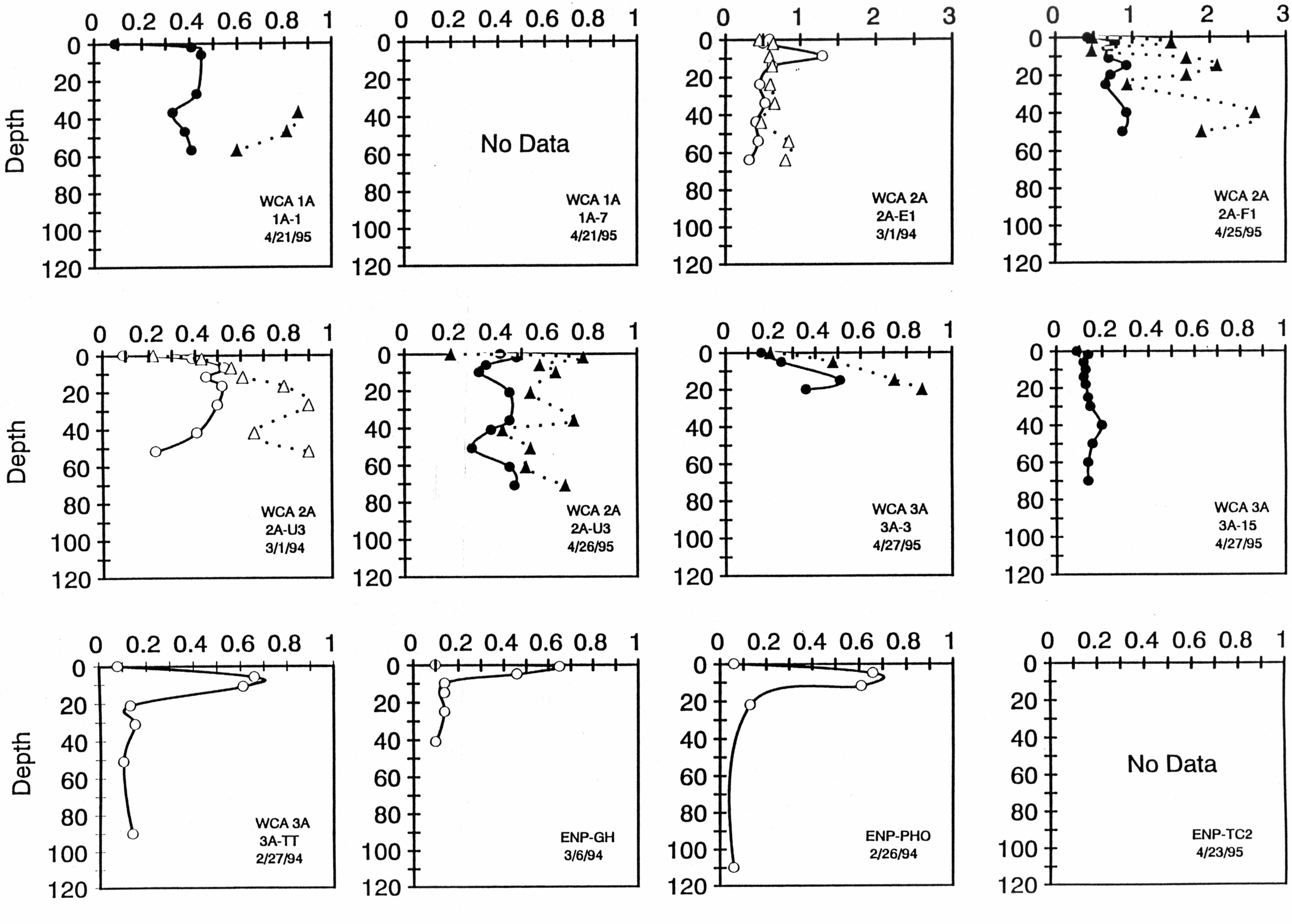


Fig. 4J

Sodium (•) and Potassium (▲) (mg/l)

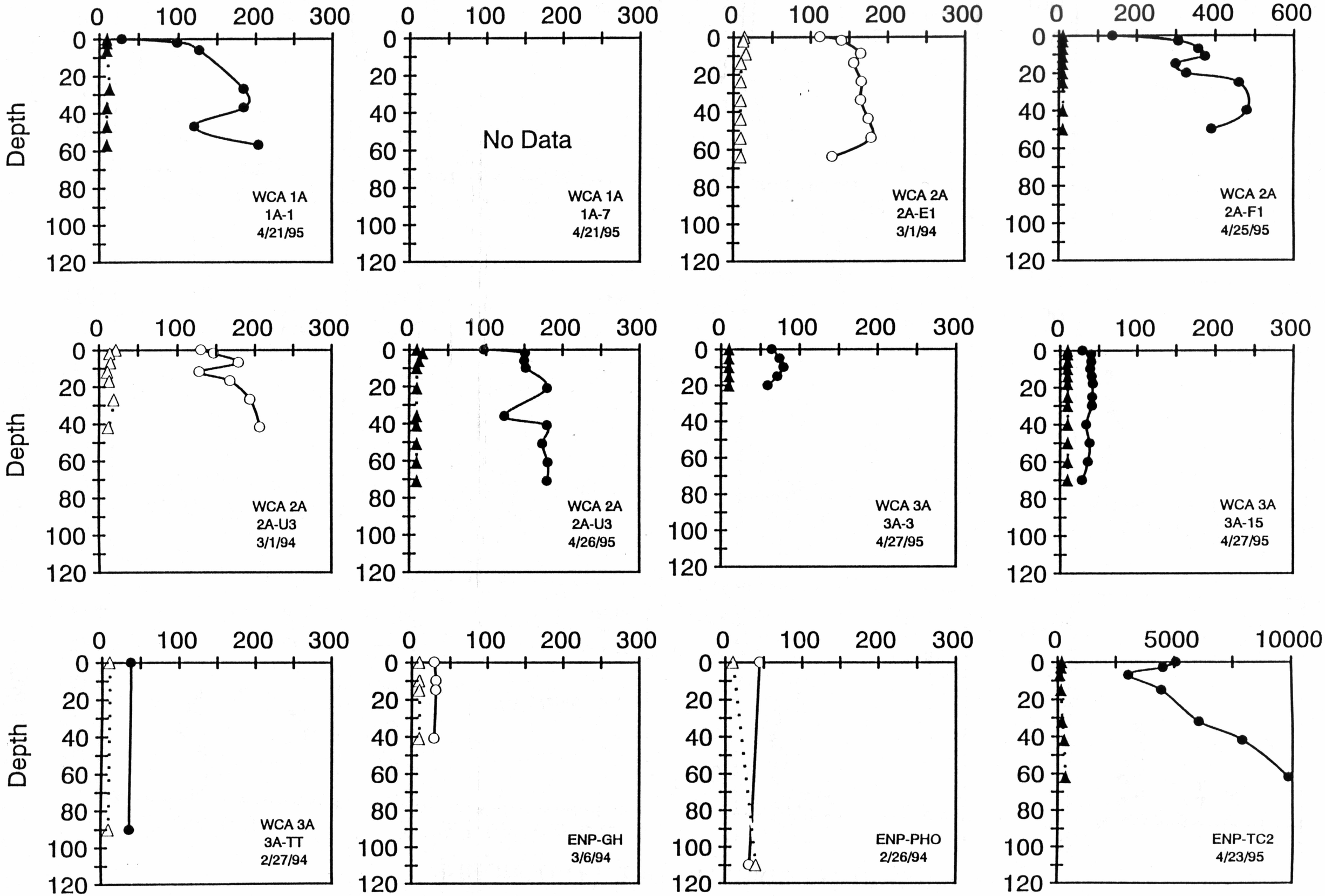


Fig. 4K

Calcium (•) and Magnesium (▲) (mg/l)

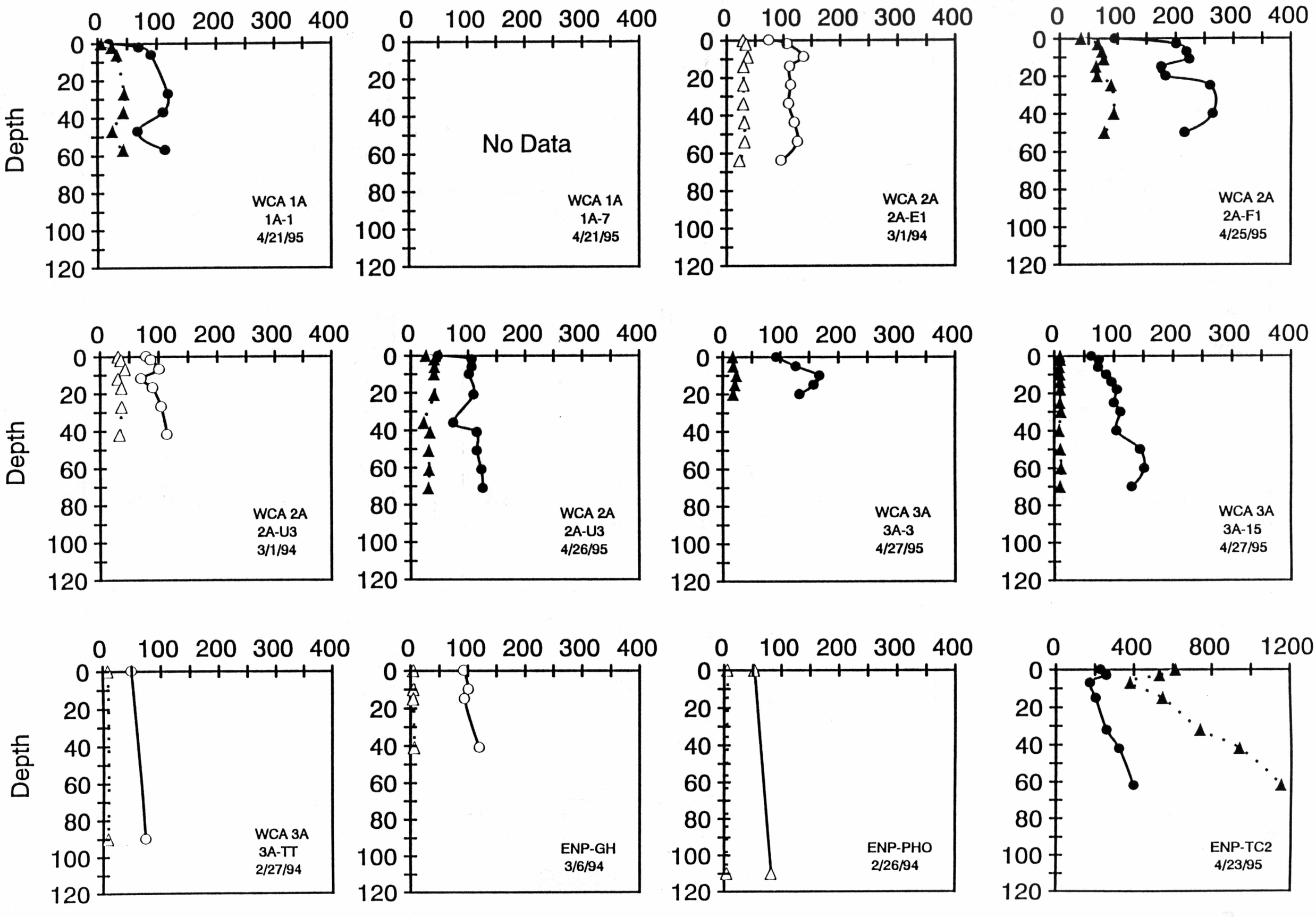
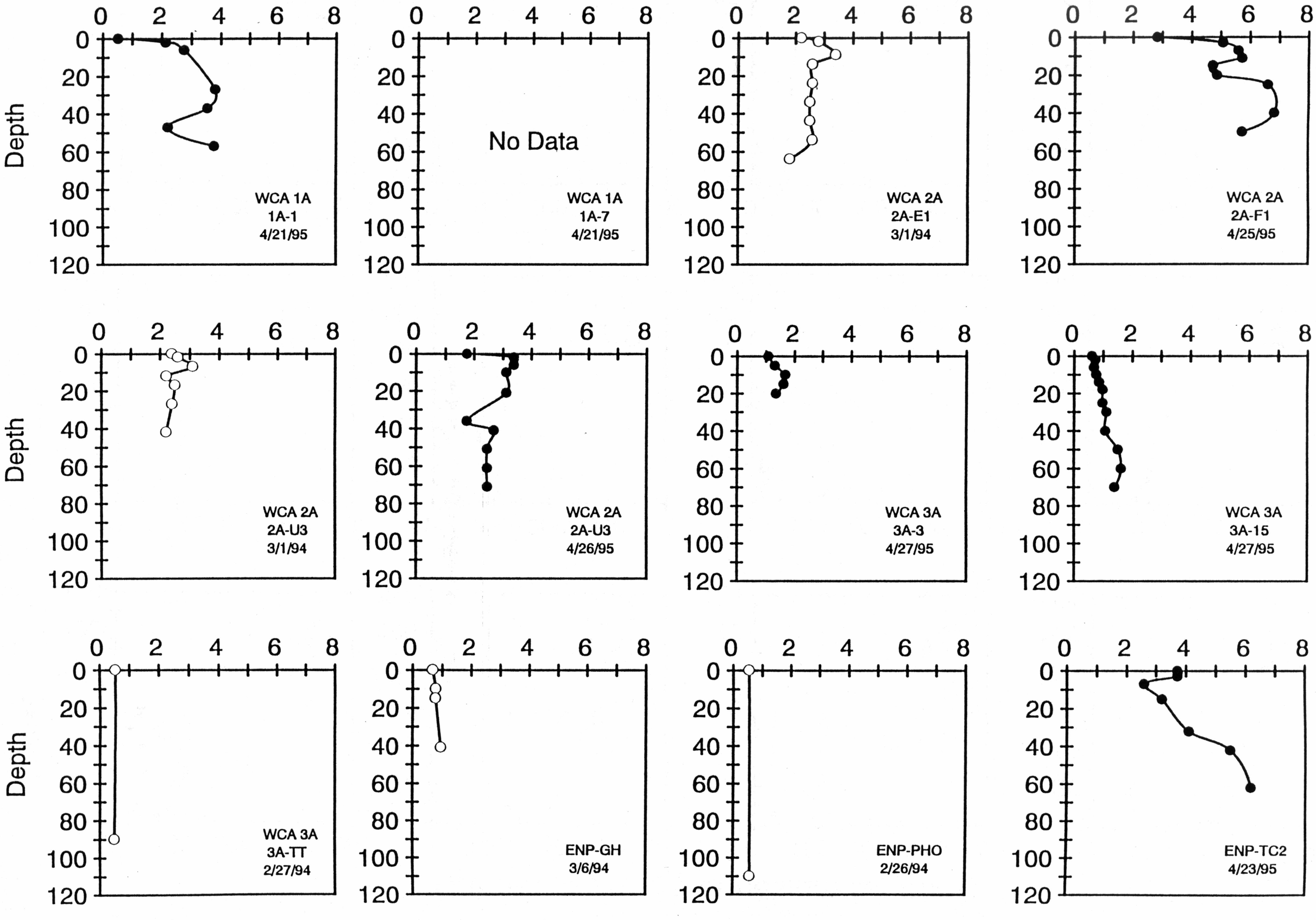


Fig. 4L

Strontium (mg/l)



show little change as a function of depth. Sodium concentrations in the freshwater marshes range from 100 to 500 ppm at sites in WCA 1A and 2A, and typically 25 to 50 ppm at sites in WCA 3A and ENP. Magnesium concentrations ranged from 24 to 94 ppm at sites in WCA 1A and 2A, but only 5 to 24 ppm at freshwater marsh sites in WCA 3A and ENP. Strontium concentrations ranged from 2 to 7 ppm at sites in WCA 1A and 2A, but only 0.5 to 2 ppm at freshwater marsh sites in WCA 3A and ENP. In contrast, calcium concentrations showed little regional variation (range of 70 to 170 ppm downcore at most sites), except for somewhat elevated concentrations at site F1 in WCA 2A (range of 66 to 265 ppm).

Concentrations of iron and silica in pore water from these sites are also listed in Table 4. In general, concentrations of these two elements were below the detection limits by ICP-AES (0.1 ppm for iron and 1.0 ppm for silica. At a few sites, however, detectable levels of these elements were observed. Silica was observed in pore water only at site F1 in WCA 2A (range of 1.3 to 4.4 ppm), possibly suggesting a source from canal water discharge although other explanations are possible. For iron, concentrations ranging from 0.1 to 2.3 ppm were observed below 36 cm at site WCA 2A-U3, and throughout the core at sites WCA 3A-15 and ENP-GH. The presence of dissolved iron at these sites implies a source of iron and low levels of dissolved sulfide. Note the low concentrations of dissolved sulfide in pore water below 25 cm at site WCA 2A-U3, and throughout the core at site WCA 3A-15 (Table 3 and Fig. 4E). The sources of iron for these sites are unclear, but the biogeochemical cycling of iron in the iron-starved environment of south Florida is likely of importance to primary productivity and deserves further study.

Summary

The results of chemical analysis of surface and pore waters from 22 selected sites throughout south Florida showed that distinct regional patterns exist in the distribution of chemical species in this wetland ecosystem. Most chemical species in both surface and pore water showed enhanced concentrations in WCA 2A, with generally decreasing concentrations to the south and west into WCA 3A, ENP, and Big Cypress National Preserve. The largest enhancements observed were for sulfide and phosphate, with concentrations in pore waters at sites near the Hillsboro Canal in WCA 2A up to 500 times higher than "pristine" sites in WCA 1A, WCA 3A, and ENP. Other chemical

species (DOC, alkalinity, chloride, fluoride, calcium, magnesium, sodium, potassium, and strontium) showed much lower enhancements of 2 to 10 times at WCA 2A near-canal sites compared to "pristine" areas. Ammonium concentrations in pore waters were quite variable, and were frequently very high (> 1,000 µg/l) at pristine sites with concentrations comparable to contaminated marsh sites near the Hillsboro Canal in WCA 2A.

Within WCA 2A, sites near the Hillsboro Canal had higher pore water concentrations of several dissolved chemical species compared to a site near the center of WCA 2A (2A-U3). This trend is most pronounced for phosphate, consistent with previous studies of the sediments which show a distinct pattern of sedimentary phosphorus enrichment proceeding toward the Hillsboro Canal (Koch and Reddy, 1992; Craft and Richardson, 1993). The phosphorus enrichment near the Hillsboro Canal apparently originates from discharge of canal water that contains phosphate derived from the Everglades Agricultural Area. This phosphate is rapidly assimilated by aquatic macrophytes (notably cattails which have recently colonized areas near the Hillsboro Canal in WCA's 1A and 2A) and ultimately deposited in the sediments. Diagenetic processes in the sediments recycle the sedimentary phosphorus, producing high pore water phosphate concentrations at the contaminated sites. Titration alkalinity and DOC concentrations are also somewhat higher at sites near the canal compared to the central marsh site in WCA 2A. This likely reflects the active decomposition of organic matter derived from macrophytes (notably cattails) that flourish in the nutrient-rich environment adjacent to canals. Other chemical species in pore water, such as chloride, fluoride, calcium, magnesium, sodium, and strontium were only nominally higher at one of the canal sites (WCA 2A-F1) compared to the center marsh site (WCA 2A-U3). Sulfate showed somewhat unusual behavior, with similar surface water sulfate concentrations and pore water sulfate profiles at both the canal and center marsh sites, but > 10x higher sulfide concentrations in pore water at the center marsh site. Rooted aquatic macrophytes (cattails at eutrophied sites and sawgrass at non-eutrophied sites) may play a key role in transporting dissolved gases such as sulfide between the sediments and the atmosphere.

In addition to the observed regional trends, the pore water data provides information on the nature of diagenetic processes occurring in the sediments. In most cores, maxima for phosphate and ammonium in the pore water occur in the upper 20 cm of sediment. This suggests that recycling of organic P and N occurs principally in the near-surface sediments where microbial activity is

highest. High concentrations of phosphate and ammonium in the pore waters establish concentration gradients between the pore water and surface water, and diffusional fluxes of pore water nutrients may represent a significant source of nutrients to marsh surface waters. Sulfate reduction is evident at most sites, but high levels of sulfide (> 100 µg/l) were only observed in pore water from sites in WCA 2A, a canal site in WCA 1A, and a brackish water site in ENP. Sulfate reduction is thought to be the principal mechanism for the microbial methylation of mercury (Gilmour et al., 1992), an important environmental issue in south Florida. When abundant sulfate (e.g. @ 5-10 mg/l or greater) is present, however, the production of high levels of sulfide in the pore water may inhibit mercury methylation by immobilizing the mercury as insoluble mercuric sulfide. Thus the high levels of sulfate and sulfide in WCA 2A may retard mercury methylation here. At sites further south (e.g. WCA 3A-15) measurable but much lower levels of sulfate and sulfide may favor mercury methylation. Preliminary results (Gilmour et al., 1997) suggest that rates of mercury methylation are in fact greater at site WCA 3A-15 compared to sites in WCA 2A. Further work is underway to better evaluate the relation between mercury methylation and sulfate reduction in various wetland areas of the south Florida.

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