Assessment of Groundwater Input and Water Quality Changes Impacting Natural Vegetation in the Loxahatchee River and Floodplain Ecosystem, Florida

By William H. Orem, Peter W. Swarzenski, Benjamin F. McPherson, Marion Hedgepath, Harry E. Lerch, Christopher Reich, Arturo E. Torres, Margo D. Corum, and Richard E. Roberts

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Table of Contents

Page

List of Figures in Text

List of Tables in Text

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
Volume		
gallon (gal)	3.785	liter (L)
cubic foot (ft^3)	28.32	liter (L)
Flow rate		
cubic foot per second (ft^3/s)	28.32	liter per second (L/s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Mass		
ounce avoirdupois (oz)	28.35	gram (g)
pound avoirdupois (lb)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F = (1.8×°C) +32
Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
°C = (°F-32)/1.8
Altitude, as used in this report, refers to distance above the vertical datum.
Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).
Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

SI to Inch/Pound

Multiply	By	To obtain
Length		
meter (m)	3.281	foot (ft)
Volume		
liter (L)	0.2642	gallon (gal)
liter (L)	0.03531	cubic foot (ft^3)
Flow rate		
liter per second (L/s)	0.03531	cubic foot per second (ft^3/s)
liter per second (L/s)	15.85	gallon per minute (gal/min)
Mass		
gram (g)	0.03527	ounce avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Abbreviations

‰ – parts per thousand (units for salinity), equivalent to gL^{-1}

μmol – micromoles

μg - micrograms

d - day

dbh – diameter at breast height (measurement of tree dimension)

DIN – dissolved inorganic nitrogen

DOC – dissolved organic carbon

dpm – disintegrations per minute (for radioactive elements)

L - liter

LT – lower tidal

m – meters

m^3 – cubic meteers

meq L^{-1} or meq/L – milliequivalents per liter

mg L^{-1} or mg/L – milligrams pre liter

MFLs – minimum flows and levels

NGVD – National Geodetic Vertical Datum

NPBC CERP – North Palm Beach County Comprehensive Everglades Restoration Plan

NW – northwest

OC – organic carbon

R – riverine

RBA – relative basal area (measurement of tree areal coverage)

RECOVER – Restoration Coordination and Verification (part of Comprehensive Everglades Restoration Plan (CERP)

%RSD – percentage relative standard deviation

SFWMD – South Florida Water Management District

SGD – submarine groundwater discharge

SPM – suspended particulate material

TC – total carbon

TN – total nitrogen

TP – total phosphorus

TS – total sulfur

USGS – United States Geological Survey

UT – upper tidal

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[1]USGS, 956 National Center, Reston, VA 20192
[2]USGS, 600 4th St. S., St. Petersburg, FL 33701
[3]USGS, 10500 University Center Dr., Suite 215, Tampa, FL 33612
[4]South Florida Water Management District, 3301 Gun Club Road, West Palm Beach, FL 33406
[5]Florida Department of Environmental Protection, Florida Park Service, District 5, P.O. Box 1246, Hobe Sound, FL 33455.

Summary

The Loxahatchee River and Estuary are small, shallow, water bodies located in southeastern Florida. Historically, the Northwest Branch (Fork) of the Loxahatchee River was primarily a freshwater system. In 1947, the river inlet at Jupiter was dredged for navigation and has remained permanently open since that time. Drainage patterns within the basin have also been altered significantly due to land development, road construction (e.g., Florida Turnpike), and construction of the C-18 and other canals. These anthropogenic activities along with sea level rise have resulted in significant adverse impacts on the ecosystem over the last several decades, including increased saltwater encroachment and undesired vegetation changes in the floodplain. The problem of saltwater intrusion and vegetation degradation in the Loxahatchee River may be partly induced by diminished freshwater input, from both surface water and ground water into the River system.

The overall objective of this project was to assess the seasonal surface water and groundwater interaction and the influence of the biogeochemical characteristics of shallow groundwater and porewater on vegetation health in the Loxahatchee floodplain. The hypothesis tested are: (1) groundwater influx constitutes a significant component of the overall flow of water into the Loxahatchee River; (2) salinity and other chemical constituents in shallow groundwater and porewater of the river floodplain may affect the distribution and health of the floodplain vegetation.

The distributions of dissolved organic carbon (DOC), silica, select trace elements (Mn, Fe, Ba, Sr, Co, V,) and a suite of naturally-occurring radionuclides in the U/Th decay series (^{222}Rn, ^{223,224,226,228}Ra, ^{238}U) were studied during high and low discharge conditions in the Loxahatchee River estuary, Florida. The zero-salinity endmember of this still relatively pristine estuary may reflect not only river-borne constituents, but also those advected during active groundwater/surface-water discharge. During low discharge conditions, with the notable exception of Co, trace metals generally mixed conservatively from a salinity of ~12‰ on through the estuary. In contrast, of the trace metals studied, only Sr, Fe, U and V exhibited conservative estuarine mixing during high discharge. Dissolved organic carbon and Si concentrations were highest at zero salinity, and generally decreased with an increase in salinity during both discharge regimes, indicating removal of land-derived dissolved organic matter and silica during estuarine transport. Suspended particulate matter (SPM) concentrations were generally lowest (< 5 mg L^{-1}) close to zero salinity, and increased to ~ 18 mg L^{-1} at low discharge towards the seaward endmember, which may be attributed to dynamic resuspension within Jupiter Inlet.

Surface water-column ^{222}Rn activities were most elevated (> 28 dpm L^{-1}) at the freshwater endmember of the estuary, and appear to identify regions of the river most influenced by active groundwater discharge. Activities of four naturally occurring isotopes of Ra (^{223,224,226,228}Ra) in this estuary and select adjacent shallow groundwater wells yield mean estuarine water mass residence times of less than 1 day; values in close agreement to those calculated by tidal prism and tidal period. A radium-based model for estimating groundwater discharge to the Loxahatchee River estuary yielded an average of 1.03 – 3.84 x 10^5 m^3 day^{-1}, depending on river discharge stage as well as slight variations in the particular Ra models used. Such calculated flux estimates are in close agreement with results obtained from a 2-day electromagnetic seepage meter (0.9 x 10^5 m^3 d^{-1}) deployment during high discharge at the confluence of Kitching Creek and the Loxahatchee River, as well as with surficial aquifer recharge estimates. Calculated groundwater discharge rates yield NH_4^+ and PO_4^{-3} flux estimates to the Loxahatchee River estuary that range from 6.27 x 10^1 to 1.06 x 10^3 μmol m^{-2} d^{-1} and 6.92 x 10^1 to 3.79 x 10^2 μmol m^{-2} d^{-1}, respectively.

Results from sampling of surface and pore water along transects in the floodplain of the Loxahatchee River on two sampling trips (September 2003 and March 2004) are reported, and tentative conclusions on the impact of saltwater intrusion on freshwater plant viability in the floodplain of the river are presented. The water chemistry data showed consistently higher ionic strength water occurring at depth in the soil/sediment pore water of the Loxahatchee River floodplain compared to surface water. This high ionic strength water at depth in the pore water may originate from a tidally driven salt wedge moving up the Loxahatchee River through the relatively porous sand layer underlying much of the floodplain. It is also possible that this higher ionic strength pore water may originate from groundwater entering the floodplain. Although the deep pore water is higher ionic strength compared to surface water, it does not have an extremely high salinity or chloride content, except along transect 9. Studies suggest that cypress trees are tolerant of high ionic strength water up to a salinity of 2‰ (g L^{-1}). Salinities this high were only observed along transect 9. Salinities of pore water along transects 1, 3, and 7 did not generally exceed 0.5‰. Thus, results of this study suggest that high salinity water may only be impacting the viability of cypress in an acute way along transect 9, and perhaps to a lesser extent along transect 6. Along transect 6, cypress and other fresh water vegetation are continually exposed to water of slightly elevated salinity compared to levels along transect 1 (upriver background site). Sulfide levels in most soil/sediment pore water in the floodplain of the Loxahatchee River were also low. Sulfide concentrations in excess of 1 mg/L (1,000 µg/L) were observed only along transect 9, and in isolated deep pore water samples along transects 6, and 7. Even along transect 9, sulfide levels were not as high as anticipated considering the levels of sulfate present. This might be due to tidal movement of sulfide in and out of deep pore water, providing an advective flux preventing buildup of high levels of sulfide in sediment pore water. Thus, buildup of sulfide in pore water is unlikely to have deleterious effects on cypress trees, except along transect 9.

Thus, movement of high salinity water appears to be a factor in cypress declines only along transect 9, and perhaps to some extent along transect 6, based on the limited results of this study. Further work, especially looking at pore water below 50 cm depth in the floodplain, and examining pore water during spring tide/neap tide monthly cycles is needed. Episodic events (hurricanes and other severe storms) may be a more important factor in moving saltwater up the Loxahatchee River than daily tidal flooding, and should also be a focus of additional study. A single storm event could conceivably move saltwater far enough upriver and into the floodplain to damage cypress vegetation.

I. Introduction

I.A. Background

The Loxahatchee River and Estuary are small, shallow water bodies located in southeastern Florida. The Loxahatchee River watershed covers an area of about 699 km^2 (270 mi^2) within northern Palm Beach and southern Martin counties (Fig. 1). The Loxahatchee River has three major tributaries: the Northwest Branch/Fork, the North Fork, and the Southwest Fork. These three tributaries drain to the central embayment discharging ultimately to the Atlantic Ocean via the Jupiter Inlet (Fig. 1). The North Fork of the Loxahatchee River is a very shallow tributary and currently provides only a small percentage of the total freshwater flow to the Estuary (Russell and McPherson, 1984). The Northwest Branch/Fork of the Loxahatchee River originates from the Loxahatchee Slough, flows north and bends to the east/southeast through the Jonathan Dickinson State Park (JDSP). The floodplain is a freshwater swamp supporting a

Fig. 1. Map showing the location of the Loxahatchee River in south Florida (top), and satellite image of the Loxahatchee River, its tributaries, and the surrounding watershed (bottom). Images modified from Google Earth.

unique ecosystem in the region. In 1985, the Northwest Branch/Fork was designated by Federal and state governments as Florida's first "Wild and Scenic River" and is often referred to as the "last free flowing river in southeast Florida". Portions of the river are also designated as an Aquatic Preserve, Outstanding Florida Water (OFW), and are included as important components of Florida's state park system (Fig 2).

Fig. 2. Canoeing the Northwest Branch/Fork of the Loxahatchee River at Jonathan Dickinson State Park.

Historically, the Northwest Branch/Fork of the Loxahatchee River was a freshwater system. In 1947, the inlet at Jupiter was dredged for navigation and has remained permanently open since then. Drainage patterns within the basin have been altered significantly due to land development, and road and canal construction (Fig. 3). These anthropogenic impacts and sea level rise have resulted in significant adverse impacts on the ecosystem, including increased saltwater encroachment and undesired vegetation changes in the floodplain (McPherson and Sabanskas, 1980; McPherson and Halley, 1996), (Fig 4). The problem of saltwater intrusion and vegetation degradation in the Loxahatchee River may be partly induced by diminished freshwater input, from both surface water and groundwater, into the river system. In 2002, the South Florida Water Management District (SFWMD) established Minimum Flows and Levels (MFLs) for the Northwest Branch (South Florida Water Management District, 2002). The Northern Palm Beach County Comprehensive Water Management Plan (South Florida Water Management District, 2002a) contains a

Fig. 3. Map of the Loxahatchee River watershed, showing major canals and drainage features, the location of wells (M_1234, M_140, Pb_565, Pb_689, Pb_1642, and Pb_ 1662) installed by the U.S. Geological Survey, and approximate locations of maps in Figures 18 and 19.

Fig. 4. Dead cypress tree along the Northwest Branch/Fork of the Loxahatchee River.

number of key projects designed to provide supplemental base flows to the Northwest Branch/Fork of the Loxahatchee River. Comprehensive restoration of the Loxahatchee ecosystem is included in the North Palm Beach County (NPBC) Project under the Comprehensive Everglades Restoration Plan (CERP).

In spite of the general observation of vegetation changes in the floodplain, it is not clear how much groundwater is discharged into the river and how the groundwater flux may be related to the MFLs and flow diversions being considered in the NPBC CERP Project. More information is needed concerning the critical biogeochemical regime that triggers the transition from freshwater vegetation to salt water tolerant mangroves. Field observations indicate that in the transitional zone, vegetation change could be dynamically related to seasonal change of salinity, groundwater levels, and micro-topography in the floodplain.

Understanding the relationships among the surface water and groundwater interaction and its influence on floodplain vegetation is critical to the future revision of the Loxahatchee MFLs and the NPBC CERP Project. The project work reported here represents a cooperative agreement between the SFWMD and the U.S. Geological Survey (USGS) to help address these issues.

I.B. Objectives

The overall objective of this project was to assess the seasonal surface water and groundwater interaction and the influence of the biogeochemical characteristics of shallow groundwater and porewater on vegetation health in the Loxahatchee River floodplain. The hypotheses being tested are: (1) groundwater influx constitutes a significant component of the overall flow of water into the Loxahatchee River; (2) salinity and other chemical constituents in shallow groundwater and porewater of the river floodplain may affect the distribution and health of the floodplain vegetation.

We investigated the distributions of dissolved organic carbon (DOC), Si, select trace elements (Mn, Fe, Ba, Sr, Co, V) and a suite of naturally occurring U/Th-series isotopes (^{222}Rn, $^{223,224,226,228}Ra$, ^{238}U) during estuarine transport and mixing in the Loxahatchee River estuary. This subtropical estuary, located just east of Lake Okeechobee, FL in a predominantly carbonate geologic environment (McPherson et al., 1982; Wanless et al., 1984; Noel et al., 1995), may consequently have a strong groundwater contribution to the surface-water budget (Russell and McPherson, 1984; Russell and Goodwin, 1987). Therefore, we utilize naturally occurring isotopes of Ra and Rn as tracers of submarine groundwater flow in our investigation of biogeochemical transport in the Loxahatchee River estuary (Cable et al., 1996, 1997; Kelly and Moran, 1999; Krest et al., 1999, 2000; Swarzenski et al., 2001; Kelly and Moran, 2002; Burnett and Dulaiova, 2003; Krest and Harvey, 2003; Charette and Buesseler, 2004; Purkl and Eisenhauer, 2004).

Estuaries are well-known biogeochemical reactors (Sholkovitz, 1976, 1977; Boyle et al., 1977; Sholkovitz et al., 1978; Shiller and Boyle, 1991; Millward and Turner, 1994; Swarzenski et al., 1995) wherein terrigenous material, carried downstream by rivers, eventually is mixed into seawater (Turekian, 1977). The reactions and processes that occur during estuarine mixing are similarly well-characterized (Mackin and Aller, 1984; Yan et al., 1990; Chiffoleau et al., 1994; Robert et al., 2004; Turner et al., 2004), and reflect an integration of diverse biogeochemical controls across land-sea margins (Martino et al., 2004). For example, many estuarine systems are variably contaminated by anthropogenic inputs that may influence estuarine transport and mixing (Shank et al., 2004). In addition, the ubiquitous nature of groundwater discharge along many coastlines may directly affect estuarine water and geochemical budgets alike (Bokuniewicz, 1980; Johannes, 1980; Oberdorfer et al., 1990; Valiela et al., 1990; Moore, 1996, 1997, 1999; Corbett et al., 1999; Li et al., 1999; Charette et al., 2001; Swarzenski et al., 2001; Burnett et al., 2001, 2002, 2003; Slomp and Cappellen, 2004; Swarzenski et al., 2004a). To better understand biogeochemical transport in the Loxahatchee River estuary, we have employed a suite of natural tracers that can provide information on traditional biogeochemical scavenging reactions initiated by an increase in salinity, as well as on the role of groundwater/surface water exchange or groundwater discharge in impacting or defining such estuarine biogeochemical transport.

The USGS has in-house radiometric techniques (Radium [Ra] and Radon [Rn] isotopes) and analytical expertise to examine freshwater-saltwater interactions and geochemical regimes of groundwater and porewater in the wetland ecosystems of South Florida (e.g., Orem et al., 1997; Swarzenski, 2001). In addition, the SFWMD has ongoing efforts in model development and groundwater and vegetation monitoring in the floodplain of the Northwest Branch/Fork of the Loxahatchee River to address project objectives.

This study addresses the following specific objectives:

- To evaluate long-term patterns in groundwater levels and rainfall in the Loxahatchee River watershed from a literature survey.
- To characterize the Ra-Rn isotopic signature of surface water and groundwater within the Loxahatchee River and Estuary; and to use these signatures and other indicators to estimate a wet season and dry season groundwater input into the river system
- To measure salinity and other selected water-quality constituents in the sediment, porewater and shallow groundwater of the river and floodplain during a wet and a dry season, and to relate these measurements to the distribution and health of wetland vegetation in the Northwest Branch/Fork of the Loxahatchee River.

To achieve these objectives, water samples from selected wells and from the surrounding surface waters were collected and analyzed for Ra and Rn isotopes. Samples of porewater and sediment were collected along selected SFWMD vegetation transects in the Loxahatchee River system (including saltwater-impacted and pristine freshwater areas) for chemical analysis of selected parameters. Parameters measured included: salinity, major ions (indicators of saltwater intrusion), sulfur species (sulfate and sulfide), nutrients (nitrate, ammonium, phosphate), pH, alkalinity, redox conditions, and dissolved oxygen. Comparing these geochemical parameters in both pristine freshwater and saltwater-impacted sites provides a first step in determining the causes of the observed vegetation community changes. An evaluation of the results in the context of existing studies of the sensitivity of freshwater vegetation to changes in water quality provides a basis for determining the most important water quality constituents. The information from our study will help support and contribute to several SFWMD efforts, including flow and salinity modeling in the Estuary and floodplain, vegetation and soil studies in the floodplain, the NPBC CERP Project and RECOVER, as well as the MFLs update and rule development for the Loxahatchee River.

II. Retrospective

II.A. General

The SFWMD (2002) conducted a comprehensive environmental study of the Loxahatchee River. The study included a literature review of environmental reports on the river over the past three decades. The review includes studies related to saltwater intrusion and the effects of salinity on freshwater vegetation, including cypress, and cites 76 references. The SFWMD study also includes an analysis of historical vegetation distribution and changes in vegetation distribution along the Northwest Branch/Fork of the Loxahatchee River. Other parts of the study document vegetation surveys, freshwater inflows, and salinity along the Northwest Branch/Fork of the river. The study also presents preliminary results of hydrodynamic and salinity models of the river and its estuary.

Studies of groundwater and its effects on wetland ecology in the vicinity of the Loxahatchee River are much less common than those of surface water and its effects on wetland ecology. Shaw and Huffman (2000) reported on the hydrology of isolated wetlands, including a wetland in Jonathan Dickenson State Park, and how wetlands are affected by water table drawdown. Earth Tech, Inc (2000) conducted a study of ground water in the Kitchen Creek basin just north of the Northwest Branch/Fork of the Loxahatchee River .

II.B. Influence of Saltwater Intrusion on Freshwater Vegetation

Saltwater intrusion has been shown to adversely impact freshwater plants. High levels of salt may cause problems of osmoregulation in plants not adapted to live in high ionic strength waters. In coastal Louisiana, intrusion of seawater into freshwater and brackish marshes has resulted in significant degradation of these wetlands through the mortality of macrophytes and other rooted plants (Flynn et al., 1995; Howard et al., 2000; Hester et al., 2001; Holm et al., 2001).

In addition to the effects of salt, sulfate is also present in high concentrations in seawater (~2.7 g/L of seawater). While sulfate itself is not harmful to macrophytes and other aquatic plants (except as it contributes to the general salt issue), sulfate entering a wetland stimulates microbial sulfate reduction and the production of toxic hydrogen sulfide. Sulfate reduction occurs in reducing environments, such as wetland sediments (Bates et al., 2001). It is typically a minor metabolic process in freshwater sediments, where methanogenesis dominates. Intrusion of saltwater or other major sources of sulfate, however, can stimulate sulfate reduction and the production of hydrogen sulfide. Hydrogen sulfide can act as a toxin to rooted aquatic vegetation in three ways: (1) reducing redox conditions in sediments and retarding transport of oxygen to plant roots, (2) reacting with metals to form insoluble metal sulfides and depriving plants of needed metal micronutrients, and (3) inhibiting uptake of nutrients from the sediments (Portnoy and Giblin, 1997; Howard et al., 1999; Flynn et al., 1999; Lamers et al., 2002). In coastal Louisiana, production of toxic hydrogen sulfide from saltwater intrusion may be the major factor in the loss of freshwater and brackish marsh vegetation (Flynn et al., 1999). Sulfate is also entering the northern Everglades at concentrations 50-100 times background (Orem et al., 1997, 1998, 2000; Orem, 2004; Gilmour et al. 2007), and may be partly responsible for the changes in macrophyte distributions (cattail replacing sawgrass) and tree island loss. In the case of the northern Everglades, however, the excess sulfate originates from agricultural sources in the Everglades Agricultural Area rather than from seawater intrusion (Orem et al., 2000; Bates et al., 2001). Regardless of the source, the sulfate entering the northern Everglades has stimulated sulfate reduction, and drastically reduced redox conditions in the most heavily affected areas (Orem et al., 1998; Gilmour et al., 2007). In the northern Everglades, excess nutrient inputs from agricultural runoff have also been implicated in observed changes in macrophytes in the ecosystem, with cattails replacing sawgrass (Vaithiyanathan and Richardson, 1999). Excess nutrient inputs can also have dramatic effects on algal communities, with green algae replacing periphyton in eutrophied areas of the Everglades (Noe et al., 2002).

II.C. Long-Term Patterns in Groundwater Levels and Rainfall

Long-term groundwater level measurements for shallow wells in the Loxahatchee River watershed (Fig. 3) extend back to at least 1950. The shallow groundwater well with one of the longest records, M-140, begins in 1950 and ends in 1990. Over this 40 year span, the groundwater level declined over 0.6 m (2 ft), or about 0.02 m/yr (0.06 ft/year), (Fig. 5). During the 1990's and early 2000's, other wells were installed and monitored. Statistical analyses generally indicate decreasing water level trends through this period (Table 1). For example, well M-1234, located a few miles from M-140, declined 0.007 m/yr (0.024 ft/yr) between 1989 and 2004. Well Pb-689 declined 0.021 m/yr or 0.069 ft/yr (linear regression) from 1993-2003 (Fig. 6). The reason for the recent decline in groundwater levels is uncertain, and may have multiple causes, including changes in long-term rainfall (Figs. 7 and 8), or various water management activities in the watershed. However, the overall decline in groundwater level from 1950 to the present spans years of heavy and light rainfall (Fig. 9). Thus the groundwater decline probably reflects drainage alterations in the watershed, rather than patterns of rainfall. Drought conditions prevailed in 1989-1990 (Fig. 9), and groundwater levels were low as a result. Groundwater levels rebounded in the early 1990's as rainfall increased. Lower rainfall in the late 1990's and early 2000's may have contributed to overall downward trends. Water management, including diversions, pumping, or impoundment, will normally affect groundwater levels, and these effects will vary with location in the watershed. The predominant trend, however, is downward, and the reduced groundwater head must have resulted in reduced groundwater inflow to the river. Undoubtedly, many of the anthropogenic and natural effects on groundwater levels in the Loxahatchee River watershed preceded recent groundwater monitoring.

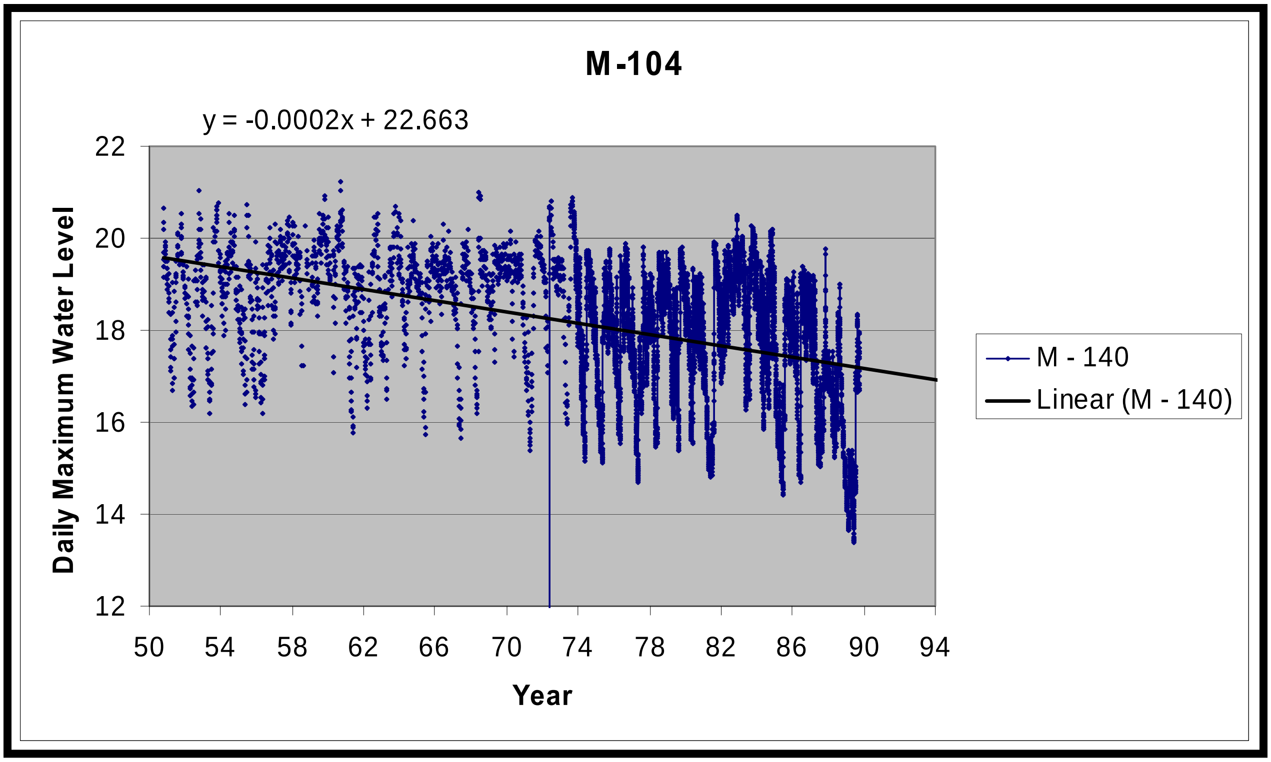


Fig. 5. Decline in the groundwater level in Loxahatchee River well M-140, from 1950-1990 in units of feet above mean sealevel (vertical axis). Both actual measurements and a linear regression line of the data are shown.

Evidence from vegetation near the Northwest Branch/Fork of the river suggests that groundwater levels were historically higher. Alexander and Crook (1975) concluded that since 1940, wet prairie and swamp hardwoods in the watershed lost ground to pineland and mangrove communities due to lowering of the groundwater table. Old aerial photographs (1940) of the watershed revealed an abundance of swamps, prairies, inland ponds, and sloughs. These communities had declined by the middle 1980's.

Various water management changes have been implemented or have been discussed to increase groundwater levels and flows to the Northwest Branch/Fork of the river. Release of canal water from C-18 is now used to increase flow to this Fork. Paul Mercado (written communication, 2004) suggested that groundwater flows to the Northwest Branch/Fork of the river from the Atlantic coastal ridge could be increased by making changes in Bridge Road to allow more conveyance of water through Kitching Creek watershed.

Table 1. Statistical analysis of groundwater levels in wells, Loxahatchee River.

Lox River	Well No.	Period of Record	Trend Period	Trend (ft./yr.)	Type Analysis	Total Decline (ft.)
	M-1234	1988-2004	1989-2004	-0.024	first order	
	PB-689	1973-2004	1994-2004	-0.069	linear	0.69 ft in 10 y
	PB-1642	1988-2004	1993-2004	-0.124	linear	
	PB-1662	1991-2004	1991-2004	0.0422	Seasonal Kendall	
	PB-831	1974-2004	1980-2004	0.01	linear	
	PB-565	1970-2004	1980-2004	-0.005	linear	
	M-140	1950-1990	1950-1990	-0.07	linear	2.8 in 40y
	M-140	1973-1990	1973-1990	-0.04	linear	0.6 in 16 y

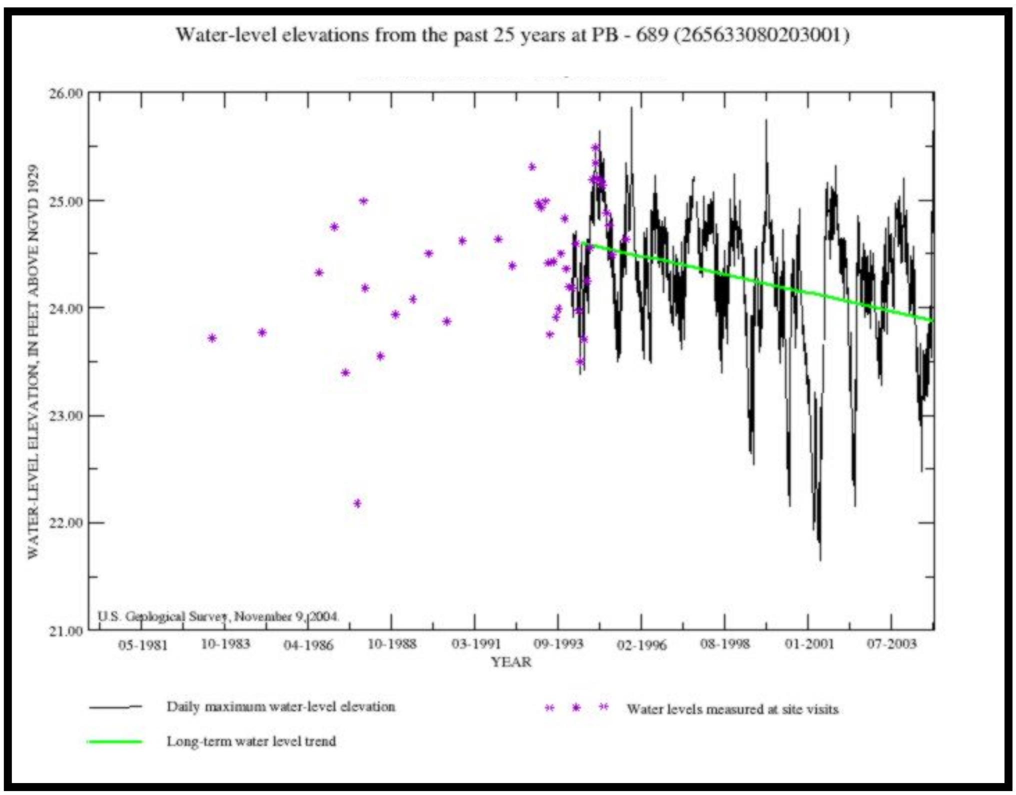


Fig. 6. Decline in the groundwater level in Loxahatchee River well Pb-689, 1993-2003.

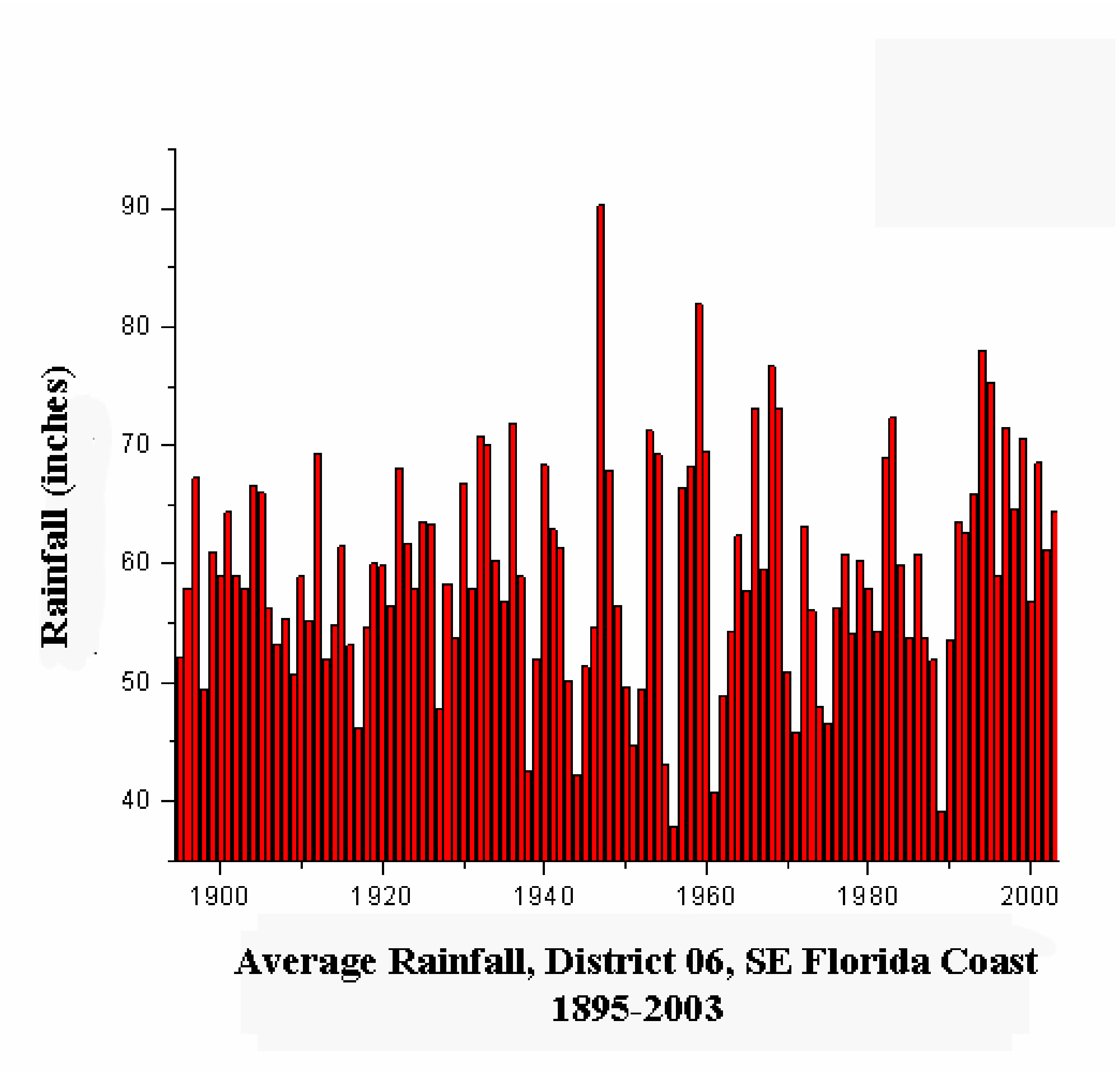


Fig. 7. Long-term rainfall patterns in southeastern coastal Florida; the average for the period 1895-2003 was 59.41 in.

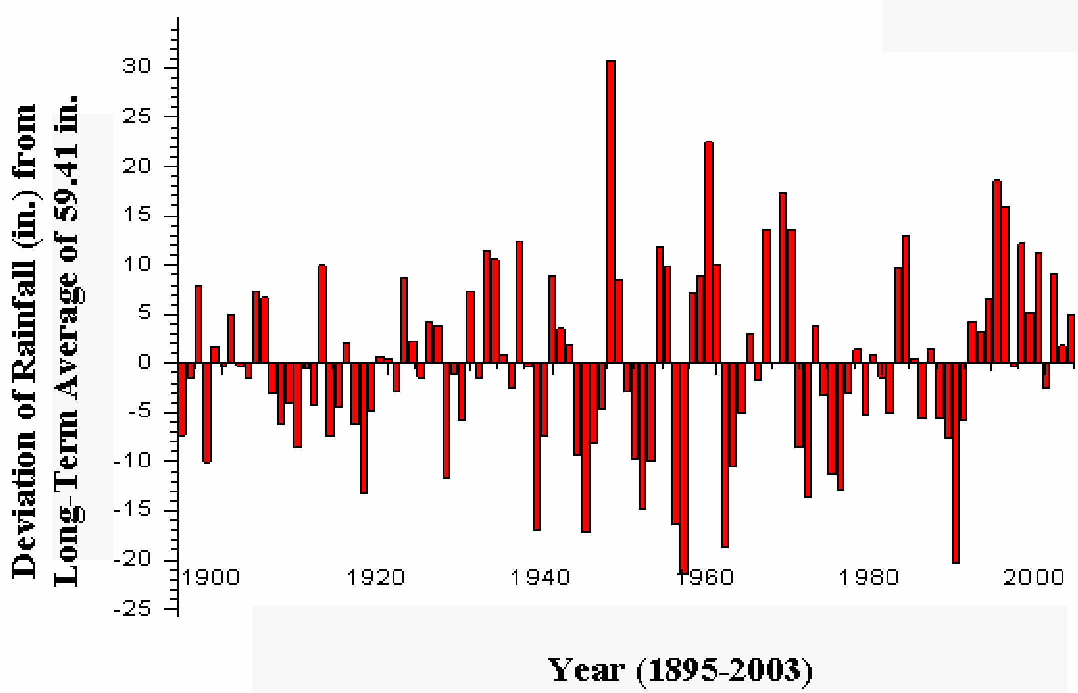


Fig. 8. Deviations in annual rainfall from the long-term average of 59.41 in. for the period of record (1895-2003) for the southeastern coast of Florida (Region 06).

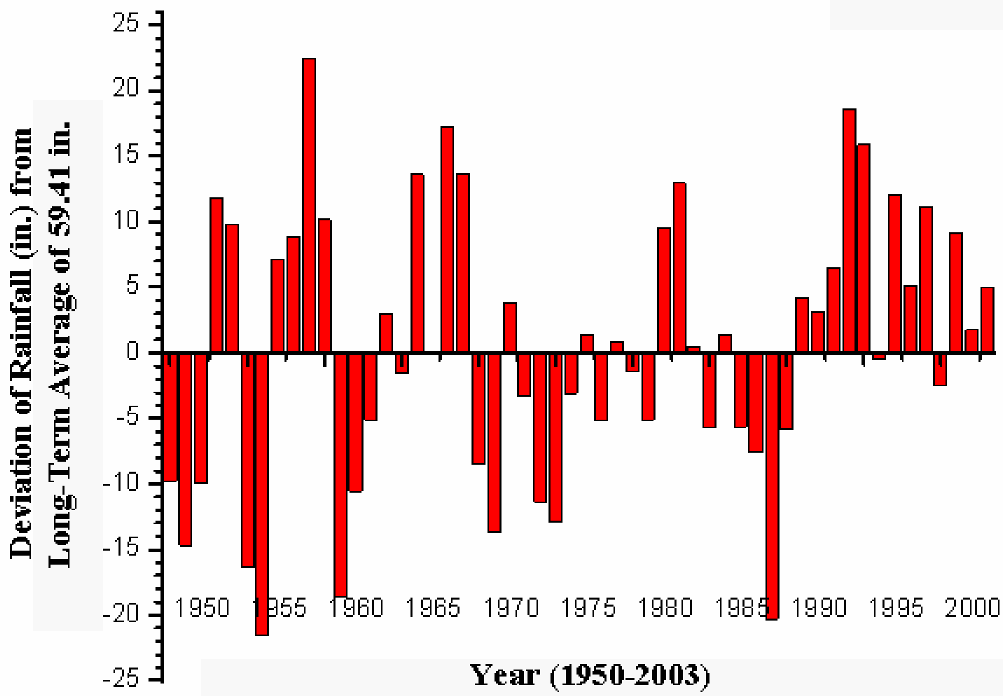


Fig. 9. Deviations in annual rainfall from the long-term (1895-2003) average of 59.41 in., for the period 1950-2003 for the southeastern coast of Florida (Region 06).

II.D. <u>Long-Term Patterns in Floodplain Vegetation</u>

Vegetative land cover in the vicinity of the Northwest Branch/Fork of the Loxahatchee River is characterized by pine forest, wet prairie, or hardwood swamps, and mangrove forests along tributaries. Freshwater hardwood swamps, of cypress, red maple, water oak, willow, bay trees and other hardwoods, grow along upstream tributaries. Mangrove forest (with three species of mangrove) grows along downstream tributaries, and mixes with hardwood trees along a transitional zone.

Hedgepeth and others (SFWMD, 2002) used existing historical aerial photography (1940, 1953, 1964, 1979, 1985, and 1995) to compare spatial and temporal changes in distribution and abundance of vegetative communities along the floodplain of the Northwest Branch/Fork of the Loxahatchee River, and to document changes in vegetation cover and correlate those changes to major events in the watershed. The total vegetative community coverage by type and by year was compared over time to quantify changes over the 55-year period 1940-1995. Over this time span, the wetland vegetative communities declined in acreage as a result of several causes, including scouring of river bed, bulkheading, development, and loss of wetland plants to transitional and upland species, as a result of flow diversions and decreasing water levels. In the lower reach, mangrove forest was displaced by urbanization, but overall mangrove forest coverage increased as it encroached upstream into predominately freshwater communities. Along the middle stretches of the river, nine miles upstream of Jupiter Inlet, there was an apparent increase in the number of plant species and a loss of cypress dominance. Along this intermediate portion of the river and downstream, cypress trees show increasing stress and many trees have died. Such changes in the freshwater vegetative communities may be due to impacts of saltwater intrusion and decreased flows of fresh surface and groundwater inflows. Changes in freshwater habitat along the Northwest Branch/Fork may be attributed to dredging of the Intracoastal Waterway (early 1900's), dredging downstream segments of the Loxahatchee River (1930's), permanent opening of the Jupiter inlet (1947), lowering of the freshwater table, and diversions of freshwater from the Northwest Branch/Fork (1950's). All these projects had a potential to allow increased upstream encroachment of seawater during tidal cycles.

III. Study Area and Sampling

III.A. General Description

The study area includes the entire Loxahatchee River watershed for the historical data review and the evaluation of historic groundwater levels for wells, while field studies focused primarily on the Northwest Branch/Fork of the Loxahatchee River (Fig. 1), its floodplain and nearby uplands, and the estuary. The study included two sampling periods, one during the wet season (September 2003) and one in the dry season (March 2004).

The 699 km^2 Loxahatchee River watershed provides water for three principal distributaries, the Northwest Branch/Fork, and North- and Southwest Forks that discharge through Jupiter Inlet to the Atlantic Ocean (Russell and McPherson, 1984). Natural and anthropogenic change in the watershed since the 1940's has resulted in increased saltwater intrusion up the Loxahatchee River estuary, and consequent dramatic ecosystem change (McPherson et al., 1982; Noel et al., 1995). Compounding the issue of saltwater intrusion may be a gradual decrease in available fresh surface- and groundwater, due to regional construction of extensive canal networks for expansive urban growth centered around Jupiter, FL (McPherson and Sonntag, 1984).

The lower Loxahatchee River estuary is mostly shallow (average depth ~ 1.2 m), although a partially dredged and natural channel 3+ m deep extends about 14 km upstream. In the upper reaches of the river, water depths are generally less than 2-3 m. The tides in the estuary are mixed-semi-diurnal, and the tidal range is <1 m. A typical tidal wave may propagate upstream for about 16 km (Russell and Goodwin, 1987) at a rate of 8-16 km hr^{-1}.

Freshwater inflows to the Loxahatchee River estuary may include local and regional upward groundwater flow, precipitation, surface-water runoff, storm drainage and canal discharge. This composite inflow, which is seasonal in nature and can be partially regulated during wet (May-November) months, may have a strong tropical weather imprint (e.g., two hurricanes made landfall very close to the estuary in September 2004). Mean monthly precipitation rates at SFWMD Station No. C18W_R (26° 52' 19" N, 80° 14' 42" W), and daily mean stream-flow upstream of the Northwest Branch/Fork of the Loxahatchee River are illustrated in Fig. 10. This two plus-year record suggests a reasonably strong relation between precipitation and stream flow. Average daily discharge rates for the upper Northwest Branch/Fork of the Loxahatchee River (USGS site ID: 2277600; 26° 56' 20" N, 80° 10' 31" W) during the high and low discharge sampling cruises were 4.02 and 0.88 m^3 sec^{-1}, respectively. A 2-yr mean stream flow rate during the two sampling efforts was 2.15 m^3 sec^{-1}. For comparison, an average discharge rate of about 300 m^3 sec^{-1} has been reported for Jupiter Inlet (Mehta et al., 1992).

Groundwater/surface water interactions are often enhanced in carbonate-dominated coastal margins and wetlands of Florida (Parker et al., 1955; Krest and Harvey, 2003). Biogeochemical transport in the Loxahatchee River estuary was, therefore, investigated from the perspective that groundwater discharge could play an important role in geochemical and water budgets of this estuarine system. Consequently, the following discussion will develop in two directions: (1) traditional biogeochemical transformations along salinity gradients, and (2) the role of groundwater discharge in impacting estuarine transport.

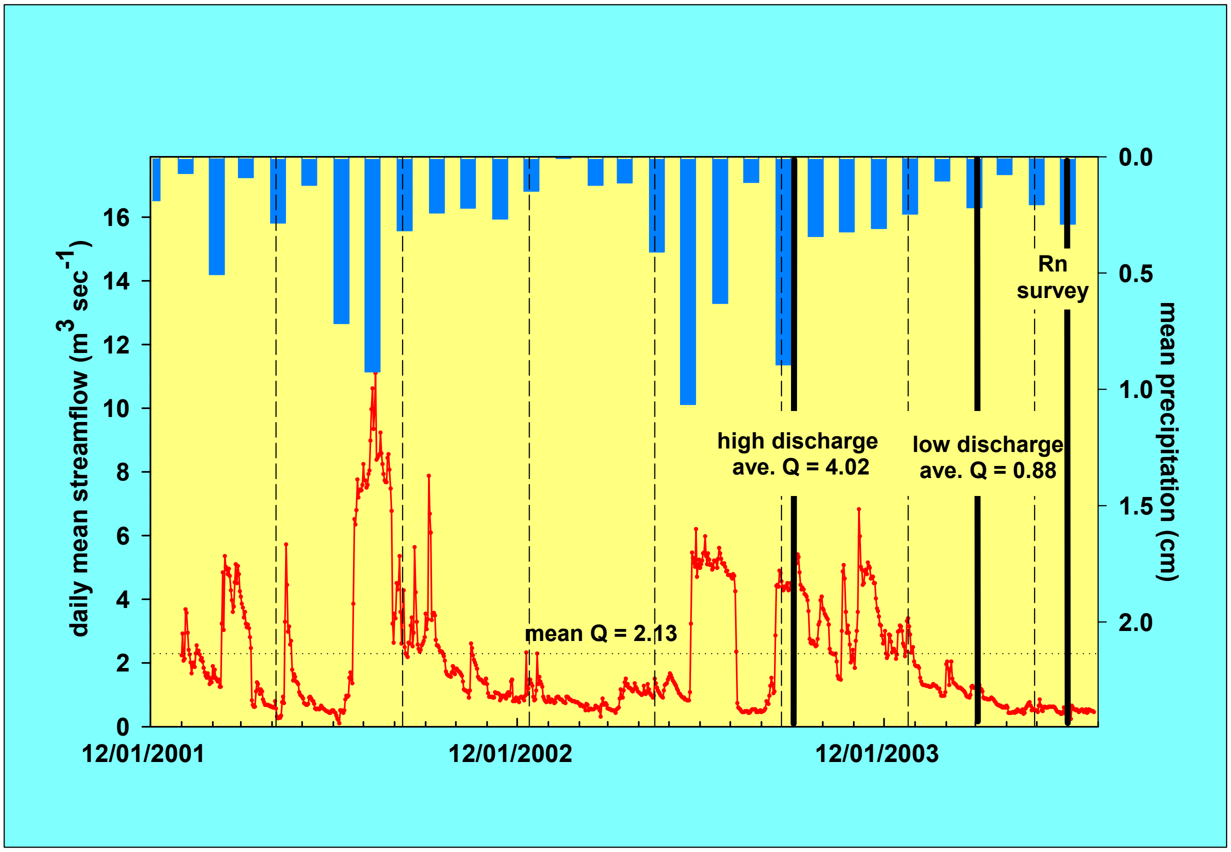


Fig. 10. Mean daily streamflow (m^3 sec^{-1}) and monthly precipitation (cm) for the Loxahatchee River estuary. Individual sampling intervals are denoted by the vertical dashed grey (Ra, elements) and black solid (Rn) bars.

III.B. Loxahatchee River and Estuarine Sites

Estuarine water samples were collected from a small boat at sites along the Loxahatchee River (Fig. 11) during two river discharge regimes (September 2003 and March 2004) for analysis of dissolved constituents using 'trace metal clean' procedures (Swarzenski et al., 2004). Uncontaminated estuarine water was collected using a gimbaled collection port from ~0.5 m below the water surface and away from the boat's hull using a small volume peristaltic pump and acid-rinsed tubing. Pre-rinsed, large surface area filter cartridges (0.4 µm cutoff) were used to filter dissolved trace metals and other chemical species in situ. Trace metal sub-samples were acidified to pH <2 in the field using SeaStar ultra-pure HNO_3, and stored chilled. Sub-samples for dissolved organic carbon (DOC) were collected using a metal bucket, a portable glass filtration system and pre-combusted GFF glass fiber filters. The DOC samples were immediately frozen until subsequent analyses. Shallow groundwater samples were collected at three well sites along transects perpendicular to the estuary during both sampling efforts.

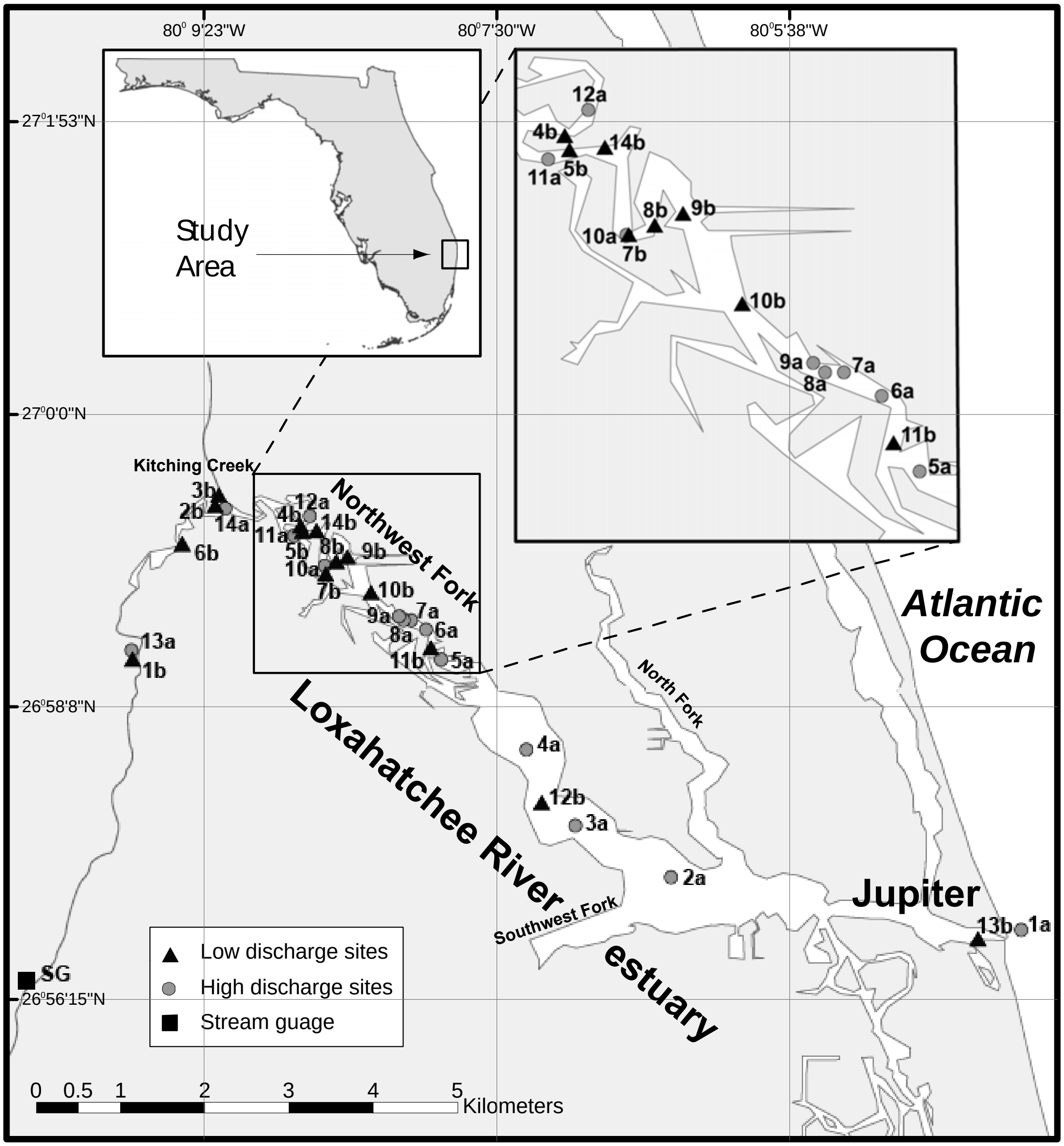


Fig. 11. Station location map for high (September 2003) and low (March 2004) discharge sampling efforts.

Samples for all four radium isotopes ($^{223,224,226,228}Ra$) were collected (using the same gimbaled arm and a 12v submersible pump) by passing a known volume of estuarine water through either 1 or 2 MnO_2 impregnated acrylic fiber cartridges (Weiss et al., 1984). Two serial cartridges were used sporadically to evaluate the Ra extraction efficiency onto the MnO_2 fiber (typically >96 %). Target salinities and water characteristics (e.g., temperature, pH, dissolved oxygen, specific conductivity, and salinity) were continuously monitored during pumping operations with a multi-parameter YSI probe. The suspended particulate matter (SPM) concentration per sample was determined gravimetrically in the lab, using pre-weighed 0.4 µm Nuclepore filters (47 mm diameter).

Near-continuous excess radon-222 activities were measured in the Loxahatchee River estuary in June 2004 using six commercial air radon detectors (RAD7 – Durridge, Co., Inc.), routed simultaneously through a single air-water exchanger (Burnett et al., 2001). By applying a temperature and solubility coefficient correction, one can calculate the activity of ^{222}Rn in water, as the Rn in air will attain equilibrium with estuarine water flowing through the exchanger after about 20 min. Utilizing six RAD7 detectors simultaneously permits almost real-time (once every 5-min) Rn data acquisition. During this survey, water column characteristics were again monitored both at the exchanger site and within the water column using an *in situ* multi-parameter sensor array, as well as WTW multi-probes.

To physically validate the Ra-derived groundwater flux rate for the estuary, direct seepage across the sediment/water interface was measured during the high discharge sampling cruise in September, 2003 at Kitching Creek (Fig 11), using an autonomous electromagnetic seepage meter (Rosenberry and Morin, 2004; Swarzenski et al., 2004b). A streaming resistivity profiling survey (Manheim et al., 2002; Belaval et al., 2003; Swarzenski et al., 2004d) was also conducted in this estuary during the June 2004 field effort to provide detailed information on the dynamic subsurface freshwater/saltwater interface of this estuary.

III.C. Loxahatchee River Floodplain Sites

In addition to studies conducted in the Loxahatchee River Estuary, surveys of vegetation, and measurements of geochemical parameters in the floodplain surface water and porewater were also conducted during the same wet and dry period cycles (September 2003 and March 2004). In 2003, the SFWMD and the Florida Park Service established vegetation monitoring studies for plant community composition and structure in order to document baseline and future plant community health along the floodplains of the North Fork and Northwest Branch/Fork of the Loxahatchee River and Kitching Creek. The project examined vegetation along six historical transects and established four new transects in areas of concern (Fig. 12). The transects are located in areas representative of riverine (predominantly non-impacted freshwater), and upper tidal (saltwater intruded with fresh and brackish water) communities. Seven transects were established at designated locations along the middle and upper segments of the Northwest Branch/Fork of the Loxahatchee River. Additional transects were established in the lower segment of Kitching and Cypress Creeks (tributaries of the Northwest Fork), and in the upper North Fork of the Loxahatchee River.

Surface water, porewater, and sediment samples were collected at points located along transects 1,

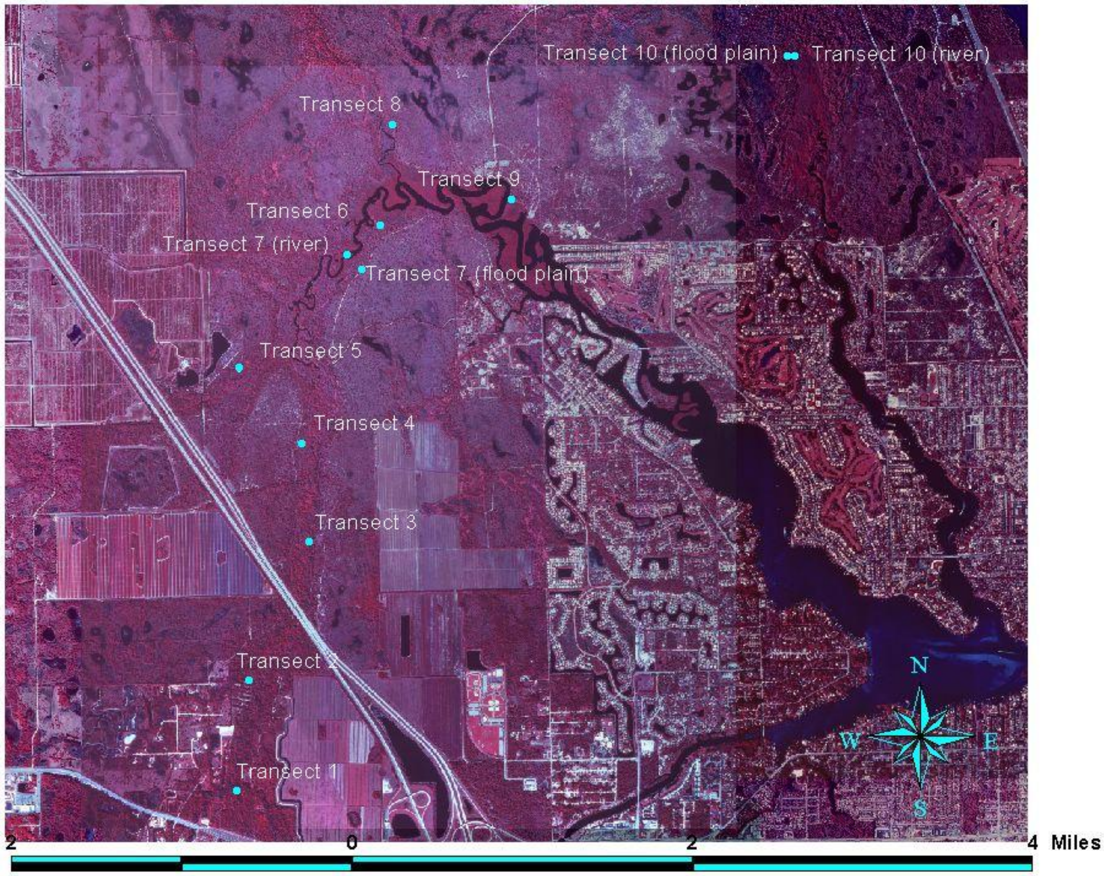


Fig. 12. Location of the 10 vegetative transects in the Loxahatchee River Floodplain.

3, 6, 7, and 9 in the Loxahatchee River floodplain. Sites along each transect were sampled during September 2003 (wet season) and March 2004 (dry season). Transect 1 is the most upriver location, and transect 9 is the location closest to the mouth of the Loxahatchee River at Jupiter Inlet. Three sites were sampled along transects 1, 3, and 9, with one site located near the river, one site near the landward end of the transect, and one site intermediate between the other two. Two sites were sampled along transects 6 and 7, one site near the river, and one site near the landward end of the transect. Elevation and distance maps indicating the sites sampled along each transect are shown in Figs. 13-17. Information on site locations is presented in Table 2 for the September 2003 (wet season) sampling, and in Table 3 for the March 2004 (dry season) sampling. Site and sampling information for sediment cores collected in March 2004 along the different transects is presented in Table 4.

Surface water (when present), and pore water samples to 40 cm depth were collected using a Teflon

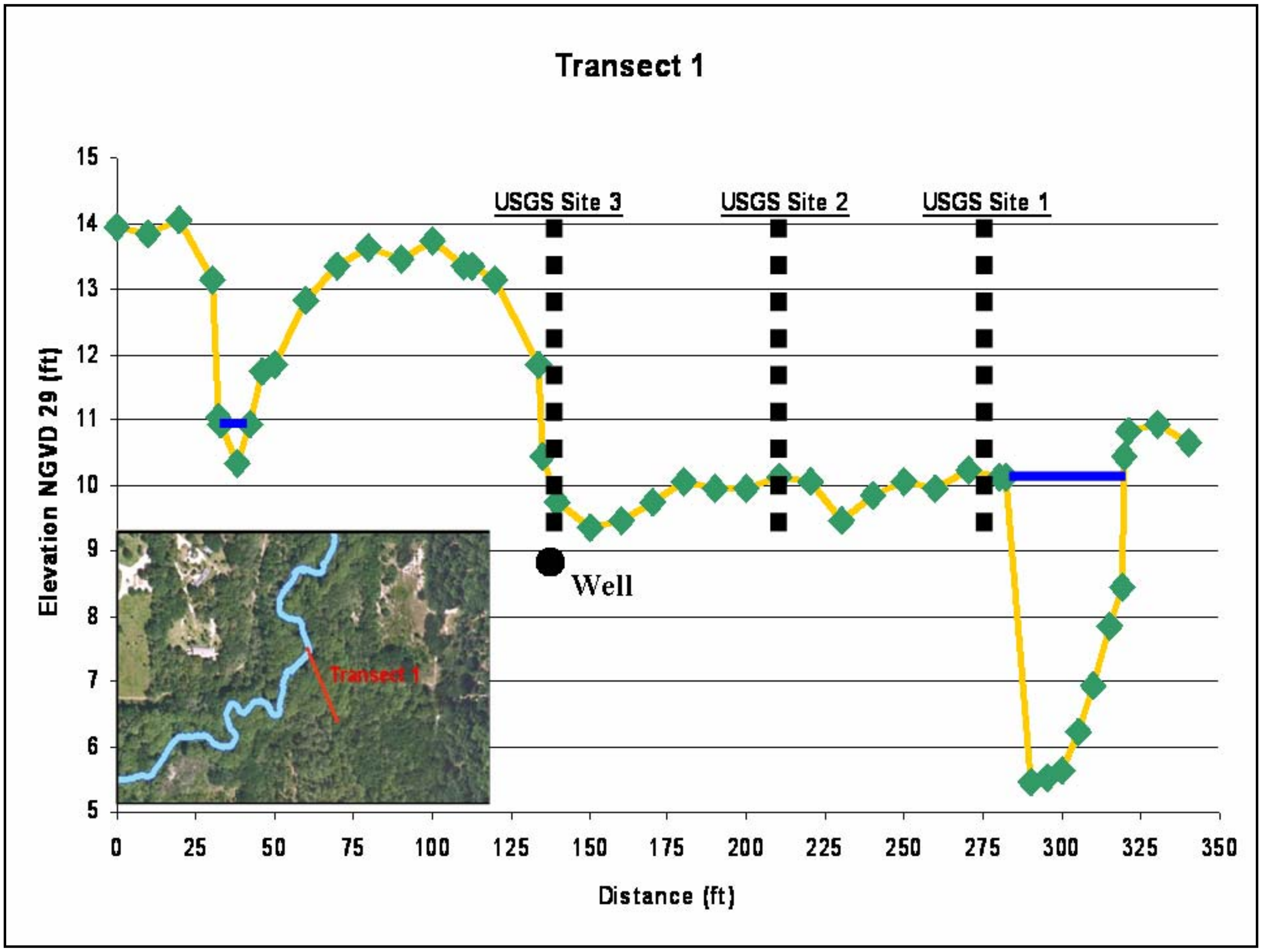


Fig. 13. Elevation map along transect 1 in the Loxahatchee River floodplain, showing sampling locations for surface water, pore water, and sediments, and the locations of wells sampled for groundwater.

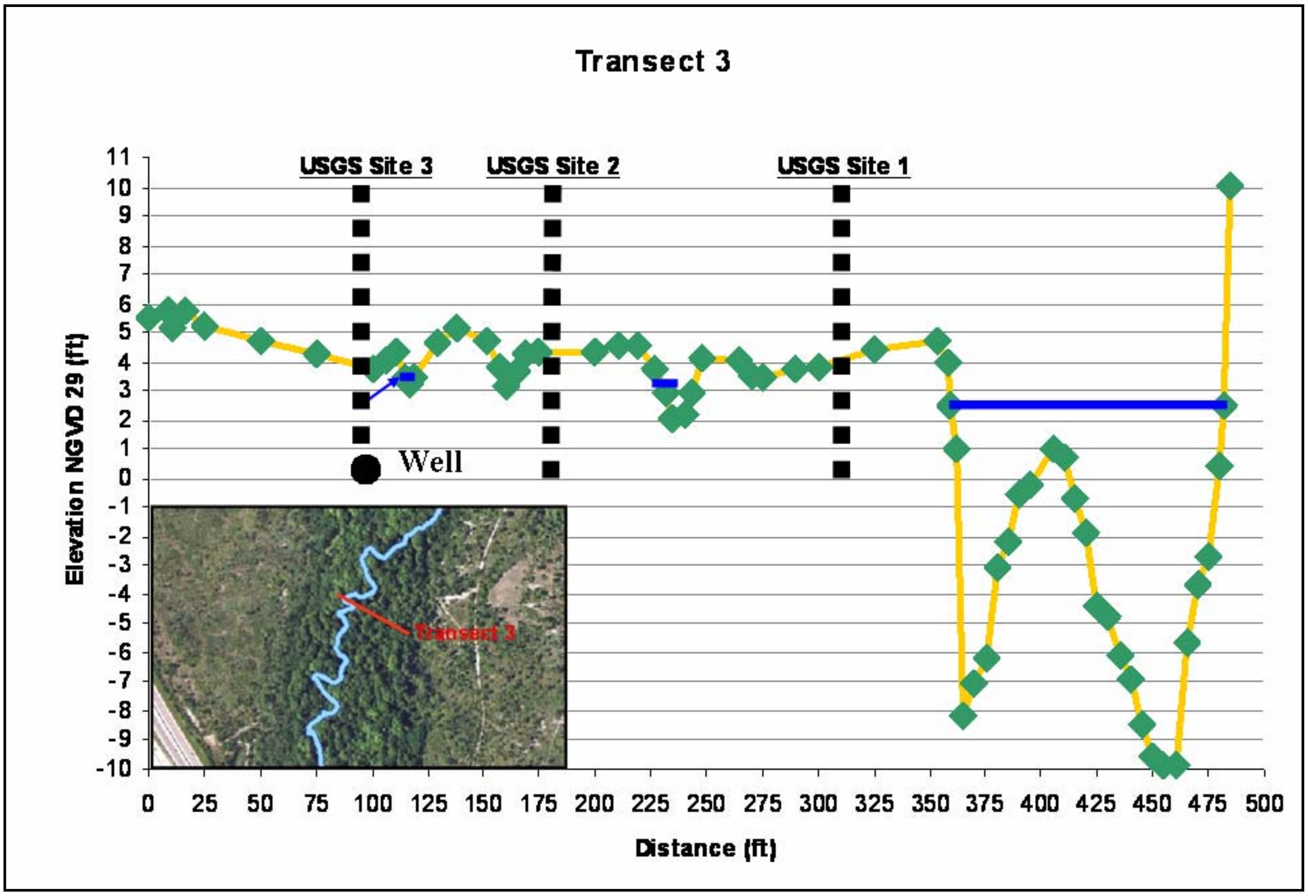


Fig. 14. Elevation map along transect 3 in the Loxahatchee River floodplain, showing sampling locations for surface water, pore water, and sediments, and the locations of wells sampled for groundwater.

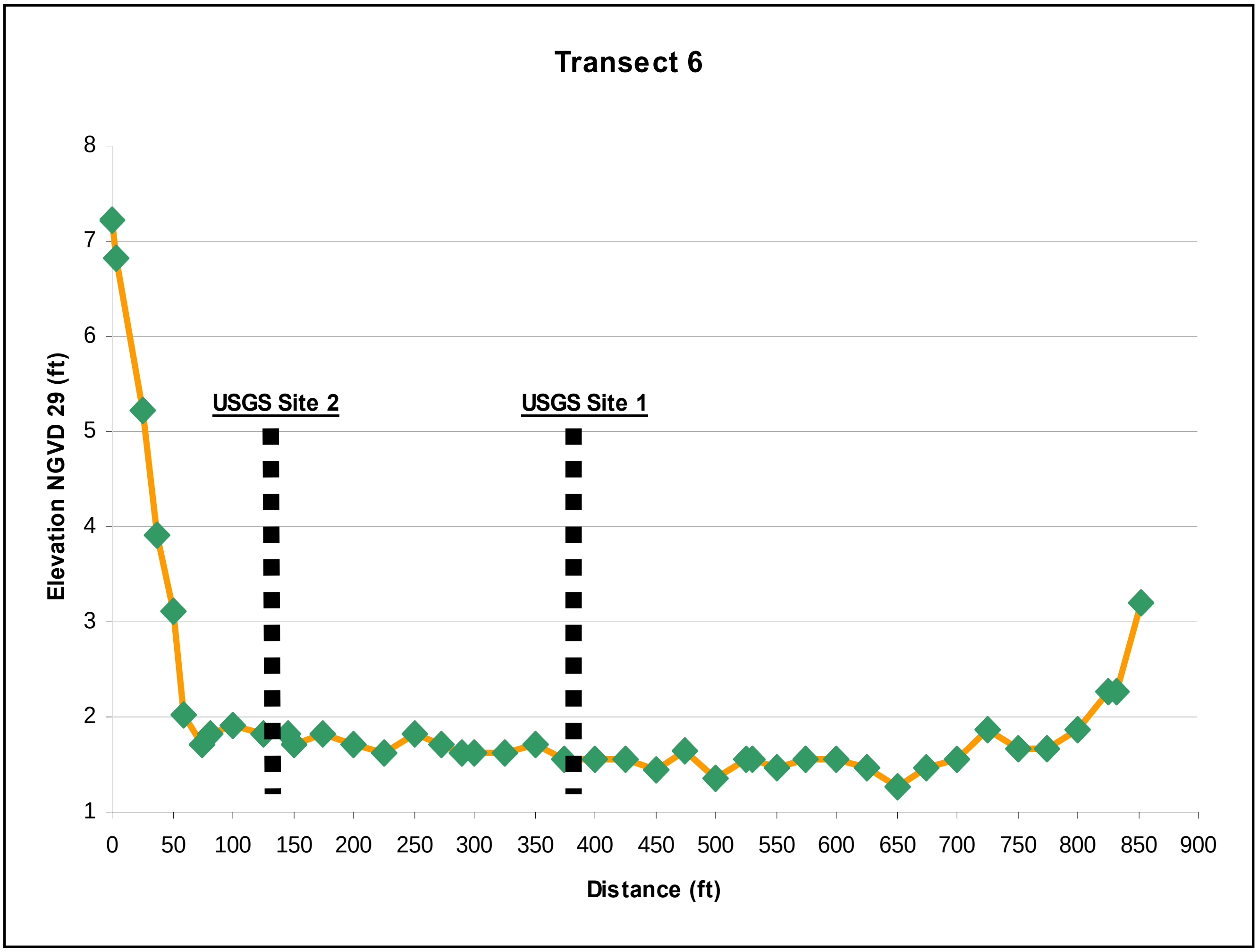


Fig. 15. Map along transect 6 in the Loxahatchee River floodplain, showing sampling locations for surface water, pore water, and sediments, and the locations of wells sampled for groundwater.

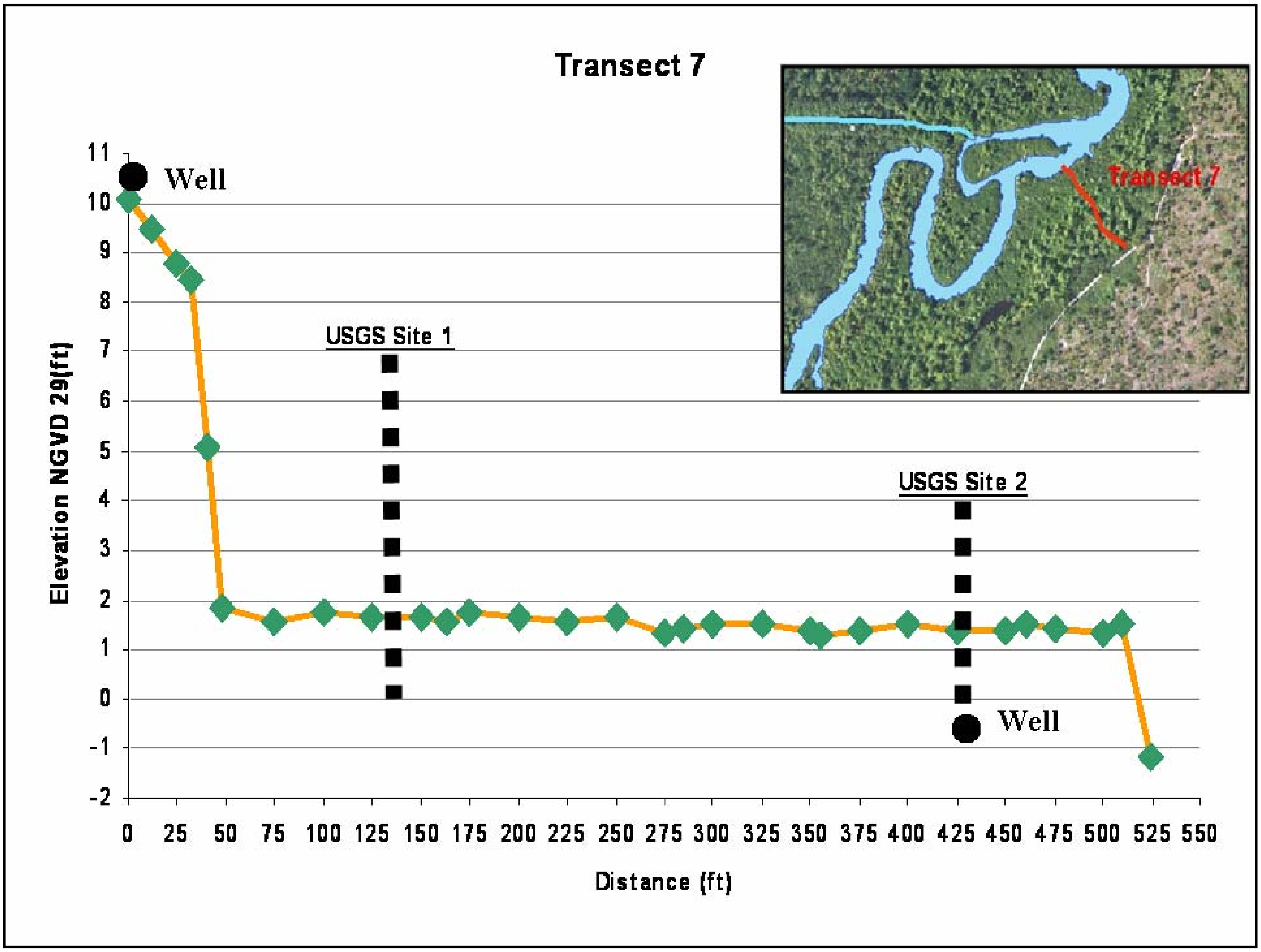


Fig. 16. Map along Transect 7 in the Loxahatchee River floodplain, showing sampling locations for surface water, pore water, and sediments, and the locations of wells sampled for groundwater.

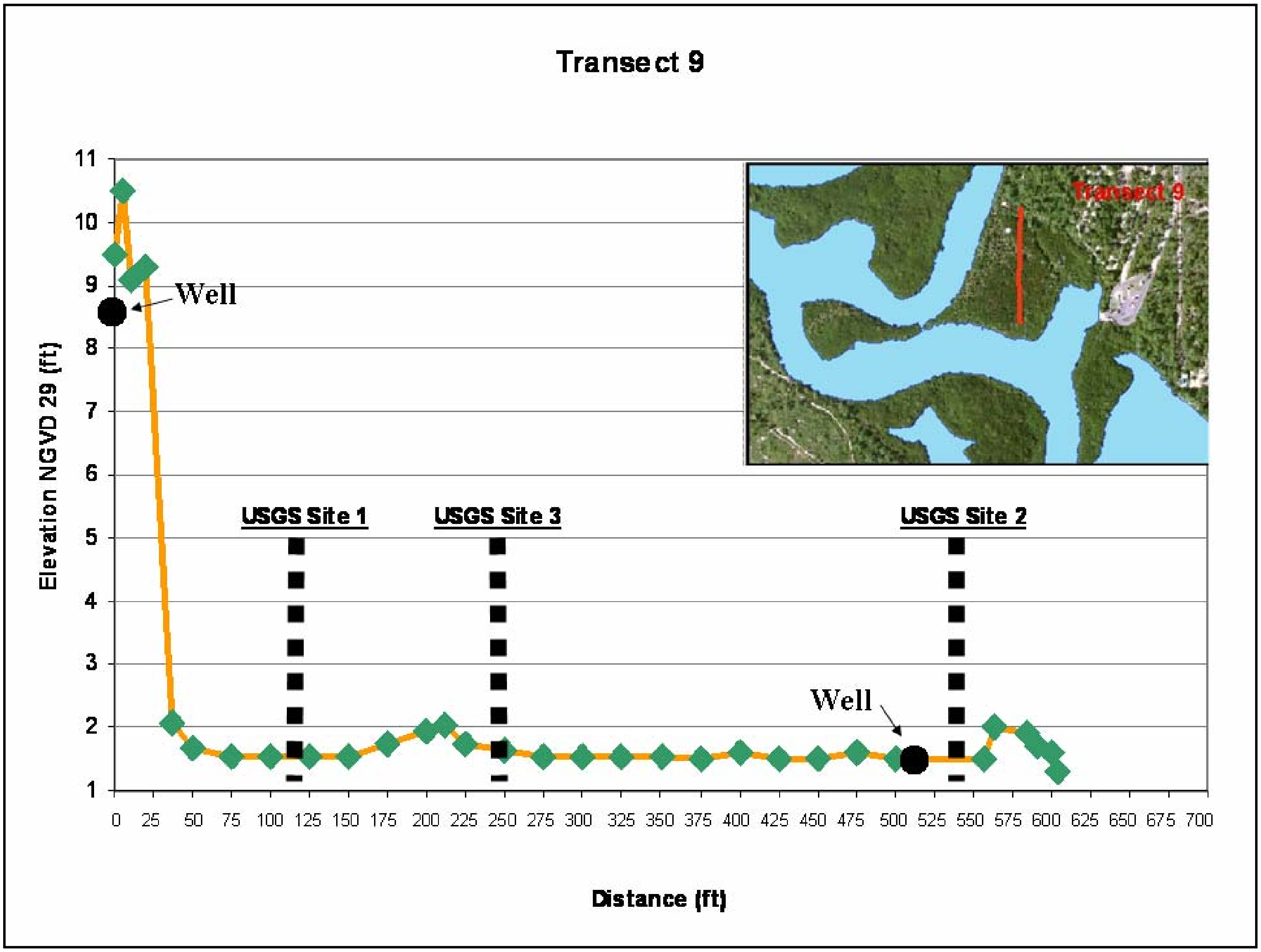


Fig. 17. Map along Transect 9 in the Loxahatchee River floodplain, showing sampling locations for surface water, pore water, and sediments, and the locations of wells sampled for groundwater.

micropiezometer probe connected via Teflon tubing to an inline filter (1.0 μm GF/C) and a battery-powered, field-portable pump (geopump). A smaller diameter stainless steel micropiezometer, operated in the same manner as the Teflon micropiezometer, was used to collect deeper pore water to a depth of 80 cm. Surface water was collected first at each site using the Teflon micropiezometer and pump. Collecting surface water first minimizes cross contamination issues, since surface water typically has lower concentrations of dissolved chemical species than porewater. A minimum of 100 ml of surface water was flushed through the micropiezometer setup prior to collection of sample in order to minimize contamination. Porewater was collected at 5 different depth intervals at most sites (Tables 2 and 3). Depths of 2, 5, 10, 20, and 40 cm were the target intervals for porewater sampling, but dry conditions near the sediment surface (especially along Transects 1 and 3 in March 2004), and a layer of highly compacted sediment below 20 cm at some sites limited water flow to the micropiezometer, and prevented collection of pore water samples from some depths at some sites. Pore water samples from depths >40 cm were collected at selected sites (Table 3) during March 2004, after it became apparent from the September 2003 sampling that higher ionic strength water was present at depth.

Water samples from wells located along transects 1, 3, 7, and 9 were also collected (Tables 2 and 3) using Teflon or plastic tubing connected to an inline filter (1.0 μm GF/C), and the portable field pump (geopump).

Sediment cores were collected at selected locations along transects 1, 3, 6, 7, and 9 (Table 4). The cores were collected using a custom piston corer with plexiglas core tube, PVC piston, and stainless steel cutter and adjustable handles. The coring device is a smaller variation of a piston corer used in the Everglades (Orem et al., 1997). The core tube is 2.5 inches in diameter and about 4 feet long, which provides sufficient material for chemical analyses, but makes the corer relatively easy to carry along the heavily forested, flooded transects.

Cores were collected in a manner similar to that described in Orem et al. (1997): connecting the piston to a small monopod using stainless steel cable, positioning the piston at the sediment surface in the core tube, and pushing the core tube into the sediment (piston remaining stationary at the sediment surface) using the adjustable stainless steel handles clamped to the core tube. Cores were retrieved by securing the piston around the handles using the stainless steel cable to maintain it in place, and manually pulling the core barrel out of the sediment using the handles (Orem et al., 1997). Cores were capped in the field, and transported upright to a convenient area (hotel parking lot) for extrusion and sampling.

Cores were extruded vertically, sectioned every 2 cm, and each section placed into a labeled plastic zip-lock bag. Sediment samples in zip-lock bags were frozen on dry ice, and shipped to laboratory facilities at the USGS in Reston, VA. At the lab, sediments were lyophilized, ground to a powder, and stored in glass vials prior to analysis.

Table 2. Transect and site information for wet season sampling, Loxahatchee River, Florida, September 15-18, 2003.

Transect	Date	Site	Marker[1,2] (m)	Lat.[2]	Long.[2]	Porewater Depths[2] (cm)	Notes[2]
1	9/15/2003	1	85	26 56.410N	80 10.362W	sw, 2, 5, 10, 20, 34.5	
	9/15/2003	2	65	26 56.417N	80 10.350W	sw, 2, 5, 10, 20, 35	
	9/15/2003	3	40	26 56.408N	80 10.338W	sw, 2, 5, 10, 20, 37	
	9/15/2003	well	35	26 56.406N	80 10.335W	well water	
3	9/16/2003	1	95	26 57.729N	80 09.918W	sw, 2, 5, 10, 20, 23	difficult pumping porewater at >23 cm
	9/16/2003	2	55	26 57.678N	80 09.891W	sw, 2, 5, 10, 20, 23.5	difficult pumping porewater at >23 cm
	9/16/2003	3	30	26 57.670N	80 09.875W	sw, 2, 5, 10	sand below 10 cm
	9/16/2003	well	30	26 57.670N	80 09.875W	well water	
6	9/17/2003	1	115	26 59.320N	80 09.407W	sw, 2, 5, 10, 20, 34	
	9/17/2003	2	40	26 59.285N	80 09.404W	sw, 2, 5, 10, 20, 40.5	
7	9/16/2003	1	40	26 59.057N	80 09.544W	sw, 2, 5, 10, 20, 41	collected during flood tide
	9/17/2003	2	130	26 59.097N	80 09.573W	sw, 2, 5, 10, 20, 34	collected during ebb tide
	9/16/2003	well #1	0	26 59.039N	80 09.533W	well water	collected during flood tide
	9/17/2003	well #2	130	26 59.097N	80 09.573W	well water	collected during ebb tide
9	9/18/2003	1	35	26 59.352N	80 08.642W	sw, 2, 5, 10, 20, 40	
	9/18/2003	2	165	26 59.288N	80 08.645W	sw, 2, 5, 10, 20, 35	
	9/18/2003	3	75	26 59.288N	80 08.645W	sw, 2, 5, 10, 20	
	9/18/2003	well #1	0	26 59.372N	80 08.640W	well water	on slope above transect
	9/18/2003	well #2	155	26 59.281N	80 08.645W	well water	

1 - Distance in m from beginning of transect based on established transect distance markers

2 - Lat. = latitude; Long. = longitude; cm = centimeters; m = meters; sw = surface water; > = greater than

Table 3. Transect and site information for dry season sampling, Loxahatchee River, Florida, March 8-11, 2004.

Transect	Date	Site	Marker[1,2] (m)	Lat.[2]	Long.[2]	Porewater Depths[2] (cm)	Notes[2]
1	3/8/2004	1	85	26 56.410N	80 10.362W	sw, 20, 40, 50	Sediment dry above 20 cm
	3/8/2004	2	65	26 56.417N	80 10.350W	20, 30, 40, 50, 60	Sediment dry above 10 cm
	3/8/2004	3	40	26 56.408N	80 10.338W	20, 30. 40, 50, 60	Sediment dry above 10 cm
	3/8/2004	well	35	26 56.406N	80 10.335W	well water	
3	3/9/2004	1	95	26 57.729N	80 09.918W	sw, 5, 10, 20, 30	Sediment dry/Highly colored porewater
	3/9/2004	2	55	26 57.678N	80 09.891W	20, 29	Sediment dry/Highly colored porewater
	3/9/2004	3	30	26 57.670N	80 09.875W	sw, 10, 20	Sediment dry/Highly colored porewater
	3/9/2004	well	30	26 57.670N	80 09.875W	well water	
6	3/10/2004	1	115	26 59.320N	80 09.407W	sw, 2, 5, 10, 20, 40	
	3/10/2004	2	40	26 59.285N	80 09.404W	sw, 2, 5, 10, 20, 40	
7	3/9/2004	1	40	26 59.057N	80 09.544W	2, 5, 10, 20, 40	No sw present
	3/9/2004	2	130	26 59.097N	80 09.573W	sw, 2, 5, 10, 20, 34	
	3/9/2004	well #1	0	26 59.039N	80 09.533W	well water	
	3/9/2004	well #2	130	26 59.097N	80 09.573W	well water	
9	3/11/2004	1	35	26 59.352N	80 08.642W	sw, 10, 20, 40, 60, 84	
	3/10/2004	2LT	165	26 59.288N	80 08.645W	sw, 2, 5, 10, 20, 40, 60, 80	Low tide sample - site 2
	3/11/2004	2HT	165	26 59.288N	80 08.645W	sw, 5, 20, 40, 80	High tide sample - site 2
	3/11/2004	3	75	26 59.329N	80 08.645W	sw, 2, 5, 10, 20, 40, 60, 80	
	3/11/2004	well #1	0	26 59.372N	80 08.640W	well water	
	3/10/2004	well #2	155	26 59.281N	80 08.645W	well water	

1 - Distance in m from beginning of transect based on established transect distance markers

2 - Lat. = latitude; Long. = longitude; cm = centimeters; m = meters; sw = surface water; > = greater than

Table 4. Transect and site information for sediment coring, Loxahatchee River, Florida, March 8-11, 2004.

Transect	Date	Site	Marker[1,2] (m)	Lat.[2]	Long.[2]	Sediment Cores[2]	Compaction[3] (%)
1	3/8/2004	1	85	26 56.410N	80 10.362W	23 cm core/46 cm hole	50
	3/8/2004	2	65	26 56.417N	80 10.350W	33 cm core/48 cm hole	31
	3/8/2004	3	40	26 56.408N	80 10.338W	26 cm core/53 cm hole	51
3	3/9/2004	1	95	26 57.729N	80 09.918W	56 cm core/67 cm hole	16
	3/9/2004	2	55	26 57.678N	80 09.891W	20 cm core/30 cm hole	33
	3/9/2004	3	30	26 57.670N	80 09.875W	26 cm core, 43 cm hole	40
6	3/10/2004	1	115	26 59.320N	80 09.407W	24 cm core/72 cm hole	67
	3/10/2004	2	40	26 59.285N	80 09.404W	20 cm core/71 cm hole	72
7	3/9/2004	1	40	26 59.057N	80 09.544W	31 cm core/34 cm hole	9
	3/9/2004	2	130	26 59.097N	80 09.573W	22 cm core/61 cm hole	64
9	3/11/2004	1	35	26 59.352N	80 08.642W	18 cm core/75 cm hole	76
	3/10/2004	2	165	26 59.288N	80 08.645W	22 cm core/78 cm hole	72
	3/11/2004	3	75	26 59.329N	80 08.645W	15 cm core/35 cm hole	57

1 - Distance in m from beginning of transect based on established transect distance markers

2 - Lat. = latitude; Long. = longitude; cm = centimeters; m = meters; sw = surface water; > = greater than

3 - % Compaction calculated as follows: [(length of core)/(depth of core hole)] x 100

IV. Methods

IV.A. Groundwater Flux Measurements

Groundwater fluxes were evaluated using isotopic tracers as described by Swarzenski (1999). Freshwater-saltwater interface processes were examined with four radium isotopes (USGS Fact Sheet FS-065-99), similar to the multiple geochemical tracer approach used to characterize the hydrogeology of the submarine spring off Crescent Beach, Florida (Swarzenski et al., 2001).

There are four radium isotopes in the ^{238}U, ^{232}Th and ^{235}U decay series; their individual half-lives (^{223}Ra: $t_{½}$ = 11.4 d, ^{224}Ra: $t_{½}$ = 3.6 d, ^{228}Ra: $t_{½}$ = 5.7 yr and ^{226}Ra: 1600 yr) make them ideally suited to study many aquatic processes that occur over time scales of days to years. Strongly particle-reactive thorium isotopes (Th half-lives range from days to 1 x10^{10} yr) decay to form radium isotopes. In freshwater, radium as a Group IIA alkaline–earth metal is also strongly bound onto particle surfaces. As these Ra-surface sites become exposed to higher ionic strength groundwater or seawater, Ra undergoes a rapid phase transformation and resides exclusively as a dissolved species. Thorium, in contrast, will continue to remain bound onto particles regardless of salinity, and will continuously generate radium. Sediments thus provide a constant source of Ra to the overlying waters, and the production rate is defined directly by the particular isotope's decay constant. Radium isotopes, therefore, provide an invaluable means for assessing the exchange of water across the sediment-water interface (Swarzenski et al., 1998)

In the Loxahatchee River system, where the underlying sediments are flushed either continuously or sporadically by groundwater, a localized disequilibrium between ^{228}Th and ^{228}Ra will develop. This occurs because Ra is rapidly released into the water column while thorium remains attached to the bottom sediments. One can use this disequilibrium to derive a groundwater flux rate (water mass mixing rate). Assuming steady state conditions, the flux of ^{228}Ra from the surface sediments will deplete the activities of its progeny, ^{228}Th and ^{224}Ra. Below this active surface sediment layer, one can expect secular equilibrium from ^{232}Th down to ^{224}Ra, which takes about 20 years. Bioturbation as well as groundwater flow will facilitate the interaction of these two sediment layers, causing an upward flux of ^{228}Ra, and ^{224}Ra. Radium isotopes removed from the surface sediment layer by upward groundwater discharge will, thus, provide information on the rate of groundwater discharge across the sediment water interface and will also provide insight on the relative contribution of groundwater to the overall movement of surface water through the Loxahatchee River system.

Marine geochemists have been able to clearly demonstrate that ^{228}Ra/^{226}Ra activity ratios can be an ideal tracer for water mass migration studies (Porcelli and Swarzenski, 2003). Unlike other tracers that may not be conservative or easily quantifiable, the ^{228}Ra/^{226}Ra activity ratio is not modified by evaporation, precipitation, or biological activity, dependent only on radioactive decay. Because of the relatively long half-life of ^{228}Ra and ^{226}Ra, these two isotopes are not too useful for determining mixing rates/processes on time scales of a few days to weeks. The shorter-lived radium isotopes ^{223}Ra and ^{224}Ra are, however, ideal to examine weekly events and can be applied with similar success.

IV.B. Groundwater Flux Calculations

To use the activity of excess ^{224}Ra in a water sample as a geochronometer for water movement or transport (residence times), a mass balance equation is written as follows:

$$^{224}Ra_{obs} = {}^{224}Ra_i f_{EM} e^{-\lambda 224t}$$

and solving for time t:

$$t = -\ln [{}^{224}Ra_{obs} / {}^{224}Ra_i f_{EM}] / \lambda_{224}$$

where λ_{224} is the decay constant for ^{224}Ra (0.189 days^{-1}), $^{224}Ra_i$ is the initial amount of ^{224}Ra in the water sample, $^{224}Ra_{obs}$ is the observed (measured) ^{224}Ra in the water sample, and f_{EM} is the fraction of the end member (well sample) remaining in the sample. Age determinations calculated in such a manner reflect the time elapsed since the water sample became enriched in Ra by the discharge of groundwater. ^{224}Ra is regenerated on the order of days. The fraction f_{EM} can be estimated either from the salinity signal or from the distribution of $^{228,226}Ra$ isotopes, but this term can be difficult to constrain in non-two endmember systems. One can write a similar equation describing the change in activity as a result of mixing and decay for ^{223}Ra and dividing this by the above equation yields: (f_{EM} drops out):

$$[{}^{223}Ra/{}^{224}Ra]_{obs} = [{}^{223}Ra/{}^{224}Ra]_i \, [e^{-\lambda 223t}/e^{-\lambda 224t}]$$

This equation should be useful for Loxahatchee River waters because the term f_{em} is removed. Using $^{223}Ra/^{224}Ra$ isotope ratios in this manner is based on the assumption that the initial $^{223}Ra/^{224}Ra$ activity ratio must remain constant. This is a reasonable assumption since the long-lived parent isotopes (^{231}Pa and ^{232}Th) have relatively constant activity ratios in sediments, and the intermediate Th isotopes (^{227}Th and ^{228}Th) are scavenged efficiently in the near-shore water column, as field tested and verified by Swarzenski and others (2003).

Radon-222 has been proven effective as a tracer of subsurface discharge to the ocean in karst ground water systems (Cable et al., 1996, 1997). In addition, activity ratios between ^{222}Rn and ^{224}Ra have indicated that unique water mass sources can be identified flowing into the near shore northeastern Gulf of Mexico (Cable and Moore, personal communication). The mass balance technique is based on measurement of the radon sources and sinks activities to obtain the groundwater derived radon component as shown:

$$C_f = [\nu_s C_{n-1} A_o + J_{ben} + (\lambda C_{Ra}) V_n] / [\nu_s A_{n+1} + \lambda V_n]$$

where C_f is the final ^{222}Rn activity exiting the transect in a horizontal plane; C_{n-1} is the ^{222}Rn activity entering each volume increment along the transect for n increments; ν_s is the velocity of the surface water along the transect; A_n is the area at the initial side of each increment (sampling station); J_{ben} is the benthic input of radon to the surface waters; λ is the ^{222}Rn decay constant (1.25×10^{-4} min^{-1}); λC_{Ra} represents the water column radon production; V_n is the volume of water in individual segments of the transect; and A_{n+1} is the area of the exit (inshore) side of the n^{th} increment. For a region where both the volume of surface water flow and groundwater flow are unknown, it is important to measure one before using this mass balance. This proposed study would assess the radon activities in the ground water. In this way, the mass balance can be solved iteratively by changing the surface water volume term until the radon budget yields a C_f similar to what is observed in the field.

IV.C. Analytical Methods for Chemical Species

IV.C.1. River and estuarine water column samples - River and estuarine water samples were analyzed for dissolved trace elements by isotope dilution inductively coupled plasma mass spectrometry. Reported detection limits (in μg L^{-1}) for the suite of trace elements are as follows: Si (50), U (0.001), V (0.05), Mn (0.05), Fe (5), Co (0.005), Sr (0.04), and Ba (0.1). Dissolved organic carbon (DOC) concentrations were quantified by high-temperature catalytic oxidation, using a Shimadzu TOC 5000 analyzer. $^{223,224}Ra$ activities ($t_{½}$ = 11.4 d and 3.7 d, respectively) were determined using delayed coincidence alpha counting techniques (Moore and Arnold, 1996; Swarzenski et al., 2001; Charette and Buessler, 2004), while the two longer-lived Ra isotopes ($^{228,226}Ra$ – $t_{1/2}$ = 5.7 y and 1620 y, respectively) were subsequently extracted quantitatively from the MnO_2 fiber and analyzed using peak energies by high-resolution gamma spectroscopy with a well-type configuration (Kim and Burnett, 1983). The short-lived Ra isotopes were recounted after ~3 weeks to correct for supported ^{224}Ra activities (^{228}Th), decay-corrected to the sampling time, and propagated errors were typically <10 %. Aqueous ^{222}Rn activities were quantified using multiple RAD7 detectors routed through a single air-water exchanger (Burnett et al., 2001; Burnett and Dulaiova, 2003).

Trade names are used in this report for descriptive purposes only; no endorsement of products by the U.S. Geological Survey is implied.

IV.C.2. Floodplain surface and pore water samples - Surface water and porewater samples from the Loxahatchee River floodplain were analyzed for the following parameters: redox, pH, titration alkalinity, conductivity, salinity, total dissolved solids, nutrients (nitrate, ammonium, and phosphate), anions (chloride, fluoride, bromide, and sulfate), sulfide, and major cations (sodium, potassium, calcium, magnesium). A synopsis of methods used for surface and pore water chemical analysis is presented in Table 5. Redox (calibrated with two point redox couple standard) was measured by electrode in the field immediately after collection of sample from the micropiezometer into a syringe. Sample (3 ml) for sulfide analysis was preserved in the field by addition of 3 ml of sulfur antioxidant buffer (SAOB) to the sample in a small plastic container. Analysis of sulfide was carried out within 6-8 hours of collection in a hotel room laboratory by sulfur electrode (sulfide electrode calibration is carried out just prior to a field trip). pH and titration alkalinity were measured within 6-8 hours of sample collection in a hotel room laboratory; pH using a semi-micro electrode and 2 point buffer calibration, and titration alkalinity by addition of 0.1 M HCl with a micro burette to the sample with pH measurement. Conductivity, salinity, and total dissolved solids measurements were carried out by electrochemical measurements within 6-8 hours of sample collection in hotel room laboratories. Samples for ammonium and phosphate analysis were frozen on dry ice within 6-8 hours of collection, and transported to laboratory facilities (USGS Labs in Reston, VA) for analysis using standard colorimetric methods. Anions and nitrate concentrations were determined by suppressed anion chromatography, using dual detectors (conductivity for chloride, fluoride, bromide, and sulfate; conductivity and uv/vis absorbance for nitrate). Major cation concentrations (Na, K, Mg, Ca) were determined by suppressed cation chromatography with conductivity detection. Identification and quantification of individual anions and cations was accomplished using external calibration standards and peak area calculation using Waters Associates Millennium chromatography software.

Percentage relative standard deviation (%RSD) for each procedure can vary somewhat from sample to sample, however, average %RSD's for each procedure are as follows: ± 10% for pH and titration alkalinity, ± 20% for redox, ± 2% for conductivity, salinity, and total dissolved solids, ± 5% for ammonium and phosphate, ±7% for sulfide, ± 4% for anion chromatography (including nitrate), and ± 7% for cation chromatography. Conservative estimates of detection limits for each method are: 0.1 ppb for sulfide, 0.05 mg/l for cations and anions (excluding major interferences), 0.5 µg/l for phosphate and ammonium, 0.1 µS for conductivity, 0.1 ppt for salinity, and 0.1 mg/l for total dissolved solids.

IV.C.3. Floodplain sediment samples - Sediments samples (dried) were analyzed for total carbon (TC), organic carbon (OC), total nitrogen (TN), total phosphorus (TP), and total sulfur (TS). All results are reported on a sediment dry weight basis. TC, OC, TN, and TS contents of sediments were determined using a Leco 932 CNS Analyzer (Leco Corporation, St. Joseph, MI, USA), as discussed by Orem et al. (1999). TC, TN, and TS were measured directly, after drying the sediment overnight at 60° C. OC was determined after removal of inorganic carbon using an acid vapor method slightly modified from that of Hedges and Stern (1984), and Yamamuro and Kayanne (1995). Sediment samples (5 to 6 mg) were weighed into prebaked (450° C) silver cups, placed in an acid vapor chamber (dessicator with beakers of concentrated HCl in the bottom), allowed to react for a minimum of 48 hrs, dried (60° C), and analyzed. Results showed virtually no inorganic carbon present in these cores, with TC and OC values virtually identical. Therefore, only TC values are reported. All samples were analyzed at least in duplicate for all parameters. Analytical precision (percentage relative standard deviation) was about 2% for TC, 4% for OC, 3% for TN, and 5% for TS.

Table 5. Methods used for sample collection and chemical analysis in the Loxahatchee River floodplain.

Sample Type	**Method**
Surface Water	hand or Niskin bottle collection (Shelton, 1994)
Sediment Pore Water	(1) piston coring and *in situ* squeezing with filtration (Orem et al., 1997)
	(2) micropiezometer with filtration (Duff et al., 1998)
Ground (Well) Water	pumping from cased wells (Koterba et al., 1995)
Soil/Sediment	piston coring (Orem et al., 1997 and 1999)
Chemical Constituent in Water Samples	**Method**
Conductivity/Salinity/TDS	electrode (U.S. EPA[1], 1982a; Method 120.1)
pH	electrode (U.S. EPA[1], 1982b; Method 150.1)
Alkalinity	titration to fixed pH, electrode (Orem et al., 1997)
Redox	Pt electrode (Orem et al., 1997)
Major Anions (Cl^-, F^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-})	ion chromatography (U.S. EPA[1], 2007; Method 4110B)
Sulfide	ion selective electrode (U.S. EPA[1], 1993; Method 4500-S2-G)
Nutrients (PO_4^{3-}, NH_4^+)	colorimetric analysis (Strickland and Parsons, 1972)
Major Cations (Na^+, K^+, Mg^{2+}, Ca^{2+})	ion chromatography (U.S. EPA[1], 20007; Method 9056)
Chemical Constituent in Soil/SedimentWater Samples	**Method**
Total C, Organic C, Total N, Total S	Leco 932 CNS elemental analyzer (Orem et al., 1999)
Total P	combustion, extraction, colorimetric analysis (Aspila et al., 1976)

[1]U.S. EPA = U.S. Environmental Protection Agency

Total phosphorus (TP) concentrations in sediments were determined by the method of Aspila et al. (1976), slightly modified for work in Loxahatchee River floodplain sediments. Samples were dried overnight (60° C), cooled to room temperature in a desiccator, weighed, and placed in precleaned (soaked in 10% HCl overnight, rinsed with deionized/distilled water, and baked at 450° C) ceramic crucibles. Generally, 0.4-0.6 g of the sediment was used for TP analysis. Weighed sediment samples were baked at 550° C for 2 hrs., cooled, then transferred into clean plastic centrifuge cones containing 45 ml of 1 M HCl. All plastic and glassware used for TP analysis was cleaned by soaking in 10% HCl overnight, followed by rinsing with deionized/distilled water. The empty crucibles were rinsed with 5 ml of 1 M HCl and the rinse was added to the centrifuge cones for a final volume of 50 ml of 1 M HCl. The samples were extracted in the 1 M HCl for 16 hrs. on a shaker to dissolve the phosphate. An aliquot of each extract was centrifuge filtered using Millipore ultrafree-CL HVPP low-binding Durapore centrifuge filters (0.4 μm pore size), then neutralized with a NaOH solution, and transferred to plastic test tubes. The filtered aliquots were analyzed for phosphate using the standard phospho-molybdate method (Strickland and Parsons, 1972), and a Brinkman PC900 fiberoptic colorimeter. Analytical precision (percentage relative standard deviation) for the TP analysis is ± 3%.

Elemental ratios (C/N, C/P, N/P) reported are atomic ratios, calculated after conversion of weights of each parameter to molar units.

IV.D. Vegetation Analysis

Vegetative belt transects were positioned perpendicular to the river and the existing elevational gradient in the floodplain, along the transects previously described. Within each 10 x 10 m segment, all trees with a diameter >5 cm (2 in) at breast height (dbh) were identified by species, and diameter at breast height (dbh) and tree height were measured. Tree heights were measured using a Haglöf Vertex III Hypsometer and T3 Transponder. Cover, by species, of all woody plants with a height >1 m. (3 ft) and dbh <10 cm were measured within a 10x1 m subplot nested within each 10x10 m plot. Cover and stem counts of all herbaceous and woody plant species <1 m were measured within three 1 m subplots nested within each 10x10 m plot. Additional information collected at each segment included: presence of hummocks, presence of cypress stumps, estimates of %open ground, %exposed roots, %leaf litter, and %fallen logs.

Plant communities of the floodplains of the Northwest Branch/Fork of the Loxahatchee River were divided into three distinct groups or reaches (Figs. 18 and 19), riverine (R), upper tidal (UT) and lower tidal (LT) based on hydrological conditions, vegetation, and soils modified from Lewis et al. (2002). The locations of reach boundaries were based on differences in canopy tree species distribution of the 1995 aerial photography and the corresponding GIS coverage. The Northwest Branch/Fork of the Loxahatchee River contains approximately 320 hectares of R, 24 hectares of UT, and 45 hectares of LT floodplain.

The R reach is that part of the floodplain forest having primarily freshwater canopy forest that is generally unaffected by tides. On the Northwest Branch/Fork of the Loxahatchee River, this area ranges from just north of the G-92 Structure to approximately Rivermile 9.5. Maps, tables and data for the R reach are presented with a green background color. Riverine reach vegetative communities are dominated by bald cypress (*Taxodium distichum*), in addition to pop ash (*Fraxinus caroliniana*), red maple (*Acer rubrum*), pond apples (*Annona glabra*), water hickory (*Carya aquatica*) and others.

The UT reach is that part of the floodplain forest having a mixed freshwater/brackish canopy forest that is partially influenced by tides. On the Northwest Branch/Fork of the Loxahatchee River this area is shown between approximately Rivermile 9.1 and Rivermile 8.2 (mouth of Kitching Creek). The UT reach extends along the riverbed into the R reach in areas where the topography of the floodplain has allowed the further introduction of mangroves into the floodplains. UT reach communities are dominated by pond apple, red and white mangrove (*Rhizophora mangle* and *Laguncularia racemosa*), and cabbage palm (*Sabel palmetto*), with some communities of bald cypress present in the inner floodplain areas away from the riverbed.

The LT reach is that part of the floodplain forest having primarily brackish water canopy forest that is highly influenced by tides and salinity in the water and soils. On the Northwest Branch/Fork of the Loxahatchee River, this area extends from approximately Rivermile 8.0 to 5.5, although several smaller areas can be found around Rivermile 4.5, and in the embayment area. The LT reach is dominated by red and white mangrove.

Forest types were determined from the observation of groups of canopy tree species that generally grow together in recognizable communities (modified after Darst et al., 2003). Tree canopy data from unpublished work by Ward and Roberts in 1995 (76 10x10 m plots), and unpublished data from a 2003 transect study by Hedgepath (130 10x10 m.plots) were examined to make the determinations using dbh measurements to calculate relative basal area (RBA) of each species within each of the 10x10 m plots. RBA is calculated by dividing the total basal area of a species (in m^2) by the total basal area of all species within a 10x10 m plot. In the RBA analysis, multi-trunk trees were considered as separate trees. The most common multi-trunk trees observed were pond apple (*Annona glabra*), red mangrove (*Rhizophora mangle*), and bald cypress (*Taxodium distichum*).

Fifteen forest community types were identified for the Northwest Branch/Fork of the Loxahatchee River and its major tributaries (Table 6). The major vegetative communities were identified as swamp (S), bottomland hardwood (low and high Blh), hydric and mesic hammock (H), and uplands (U). A total of 28 canopy species were identified during the 2003 belt transect survey and were categorized by

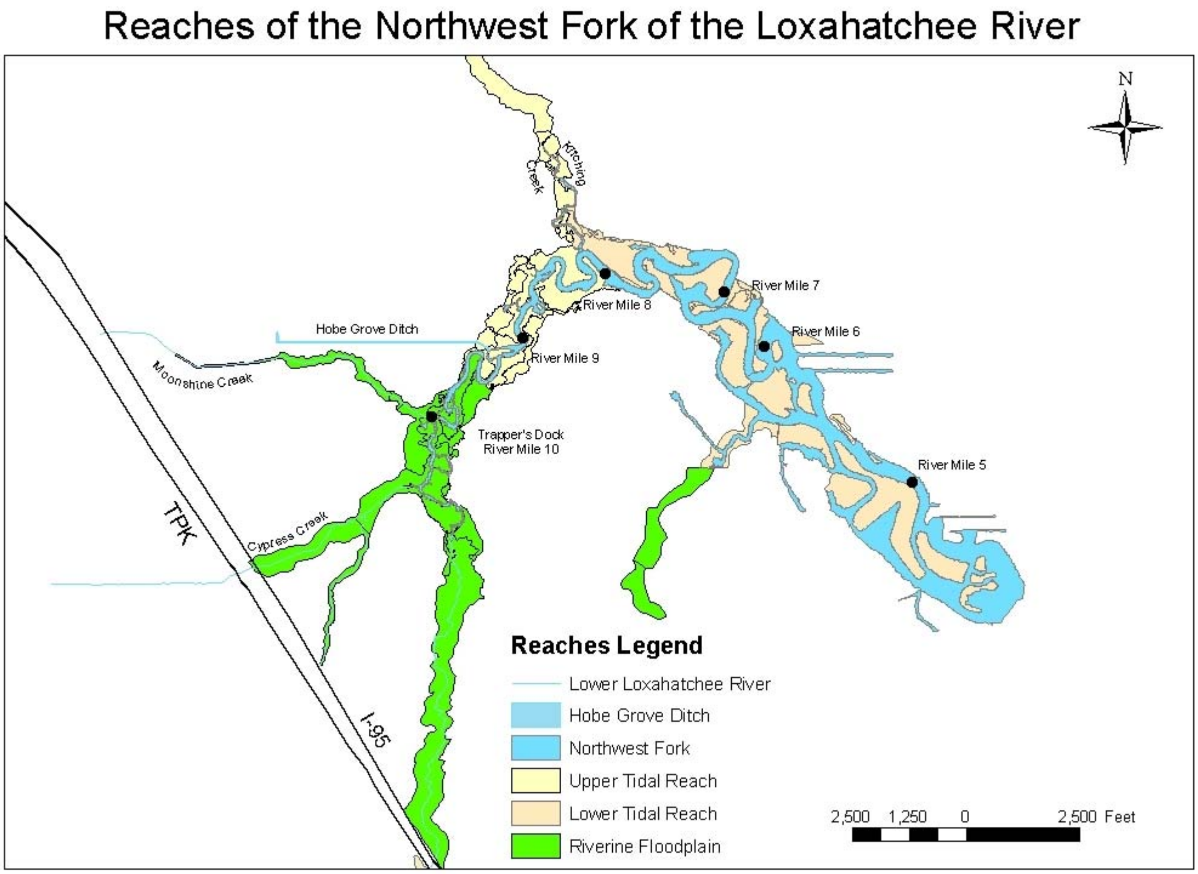


Fig. 18. Reaches of the Northwest Fork of the Loxahatchee River between river miles 4.5 and 13.

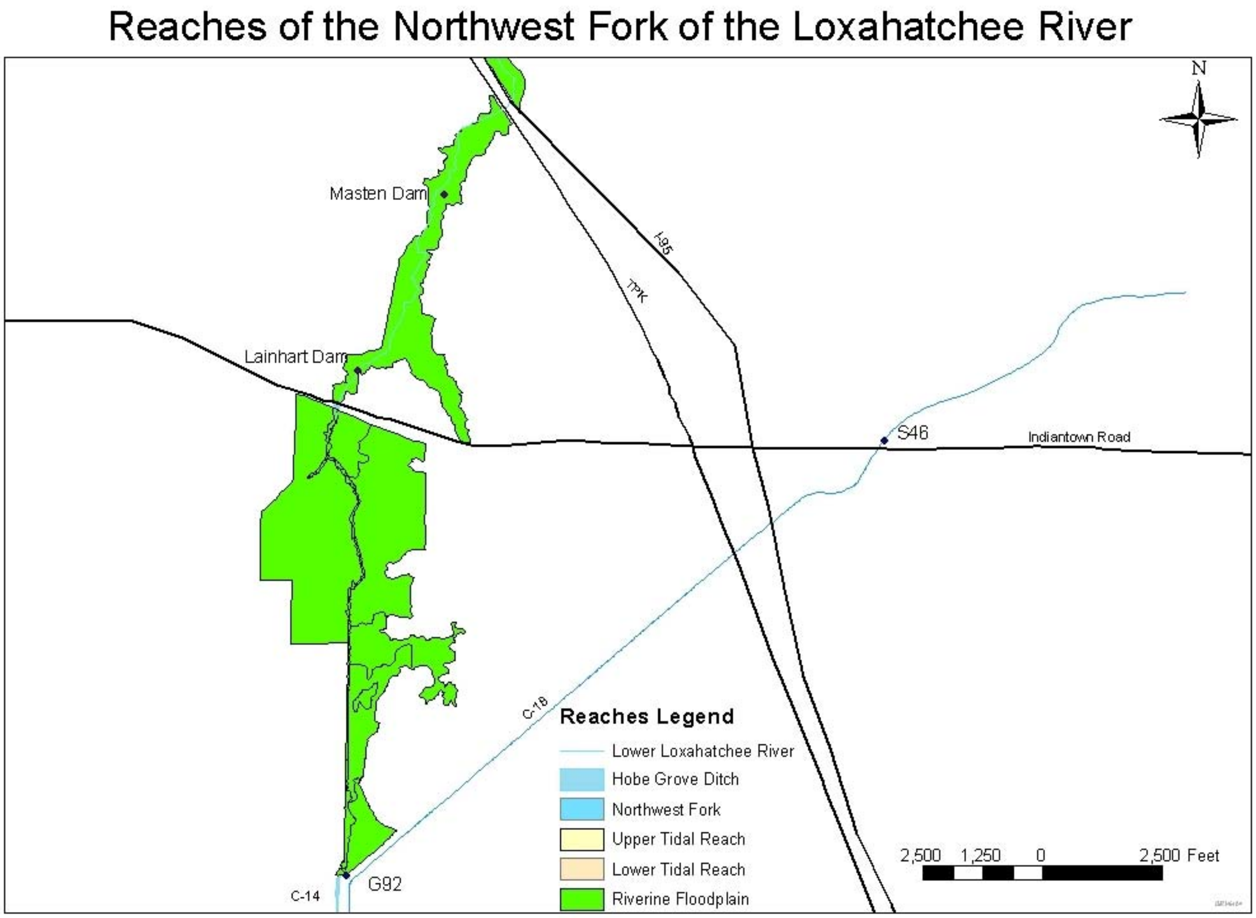


Fig. 19. Upper riverine reach of the Northwest Fork of the Loxahatchee between I-95 and the G-92 structure.

Table 6. Forest community types by reach for the Loxahatchee River and its major tributaries.

Forest Type	Riverine	Upper Tidal	Lower Tidal
Swamp	RSW1 RSW2 (FPsw1)	UTsw1 UTsw2 (FPsw1*) UTsw3 (LRsw3*)	LTsw1 (RMsw1*) LTsw2
Low Bottomland Hardwood	Rblh1 Rmix Rblh2	UTmix	LTmix
High Bottomland Hardwood	Rblh3		
Mesic and Hydric Hammock	H	H	H
Upland	U	U	U

*Another name for *Fraxinus Caroliniana*, *Laguncularia racemosa*, and *Rhizophora mangle* swamps

their most common occurrence in the floodplains. Forest types clearly differ as a result of changes in hydrology, topography, vegetation, soils, and proximity to the coast (Darst et al., 2003). Other factors include logging and fire history, presence or absence of exotics, and the availability of nutrients and light.

V. Results

V.A. Loxahatchee River Water Column Chemical Measurements

V.A.1. General - The Loxahatchee River estuary was sampled during high and low discharge conditions along a transect that extended from just seaward of Jupiter Inlet, where salinities were > 30‰, to the upper reaches of the Northwest Branch/Fork, where salinities approach zero (<0.1‰; Table 7). The freshwater/estuarine/saltwater mixing zone exhibited an expectedly strong dependency on river discharge stage. In general, the entire salinity regime was pushed upstream several km during low flow conditions (Russell and McPherson, 1983). During low discharge sampling, an Atlantic Ocean endmember sample was obtained just seaward of Jupiter Inlet with a salinity of 34.42‰.

During both river discharge regimes, pH and specific conductance values of the two most freshwater endmember samples (13a, 1b; see Fig. 11) remained consistent at ~7.7 and 0.5 mS cm^{-1}, respectively. In contrast, suspended particulate matter (SPM) concentrations in the headwater samples were noticeably lower during low flow conditions, and both profiles uncharacteristically increased in concentration with

Table 7. Measurements of surface water in the Loxahatchee River in a transect from seaward of Jupiter Inlet to the farthest reaches of the Northwest Fork, 2003-2004.

Date	ID	Lat. (N)[1]	Long. (W)[1]	pH	Cond.[1] (mS/cm)	Sal.[1] (ppt)	Temp.[1] (°C)	DO[1] (mg/l)	SPM[1] (mg/l)
High Discharge									
9/15/2003	1a	26.9451	-80.0692	7.82	46.8	30.6	28.8	4.51	8.13
9/15/2003	2a	26.9507	-80.1065	8.13	38.2	24.4	29.3	3.66	9.4
9/15/2003	3a	26.9562	-80.1167	8	29.3	18.2	29.8	3.64	8.2
9/15/2003	4a	26.9643	-80.1219	7.91	23.4	14.3	30.1	3.56	4.6
9/15/2003	5a	26.9739	-80.131	7.78	20.3	12.3	30.6	3.04	4.6
9/15/2003	6a	26.9771	-80.1326	7.7	17.6	10.5	30.9	3.09	5
9/15/2003	7a	26.9781	-80.1342	7.62	14.42	8	31.5	3.04	4
9/15/2003	8a	26.9781	-80.135	7.74	9.59	5.5	31.3	3.16	4.6
9/15/2003	9a	26.9785	-80.1355	7.62	7.35	4.1	31.4	2.89	4.4
9/15/2003	10a	26.9839	-80.1434	7.49	4.79	2.5	30.2	2.55	3.8
9/15/2003	11a	26.9871	-80.1467	7.51	2.25	1	29.8	2.44	5.2
9/15/2003	12a	26.9892	-80.145	7.59	0.54	0	29.4	2.66	5.6
9/16/2003	13a	26.9749	-80.164	7.67	0.42	0	28.5	2.75	4.6
9/16/2003	14a	26.9914	-80.15	7.97	0.41	0	28.8	3.3	4.8
Low Discharge									
3/10/2004	1b	26.9739	-80.1639	7.69	0.64	0.31	21.5	5.94	1.5
3/10/2004	2b	26.9914	-80.1547	7.66	1.01	0.92	21.4	6.1	3.5
3/10/2004	3b	26.9903	-80.1551	7.65	4.6	2.48	21.87	6.02	3
3/10/2004	4b	26.9881	-80.146	7.65	6.74	3.69	22.05	5.91	6.2
3/10/2004	5b	26.9875	-80.1458	7.68	8.27	4.6	22.11	5.96	3.4
3/10/2004	6b	26.9862	-80.1586	7.68	11.16	6.37	22.2	5.8	3.4
3/11/2004	7b	26.9839	-80.1433	7.65	13.9	8.05	20.25	6.03	5.2
3/11/2004	14b	26.9876	-80.1443	7.77	15.74	9.28	21.51	6.62	6.4
3/11/2004	8b	26.9843	-80.1422	7.72	22.06	13.3	20.83	6.02	4.8
3/11/2004	9b	26.9848	-80.141	7.78	23.35	14.14	20.81	6.29	5.8
3/11/2004	10b	26.981	-80.1385	7.87	30.81	19.34	20.86	6.35	6.4
3/11/2004	11b	26.9751	-80.1321	8.04	38.73	24.72	21.25	6.75	13.4
3/11/2004	12b	26.9586	-80.1203	8.1	45.41	29.48	21.33	7.12	15
3/11/2004	13b	26.9441	-80.0738	8.17	52.2	34.42	21.6	7.58	18.6

1- lat. = latitude; long. = longitude; Cond = Conductivity; Sal. = Salinity; Temp. = Temperature;
DO = Dissolved Oxygen; SPM = Suspended

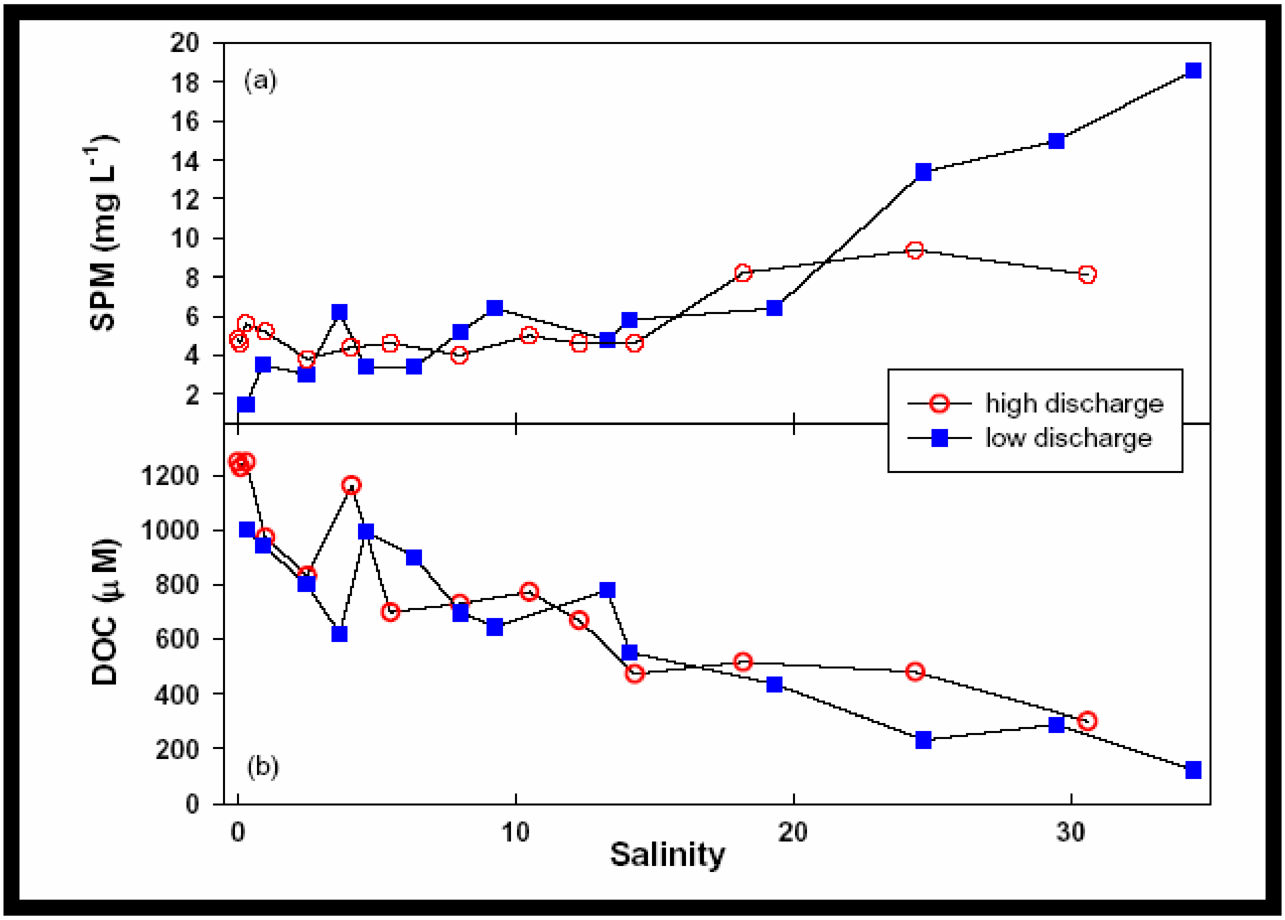


Fig. 20. Salinity versus suspended particulate material (SPM), (a) and Dissolved Organic Carbon (DOC), (b), for the two sampling periods.

Table 8. Dissolved organic carbon (DOC) and select trace element concentrations per discharge (season) for the Loxahatchee. River, 2003-2004.

Date	ID[1]	DOC[2] (μM)	Si (μM)	U (nM)	V (nM)	Mn (nM)	Fe (μM)	Co (nM)	Sr (μM)	Ba (nM)
High Discharge										
9/15/2003	1a	300.11	16.63	10.59	1794.21	28.21	22.74	26.3	111.05	76.46
9/15/2003	2a	481.51	53.05	7.65	1268.12	117.95	18.26	14.58	74.3	91.75
9/15/2003	3a	517.55	68.36	7.1	1099.3	141.8	17.48	13.64	66.65	96.12
9/15/2003	4a	472.98	74.41	6.09	961.89	166.37	14.7	10.76	52.04	93.93
9/15/2003	5a	669.07	89.37	4.62	796.99	212.97	11.62	8.08	38.69	95.39
9/15/2003	6a	773.68	90.44	4.05	706.69	218.43	9.99	8.45	33.67	94.66
9/15/2003	7a	730.07	120.7	3.25	557.5	240.27	9.94	10.84	32.07	101.94
9/15/2003	8a	698.92	121.77	2.63	437.76	232.99	8.17	9.25	23.74	100.49
9/15/2003	9a	1162.36	130.31	2.04	355.31	238.45	6.68	6.58	16.09	98.3
9/15/2003	10a	831.54	132.81	1.74	304.27	231.17	5.78	4.16	11.53	101.22
9/15/2003	11a	973.08	133.16	1.31	231.64	207.51	5.19	2.58	6.37	96.85
9/15/2003	12a	1248.34	131.38	1.09	223.79	253.01	4.91	1.78	4.31	96.85
9/16/2003	13a	1228.53	141.35	1	237.53	318.54	6.86	2.21	4.78	102.67
9/16/2003	14a	1249.13	129.6	1.07	227.71	347.66	5.09	1.82	4.26	100.49
Low Discharge										
3/10/2004	1b	1003.47	156.66	1.63	17.55	128.69	7.97	3.12	6.13	142.72
3/10/2004	2b	941.78	132.09	2.58	40.63	146.53	7.72	3.95	7.46	152.92
3/10/2004	3b	802.17	136.72	2.83	87.16	163.64	10.28	5.85	10.97	145.63
3/10/2004	4b	620.35	138.86	3.29	134.47	182.02	11.41	5.85	15.75	149.28
3/10/2004	5b	996.32	128.53	3.53	176.08	179.29	12.28	10.76	18.83	145.63
3/10/2004	6b	900.15	131.03	4.11	522.17	192.94	15.02	8.38	21.34	144.18
3/11/2004	7b	696.62	124.26	4.33	685.1	175.11	17.03	8.11	25.45	139.81
3/11/2004	14b	644.94	104.32	4.96	667.43	168.55	17.39	9.82	28.3	131.07
3/11/2004	8b	779.98	114.29	5.42	796.99	164.55	20.06	10.55	33.9	130.34
3/11/2004	9b	552.66	103.25	6.09	869.62	147.07	22.38	10.83	39.6	126.7
3/11/2004	10b	435.98	89.72	7.9	1118.93	123.59	29.01	16.97	54.78	106.31
3/11/2004	11b	231.79	69.07	9.49	1313.27	93.2	36.17	24.94	68.25	92.48
3/11/2004	12b	289.44	55.54	11.3	1425.16	66.44	40.83	25.11	79.43	80.1
3/11/2004	13b	122.37	30.83	12.98	1595.95	28.94	46.92	32.75	92.56	63.13

1 - See Fig. 11.

2 - DOC = dissolved organic carbon

an increase in salinity (Fig. 20a). Average SPM concentrations for each set of estuarine samples were just slightly higher during low flow conditions (6.9 versus 5.5 mg L^{-1}), but both SPM datasets indicate a general paucity of organic/inorganic particulates retained on a 0.4 µm filter.

V.A.2. Trace elements and DOC - Select trace element (Si, U, V, Mn, Fe, Co, Sr, and Ba) and dissolved organic carbon (DOC) concentrations in estuarine surface water samples are presented in Table 8. DOC concentrations decreased ten-fold (Figure 20b) from values just over 1200 µM in fresh-water samples to 100-300 µM for samples from the in the most saline surface waters. Of the studied elements, only Mn and Ba exhibited similar decreasing trends with an increase in salinity. In contrast, U, Sr, V, Co and Fe all showed a positive trend with salinity (i.e. their respective concentrations increased as salinity also increased).

V.A.3. Surface water Ra and Rn isotopes – ^{223,224,228,226}Ra isotope activities in shallow groundwater and estuarine surface water are presented in Tables 9 and 10, respectively. The highest Ra activities in estuarine surface water were generally observed in the freshwater endmember samples (Figs. 21 and 22). ^{226}Ra ($t_{1/2}$ = 1600 y) activities during both high and low discharge conditions ranged from 70 dpm 100 L^{-1} in the headwater fresh water samples to about 15 dpm 100 L^{-1} in the seawater endmember sample (salinity = 34.42‰). ^{228}Ra similarly ranged from about 6 – 15 dpm 100 L^{-1} (seawater endmember samples) to more than 18 dpm 100 L^{-1} (fresh water endmember samples) during both river discharge regimes. The two

Table 9. Dissolved ^{226,228,223,224}Ra activities and salinity in shallow groundwater wells adjacent to the Loxahatchee River estuary per river discharge (season), 2003-2004.

Date	ID[1]	^{226}Ra (dpm/100l)	^{226}Ra error ±dpm/1001	^{228}Ra (dpm/100l)	^{228}Ra error ±dpm/1001	^{223}Ra (dpm/100l)	^{224}Ra (dpm/100l)	Salinity[2] (ppt)
High Discharge								
9/15/2003	WELL1	108.53	13.7	59.56	16.6	78.53	161.84	0.3
9/16/2003	WELL3	88.11	14.36	58.21	19.59	54.23	145.97	0.1
9/15/2003	WELL7	47.43	12.44	bd	bd	34.35	82.2	0
Average		81.35		58.89		55.7	130	
Low Discharge								
3/8/2004	WELL1	88.52	12.57	42.44	17.58	57.4	121.84	0.2
3/9/2004	WELL3	520.72	21.8	152.37	25.4	106.78	269.4	0.1
3/8/2004	WELL7	34.14	10.99	42.43	19.35	46.43	131.08	0
Average		214.46		79.08		70.2	174.1	

1 - see Figs. 13, 14, and 16, and Tables 2 and 3 for well locations.
2 - ppt = parts per thousand

Table 10. Dissolved $^{226,228,223,224}Ra$ activities and salinity in the Loxahatchee River estuary, per river discharge (season), 2003-2004.

Date	ID[1]	^{226}Ra (dpm/100l)	^{226}Ra error ±dpm/1001	^{228}Ra (dpm/100l)	^{228}Ra error ±dpm/1001	^{223}Ra (dpm/100l)	^{224}Ra (dpm/100l)	Salinity[2] (ppt)
High Discharge								
9/15/2003	1a	27.98	0.45	14.72	2	3.78	21.19	30.6
9/15/2003	2a	43.89	0.53	18.26	1.77	7	26.13	24.4
9/15/2003	3a	63.83	0.79	23.99	1.79	3.65	34.74	18.2
9/15/2003	4a	57.42	0.7	19.87	1.36	4.26	26.73	14.3
9/15/2003	5a	58.31	0.71	22.56	1.47	7.29	30.12	12.3
9/15/2003	6a	59.46	0.71	17.67	1.45	7.33	23.59	10.5
9/15/2003	7a	47.69	0.61	18.03	1.61	6.11	24.96	8
9/15/2003	8a	59.89	0.71	16.96	1.28	4.31	23.45	5.5
9/15/2003	9a	59.54	0.72	16.72	1.66	3.04	24.27	4.1
9/15/2003	10a	64.23	0.79	17.52	2	2.96	24.99	2.5
9/15/2003	11a	63.27	0.67	19.53	1.58	2.09	29.2	1
9/15/2003	12a	67.89	0.72	16.34	2.11	2.33	24.5	0.3
9/16/2003	14a	69.84	0.73	16.26	1.83	2.23	23.62	0.1
9/16/2003	13a	67.49	0.71	18.33	1.69	4.47	28.29	0.01
Low Discharge								
3/10/2004	1b	67.04	3.46	16.08	4.47	3.23	23.13	0.31
3/10/2004	2b	0.62	0.85	1.3	1.81	2.61	15.23	0.92
3/10/2004	3b	27.59	1.73	8.35	2.6	2.09	12.17	2.48
3/10/2004	4b	26.48	1.66	4.55	2.17	9.7	35.7	3.69
3/10/2004	5b	59.03	2.36	16.13	2.83	13.4	23.42	4.6
3/10/2004	6b	72.52	2.58	18.11	3.14	10.13	26.01	6.37
3/11/2004	7b	75.43	2.49	21.41	3.14	10.63	30.12	8.05
3/11/2004	14b	73.75	2.69	21.38	2.89	8.43	30.68	9.28
3/11/2004	8b	63.85	2.36	18.32	2.86	3.55	26.2	13.3
3/11/2004	9b	73.31	2.51	19.54	2.92	6.23	27.6	14.14
3/11/2004	10b	48.15	2.05	18.86	2.79	6.28	25.95	19.34
3/11/2004	11b	43.6	2.06	17.08	2.81	7.28	23.04	24.72
3/11/2004	12b	47.16	1.6	14.37	1.86	6.14	18.97	29.48
3/11/2004	13b	14.93	1.04	6.71	1.7	4.25	9.22	34.42

1 - see Fig. 11 for locations in the Loxahatchee River estuary

2 - ppt = parts per thousand

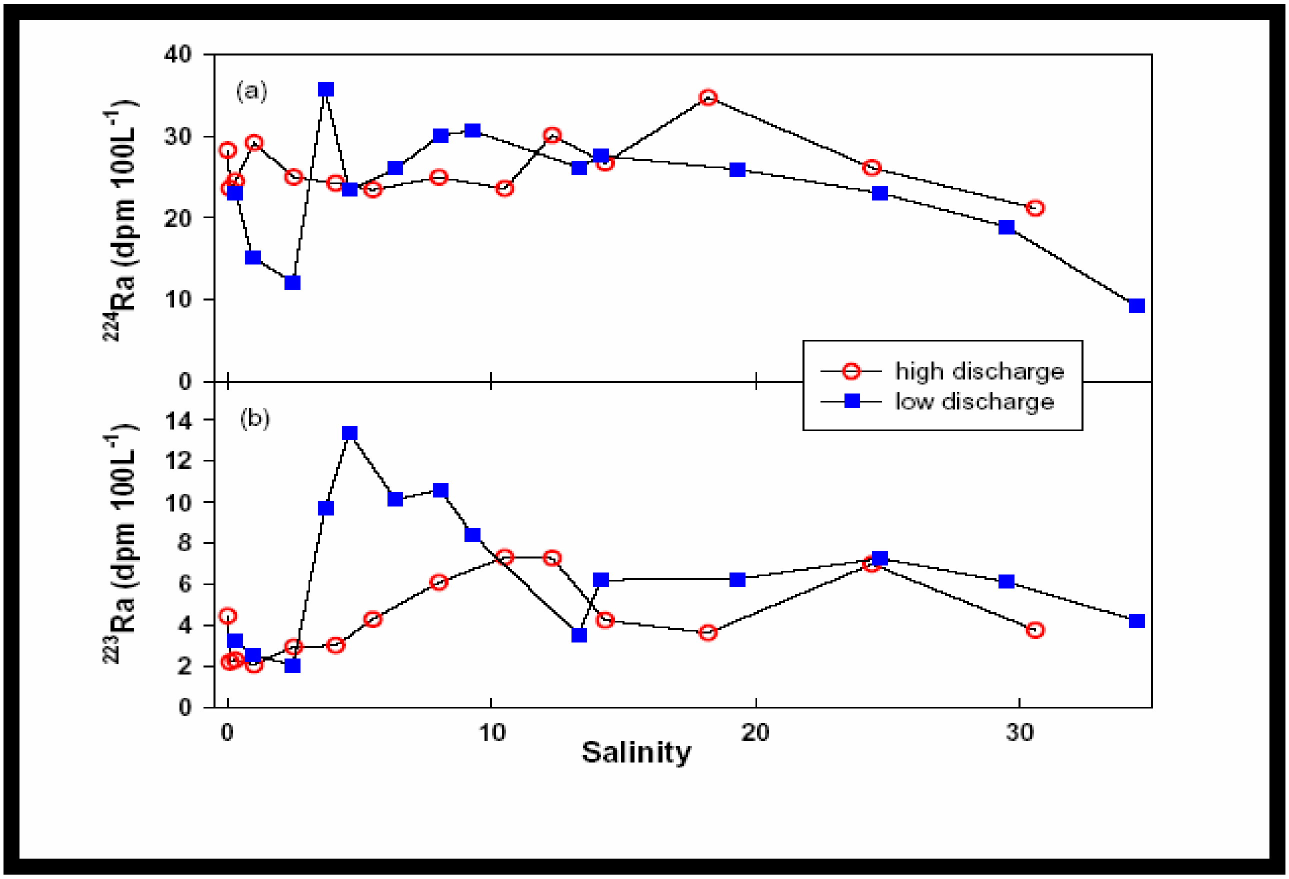


Fig. 21. Plots of salinity versus dissolved ^{224}Ra (a) and ^{223}Ra (b) for the two sampling periods.

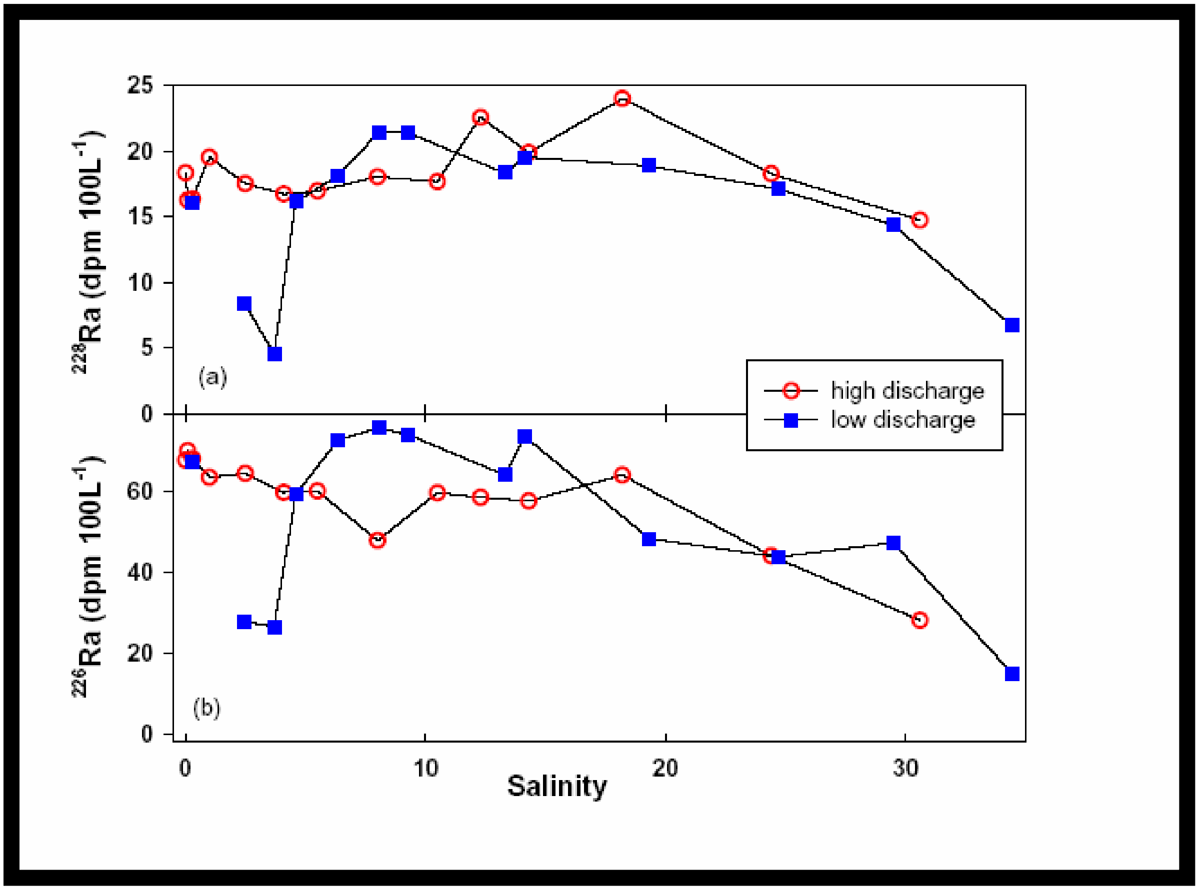


Fig. 22. Plots of salinity versus dissolved ^{228}Ra (a) and ^{226}Ra (b) for the two sampling periods.

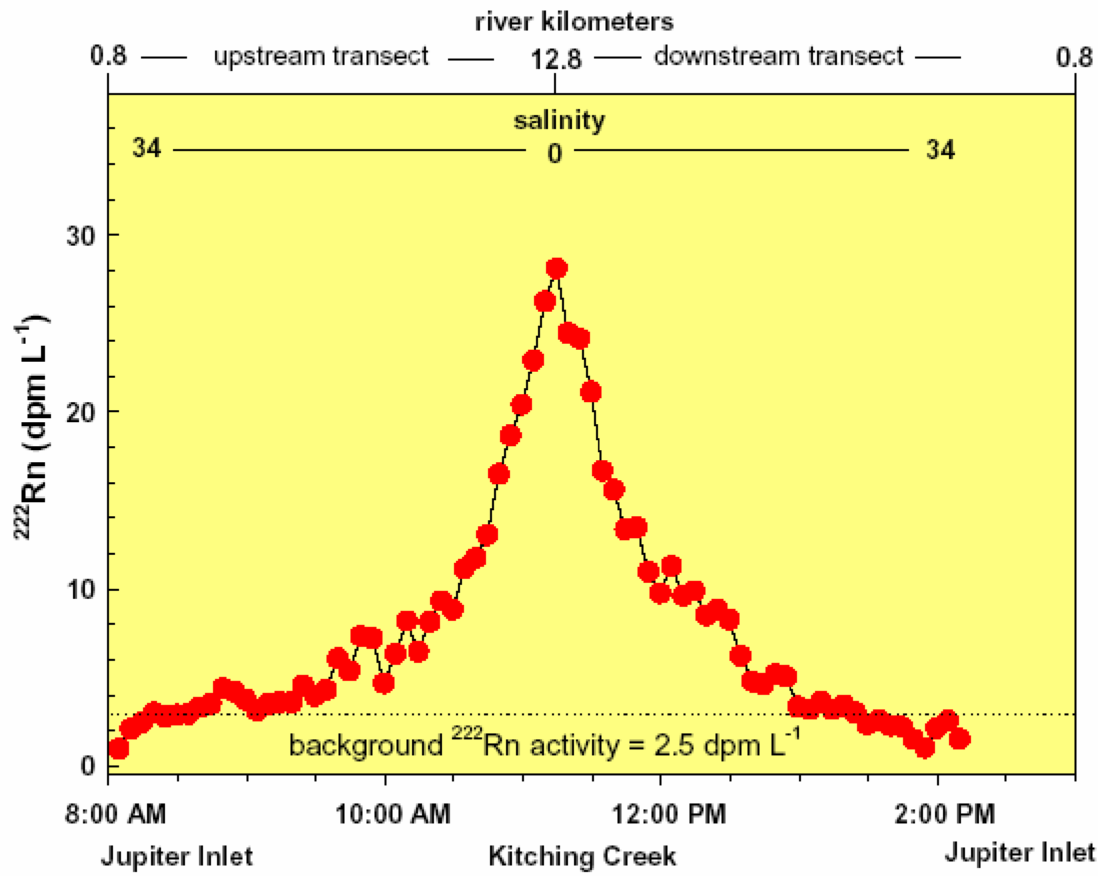


Fig. 23. Dissolved ^{222}Rn activities (dpm L-1) in the Loxahatchee River estuary.

short-lived Ra isotopes, ^{223}Ra and ^{224}Ra, ranged in activity from generally < 14 dpm 100 L^{-1} to 10 – 35 dpm $100L^{-1}$, respectively. There is no obvious trend between $^{223,224}Ra$ and salinity. Excluding the thermal spring-derived discharge off west-central Florida (Fanning et al., 1981), and the phosphate-enhanced Ra isotopes observed in Tampa Bay, such Ra activities are typicalfor Florida coastal waters and estuaries (Burnett et al., 1990; Swarzenski et al., 2001; Swarzenski et al., 2004; Cable et al., 2004).

^{222}Rn activities were measured almost real-time from the seaward endmember close to the Jupiter Inlet (salinity ~ 34‰) upstream to the confluence of Kitching Creek and the Loxahatchee River, where salinities approach zero. During this Rn survey, activities were inversely related to salinity (Fig. 23), and ranged from a background value of ~2.5 dpm L^{-1} at Jupiter Inlet to more than 28 dpm L^{-1} at Kitching Creek.

V.B. Loxahatchee River Floodplain Water Quality Measurements

V.B.1. General - Results of chemical analyses of surface water, porewater, and well water samples from the Loxahatchee River floodplain sites (transect sites) are presented in tabular form in Appendix A for both the wet season (September 2003) and dry season (March 2004) sampling**.** Selected parameters for surface water and porewater for all sites sampled along transects 1, 3, 6, 7, and 9 for both the wet season and dry season are plotted versus depth and along the transects in the figures in Appendix B.

V.B.2. pH, alkalinity, and redox – Values for pH at all sites are tabulated in Tables 1 and 3, in Appendix A, representing the wet and dry season sampling, respectively. Results are plotted in Appendix B, Figs. 1A-1E. Surface water and porewater pH values ranged from 5.74 to 7.90, but with most samples having pH values in the range of 6.5-7.8 (circumneutral pH). No major differences in pH were noted among the different transects, and dry season pH values were generally similar to wet season values at most sites. Upland wells on Transects 7 and 9 had much more acidic pH values of around 5. These wells also tended to have low ionic strength. At most sites, pH values tended to decrease with increasing depth in the sediment, reflecting production of protolytic chemical species (e.g organic acids) during sedimentary decomposition of organic matter. Along transect 1, a large decrease in pH was seen at site 3 below 5 cm. This may reflect the influence of more acidic groundwater at this most upland site.

Values for titration alkalinity are presented in Appendix A Tables 1 and 3 for the wet and dry seasons, respectively. Alkalinity values are plotted in Appendix B, Figs. 2A-2E. Alkalinities ranged from 1 to 23 meq/L, but with most samples in the 2 to 5 meq/L range. These are relatively low alkalinities for porewater. Typically, alkalinities are higher in pore water than surface water, and increase with depth in pore water due to accumulation of dissolved CO_2 from microbial degradation of organic matter in sediments. The reason(s) for the relatively low alkalinities in the Loxahatchee River floodplain is unclear. One hypothesis is that tidal effects or upwelling groundwater continually strip dissolved chemical species from pore water. No pattern was observed in the downcore profiles of alkalinity, with some sites exhibiting increasing alkalinity with depth, some sites showing decreasing alkalinity with depth, and some sites showing no pattern. Similarly, no consistent pattern was observed in alkalinity between the wet and dry seasons. Some sites showed slightly higher wet season alkalinities, some showed slightly higher dry season alkalinities, and some sites showed no difference. Wells had variable alkalinities, but the two lowest alkalinities observed were from upland wells along Transects 7 and 9. These wells also had low pH and ionic strength.

Redox values for all sites are presented in Appendix A Tables 1 and 3, for the wet season and dry season, respectively. Results are plotted in Appendix B Figs. 3A-3E. Redox values range from 219 (highly oxidizing) to -260 mv (highly reducing) in surface and porewater, although most samples had redox values of 100 to -150 mv. Most surface water redox values were positive, reflecting oxidizing conditions. Some surface waters, especially from wet season sites along transects 1 and 3, had slightly negative redox values, suggesting reducing conditions. This could reflect stagnant water conditions, as well as high levels of dissolved humic substances in the surface water, which can also influence redox measurements. The most negative (reducing) redox values in porewater were observed along transect 9, due to the high levels of sulfide in the brackish waters on this transect. Transect 1 had much lower (more reducing) porewater redox values in the wet season than in the dry season. This is due to the generally dry (oxidizing) conditions of the sediments during the dry season. Changes in redox values with depth varied along the different transects. Redox values along transects 1 and 3 initially decreased with depth over the upper 10 cm, and then increased below this. Redox values at sites on transect 6 showed slight increases with depth over the upper 15 cm, and then decreased sharply with depth below 15 cm. Redox values along transect 7 showed little change or a slight decrease with depth, and redox values along transect 9 sharply decreased with depth, especially during the dry season. Wells had variable redox values, but with the majority having negative values (reducing conditions). More wells had positive (oxidizing) redox values in the dry season compared to the wet season.

V.B.3. Conductivity, salinity, total dissolved solids – Values for conductivity, salinity, and total dissolved solids (TDS) are presented in Appendix A Tables 1 (wet season) and 3 (dry season). Results for conductivity are plotted in Appendix B, Figs. 4A-4E. Plots of salinity and TDS are not included in Appendix B, but these closely parallel the conductivity plots (from which they are derived). Overall, conductivity, salinity, and TDS were highest at transect 9 (most downstream transect), and lowest at transects 1 and 3. At most (but not all) sites, higher conductivity, salinity and TDS values were observed during the dry season, presumably due to evaporative concentration of salts. Sites exhibiting higher wet season values for conductivity, salinity, and TDS tended to be those farthest from the river, and potentially more influenced by groundwater.

Conductivity values ranged from 400-900 µS along both transects 1 and 3 during the wet season, and from 148-1788 µS along transect 1 during the dry season (March 2004). Dry season conductivity results from transect 3 were somewhat limited due to extremely dry conditions, but results available ranged from 127-776 µS. Depth profiles for conductivity along transects 1 and 3 were similar. Conductivity values were higher in porewater than in surface for all wet season sites along transects 1 and 3. During the dry season, however, the more upland sites (site 3 along transect 1, and sites 2 and 3 along transect 3) had higher surface water conductivity compared to porewater. At sites 2 and 3 along transects 1 and 3, conductivity had a subsurface maximum at about 10-20 cm during the wet season. At site 2 along transect 1, conductivity increased sharply with depth during the dry season sampling, indicating a source of higher ionic strength water coming in from below the unconsolidated peat zone. At sites 1 and 3 along transect 1, dry season conductivity had unsystematic depth profiles, possibly reflecting the influence of evaporative concentration by drying in the surface sediments and input of saltier water from below the surface.

Conductivity values along transect 6 are 3 to 4 times higher than along transects 1 and 3, reflecting the closer proximity to the Loxahatchee River mouth at Jupiter Inlet. In the wet season conductivity increased from 400 to 2,300 µS with depth in porewater along transect 6. During the dry season the increase in conductivity with depth was much less, from 1500-2000 µS due to higher overall conductivity values in the surface water and near-surface porewater.

Although transect 7 is in relatively close proximity to transect 6, there are significant differences in many of the chemical parameters between these two transects. Overall, transect 7 more closely resembles transect 3 than Transect 6 in its surface and pore water geochemistry. Transect 7 has generally lower conductivity values compared to transect 6, irrespective of tidal level. For example, conductivity reaches only about 600 µS along transect 7, compared to nearly 2,500 µS at transect 6. Note that transect 7 was sampled on 2 different days and over different tidal levels (site 1 at high tide, and site 2 at low tide) during the wet season. The difference in the tidal level is reflected in lower conductivity values at site 2 compared to site 1. Conductivity shows a slight increase with depth at both sites on transect 7.

As expected, transect 9 had the highest conductivity values, up to nearly 8,000 µS in the wet season and more than 14,000 µS in the dry season. Interestingly, site 2 on this transect (site closest to the river) had the lowest conductivity and chloride concentrations, and site 1 (the most landward site) had the highest, during both the wet and dry seasons. This particular transect is on a small peninsula in the river, and the orientation of the transect on the peninsula combined with salt wedge movement may explain the saltier water at the most landward site. Conductivity values increased with depth in the porewater during the wet season. During the dry season conductivity was generally highest in the surface water and showed little change with depth until below about 50 cm, where values decreased. Dry season results from site 2 (nearest the river) indicated higher conductivity values during high tide compared to low tide.

V.B.4. Chloride, fluoride, bromide – Values for chloride, fluoride, and bromide are presented in Appendix A Tables 1 (wet season) and 3 (dry season). Results for chloride are plotted in Appendix B, Figs. 5A-5E. Plots of fluoride and bromide are not included in the Appendix, but these closely parallel the chloride plots. Chloride, fluoride, and bromide values are generally lowest at the upriver transects (1 and 3), and highest along transect 9 (most marine site), as expected.

Along transect 1, chloride concentrations range from 19-36 mg/L during the wet season, and 28-151 mg/L in the dry season, in surface and porewater. Dry season chloride concentrations are generally higher at sites 1 and 2, but wet season chloride concentrations are higher at site 3 (most upland site). Site 3 chloride concentrations show little change with depth during the dry season, but an increase with depth and maximum at 20 cm depth during the wet season. Site 2 chloride concentrations showed a subsurface maximum at about 10-20cm, that was much more pronounced during the dry season. At site 1 (nearest the river) chloride concentration increased with depth during the wet season, but decreased with depth during the dry season.

Chloride concentrations along transect 3 were similar to those along transect 1, and ranged from 17-105 mg/L during the wet season, and from 14-267 mg/L during the dry season. Chloride concentrations were the same to slightly higher overall during the dry season at all sites along transect 3.

Along transect 6, chloride concentrations ranged from 44-612 mg/L during the wet season, and 223-563 mg/L during the dry season. Concentrations at sites 1 and 2 were similar. At site 1 (near river), chloride concentrations were generally higher during the dry season, and chloride concentrations increased with depth during both the wet and dry seasons. At site 2, chloride concentrations increased with depth during the wet season, but a more complex depth profile was observed during the dry season.

Transect 7 chloride concentrations ranged from 21-115 mg/L during the wet season, and 69-200 mg/L during the dry season. Overall concentrations were slightly higher at site 1 (upland site). Chloride concentrations showed little change with depth, except for a maximum at about 10 cm in the site 1 dry season data. As with conductivity, transect 7 results for chloride more closely resembled those for transects 1 and 3 than the nearby transect 6.

Transect 9 had the highest chloride concentrations, ranging from 279-6773 mg/L in the wet season, and 1414-7720 mg/L in the dry season. Dry season chloride concentrations were generally lower than wet season concentrations at all sites. As with conductivity, the highest chloride concentrations were observed at site 1 (most upland site). Transect 9 is on a small peninsula in the river, as previously mentioned, and the orientation of the transect on the peninsula combined with salt wedge movement may explain the higher chloride contents at the most landward site. Chloride concentrations at most sites along transect 9 increased with depth to a subsurface maximum, during both the wet and dry seasons. These subsurface maxima are typically at depths of about 10-20 cm, except for the wet season results from site 1, where the maximum is at 40 cm.

V.B.5. Sulfate and sulfide – Concentrations of sulfate and sulfide are tabulated in Appendix A Tables 1 (wet season) and 3 (dry season), and plotted in Appendix B, Figs. 6A-6E.(sulfate) and 7A-7E (sulfide). Overall sulfate and sulfide concentrations were highest at transect 9, and lowest at transects 1 and 3.

Along transect 1, sulfate concentrations ranged from <1-47 mg/L in the wet season, and from 1.6-209 mg/L in the dry season. Sulfate concentrations were somewhat higher at the river site (site 1) compared to the more upland sites. Sulfate concentrations were slightly or moderately higher during the dry season, with the dry season-wet season difference being least at the most upland site. Changes in sulfate concentration with depth were complex, but for most cores involved an initial decrease in concentration from the surface water into the pore water, followed by an increase toward the bottom of the profile. This overall trend is consistent with microbial sulfate reduction occurring in the near surface sediment zone, and a source of sulfate at depth. Well water from transect 1 (site 1) had significantly higher sulfate concentration in the wet season.

Sulfide concentrations in the surface and porewater along transect 1 were low, but measurable, ranging from 1-32 μg/L during the wet season, and <0.1-184 μg/L during the dry season. The presence of sulfide indicates that microbial sulfate reduction is occurring in these sediments, but with sulfide buildup limited by sulfate availability, daily tidal pumping, and precipitation of insoluble metal sulfides. Sulfide concentrations were similar during the wet and dry seasons at transect 1 sites 1 and 2, but were significantly higher during the dry season at transect 1 site 3. Sulfide profiles generally exhibited a mid-depth maximum, indicating the zone where maximal microbial sulfate reducing activity is occurring, and where sulfide advection/diffusion out of the porewater is limited. Well water had sulfide concentrations of 52 μg/L in the wet season, and 26 μg/L in the dry season.

Transect 3 had sulfate concentrations ranging from 1-63 mg/L in the wet season, and 1-44 mg/L in the dry season, similar to values observed along transect 1. Transect 3 also had somewhat lower sulfate concentrations at site 3 (upland site), similar to what was observed at transect 1. In contrast to transect 1, however, dry season sulfate concentrations along transect 3 were either about the same, or higher compared to the wet season. As with transect 1, sulfate concentrations along transect 3 commonly showed an initial decrease with depth, followed by an increase toward the bottom of the profile. Again, this is consistent with microbial sulfate reduction in the near surface zone, and a source of sulfate at depth.

Sulfide concentrations along Transect 3 were similar to those observed along transect 1. Wet season sulfide concentrations ranged from 2-37 μg/L, and dry season concentrations from <0.1-165 μg/L. Higher overall dry season sulfide concentrations along transect 3 reflect overall higher dry season sulfate concentrations. Downcore sulfide profiles showed generally increasing concentrations with depth to the bottom of the profile. This reflects the high sulfate concentrations found at the base of many of the profiles along transect 3. Well water from near transect 3 site 1 had much higher dry season sulfide concentrations (204 μg/L) compared to the wet season (11.8 μg/L), although higher sulfate concentrations were observed in the well water during the wet season. This result is somewhat surprising, since one normally anticipates higher rates of microbial sulfate reduction with higher levels of sulfide and lower sulfate during the warmer wet season.

Transect 6 had sulfate concentrations slightly higher than those at transects 1 and 3. Sulfate concentrations along transect 6 ranged from <1-139 mg/L in the wet season, and 21-84 mg/L in the dry season. Sulfate concentrations were approximately the same at both sites along the transect. Dry season sulfate concentrations were higher than wet season concentrations, except at the base of each profile. The wet season profiles at both sites showed a sharp increase in sulfate concentrations at the bottom of the profile, suggesting a source of sulfate at depth. This increase in sulfate concentrations at the base of the profile was not observed in the dry season. The wet season depth profiles for sulfate were similar to those observed at transects 1 and 3: an initial decrease in sulfate concentration (microbial sulfate reduction), followed by an increase in sulfate near the base of the profile suggesting a sulfate source at depth. The dry season sulfate profiles along transect 6 showed only a slow decrease in sulfate concentration with depth.

Sulfide concentrations along transect 6 ranged from 1-1840 μg/L in the wet season, and <1-2557 μg/L in the dry season. The major characteristic of the sulfide data along transect 6 is the large increase in concentration below 20 cm, especially at the more upland site (site 2). This indicates that microbial sulfate reduction and accumulation of sulfide in porewater is occurring below 20 cm at this transect. Normally, maximum microbial sulfate reduction activity is located in the near surface zone. It may be that microbial sulfate reduction is high near the surface, but that sulfide is being continuously removed by advective flux, such as tidal action. The sulfate data also indicates a source of sulfate at depth at these sites, and this likely stimulates microbial sulfate reduction and sulfide accumulation at depth along this transect.

Transect 7 had overall sulfate concentrations more similar to transects 1 and 3 than to nearby transect 6, which is consistent with the chloride and conductivity results discussed earlier. Sulfate concentrations ranged from <1-19 mg/L during the wet season, and 1-105 mg/L in the dry season. Overall higher sulfate concentrations were observed during the dry season along transect 7. During the wet season, sulfate concentrations generally showed a decrease with depth, followed by an increase near the base of the profile. Again, this is consistent with microbial sulfate reduction in the near surface zone, and a source of sulfate at depth. The dry season data, however, showed an initial increase in sulfate with depth to a subsurface maximum, followed by a decrease in sulfate concentration to the bottom of the profile. This may reflect decreased freshwater flow during the dry season, and increased sulfate in near surface porewater from tidal action. The decrease in sulfate concentration toward the base of the profile may reflect the microbial sulfate reduction zone during the dry season along this transect. Well water from the river site (site 2) had much higher sulfate concentrations compared to the upland site (site 1). No differences in sulfate concentration between the wet and dry seasons were observed at either well along transect 7.

Sulfide concentrations along transect 7 ranged from 1-1458 μg/L during the wet season, and <1-710 μg/L during the dry season. As at transect 6, the most interesting characteristic of the sulfide data was the dramatic increase in concentration below 20 cm at both sites, but especially at the more upland site (site 1). Again, this feature of the sulfide data may reflect advective tidal flux of sulfide from porewater in the near surface zone, and a source of sulfate at depth that stimulates microbial sulfate reduction and accumulation of sulfide. Sulfide in the well water was somewhat higher at the upland site (site 1). This is in contrast to the sulfate data, which was much higher at the river site (site 2). Sulfide concentrations were somewhat higher at both wells sampled along transect 7 during the dry season.

Sulfate concentrations along transect 9 ranged from 16-1259 mg/L during the wet season, and 284-1067 mg/L during the dry season. As with chloride and conductivity, the overall highest sulfate concentrations were observed at the most upland site (site 1) along transect 9. Dry season sulfate concentrations were generally significantly higher than wet season sulfate concentrations, reflecting decreased freshwater flow (increased marine influence) during the dry season. Sulfate had differing wet season-dry season profiles. Wet season profiles had lower overall sulfate concentrations, and showed a general pattern of initial decreasing sulfate concentration over the upper 2-10 cm, followed by increasing sulfate concentration to the bottom of the profile. During the dry season, sulfate depth profiles showed either a gradual decrease in sulfate with depth (site 3), or an initial increase to a subsurface maximum at about 20 cm, followed by a decrease, and then another increase to the base of the profile (sites 1 and 2). The upland well along transect 9 had >10 fold lower sulfate concentrations than the river well (near site 2). The upland well had higher wet season sulfate concentrations, while the river well had higher dry season sulfate concentrations.

Sulfide concentrations along transect 9 ranged from 2-179 μg/L during the wet season, and <1-3007 μg/L during the dry season. However, sulfide levels were relatively low in the near-surface zone (above 20 cm) at all sites, and were especially low overall during the wet season. As with transects 6 and 7, the characteristic feature of the sulfide data along transect 9 was the very large increase in concentration below 20 cm. Again, this type of profile is likely driven by advective tidal flux of sulfide from pore water in the near-surface zone, and by a source of sulfate at depth along this transect. Although sulfate concentrations were highest at the most upland site along this transect (site 1), sulfide concentrations were highest at the river site (site 2), and lowest at the upland site (site 1). Higher sulfide concentrations (much higher at sites 2 and 3) were observed during the dry season; probably reflecting decreased freshwater flux and greater marine influence during the dry season. Sulfide concentrations in wells were higher at the river end well, and lower at the upland well, consistent with the sulfate data.

V.B.6. Nitrate, ammonium, and phosphate – Concentrations of nutrients (nitrate, ammonium, and phosphate) are tabulated in Appendix A Tables 2 (wet season) and 4 (dry season), and plotted in Appendix B, Figs. 8A-8E (nitrate), 9A-9E (ammonium), and 10A-10E (phosphate). In contrast to parameters such as conductivity, salinity, chloride, and sulfate that are linked to the increasing influence of saltwater progressing downstream, nutrients do not generally increase from Transect 1 to Transect 9. Indeed, for phosphate and nitrate, the upstream transects (1 and 3) have the overall highest concentrations. Also, at most sites wet season nutrient concentrations were significantly higher than dry season concentrations.

The principal feature of the nutrient (nitrate, ammonium, and phosphate) profiles along transect 1 at all sites is a subsurface maximum in concentration. The depth of this maximum varies from site to site, but at each site is at the same depth for nitrate, ammonium, and phosphate. This maximum represents the zone of primary organic matter decomposition, and recycling of N and P from organic matter deposited in the sediments. Concentrations of nutrients at all three sites along transect 1 were higher during the wet season, especially at sites 2 and 3. Phosphorus levels were uniformly high, and in many instances exceeded the combined nitrate and ammonium concentrations. Thus, primary production along this transect may be nitrogen limited, although further verification of this is certainly needed. Concentrations of nutrients in the well from transect 1 (located near site 3) were significantly lower than the maximum concentrations observed in the porewater during the wet season, but comparable to the dry season concentrations. There was little difference between wet season and dry season concentrations for phosphate and ammonium in the well water, but nitrate was significantly higher in the wet season.

Transect 3 had overall lower nitrate concentrations compared to transect 1, especially during the wet season. Ammonium and phosphate concentrations, however, were generally higher along transect 3 compared to transect 1. Wet season phosphate concentrations were significantly higher than dry season concentrations along transect 3, as was also observed along transect 1. Overall, wet season concentrations for nitrate and ammonium were also higher than dry season concentrations, but not in all instances, and not to the extent seen along transect 1. Depth profiles of nutrient elements along transect 3 also exhibited generally increasing concentrations from surface water into the porewater, and mid-depth concentration maxima, as also observed along transect 1. The concentration maxima represent zones of highest biodegradation of organic N and P in the sediments and production of dissolved nutrient species. As along transect 1, phosphate concentrations in porewater along transect 3 are elevated relative to ammonium and nitrate concentrations, in many cases exceeding the combined nitrate plus ammonium concentration. Again, this suggests the possibility that the floodplain vegetation is nitrogen limited. Well water from transect 3 (well located near site 3) had nutrient concentrations generally lower than wet season porewater nutrient concentrations, but comparable to dry season porewater nutrient concentrations. Nitrate, ammonium, and phosphate concentrations in well water from transect 3 were all higher in the wet season. As with the porewater, well water also had phosphate values that exceeded the total nitrate and ammonium concentrations.

Overall nitrate concentrations along transect 6 are similar to those observed along transect 3, and lower than values observed along transect 1. Ammonium and phosphate concentrations are generally lower than those observed along transects 1 and 3. Wet season concentrations for nitrate, ammonium, and phosphate were generally much higher than dry season concentrations, as observed along transects 1 and 3. Indeed, along transect 6 dry season porewater concentrations of nutrients were actually less than those observed in the surface water. Depth profiles, especially during the wet season, exhibited increasing concentrations of all nutrients from surface water into the porewater building to a subsurface maximum concentration at about 10 cm for ammonium and phosphate, and 10-20 cm for nitrate.

The two sites along transect 7 have similar nitrate concentrations, but phosphate and ammonium concentrations during the wet season are much higher at the landward site (site 1). As along transect 6, dry season concentrations of nutrients are generally lower in porewater than in surface water. As on other transects, depth profiles for ammonium and phosphate during the wet season along transect 7 exhibit subsurface maxima. This is especially apparent in the landward (site 1) profile. Well water samples had higher concentrations of nitrate at the upland well site during the wet season, but much higher concentrations of phosphate and ammonium at the well near the river. Thus, the well water results are exactly the reverse of the porewater results, and concentrations of ammonium and phosphate in the well near the river are considerably higher than those observed in porewater at the river site. Reasons for this difference are unclear. All well water nutrient concentrations were higher in the wet season.

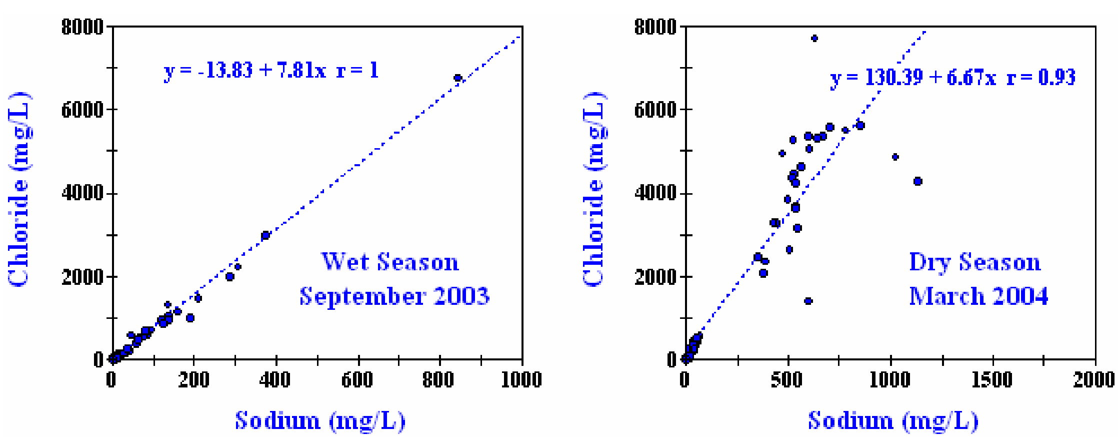
Nitrate concentrations along transect 9 were generally comparable to those observed along transects 3, 6, and 7, but lower than those from transect 1. Ammonium and phosphate concentrations were generally comparable to those along transect 7. As elsewhere, nutrient concentrations in porewater along transect 9 were generally higher during the wet season. Vertical profiles, especially for ammonium and phosphate showed a sharp increase from surface water into porewater to a subsurface maximum during the wet season. This was also observed along most other transects. Ammonium and phosphate concentrations were highest in porewater from the most landward site (site 1). The upland well also had higher phosphate and ammonium values compared to the river well, exactly the opposite of what was observed in wells from transect 7. All of the well nutrient data was higher during the wet season, except for phosphate at the river well. Ammonium and phosphate at the upland well had much higher concentrations during the wet season.

V.B.7. Sodium, potassium, magnesium, and calcium - Concentrations of major cations (sodium, potassium, magnesium, and calcium) are tabulated in Appendix A Tables 3 (wet season) and 4 (dry season), and plotted in Appendix B, Figs. 11A-11E (sodium), 12A-12E (potassium), 13A-13E (magnesium), and 14A-14E (calcium). Overall, sodium, potassium, and magnesium concentrations appear to be directly linked to degree of saltwater influence, and tend to increase downstream. Calcium concentrations, however, show no significant changes downstream. Calcium in surface and porewater may be controlled by diagenetic factors that determine equilibrium concentrations of calcium between the porewater and the soils/sediments. All four major cations show generally higher concentrations in porewater along transects 6 and 9 (the most marine sites) during the dry season, reflecting lower freshwater discharge. No consistent trends in the major cations were observed between the wet and dry seasons along transects 1, 3, and 7.

Sodium concentrations in surface and porewater range from 2-843 mg/L during the wet season, and from 0.3-1132 mg/L during the dry season. During the wet season, most sites showed increasing sodium concentrations from surface water to porewater, and increasing sodium concentrations with depth in the porewater. During the dry season, however, changes in sodium concentration between surface water and porewater, and with depth in the porewater were inconsistent. Sodium concentrations were highly correlated with chloride during the wet season (Fig. 24A), however, this correlation broke down during the dry season, especially at higher salinities (Fig. 24B). Correlation coefficients (r^2 values) between sodium and chloride were 1.0 during the wet season and 0.86 during the dry season. This suggests that mixing of salt and fresh water dominates both chloride and sodium concentrations during the wet season, but other processes may dominate during the dry season. All wells, except the well closest to the river along transect 9, showed higher wet season concentrations of sodium. Upland wells had generally lower sodium concentrations than wells nearer the river.

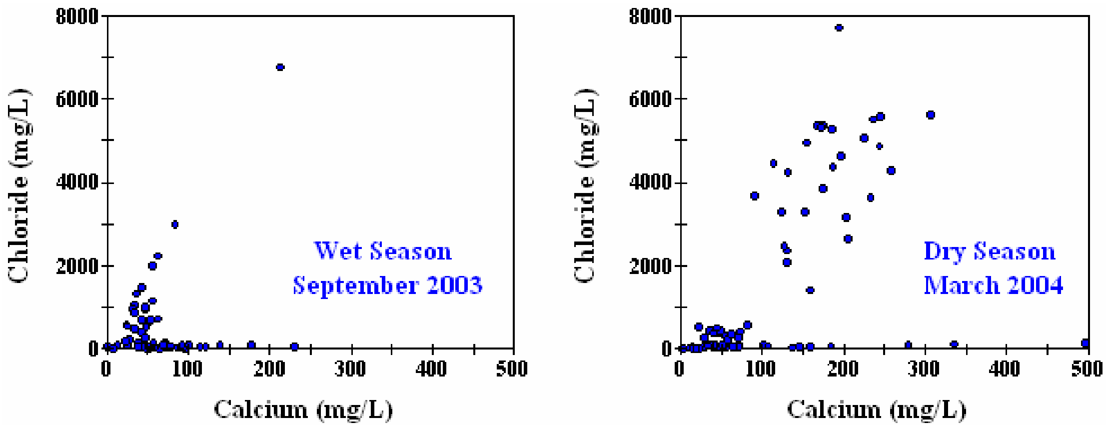
Potassium concentrations in surface and porewater ranged from <1-168 mg/L in the wet season, and <1-119 mg/L in the dry season. Magnesium concentrations in surface and pore water ranged from <1-470 mg/L in the wet season, and from <1-514 mg/L in the dry season. Potassium and magnesium concentrations in surface and porewater were generally correlated with sodium concentrations, though more strongly during the wet season compared to the dry season. Correlation coefficients (r^2 values) between potassium and sodium were 0.98 in the wet season, and 0.86 during the dry season; and between magnesium and sodium were 0.96 in both the wet and dry season. As with sodium, both potassium and magnesium concentrations were strongly correlated with chloride concentrations, especially during the wet season. Changes in potassium and magnesium concentrations from surface water to porewater, and with depth in the porewater tended to parallel those for sodium in general. Upland wells had lower concentrations of both potassium and magnesium compared to river end wells along transects. No consistent wet season-dry season patterns were apparent in the well water data for potassium or magnesium.

Calcium concentrations in surface and pore water ranged from 13-230 mg/L in the wet season, and 11-496 mg/L in the dry season. As noted earlier, no distinct downstream trend in calcium concentrations were observed. The most marine transects (6 and 9) exhibited higher dry season calcium concentrations, but at the other sites no particular seasonal trend was observed. Calcium concentrations plotted versus chloride (Fig. 25) suggest both marine and freshwater sources for calcium in the Loxahatchee River. Overall calcium concentrations were highest along transects 1 and 9, consistent with the idea of both a freshwater and marine source for calcium in this river system. Calcium concentrations generally showed an increase from surface water into the porewater, but exhibited no consistent pattern versus depth in the porewater. This suggests that differential sources, and diagenetic processes all control the observed calcium concentrations. In the wells, calcium concentrations were much lower in the upland wells (especially at transects 7 and 9) compared to the river end wells, similar to the other major cations. Calcium concentrations in the well water were generally higher during the wet season, except at the river end well along transect 9.



(A) **(B)**

Fig. 24. Plots of concentrations of sodium (mg/L) versus chloride (mg/L) for pore water and surface water from the floodplain of the Loxahatchee River during the wet season (A) and the dry season (B).



(A) (B)

Fig. 25. Plots of concentrations of calcium (mg/L) versus chloride (mg/L) for pore water and surface water from the floodplain of the Loxahatchee River during the wet season (A) and the dry season (B).

V.C. Loxahatchee River Floodplain Sediment Chemistry

Soils/sediments from selected locations along the floodplain transects in the Loxahatchee River were collected by piston coring for total carbon (TC), organic carbon (OC), total nitrogen (TN), total sulfur (TS), and total phosphorus (TP) analysis, as described earlier. Results are presented in tabular form in Appendix C, and as depth profiles in the figures in Appendix D. All concentrations are reported on a dry weight basis. OC concentrations were determined, but are not shown in the Table in Appendix C because TC and OC values in these cores were virtually identical, indicating that nearly all of the carbon is present in organic form.

TC concentrations in soils/sediments are plotted versus depth along each transect in Appendix D Figs. 1A-1E. TC values vary from transect to transect and with depth. TC values gradually increased in a downstream direction, with the lowest TC concentrations along transect 1, and the highest TC concentrations along transect 9. TC concentrations along transects 6, 7, and 9 exceeded 30% near the surface, and transects 7 and 9 maintained TC contents of about 30% to a depth of 40 cm. Thus, transects 7 and 9 have developed what would be considered to be a true peat deposit of 40 cm thickness, with peaty muck below this. Transect 6 is peaty near the surface (30% TC above 10 cm), but rapidly transitions to an organic matter-rich soil with increasing depth (21% TC at 20 cm, and 6-11% TC at 30 cm). Surficial deposits along transects 1 and 3 transition from organic matter-rich soils near the surface (15-26% TC) to more mineral soil at depth (1-5% TC near the base of each core). The surficial peats and soils appear to be underlain by sand in many locations. Site 1 along transect 3 had an interesting TC profile, with peaty soil to a depth of 30 cm, then a low TC soil layer (1-2% TC) from 30-50 cm, then a peaty soil layer (up to

30% TC) from 50-65 cm, and transitioning into sand at the base of the core. The mineral soil layer from 30-50 cm at transect 3 site 1 was very difficult to extract porewater from, and may be composed of highly clastic material.

TN concentrations in soils/sediments plotted versus depth and across each transect are presented in Appendix D, Figs. 2A-2E. TN concentration trends with depth closely parallel those for TC. However, TN concentrations do not vary as much among transects as TC values. While transect 1 has the lowest maximum TN concentrations (as was also true for TC), there is little difference between maximum TN concentrations among the other sites, all of which seem to have maximum concentrations of around 2%. In contrast, TC concentrations increased gradually downstream, as discussed above.

TS concentrations in soils/sediments are shown in Appendix D, Figs. 3A-3E, plotted versus depth and across each transect. As with TC, TS values generally increase in a down stream direction, with transect 1 having the lowest concentrations, and transect 9 the highest. Downcore profiles of TS generally resemble the TC and TN vertical profiles in the upper portions of these cores. However, at all transects except transect 1 there is an increase in TS toward the base of the core. This increase in TS at depth in cores from transects 3, 6, 7, and 9 is most dramatic at transect 3 site 1, where TS increases sharply from <0.1% to 2.6% between 40 and 50 cm depth. Similar peaks occur along transect 6 (20-30 cm), transect 7 (35-45 cm), and transect 9 (below 60 cm). This increase in TS at depth in these cores could represent deposition of sediments with a higher TS content at an earlier time. However, it is more likely that the increase represents the infiltration of sulfate-containing fluids into the sediment at depth, stimulating microbial sulfate reduction and the production of hydrogen sulfide. Hydrogen sulfide is highly reactive, and may form insoluble metal sulfides in the sediments by reaction with metals (principally iron), and/or may react with organic matter in the sediments to form organic sulfur species. This idea is supported by the pore water chemistry, which indicates infiltration of high conductivity, high chloride, high sulfate/sulfide water at depth along transects 3, 6, 7, and 9.

TP concentrations in soils/sediments are shown in Appendix D, Figs. 4A-4E, plotted versus depth and across each transect. TP concentrations show no general downstream trend, and the overall highest values were observed along transect 3. Concentrations of TP generally decrease with depth, sharply at some sites (e.g. along transects 1, 3, and 6), and more gradually at other sites (e.g. along transects 7 and 9).

V.D. Floodplain Vegetation Communities

Distributions of plant species and the determination of forest types in the Loxahatchee River floodplain transects 1, 3, 6, 7, and 9 were investigated using methods discussed earlier. Results are presented in Figs. 25-29, and in Appendix E. A list of identified species along all transects and their codes are presented in Table 11 (SFWMD and Florida Department of Environmental Protection, 2005).

Table 11. Canopy plant and code list for the Loxahatchee River (Hedgepath, written communication, 2005).

Scientific Name	Common Name	Code Name
Acer rubrum	Red maple	**AR**
Annona glabra	Pond apple	**AG**
Carya aquatica	Water hickory	**CA**
Cephalanthus occidentalis	Buttonbush	**CO**
Chrysobalanus icaco	Cocoplum	**CI**
Citrus sp. (EXOTIC)		**CS**
Ficus aurea	Strangler ficus	**FA**
Fraxinus caroliniana	Pop ash	**FC**
Ilex cassine	Dahoon holly	**IC**
Laguncularia racemosa	White mangrove	**LR**
Myrica cerifera	Wax myrtle	**MC**
Persea borbonia	Red bay	**PB**
Persea palustris	Swamp bay	**PP**
Pinus elliottii	Slash pine	**PE**
Psidium cattleianum	Strawberry guava	**PC**
Quercus laurifolia	Laurel oak	**QL**
Quercus myrtifolia	Myrtle oak	**QM**
Quercus virginiana	Live oak	**QV**
Rhizophora mangle	Red mangrove	**RM**
Roystonea regia	Royal palm	**RR**
Sabal palmetto	Cabbage palm	**SP**
Salix caroliniana	Carolina willow	**SaC**
Schinus terebinthifolius (EXOTIC)	Brazilian pepper	**ST**
Syzgium cumini	Java plum	**SC**
Taxodium distichum	Bald cypress	**TD**

Transect 1 is located just downstream of Lainhart Dam at Rivermile 14.7. This transect transverses the north and south sides of the Northwest Fork with 15 10x10m plots (Figs. 12 and 13). It has several elevation changes from 13.74 NGVD at the top of the mesic hammock to about 9.34 NGVD in the deeper swamp areas and 5.44 NGVD in the river channel. The distribution of canopy species along this transect is shown in Fig. 26. The exterior sides of transect 1 are dominated by several plots of upland and hammock before dropping down into the floodplains as a cypress swamp that borders the riverbed. One higher area adjacent to the bank of the river is classified as Rblh1 because of red maple within the plot and water hickory just outside of the measured plot. Cabbage palm, live oak (*Quercus virginiana*), and slash pine dominate the hammock and uplands plots while a stand of mostly very old bald cypress with an average dbh of 49cm. dominate the Rsw1 plots. The smallest bald cypress has a dbh of 9.9cm. Because the canopy is so well established in this area, and also because of high flow velocities, there is very little indication of a subcanopy present at this transect. In addition, there are no indications of logging (i.e. stumps only) in this area. Shrubs and groundcover in the Rsw1 areas are dominated by swamp lily (*Crinum americanum*), tri-veined fern (*Thelypteris interrupta*), and downy shield fern (*Thelypteris dentata*). The exotics elephant ear (*Xanthosoma sagittifolium*), and arrowhead vine (*Syngonium podophyllum*) were also present as groundcover within the swamp community.

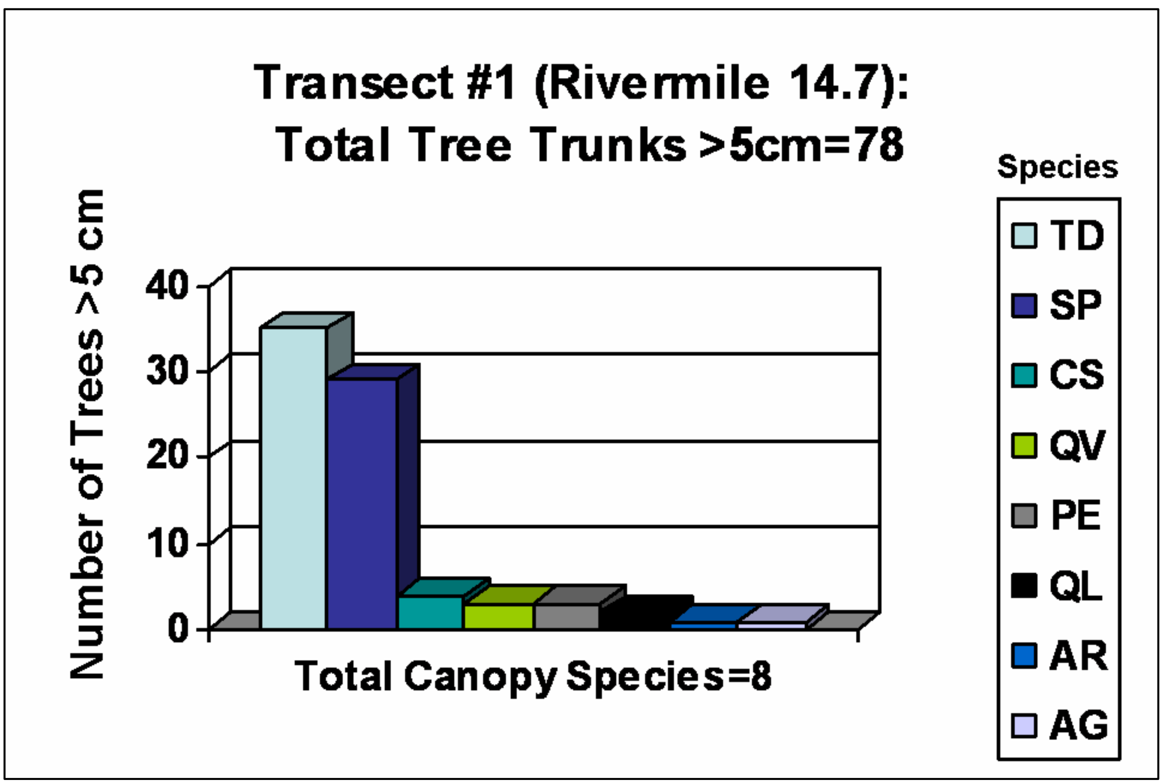


Fig. 26. Canopy species along transect 1 in the Loxahatchee River floodplain.

Transect 3 is located at Rivermile 12 downstream of I-95 and the Florida Turnpike on the east side of the river (Fig. 12). The site has been heavily impacted by selective logging in the past and by the presence of Old World climbing fern (*Lygodium microphyllum*). Also, there are multiple braided streams within the floodplains at this site. Elevations range from 5.54 NGVD at the benchmark to 2.03 NGVD at the bottom of the braided streams, and -9.87 NGVD in the river channel (Fig. 14). The majority of the floodplain is at an elevation of approximately 4 NGVD in this area. The distribution of canopy species along transect 3 is shown in Fig. 27. Nine of the 13 plots are either Rsw1or Rsw2. Bottomland hardwood and hammock are apples and red maple are also present with average dbhs of 7.1cm and 14.4cm, respectively. Shrubs and groundcover on transect 3 are primarily leather fern, maiden fern, meniscium fern, and lizard's tail present near the uplands and adjacent to the riverbed. Transect 3 has the highest concentration of pop ash of any of the ten transects. Their average dbh is 17cm; however, the range is 5-41cm. Only 4 bald cypress are within the transect canopy and they are very large with an average dbh of 91.5cm. Pond apples and red maple are also present with average dbhs of 7.1cm and 14.4cm, respectively. Shrubs and groundcover on transect 3 are primarily leather fern, maiden fern, meniscium fern, and lizard's tail.

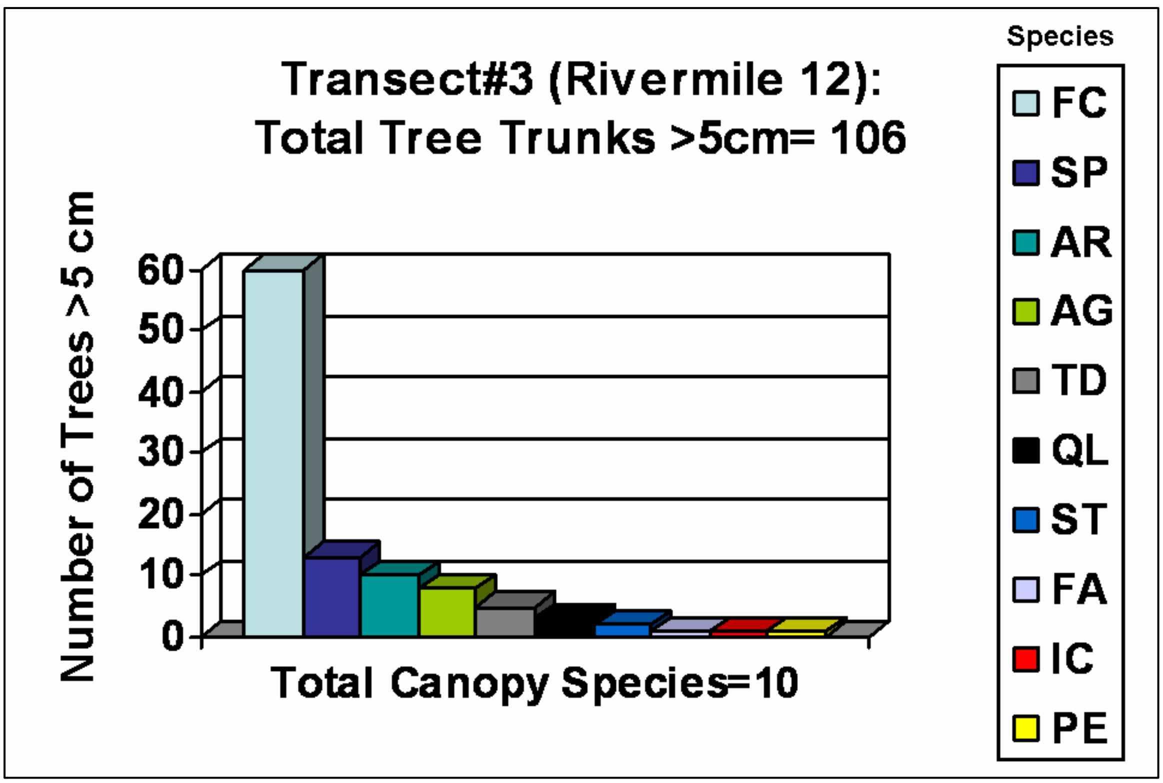


Fig. 27. Canopy species along transect 3 in the Loxahatchee River floodplain.

Transect 6 is located at Rivermile 8.5 on a peninsula just upstream of Kitching Creek and adjacent to National Audubon's Ornamental Garden (Kitching Creek Sanctuary), (Fig. 12). This peninsula has been selectively logged in the past and contains the remnants of many dead cypress. Today, there are still live cypress growing among the pond apple and mangrove and a band of cypress still exist adjacent to the uplands (again probably provided with some protection by adjacent surface and groundwater runoff from the uplands). Elevations range from 6.82 NGVD in the uplands to an average elevation of 1.59 NGVD over the remaining transect (Fig. 15). The distribution of species in the canopy along transect 6 is shown in Fig. 28. Of the 16 plots on transect 6, there are 2 Upland, 1 Rsw1, 6 UTsw1, 6UTsw3, and 1 UTmix plots. The most prevalent species are red and white mangrove and pond apple (average dbh 8.3cm.). Red maple (dbh 17.5cm) and pop ash (average dbh. 5.7cm.) are present in much smaller numbers. The average dbh of the living bald cypress are 29.8cm. At approximately 85 meters from the uplands on transect 6, there is a large bald cypress (live and healthy looking) totally surrounded by red mangroves. Red mangrove and pond apple are more prevalent in the plots beyond 110 meters from the uplands, which again indicates the significance of floodplain topography in species distribution. Shrubs and groundcover consist primarily of very young red and white mangrove, leather fern, pond apple, buttonbush, maiden fern, swamp fern, and rubber vine (*Rhabdadenia biflora*).

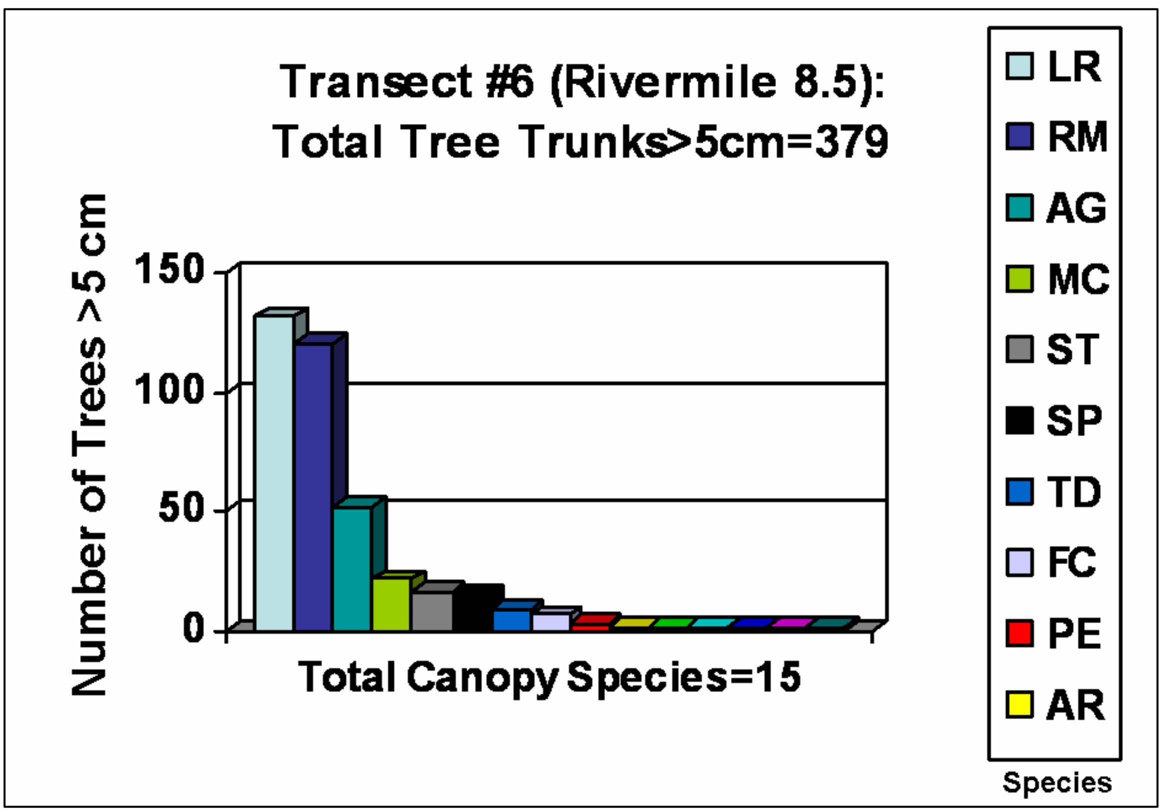


Fig. 28. Canopy species along transect 6 in the Loxahatchee River floodplain.

Transect 7 is located at Rivermile 9.1 on the south side of the mid Northwest Fork across from the eastern end of Hobe Grove Ditch (Fig. 12). This transect has been impacted by salt water intrusion, exotics (mostly Old World climbing fern, Brazilian pepper, and java plum) and logging. It is a very long transect (Fig. 16), with 15 plots that contain a mixture of 8 riverine and 7 upper tidal forest type plots. Elevations change from 10.06 NGVD at the benchmark to an average of 1.58 NGVD across most of the floodplain. The distribution of canopy species along transect 7 is shown in Fig. 29. The riverine section of the transect consist of first a mixed plot (Hammock/Rsw1) with live oak, wax myrtle, and a large cypress (50.1cm dbh) followed by 2 plots of Rsw1, and 5 plots of Rmix (primarily bald cypress, cabbage palm and wax myrtle). Cabbage palm and wax myrtle are surviving with the swamp species by living on small hummocks, old logged cypress stumps, and other fallen logs. The Upper Tidal segment of transect 7 follows with 4 plots of UTsw1, 2 plots of UTsw2, and a UTmix at the riverbed. From a distance of 120m from the upland, red mangroves begin to appear and become more abundant along with pond apple. White mangrove were present but too small to be considered canopy (i.e. >5cm. dbh). Live bald cypress are present from the edge of the uplands out to 120 m of the 150 m transect. Bald cypress have an average dbh of 28.3cm and range in size from 7.2cm to 50.1cm dbh. Shrubs and ground cover consist primarily of

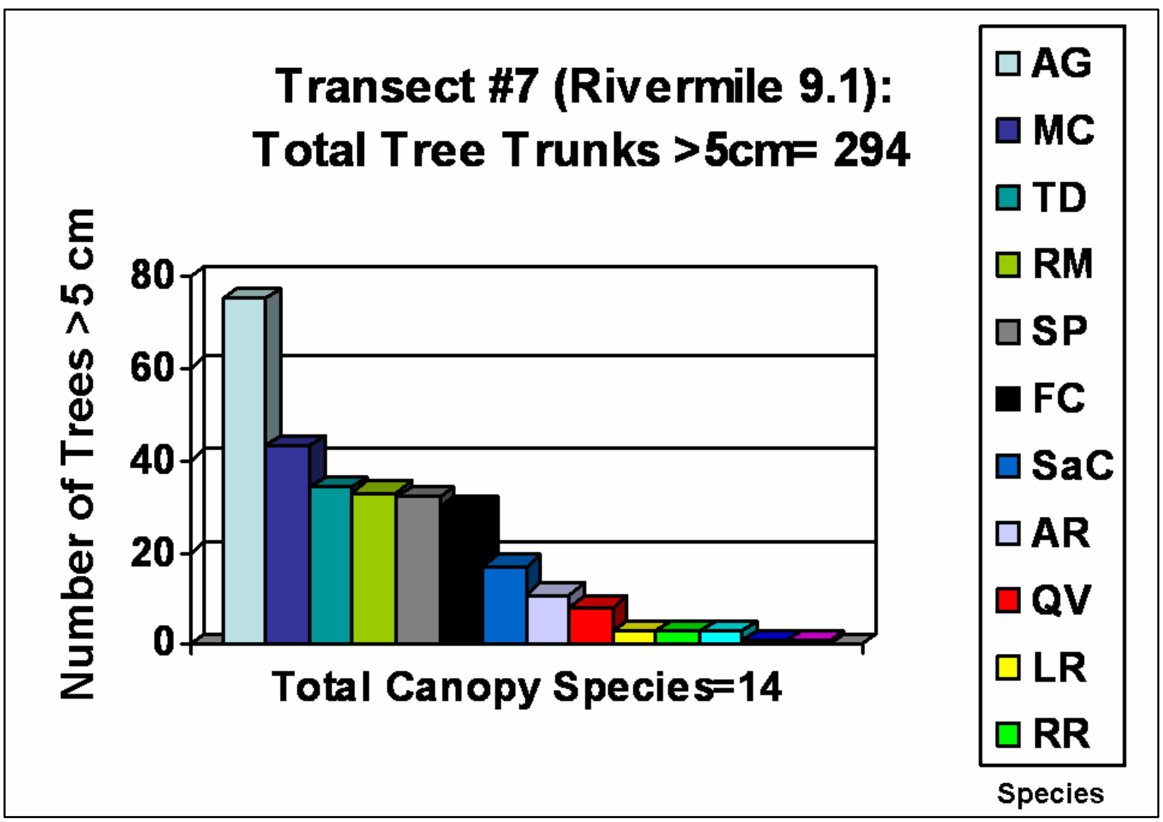


Fig. 29. Canopy species along transect 7 in the Loxahatchee River floodplain.

leather fern, wax myrtle, button bush, salt bush, primrose willow, poison ivy, swamp fern, marsh fern, meniscium fern, royal fern, swamp lily, milk vine and young mangroves, pond apples and pop ash. The riverine plots appear to have muck soils while the upper tidal plots appear to have sandy soils.

In the late fall of 2003, it was noted that transect 7 had an extremely high amount of cypress seedlings (5-7.6 cm in height). Germination of new seedlings continued well into the late spring. The dry season (December to May 2004) was very dry. Tides were not reaching the entire transect during this period and rains did not come until mid-July. It was thought that this period of dryness was advantageous for germination and early bald cypress seedling growth. On a field trip to the site, Helen Light and Melanie Darst (USGS botanists) suggested that perhaps the stress of the salt may have made the trees more reproductively active. It was also noted that the bald cypress on this site are probably younger than their counterparts in the riverine reaches of the river. The literature suggests that older bald cypress trees are less reproductively active plus we noted that the canopy was much higher and thicker in the riverine portion of the river. Therefore, less light is available for the development of an extensive subcanopy in the riverine reach. Also, the literature would suggest that a good recruitment season for bald cypress may take place every 30-40 years. Recently upon visitation to transect 7 in August 2004, we noted that many of the fall 2003 bald cypress seedlings were gone. Daily tides had returned to the interior of the transect. We do not know whether or not the seedlings were too short to survive the periods of tidal flooding (twice a day) or whether salinity was a factor. Some of these questions will be answered by additional bald cypress seedling study

Transect 9 is located at Rivermile 6.6 on a peninsula near the Jonathan Dickinson State Park boat ramp (Figs. 12 and 17). The hydrology of the floodplain in this area has been impacted by the placement of a trail that circles the peninsula. During extreme high tides, the trail acts as a barrier and traps saltwater behind in the wetland system. Elevations across transect 9 range from 9.48 NGVD at the benchmark to a very low area (1.31 NGVD) located adjacent to the river. Between 50 and 70 meters from the upland a quite pronounced hammock area exists. Elevations in the hammock are 1.95-2.05 NGVD and along the trail are 2.01 NGVD while remaining areas in the floodplain are approximately 1.63 NGVD. Distributions of canopy species along transect 9 are shown in Fig. 30. Of the 20 plots on this transect, 17 are lower tidal swamp (LTsw1 and LTsw2). The other 3 plots are upland, hammock, and LTmixed. The most prevalent species in the canopy, shrub and groundcover layers are red and white mangroves in the swamp areas and cabbage palm in the hammock areas. Pond apples in the canopy are rare. They are found predominately in the deeper swamp area at the back of the floodplains and average 7.2cm dbh. Again there is a noticeable difference between the distribution of red and white mangroves. White mangroves are dominant from the toe of the slope out to approximately 160 m. The remaining four plots (160m to 200m) are dominated by red mangrove. Leather fern dominate the shrub layer while water hyssop, leather fern

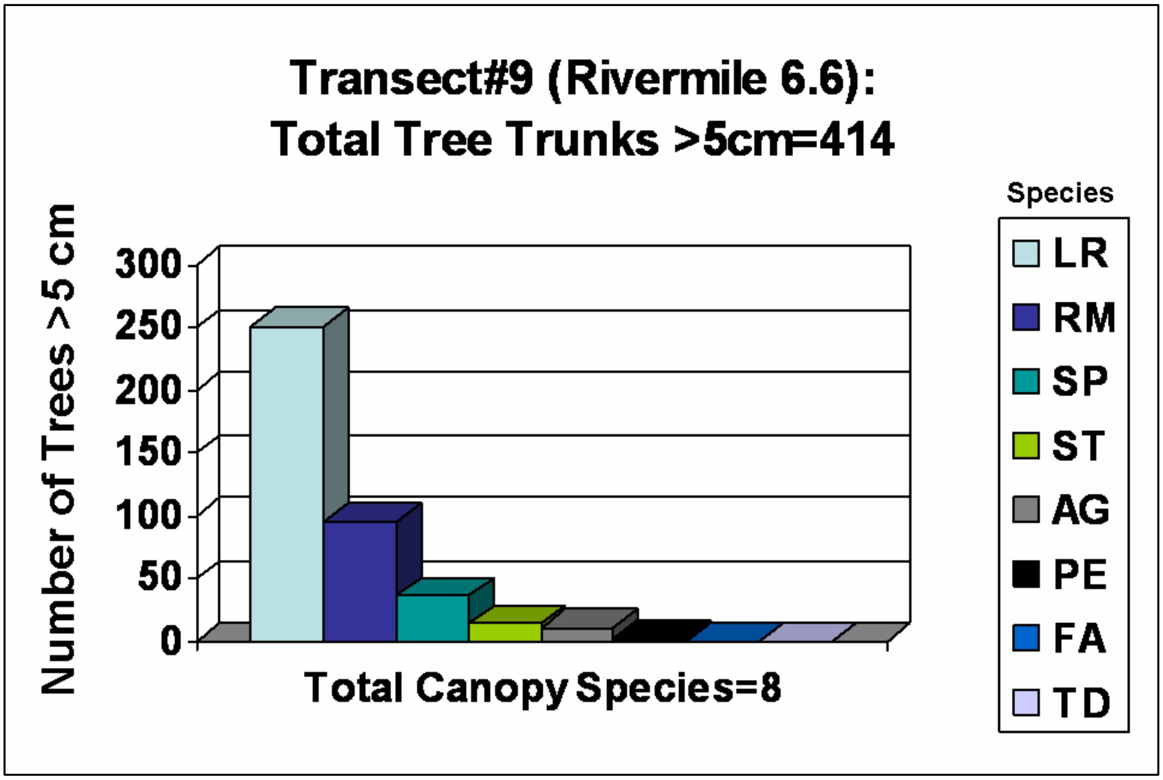


Fig. 30. Canopy species along transect 9 in the Loxahatchee River floodplain.

and rubber vine dominate the groundcover. In August 2004, we returned to this transect to verify forest type determinations and we noted that the majority of the cabbage palms that we had been recorded as alive were now dead. The only remaining live cabbage palms were associated with the trail and the hammock areas. Historically, the canopy on transect 9 was dominated by bald cypress; however, most of these trees are dead now. In his 1967 plant survey of this transect, Taylor Alexander reported live bald cypress at a frequency of 22.2 and a density of 0.39 (14 live and 28 dead). Red and white mangroves were at a frequency and density of 52.8/1.31 and 36.1/2.64 (47 red and 95 white). In addition, Alexander reported the presence of several other freshwater species in small numbers including sawgrass (*Cladium jamaicense*), swamp lily, red bay, pop ash, red maple, and button bush. In a 1975 Jonathan Dickinson State Park survey of 100 bald cypress trees on the peninsula, 71 were dead, 21 were healthy and 8 wer e stressed. In our 2003 survey, there were no live cypress within Transect 9 and red and white mangroves were at a frequency and density of 47/5.79 and 100/12.32. In an April 2004 resurvey of bald cypress on the peninsula, 151 were dead, 7 were stressed and 3 were living. The three living bald cypress are directly adjacent to or on the trail.

VI. Discussion

VI.A. Loxahatchee River Geochemistry

VI.A.1. General - The conservative nature of most of the studied element-salinity plots suggests that physical mixing dominates over any removal or release processes in the Loxahatchee River estuary. Such trends set this estuary apart from many other estuaries, wherein biological and inorganic removal processes directly impact the estuarine distribution of many constituents (Chester, 1999). The concentration profile of suspended particulate matter in the estuary indicate that resuspension of particles is greatest within the tidally-flushed waters of Jupiter Inlet (Noel et al., 1995). To evaluate the physical controls of this system, water mass residence times (i.e., flushing times) and the potential contribution of submarine groundwater discharge in the Loxahatchee River estuary were investigated.

VI.A.2. Biogeochemical estuarine trace element transport - During both discharge conditions, dissolved Si (Figure 31b) concentrations decreased approximately linearly as salinity increased, indicating that physical mixing in the Loxahatchee River estuary prevails over any biological or inorganic removal and supply processes. This observation appears to influence most of the elements studied in this estuarine system. Both the low and high discharge dissolved Fe profiles do not show characteristic removal patterns (Figure 32b) commonly initiated in many estuaries at low salinities (Boyle et al., 1977). Instead, rather typical zero-salinity dissolved Fe concentrations increase linearly with an increase in salinity during both discharge regimes. It is likely that the low observed SPM concentrations contribute to the unusual conservative nature of Fe in this system. In contrast, dissolved Mn concentrations during high discharge decreased systematically from ~350 to 200 nM at salinities < 1 (Figure 32a). However, at salinities > 5, Mn concentrations from both profiles decreased almost linearly as salinity increased. Removal of Mn could be attributed to the removal of oxy-hydroxides within low salinity surface waters (Sholkovitz, 1977).

The concentration of U at the freshwater endmember is significantly lower than the global average value for the world rivers, and this lower concentration suggests possible input from reducing groundwater, i.e., U(IV). The observed low Fe, U and higher Mn concentrations within the freshwater endmember sample is likely controlled by the redox state of the source waters (groundwater and surface runoff). Thermodynamics suggest that the redox sequence of U closely follows Mn and Fe, and hence partially-reduced groundwater could contribute to the observed behavior of Mn, U and Fe in these source waters. Dissolved Sr (Figure 33b), U (Figure 34a) and V (Figure 34b) exhibit an approximately linear increase in concentration with an increase in salinity. Slight deviations in ideal or conservative mixing for these elements are most pronounced during low discharge conditions, when discharge rates of the Loxahatchee River are lower and expected water mass residence times somewhat longer. Of all elements

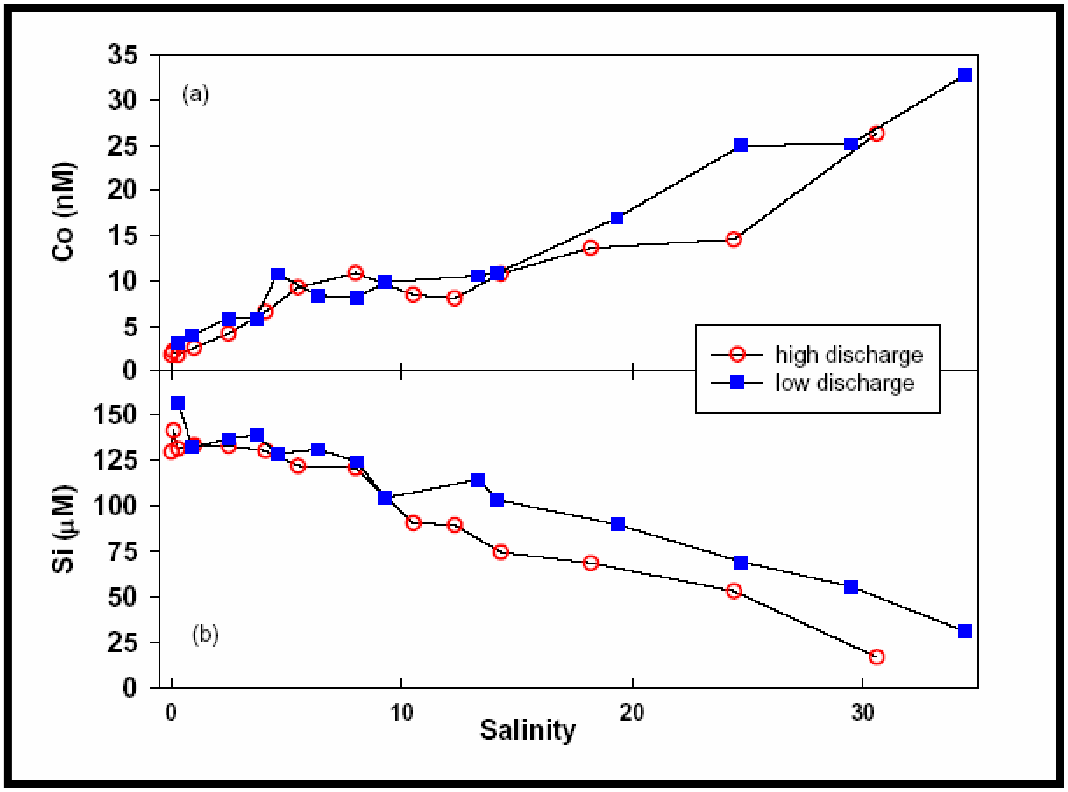


Fig. 31. Salinity versus Cobalt (a) and Silicon (b), for the two sampling periods.

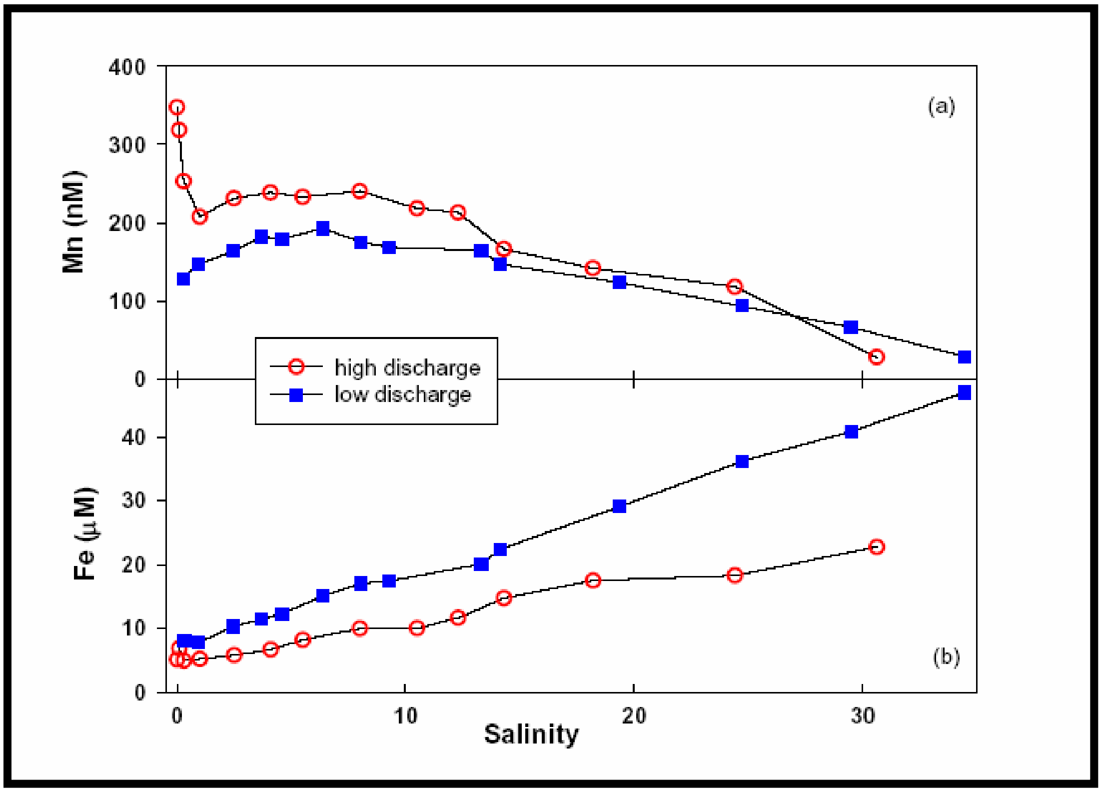


Fig. 32. Salinity versus Manganese (a) and Iron (b), for the two sampling periods.

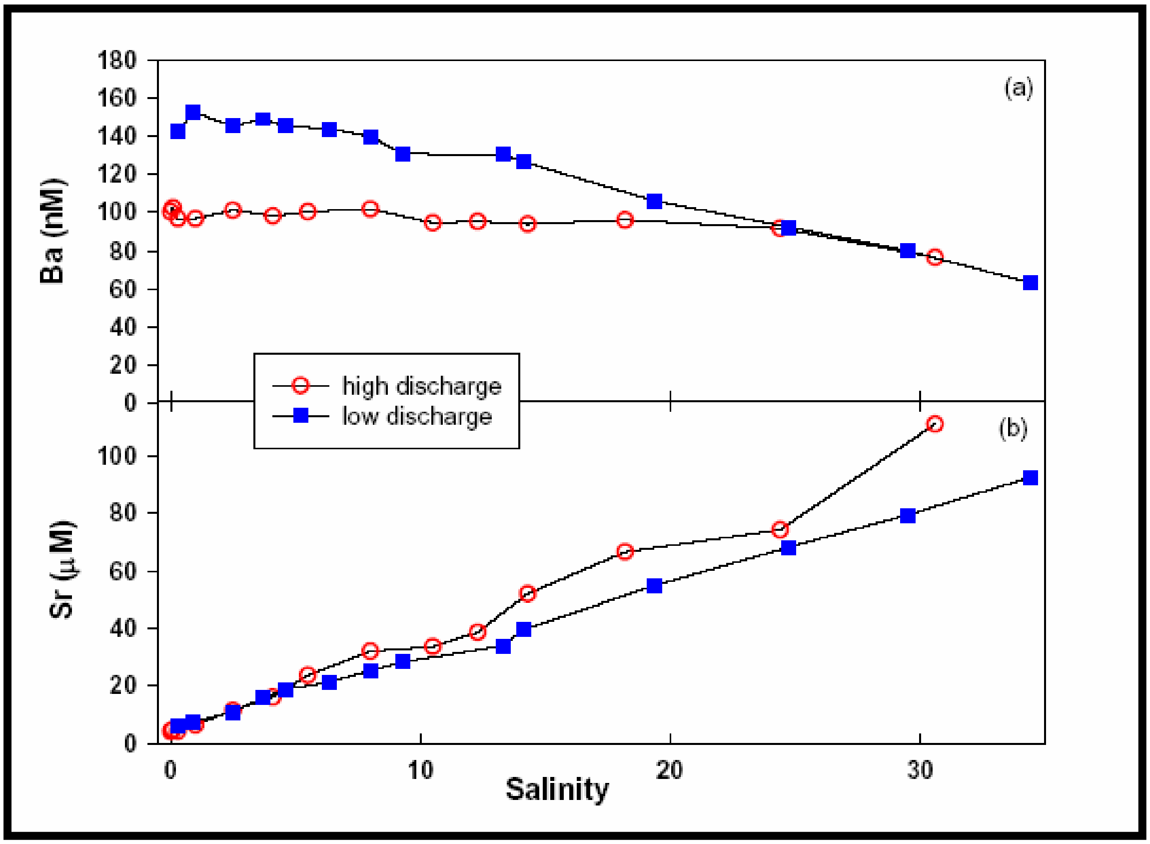


Fig. 33. Salinity versus Barium (a), and Strontium (b), for the two sampling periods.

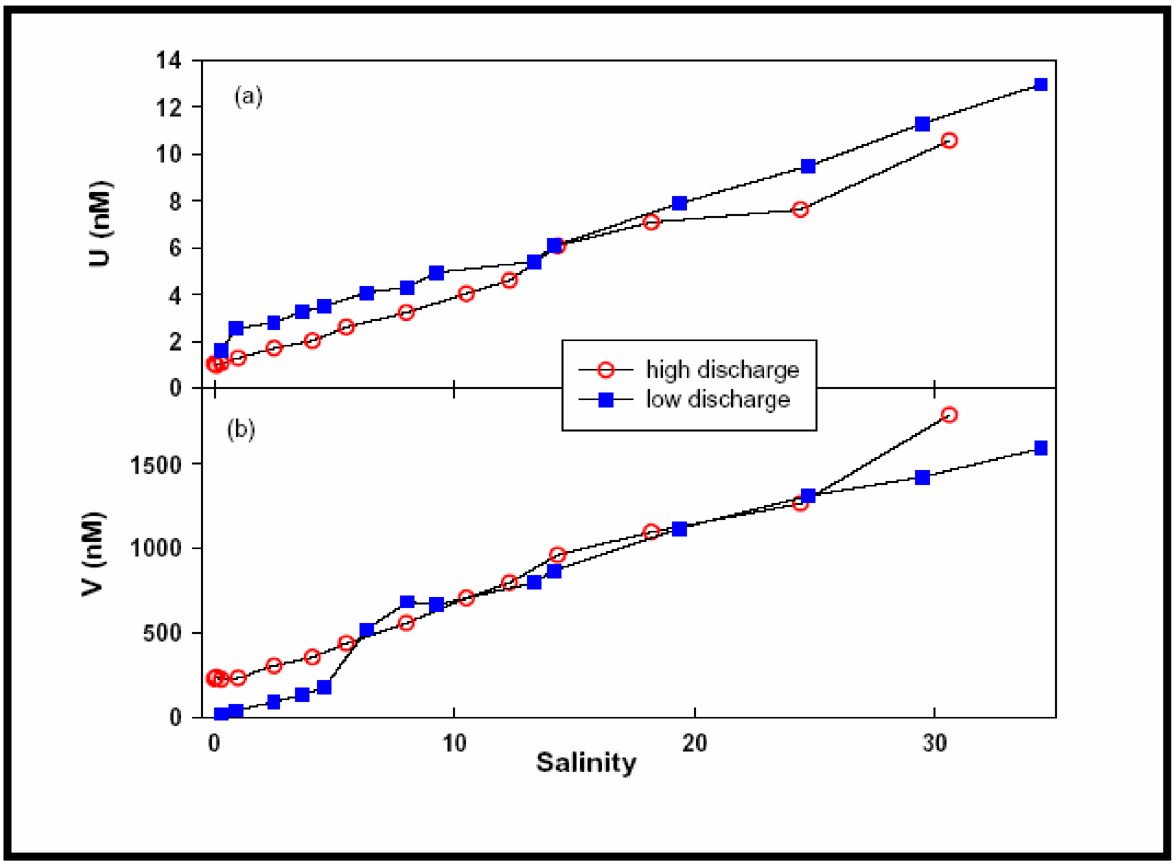


Fig. 34. Salinity versus Uranium (a), and Vanadium (b), for the two sampling periods.

studied, dissolved Ba concentrations (Figure 33a) in the two endmember samples varied the most between the two discharge stages. Cobalt concentrations (Figure 30a) were lowest (2-3 nM) in the fresh-watersurface samples and increased to above 30 nM in the most saline samples. The general absence of Co in the head waters of this river system implies that the source waters, which may be a composite of reduced groundwater and surface runoff, are still not notably impacted by the rapid and wide-spread development adjacent to the Loxahatchee River watershed.

Dissolved organic carbon (DOC) concentrations show similar decreasing trends with respect to an increase in salinity for both river discharge conditions (Figure 19b). DOC in the freshwater endmember samples ranged from ~1000 μM (low discharge) to ~1200 μM (high discharge), and decreased in concentration to just above 100 μM at the high salinity (34.42) endmember (low discharge). Observations in non-linear estuarine DOC mixing were most pronounced during both discharge regimes at salinities between 0 and 15. DOC values in the upper Loxahatchee River estuary are elevated considerably relative to 'average' DOC values for small streams (Thurman, 1985). In spite of the general paucity of suspended particulate matter present in the estuarine water column, the observed decrease in DOC concentrations with an increase in salinity may be attributed to the classic removal of terrestrial dissolved organic matter (i.e., aggregation, coagulation) during estuarine transport.

VI.B. Groundwater Flux in Loxahatchee River

VI.B.1. Ra-derived estuarine water mass ages – The construction of a Ra-derived groundwater flux model for the Loxahatchee River and its estuary, which builds upon a mass balance of source and removal terms, relies on the derivation of an accurate estuarine residence time. The residence time of a water parcel transported through an estuary, T_r, can be defined as a composite of various physical parameters such as the hydraulic gradient, the rate and seasonality of stream flow, the tidal range and amplitude, as well as anthropogenic demand on coastal fresh water resources. Such a residence time can be calculated using either physical (Pilson, 1985) volume and area estimates (i.e., tidal prism) or isotopic tracers (Charette et al., 2001). In the Loxahatchee River estuary, the residence time of water calculated using a best-estimate for the tidal prism volume (tp_{vol} = 3.98 x 10^6 m^3; McPherson et al., 1982), the surface volume (6.29 x 10^6 m^3) and the tidal period (tp_{er} = 1.9 d^{-1}) is less than one day, ~0.8 d. Such a short residence time confirms the energetic exchange that occurs through Jupiter Inlet, and implies rapid estuarine flushing rates into the Atlantic Ocean.

To alternatively calculate T_r values using Ra isotopes, an approach that compares excess isotopic ratios (^{224}Ra/xs^{228}Ra) in surface waters to such ratios in groundwater can be expressed as (after Moore, 2000; Charette et al., 2002):

$$[^{224}\mathrm{Ra/xs}^{228}\mathrm{Ra}]_{estu} = [^{224}\mathrm{Ra/xs}^{228}\mathrm{Ra}]_{gw} e^{-\lambda_{224} T_r} \quad (1)$$

Where $[^{224}Ra/xs^{228}Ra]_{estu}$ represents the observed activity ratio of the estuarine sample, $[^{224}Ra/xs^{228}Ra]_{gw}$ the average activity ratio in groundwater, and λ_{224} is the decay constant for ^{224}Ra, 0.1894 d^{-1}. Excess Ra activities are calculated here by simply subtracting an oceanic endmember activity (e.g., 228Ra = 6.71 dpm 100 L^{-1}) from the observed activities. Rearranging Eq. 1 allows one to solve for T_r:

$$\mathbf{T_r = \ln[(^{224}Ra/xs^{228}Ra)_{gw} - (^{224}Ra/xs^{228}Ra)_{estu}] / \lambda_{224}} \quad \mathbf{(2)}$$

For each station, a residence time was calculated based on Eq. 2 using average $(^{224}Ra/xs^{228}Ra)_{gw}$ values of 2.63 (high discharge) and 2.58 (low discharge). The range in calculated residence time estimates spans from ~0.44 to 1.39 days, for both sampling efforts. Such individual residence time estimates were averaged to yield composite estuarine T_r rates of 0.97 d and 0.83 d for high and low flow conditions, respectively, which are in close agreement with those calculated via the tidal prism method. Calculated residence times are shorter at the high salinity samples for both sampling efforts and suggest that such a technique might be sensitive enough to resolve local fluctuations in the estuarine flushing efficiency.

VI.B.2. Ra-derived groundwater discharge - To quantify the role of groundwater discharge to the Loxahatchee River and its estuary, an equation can be written that identifies known source terms of Ra in an estuary. The calculated activity of Ra_c may thus be defined as the sum of the fractional contribution of Ra present in seawater (Ra_s), river water (Ra_r), as well as the fractional contribution of Ra desorbed from riverine particulates (Ra_{des}) (Krest et al., 1999; Kelly and Moran, 2002):

$$\mathbf{Ra_c = f(Ra_s) + (1-f)(Ra_r) + ((1-f)Ra_{des})(1-e^{[-S_{estu}/\xi]})} \quad \mathbf{(3)}$$

Here, S_{estu} denotes the sample salinity, and ξ represents the salinity at which the particulate-bound Ra activity is thought to be reduced to e^{-1} of its initial activity due to a change in ionic strength; salinity = 5‰ (Krest et al., 1999; Kelly and Moran, 2002). In Eq. 3, the term *f* represents the fractional contribution of a sample's salinity derived by the seawater and freshwater endmembers (Krest et al., 1999) as follows:

$$\mathbf{f = (S_{estu} - S_r) / (S_{sea} - S_r)} \quad \mathbf{(4)}$$

where S_{sea} and S_r represent seawater and freshwater endmember salinities, respectively. Applying Eq. 4, one can quantitatively evaluate the relative contribution of each of the Ra source terms against observed Ra distributions. In general, such calculated activities are consistently less than observed activities present in the estuary for all four Ra isotopes, which suggests that either Ra is being actively advected into the estuarine water column by groundwater discharge, and/or, Ra production via the decay of parent Th ubiquitously-present in bottom sediment contributes substantially to the estuarine Ra mass balance.

To demonstrate that the production or regeneration rate of Ra within Loxahatchee River estuary bottom sediments is a minor contributor to the overall Ra mass balance, we collected six bottom sediment samples (3 sites per cruise) from sites within the entire estuary (salinity 0 to 34‰) that represent the spectrum of geologic strata present in this estuary. An average production rate of ^{226}Ra, derived from the disequilibrium between ^{226}Ra and its immediate parent, 230Th ($t½ = 1.4 \times 10^{10}$ yr), and integrated over the entire Loxahatchee River estuary area was calculated to be 1.45 x 104 dpm d^{-1}. Such a calculation assumes that ~75 % of the sediment-bound Ra is available for desorption and subsequent transport into estuarine waters (Rama and Moore, 1996). By deriving estimates for Ra_c, T_r and Ra_{des}, one can then establish an equation the describes that mass balance of excess 226Ra in the estuary (Charette et al., 2001; Kelly and Moran, 2002) as follows:

$$\mathbf{^{226}Ra_{\mathit{xs}} = [(^{226}Ra_{\mathit{ave}} - {}^{226}Ra_{\mathit{sea}}) *V_{\mathit{estu}} / T_{\mathit{r}}] - [^{226}Ra_{\mathit{r}} *Q_{\mathit{r}}] - [^{226}Ra_{\mathit{des}} *A_{\mathit{estu}}]} \quad \textbf{(5)}$$

where $^{226}Ra_{ave}$ is the average measured activity in the estuary, $^{226}Ra_{sea}$ is the activity in the adjacent Atlantic Ocean that can be tidally-exchanged through Jupiter Inlet, T_r is the Ra-derived estuarine residence time calculated from Eq. 2, V_{estu} and A_{estu} are volume and area estimates for the estuary, respectively (Russell and McPherson, 1984), Q_r is the river discharge rate, and $^{226}Ra_{des}$ is the calculated estuarine-wide regeneration rate of ^{226}Ra from bottom sediments.

The calculated estuarine $^{226}Ra_{xs}$ activity or removal flux using Eq. 5 ranged 2.89 x 10^8 to 6.37 x 10^8 dpm d^{-1}, during high and low river discharge conditions, respectively. To confirm such estimates, one can also calculate such estuarine removal flux estimates using tidal prism characteristics for the Loxahatchee River estuary and calculated Ra_{xs} values (Kelly and Moran, 2002), such that:

$$\mathbf{Ra_{\mathit{xs}} = Ra_{\mathit{obs}} - Ra_{\mathit{c}}} \quad \textbf{(6)}$$

where Ra_{obs} represents the observed estuarine Ra activities and Ra_c the calculated activities, after Eq. 3, and,

$$\mathbf{^{226}Ra_{\mathit{xs}} = [Ra_{\mathit{xs}} *t_{\mathit{per}} *tp_{\mathit{vol}} *10]} \quad \textbf{(7).}$$

In Eq. 7, $^{226}Ra_{xs}$ is expressed as a function of the tidal prism volume *(tp_{vol})*, the tidal period *(t_{per})* and the calculated excess Ra present in the estuarine water column, and ranged from 0.13 to 3.48 x 10^8 dpm d^{-1}, during both low and high discharge, respectively. During high-flow conditions, the two independent methods provide removal flux estimates that are in close agreement. Slight differences in the two calculated removal flux estimates during low discharge are likely influenced by the lower ^{226}Ra activities observed at salinities between 0.92 to 3.69‰. Such results validate some of the inherent assumptions in these groundwater discharge techniques, which imply, for example, that the Ra-derived residence times are truly representative of the entire estuary, or that the endmember Ra activities (including ground-water activities) are reasonably constant for the entire duration of the sampling effort.

To quantify the rate of groundwater discharge for the Loxahatchee River estuary, the estuarine removal flux estimate derived using Eqs. 5 or 7 is assumed to be in steady-state with respect to the groundwater input. Therefore, one can calculate an estuarine-wide groundwater discharge rate, as follows,

$$\boldsymbol{SGD} = \mathbf{(^{226}Ra_{\mathit{xs}}/^{226}Ra_{\mathit{GW}})} \quad \textbf{(8)}$$

where $^{226}Ra_{GW}$ represents an average groundwater ^{226}Ra activity per sampling cruise. Based on the tidal prism approach (Eq. 7), the Ra-derived input of groundwater to the estuary (Table 12) during high discharge conditions ranged from 6.00 x10^3 – 4.27 x 10^5 m^3 d^{-1}, while the Ra-derived residence time method produced a rate of groundwater discharge that varied from 6.05 x10^3 – 3.70 x 10^5 m^3 d^{-1}. In comparison, by applying a simple mass balance approach to derive a $^{226}Ra_{xs}$ estimate (i.e., Eq. 5), the calculated groundwater discharge varied little with a change in discharge stage: 3.55 x 10^5 m^3 d^{-1} and

Table 12. Radium-derived, and electromagnetic (EM) seepage meter-derived groundwater discharge (GD) rate estimates for the Loxahatchee River estuary, per river discharge (season).

Season	GD Tidal Prism (m^3 d^{-1})	Ra-Derived GD Residence Time (m^3 d^{-1})	GD Residence Time (m^3 d^{-1})	EM Seepage Meter (m^3 d^{-1})	Average GD Rate (m^3 d^{-1})
High Discharge (September 2003)	4.27E+05	3.70E+05	3.55E+05	8.86E+04	3.84E+05
Low Discharge (March 2004)	6.00E+03	6.05E+03	2.97E+05	n/a	1.03E+05

2.97 x 10^5 m^3 d^{-1}, during high and low flow conditions, respectively. Overall, the magnitude of such groundwater discharge rate estimates compare favorably with the Ra-derived SGD flux (3 x 10^6 m^3 d^{-1}) to the South Atlantic Bight region (Moore, 1996), or the single submarine vent feature of Crescent Beach Spring, FL (Swarzenski et al., 2001). For comparison, Hussain et al. (1999) computed a ^{222}Rn-derived SGD rate for the entire Chesapeake Bay system to be about 17 x 10^6 m^3 d^{-1}. While these estimates are difficult to compare without normalizing the data to a specific geographic area, average Loxachatee River estuarine SGD rates calculated here (20 – 75 L m^{-2} d^{-1}) fall well within the range (6 – 500 L m^{-2} d^{-1}) of values observed in the literature (Kim et al., 2001).

VI.B.3. Groundwater recharge estimates - One can independently evaluate the accuracy of such Ra-derived groundwater discharge rates using simple surficial aquifer parameters to estimate groundwater recharge for the Loxahatchee River watershed. The assumption for such a comparison is that the total volume of precipitation (PR) per unit time interval in the watershed available for recharge is a function of:

$$\mathbf{P_{\mathit{R}} = [\Sigma \mathit{P} * \varphi * A_{\mathit{w}}] / d} \qquad \textbf{(9)}$$

where ΣP is the cumulative precipitation to the watershed (0.5207 m), φ is a dimensionless term that incorporates evapotranspiration and surface water runoff (0.60 – 0.85; B. McPherson, pers. communication), A_w defines the watershed area (5.44 x 10^8 m^2) and d represents the defined time interval (in this case 212 days). By applying the range in φ values, an average PR value or ground-water recharge rate to the Loxahatchee river estuary is estimated to be 1 x 10^6 m^3 d^{-1}. In spite of the inherent simplicity in such calculations, it is encouraging that this recharge estimate is slightly greater than the average Ra-derived ground-water discharge rate. The difference in these two flux estimates may be due to some small component of groundwater that discharges directly into the Loxahatchee River estuary from a deeper aquifer.

VI.B.4. Electromagnetic seepage meter measurements - In order to validate the calculated Ra-derived submarine groundwater discharge rates for this estuary, we also deployed an autonomous electromagnetic (EM) seepage meter (Rosenberry and Morin, 2004; Swarzenski et al., 2004) at the confluence of Kitching Creek and the Loxahatchee River estuary, close to 12 km upstream from Jupiter Inlet (Fig. 11). An advantage of such an automatic instrument is that the wide range of bi-directional sediment/water interface exchange rates that can be measured rapidly and precisely can provide a precise, although very point-specific, groundwater/surface water exchange rate. There are well-known limitations in the accuracy and interpretation of some manual seepage meter results (Lee, 1977; Tanaguchi and Fukuo, 1993), and these can potentially be identified and minimized using autonomous instruments such as the EM seepage meters. Nonetheless, seepage meter results should be interpreted cautiously, as here in this system they record groundwater/surface water exchange conditions at only one site. For a 2-day deployment in September 2003, a 10-min. averaged SGD rate of 1.71 cm d^{-1} yielded an estuarine-wide upward submarine ground-water discharge rate of ~ 0.9 x 10^5 m^3 d^{-1}; a value very close in magnitude to the Ra-derived estimate. Thus, it appears that two independent techniques provide at least a first-order, reliable estimate of submarine ground-water discharge for this estuary. Observed variations in the calculated estimates of submarine ground-water discharge from these two very different techniques may result from the EM seepage work being only from one site in the estuary, while the Ra-derived estimates incorporate data that was derived from samples collected across the entire salinity gradient.

VI.B.5. Surface water Rn-222 activities - It has been repeatedly shown that ^{222}Rn ($t_{1/2}$ = 3.8 d) activities, when measured in surface waters, may provide useful insight into rates and magnitudes of groundwater/surface exchange (Cable et al., 1996; Corbett et al., 1999; Burnett et al., 2001, Burnett and Dulaiova, 2003, Oliveira et al., 2003; Lambert and Burnett, 2003; Purkl and Eisenhauer, 2004). To evaluate the contribution of groundwater discharge to the Loxahatchee River estuary using ^{222}Rn as a tracer, we surveyed the surface water column using six commercial radon detectors, plumbed in parallel through one air/water exchanger (Burnett et al., 2001; Burnett et al., 2003; Swarzenski et al., 2004). These new techniques have greatly simplified the collection and subsequent detection of Rn, such that one now can obtain almost real-time excess ^{222}Rn activities *in situ*.

From a river survey initiated close to the Atlantic Ocean at Jupiter Inlet, ^{222}Rn activities increased rapidly from near-background activities (~2.5 dpm L^{-1}) to values in excess of 28 dpm L^{-1} in the

Loxahatchee River close to the Kitching Creek confluence (Figure 23). The near-symmetrical shape of the Rn profile as a function salinity or distance from Jupiter Inlet suggests that submarine ground-water discharge occurs prevalently in the headwaters of the river system, and that the short residence time within the estuary (< one day) and the ubiquitous nature of SGD upstream, appear to offset any expected tidal control on SGD rates. The ^{222}Rn profile in the Loxahatchee River estuary very clearly demonstrates the utility of this tracer to identify specific regions of a river/estuary that are active sites of submarine groundwater discharge.

VI.B.6. Subsurface streaming resistivity profiling measurements - Streaming resistivity profiling techniques were used in the Loxahatchee River estuary to investigate subsurface fresh water/saltwater interface dynamics in light of the enriched ^{222}Rn activities in the source waters of the Loxahatchee River. One example of an inverse modeled streaming resistivity profile result from the June 2004 survey is shown in Fig. 35; a) depicts a East-West transect line close to Jupiter Inlet, while b) illustrates a transect line upstream in the vicinity of the Kitching Creek/Loxahatchee River confluence. Sediments that are saturated in freshened interstitial water masses generally have higher resistivity ranges (up to 20 Ω m), while more saline interstitial waters would correspond to lower resistivity values. If one assumes (as a first approximation) that the sediments underlying the Loxahatchee River estuary are homogenous in composition, and that down-core porosity is held constant, then an observed shift towards higher resistivity would imply freshened pore waters. Such streaming resistivity results clearly show that the sediments underlying the Loxahatchee River estuary reflect the dynamic nature of the freshwater/saltwater interface; upstream at Kitching Creek, the sediments show little influence of saltwater, while in the vicinity of Jupiter Inlet, the sediments are largely seawater-saturated.

VI.B.7. Groundwater-derived nutrient fluxes - The delivery and potential diagenetic transformation of select nutrients during submarine ground-water discharge may negatively impact coastal ecosystems (Howes and Weiskel, 1996; Harvey and Odum, 1990; Giblin and Gaines, 1990; Krest et al., 2000; Gobler and Sandu-Wilhelmy, 2001; Crotwell and Moore, 2003; Slomp and Cappellen, 2004). For example, N and P concentrations are often elevated in coastal groundwater relative to river water, and the stoichiometry of N:P in submarine groundwater most often diverges drastically from the Redfield ratio (16:1) (Capone and Bautista, 1985; Lapointe et al., 1990; Valiela et al., 1990; Weiskel and Howes, 1992; Gallagher et al., 1996; Corbett et al., 1996,1997; LaRoche et al., 1997; Herrera-Silveira, 1998; Miller and Ullman, 2004). By applying our calculated Ra-derived submarine groundwater discharge rate estimates, one can evaluate the groundwater-derived nutrient inputs to the Loxahatchee River estuary per discharge period (Table 13), using average ground-water nutrient concentrations. We used NH_4^+ and PO_4^{-3} values representing a composite average (n > 50) per river discharge stage that were collected from a series of vertical porewater sites in the Loxahatchee River floodplain along a series of transects (1,3,6,7,

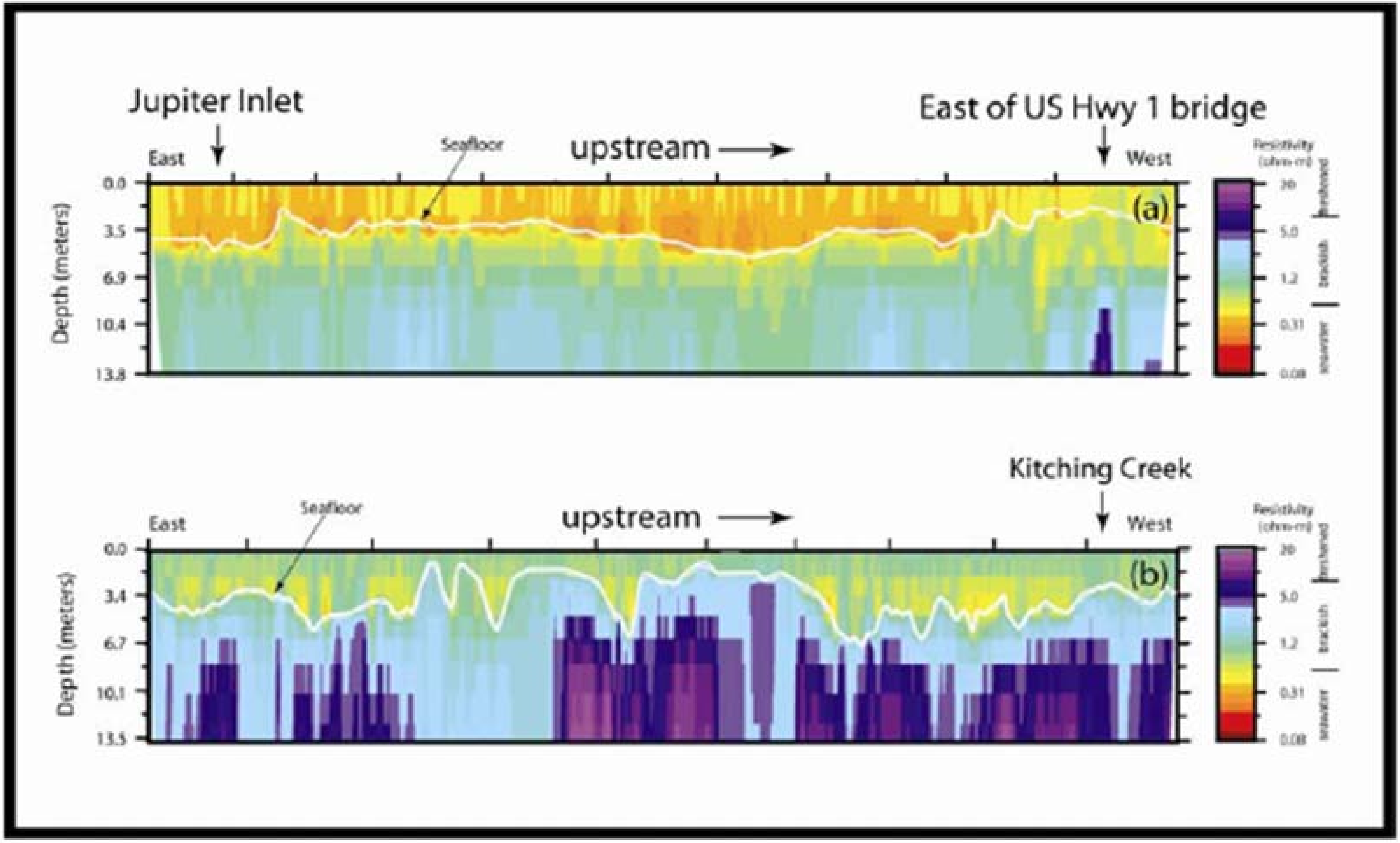


Fig. 35. A comparison of two modeled streaming resisitivity profiles, one proximal to Jupiter Inlet in a saline environment (a), and one close to the confluence of Kitching Creek and the Loxahatchee River (b).

Table 13. Radium-derived fluxes of nutrients (NH_4^+, PO_4^{3-}) to the Loxahatchee River estuary, per river discharge (season).

Season	**Average Ammonium (mmol m^{-3})**	**Average Phosphate (mmol m^{-3})**	**Average GD[1] rate (m^3 d^{-1})**	**Flux Ammonium (mmol d^{-1})**	**Flux Phosphate (mmol d^{-1})**	**Flux Ammonium (kg d^{-1})**	**Flux Phosphate (kg d^{-1})**
High Discharge (September 2003)	14.34	5.11	3.84E+05	5.51E+06	1.96E+06	99.34	186.21
Low Discharge (March 2004)	4.86	2.56	1.03E+05	3.25E+05	3.58E+05	5.86	34.02

[1]GD = Groundwater Discharge

and 9), as discussed earlier in this report. The floodplain porewater nutrients likely represent a significant fraction of the total nutrients discharged into the Loxahatchee River system from groundwater, given the large size of the floodplain compared to the river channel. However, the floodplain porewater does not represent the only source of subsurface nutrients to the river and estuary, and we have no data, for example, for nutrient concentrations in river bottom sediment porewater. Thus, the nutrient discharge estimates calculated here represent only the estimated discharge from groundwater sourced within the floodplain.

From such porewater values, the average NH_4^+ concentration ranged from 4.86 to 14.34 mmol m^{-3} during low and high discharge, respectively, while PO_4^{-3} ranged from 2.56 to 5.11 mmol m^{-3}, respectively. Multiplying these average nutrient concentrations by seasonally-averaged SGD rates, yields daily NH_4^+ fluxes into the estuary that range from 0.33 – 5.51 x 10^6 mmol (6.3 x 10^1 – 1.1 x 10^3 µmol m^{-2} d^{-1}), depending on the river discharge stage. The flux of PO_4^{-3} similarly ranged from 0.36 – 1.96 x 10^6 mmol (6.9 x 10^1 – 3.8 x 10^2 µmol m^{-2} d^{-1}) per day, during low and high discharge, respectively.

Such estimates for nutrient transport into the Loxahatchee River estuary may be compared to other SGD-influenced coastal waters. For example, in Waquoit Bay, MA, Charette et al. (2001) observed a SGD- derived DIN (NO_3^- + NH_4^+) flux of about 550 µmol m^{-2} d^{-1}. In a recent review of SGD-enhanced nutrient transport, Slomp and Capellen (2004) report that the range in N-flux extends from 160 µmol m^{-2} d^{-1} off Hawaii (Garrison et al., 2003) to 72,000 µmol m^{-2} d^{-1} in a small estuary off New England (Portnoy et al., 1998). Comparable SGD-derived P-flux estimates are much more infrequent, and range from <1.0 µmol m^{-2} d^{-1} in Florida Bay (Corbett et al., 1999) to 900 µmol m^{-2} d^{-1} off North Inlet, NC (Krest et al., 2000). The range in reported nutrient flux estimates reflects the underlying geology as well as potential anthropogenic perturbations.

VI.C. Water Chemistry - Loxahatchee River Floodplain

Perhaps the factor of most interest in the surface and pore water data is the presence of high ionic strength water at depth in the sediment pore water at most sites. At the beginning of this study, it was hypothesized that the loss of freshwater vegetation (notably Taxodium) and replacement by mangrove swamp forest along portions of the Loxahatchee River was due to saltwater intrusion up the river. This saltwater intrusion was thought to be a result of the opening of Jupiter Inlet, and net decreased freshwater flow within the Loxahatchee River watershed resulting from urbanization and development. Saltwater intrusion was visualized as occurring by saltwater movement up the river, and surface overflow into the floodplain. However, this is not what is observed. While it does appear that high ionic strength water is observed as far upstream as Transect 3, this water appears at depth in pore water, not at the surface. Even at the most downstream location (transect 9), more saline water appears at depth. The high ionic strength water at depth cannot be a result of evaporative concentration during the dry season, because of the high sulfate concentrations. Sulfate resident for a period of time would be quickly reduced by microbial sulfate reduction to sulfide, under the anoxic conditions present in the sediments. The high sulfate levels at depth, therefore, suggest a continuous source of new sulfate from below. Two possibilities might explain the more saline water at depth in the floodplain pore water: (1) saltwater moving upstream as a saltwater wedge through the permeable sand underlying the surficial sediments, and (2) high ionic strength groundwater in the floodplain. The difficulty with the groundwater explanation is that the groundwater from upland wells (e.g. wells at the upland edge of the floodplain) has very low ionic strength. Thus, results from the brief floodplain study suggest that saltwater is moving upriver at depth in a kind of tidal wedge, with less dense fresher water at the surface. However, this result is not definitive, and further study of this is needed.

Preliminary nutrient results from the floodplains showed that primary production may be N-limited rather than the more usual P-limitation (see section V.B.6). The relatively low N/P values may reflect both denitrification within the floodplain sediments and a source of excess P within the system. In general, the major limiting factor in riparian ecosystems is the physical stress of inadequate root oxygen during flooding rather than an inadequate supply of minerals (Spink and Rogers, 1996). Nitrate levels along Transect 1 were relatively low ($<10 \mu g/l$), while phosphate levels were high (exceeding 1,300 μg/l in some intervals).

Cations and anions showed overall large differences among the different transects. Upriver transects (Transects 1, 3, and 7) had cations dominated by calcium and anions dominated by alkalinity (probably predominantly bicarbonate). In contrast, downstream Transects 6 and 9 had cations dominated by sodium and magnesium, and anions dominated by chloride, and to a lesser extent sulfate. There was a net cationic charge deficit at all sites, in pore water and surface water, and in both the wet and dry season. For example, Transect 1 surface water had average anionic charge of about 4.24 and 6.69 meq/l in the wet and dry seasons, respectively, but average cationic charge of only 3.26 and 3.95 meq/l in the wet and dry seasons, respectively. Pore water along Transect 1 had average anionic charge of 6.32 (wet season) and 12.4 (dry season) meq/l, compared to average cationic charge of 5.23 (wet season) and 7.98 (dry season) meq/l. Similar anionic/cationic charge imbalances were observed along other transects for the measured species. There are several possible explanations for the observed charge imbalance, including excess cationic charge in absorbed species on the solid phase, and cationic species (e.g. iron) not measured in this study.

VI.D. Sediment Geochemistry - Floodplain

Sediments in the Loxahatchee River floodplain vary from an organic matter-rich soil, to a true peat progressing downstream. This organic matter-rich soil/peat overlies sand, and varies in thickness from 30 cm to nearly 100 cm, depending on the Transect and location. The downstream locations (Transects 6, 7, and 9) generally have thicker and more organic matter-rich soil/sediment overlying the underlying sand, reflecting the twice daily tide effects at these transects. The more upriver transects (1 and 3) do not experience twice daily tidal inundation in the floodplain. The floodplain along the upriver transects have virtually no surface water present during the November-May dry season, and the soils here thus are more subject to oxidation of deposited organic matter.

Concentrations of TC, OC, TN, TP and TS in soils/sediments along Transects 1, 3, and 6 generally decrease with increasing depth, reflecting both an increase in admixed mineral matter (sand, silt, clay), and microbial decomposition of deposited organic matter (Appendices C and D). The more peat-like deposits along Transects 7 and 9 show unsystematic profiles of TC, OC, TN, TP, and TS concentrations with increasing depth, largely reflecting differential influx of mineral matter material deposited from the river. Subsurface peaks in TS observed at some sites likely reflect deposition of sulfide mineral phases (monosulfides, and disulfides), and reaction of sulfide with organic matter to form organic sulfur compounds. The deposition of the sulfide mineral phases and formation of organic sulfur phases at depth in these soils/sediments appear to be driven by high ionic strength water containing sulfate at depth in pore water. Under the generally anoxic conditions present, microbial sulfate reduction produces sulfide as a metabolic byproduct, and the reactive sulfide may form the sulfide mineral and organic sulfur compounds contributing to the high TS in the soils/sediments. This production of TS from high levels of sulfate and sulfide in deep pore water was observed as far north as Transect 3.

VI.E. Water Levels, Water Quality and Vegetation Changes in the Floodplain

Three distinct reaches (riverine, and upper and lower tidal) and four major forest community types (swamp, bottomland hardwood, hammock, and uplands) were identified on the floodplains of the Northwest Fork of the Loxahatchee River (SFWMD, 2002). Riverine floodplain communities were predominately bald cypress and bald cypress/pop ash swamps with mixed areas of low bottomland hardwood and hammock. Younger subcanopies were present in disturbed areas and were evident by their smaller trunks (i.e. diameter at breast height). In impacted areas where large trees were historically logged, it appears that bald cypress are being replaced by pop ash and bottomland hardwood species that require shorter hydroperiods and are faster growing. Very few bald cypress seedlings or saplings are noted in the shrub and groundcover of the riverine reach. This could be a factor of light availability, low nutrients, or the age of the trees.

The Comprehensive Everglades Restoration Plan (North Palm Beach County) calls for the improvement of the quality, quantity, timing, and distribution of water delivery to the the NW Branch (Fork) of the Loxahatchee River in order to enhance and restore the remaining ecosystem. For restoration and enhancement measures in this reach, the goal is to promote the sustainable health of the existing forest types (including canopy, subcanopy, and groundcover components of the community), and target species by improving wet and dry season hydrological conditions and reducing sedimentation. In the future, the riverine reach will require new canopy recruitment to replace the older generation of deciduous trees. Future community composition of the shrub and ground cover species in the swamp habitats will likely reflect the improved hydrological conditions. Transitional and upland species should be reduced and or eliminated from the swamp habitat areas.

Upper tidal floodplain communities are dominated by mixed swamps and hammock. Although bottomland hardwood indictor species were present, distinct areas of bottomland hardwood were not present probably due to the lack of topographical change and low existing elevations. Hammock and bottomland hardwood species are adapting to this ecosystem by growing on hummocks, cypress stumps and fallen logs. Where present on the riverine plots, bald cypress comprised most of the canopy with pop ash and pond apple present as subcanopy. Canopy in the upper tidal plots were comprised of predominantly pond apple and red and white mangroves. Bald cypress and pond apple seedlings and saplings were noted in the shrub and ground cover vegetation of the upper tidal reach. With regards to restoration and enhancement measures in the upper tidal reach, the goal of the Restoration Plan would be to promote the increase in abundance and distribution of freshwater forest species in the canopy, subcanopy, shrub and groundcover components of the floodplain community and reduce the spread of mangroves and exotic plant species.

In the lower tidal floodplain communities the canopy was composed of mostly red and white mangrove, depending on elevation. There was no evidence of freshwater seedling/sapling production in the lower tidal areas, with the exception of pond apple, which appears to be salt tolerant. Therefore, reducing salt concentrations and increasing freshwater inundation will likely promote healthier sustainable habitats within the swamp and hydric hammock areas. Reducing the recruitment of new individuals of mangrove and controlling exotic species may also assist in establishing sustainable swamp and hydric hummock habitat.

The dominant canopy species (exotic and native species) are listed in Table 11. The native species reflect those species that represent best restoration targets for each forest community. Their current abundance is expressed in the vegetation transect histograms in Figs 25-29. Bald cypress would typically be the dominant species with some pop ash in the swamp communities. Low bottomland hardwood communities would typically be dominated by red maple, buttonbush, swamp bay, and Carolina willow, while high bottomland hardwood would be dominated by water hickory, laurel oak, dahoon holly and cocoplum. Hydric hammock communities should be dominated by cabbage palm with some wax myrtle, live oak, and red bay.

Enhancement and restoration in the upper and lower tidal reaches would include predominantly bald cypress and pond apple in the swamp areas and cabbage palm in the hydric hammock areas. Pop ash, red maple, Carolina willow and other freshwater canopy species should increase their recruitment in areas where there are higher elevations, hummocks, old cypress stumps, or fallen logs. As these species slowly return to the canopy, mangroves would occupy the subcanopy layer as currently exhibited in the floodplains of lower Kitching Creek.

One of the major concerns for restoration and enhancement in the riverine reach of the Loxahatchee River is the effect of no or little water flowing across the floodplains during peak growth periods when water and nutrients are needed for tree growth and seed production. To address this need restoration could include enhanced freshwater flow and inundation of riverine swamps and bottomland hardwoods during the annual growth season (June-October) in an average year.

In examining the restoration of preferred freshwater forest types within the tidal reaches, it is important to note that mangroves can survive as communities in freshwater environments according to the literature. Therefore, we would not expect to see a die-off of mangroves, if salinities were lowered and freshwater flows were increased across the floodplains. However, reductions in mangrove growth have occurred in the past as a result of freezes and/or damage from hurricanes.

Of particular concern regarding restoration in the tidal reaches of the river is the current and future distribution of white mangrove. This species appears to overlap the preferred elevations of pond apple communities. On the Loxahatchee River, we noted that most white mangroves are single trunk with limited branches while most pond apples are multi-trunk. These adaptive strategies appear to be directed at maximizing light availability for white mangrove and maximizing root structure for pond apple. On several transects, it appears that white mangroves are shading out the older pond apple communities, although the growth of pond apples may also be stunted by saline water and soils.

One of the major concerns regarding restoration in the tidal floodplains of the Northwest Fork of the Loxahatchee River is the effect of saltwater intrusion on seed production, germination and seedling/sapling/adult growth and survival of bald cypress and other freshwater deciduous trees. Bald cypress comprise the dominant canopy vegetation of the floodplain swamp community of the Northwest Fork of the Loxahatchee River; therefore, intra-seasonal biological and inter-seasonal hydrological needs for seed production, germination and growth of bald cypress should be considered. From existing literature, it has been suggested that bald cypress seedlings and adult trees are slightly salt tolerant. Wicker et al. (1981) concluded that bald cypress wetlands are limited to areas where salinity does not exceed 2 gL^{-1} for more than 50% of the time that the trees are exposed to inundation or soil saturation. Salinity tolerance appears to increase with age, but salinity levels tolerated by adult trees do not ensure forest sustainability. Specific salinity values tested in various experiments on bald cypress seedlings (Krauss et. al., 1998; 2000; Conner, 1992; 1994; Allen et. al., 1997) is summarized in South Florida Water Management District (2002), Appendix A. Generally, germination capacity and survival decreased over the salinity range 0 to 4 gL^{-1} (ppt).

Also, existing literature has shown that bald cypress seedlings can survive and grow when flooded, although their physiological performance is initially impaired (South Florida Water Management District, 2002, Appendix A). Several studies in the literature have shown that a combination of flooding and salinity is very detrimental to bald cypress seedlings than the effect of either stress alone. Conner (1994) showed that seedlings watered with 10gL^{-1} saltwater survived and grew reasonably well, whereas seedlings continuously flooded with 10gL^{-1} saltwater all died within 2 weeks.

VII. Conclusions

VII.A. Groundwater and Chemical Flux

This study has demonstrated the utility of four naturally occurring isotopes of radium in estimating rates of submarine groundwater discharge to the Loxahatchee River estuary during two sampling events that target high and low discharge conditions. Groundwater sources to this system are most likely the surficial aquifer system, and based on measured surface water ^{222}Rn activities, most groundwater is discharged upstream, in the vicinity of where Kitching Creek enters the Loxahatchee River. The mean residence time of a water parcel in the estuary as calculated by Ra isotopes is ~ 1 day, a value in close agreement with such a value estimated by tidal prism. Ra-derived submarine groundwater discharge estimates compare favorably to a short, 2-day electromagnetic seepage meter deployment at the confluence of Kitching Creek and Loxahatchee River, as well as simple watershed recharge estimates. Average submarine groundwater discharge estimates ranged from 1.03 to 3.84 $x10^5$ m^3 d^{-1}, depending on river discharge. Such values yield NH_4^+ and PO_4^{-3} fluxes that range from 6.27 x 10^1 – 1.06 x 10^3 µmol m^{-2} d^{-1} and 6.92 x 10^1 – 3.79 x 10^2 µmol m^{-2} d^{-1}, respectively.

VII.B. Floodplain Water Quality and Vegetation Change

Results from sampling of surface and pore water along transects in the floodplain of the Loxahatchee River on two sampling trips (September 2003 and March 2004) were reported above. It would be premature to present definitive conclusions based on two sampling trips to the study area, and therefore, conclusions on this theme presented in this paper must be considered tentative. Additional work would be needed to fully understand the causes of the decline of cypress and other freshwater plant species from the Loxahatchee River floodplain.

The water chemistry data consistently showed higher ionic strength water occurring at depth in the soil/sediment pore water of the Loxahatchee River floodplain compared to surface water. This high ionic strength water at depth in the pore water may originate from a tidally driven salt wedge moving up the Loxahatchee River through the relatively porous sand layer underlying much of the floodplain. It is also possible that this higher ionic strength pore water may originate from groundwater entering the floodplain. Although the deep pore water has higher ionic strength compared to surface water, it does not have an extremely high salinity or chloride content, except along Transect 9. Studies suggest that bald cypress trees are tolerant of high ionic strength water up to a salinity of 2‰ (gL^{-1}). Salinities this high were only observed along Transect 9. Salinities of pore water along Transects 1, 3, and 7 did not generally exceed 0.5‰ (gL^{-1}). Thus, results of this study suggest that high salinity water may only be impacting the viability of Cypress in an acute way along Transect 9, and perhaps to a lesser extent along Transect 6. Along Transect 6, Cypress and other fresh water vegetation are continually exposed to water of slightly elevated salinity compared to levels along Transect 1 (upriver background site). Although saltwater is known to negatively impact bald cypress at high levels of salt (acute toxicity), (Pezeshki et al., 1988), the effects of chronic (long-term) exposure of cypress and other freshwater vegetation to water of slightly elevated salinity is not known.

Another hypothesized cause of freshwater plant decline in the floodplain of the Loxahatchee River was buildup of sulfide in pore water from input of sulfate from high ionic strength water, and microbial sulfate reduction in sediments. High levels of sulfide in sediment pore water may have deleterious effects on rooted plants not adapted to living in sulfidic sediments through: (1) reduction in oxygen fugacity in sediments, (2) precipitation of micronutrient metals as metal sulfides, making them biologically unavailable, and (3) impacting nutrient uptake in plant roots. However, sulfide levels in most soil/sediment pore water in the floodplain of the Loxahatchee River were low. Sulfide concentrations in excess of 1 mg/L (1,000 μg/L) were observed only along Transect 9, and in isolated deep pore water samples along Transects 6, and 7. Even along Transect 9, sulfide levels were not as high as anticipated considering the levels of sulfate present. This might be due to tidal movement of sulfide in and out of deep pore water, providing an advective flux preventing buildup of high levels of sulfide in sediment pore water. Thus, buildup of sulfide in pore water is unlikely to have deleterious effects on cypress trees, except along Transect 9.

Thus, movement of high salinity water appears to be a factor in cypress declines only along Transect 9, and perhaps to some extent along Transect 6, based on the limited results of this study. Further work, especially looking at pore water below 50 cm depth in the floodplain, and examining pore water during spring tide/neap tide monthly cycles is needed. Episodic events (hurricanes, “noreasters”) may be a more important factor in moving saltwater up the Loxahatchee River than daily tidal flooding, and should also be a focus of additional study. A single storm event could conceivably move saltwater far enough upriver and into the floodplain to damage cypress vegetation.

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