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DOCTORAL DISSERTATION

A Radiocarbon Method and Multi-Tracer Approach to Quantifying Groundwater Discharge to Coastal Waters

by

Carolyn M. Gramling

September 2003

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Funding was provided by grants from the Rinehart Coastal Research Center/Coastal Ocean Institute at WHOI (RCRC/COI Awards 25035057, 27040014 and 27040048), WHOI SeaGrant Project R/M-47, the National Ocean Sciences Accelerator Mass Spectrometer at WHOI, and the WHOI Academic Programs Office and its Ocean Ventures Fund.

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A RADIOCARBON METHOD AND MULTI-TRACER APPROACH TO QUANTIFYING GROUNDWATER DISCHARGE TO COASTAL WATERS

By

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Submitted in partial fulfillment of the requirements of the degree of

Doctor of Philosophy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
and the
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A RADIOCARBON METHOD AND MULTI-TRACER APPROACH TO QUANTIFYING GROUNDWATER DISCHARGE TO COASTAL WATERS

by

Carolyn M. Gramling

Groundwater discharge into estuaries and the coastal ocean is an important mechanism for the transport of dissolved chemical species to coastal waters. Because many dissolved species are present in groundwater in concentrations that are orders of magnitude higher than typical river concentrations, groundwater-borne nutrients and pollutants can have a substantial impact on the chemistry and biology of estuaries and the coastal ocean. However, direct fluxes of groundwater into the coastal ocean (submarine groundwater discharge, or SGD) can be difficult to quantify. Geochemical tracers of groundwater discharge can reflect the cumulative SGD flux from numerous small, widely dispersed, and perhaps ephemeral sources such as springs, seeps, and diffuse discharge.

The natural radiocarbon content ($\Delta^{14}C$) of dissolved inorganic carbon (DIC) was developed as a tracer of fresh, terrestrially driven fluxes from confined aquifers. This $\Delta^{14}C$ method was tested during five sampling periods from November 1999 to April 2002 in two small estuaries in southeastern North Carolina. In coastal North Carolina, fresh water artesian discharge is characterized by a low $\Delta^{14}C$ signature acquired from the carbonate aquifer rock. Mixing models were used to evaluate the inputs from potential sources of DIC-$\Delta^{14}C$ to each estuary, including seawater, springs, fresh water stream inputs, and salt marsh respiration DIC additions. These calculations showed that artesian discharge dominated the total fresh water input to these estuaries during nearly all sampling periods.

These new $\Delta^{14}C$-based SGD estimates were compared with groundwater flux estimates derived from radium isotopes and from radon-222. It is clear that these tracers reflect different components of the total SGD. The fluxes of low-$\Delta^{14}C$ and of ^{222}Rn were dominated by artesian discharge. Estuarine ^{226}Ra showed strong artesian influence, but also reflected the salt water SGD processes that controlled the other three radium isotopes. The flux of ^{228}Ra seemed to reflect seepage from the terrestrial surficial aquifer as well as salt water recirculation through estuarine sediments. The fluxes of ^{224}Ra and ^{223}Ra were dominated by salt water recirculation through salt marsh sediments. This multi-tracer approach provides a comprehensive assessment of the various components contributing to the total SGD.

Dedication

This thesis is dedicated to my mother

Acknowledgments

This thesis has truly been a collaborative effort, and I owe thanks to many people. First and foremost, I want to thank Dan McCorkle, who has been integral to every aspect of this thesis. He is not only a thoughtful and dedicated scientist himself, but has also always been unselfishly committed to helping students learn the art of science.

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I want to thank all of the people who have also, at one time or another, haunted the "Dungeon" lab at McLean and made it a lot more cheerful – especially Karen Coluzzi, who was helpful in too many ways to count, and the other (at times) denizens of the Dungeon: Becky Belastock, Emily Burns, and Shelley Ugstad. I also want to thank John Hayes, Ann McNichol, Al Gagnon, and the folks at the NOSAMS facility at WHOI for all of their work on the processing and preparation of the radiocarbon samples collected in this study.

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...it is an ever-fixed mark / That looks on tempests / and is never shaken.

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Chapter I. Introduction

Motivation and Background

Groundwater discharge into estuaries and the coastal ocean is an important mechanism for the transport of nutrients and other dissolved chemical species to coastal waters. Because many dissolved chemical species are present in groundwater in concentrations that are orders of magnitude higher than typical river concentrations, groundwater-borne nutrients and pollutants can have a substantial impact on the chemistry and biology of estuaries and the coastal ocean (e.g. Capone and Bautista 1985; Valiela et al 1990; Giblin and Gaines 1990; Simmons 1992).

Direct fluxes of groundwater into the coastal ocean (called submarine groundwater discharge, or SGD) can be difficult to quantify. This is partially due to some variability in the definition of SGD itself. While the term has, in the past, been used to describe various land-sea fluxes of fresh water, including diffuse seepage of groundwater where the water table intersects the coast and focused artesian flow from seafloor springs (Stringfield, 1966; Manheim 1967; Rosenau et al. 1977; Johannes 1980), it is now more generally used to include all subsurface water, at a range of salinities and chemical compositions, discharging at or near the coast (Moore 1999; Burnett et al 2002). This can include, in addition to fresh, terrestrially-driven fluxes, seawater recirculation through coastal sediments resulting from the entrainment of salt water as seaward-flowing fresh groundwater overrides a landward-penetrating saltwater wedge, and wave- or tide-driven infiltration of salt water into coastal sediments (beaches, mud flats, salt marshes) that contain some fresh groundwater (Bollinger and Moore 1984; Moore 1999).

Hydrologic methods, including direct seepage meter measurements of benthic water fluxes and flow calculations using piezometer data, yield point estimates of groundwater discharge, but these estimates may be difficult to extrapolate to a larger area due to the spatial and temporal heterogeneity of SGD along a shoreline (Valiela et al 1990; Bokuniewicz 1992; Simmons 1992; Robinson et al 1998).

Geochemical tracers of groundwater discharge can reflect the cumulative SGD flux from numerous small, widely dispersed, and perhaps ephemeral sources such as springs, seeps, and diffuse discharge. However, geochemical tracers of SGD have different input mechanisms, and therefore can provide different estimates of the total flux. Deciding which geochemical tracer to use to estimate SGD may be a matter of determining which of its components is of greatest interest in a particular setting. As an example, nutrient loading in an estuary may result from the oxidation and release of buried nutrients due to recirculating seawater through bottom sediments, or from localized, artesian discharge from springs originating in a nutrient-enriched aquifer. To predict nutrient loading, therefore, it may be essential to understand the relative importance of several different components of SGD.

The four isotopes of radium (^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra) and the dissolved gas ^{222}Rn are used as geochemical tracers of SGD because they tend to be highly enriched in groundwater relative to seawater, behave conservatively with respect to biological processes, and radioactively decay over a range of half-lives that make them useful for measuring the mixing of water masses over different time scales (e.g. Bollinger and Moore 1993; Rama and Moore 1996; Cable et al 1996; Krest et al 2000; Corbett et al 1999, 2000).

Radium desorption from aquifer or riverine particles is enhanced in waters of increasing ionic strength, and the groundwater radium flux is almost certainly elevated as radium is desorbed from aquifer sediments by salt water intrusion (e.g. Elsinger and Moore 1980; Burnett et al 1990; Moore 1996). Therefore, fluxes of radium are likely to provide an estimate of the total SGD – including terrestrially-driven groundwater flux, the recirculation of seawater through surface sediments and through sub-bottom rock units on continental shelves, and the tidal filling and draining of salt marsh sediments – rather than of fresh, land-sea fluxes alone (e.g. Moore 1999; Burnett et al 2002; Cable et al 2003). Radon is not sensitive to salinity-linked desorption reactions, but it is quickly lost to the atmosphere via gas exchange once groundwater is exposed at the land surface. As a result, coastal ^{222}Rn activities may provide only a minimum estimate of the total groundwater flux (Corbett et al 1999; Swarzenski et al 2001).

In principle, $\Delta^{14}C$ can be used to trace SGD inputs from any water source with a distinct radiocarbon content. In coastal North Carolina, fresh water artesian discharge is characterized by a low $\Delta^{14}C$ signature acquired from the carbonate aquifer rock. This work demonstrates that coupled analyses of dissolved inorganic carbon concentrations (DIC) and carbon isotopic compositions ($\Delta^{14}C$ and $\delta^{13}C$ values) can provide a tracer of one component of the total SGD flux – the fresh groundwater discharge from confined aquifers. After determining the total fresh water input to an estuary by a salinity mass balance, a radiocarbon mass balance is then used to partition between surface water sources (including stream flow and seepage from the surficial aquifer) and artesian flow from confined aquifers.

In this dissertation, $\Delta^{14}C$ is developed as a tracer of fresh, terrestrially driven fluxes from confined aquifers. Groundwater flux estimates were derived from two other geochemical tracers of groundwater discharge, radium and radon, to determine the processes that influenced each tracer in two small estuaries in southeastern North Carolina. This suite of tracers was then used to show that artesian springs dominated the fresh water budgets of these estuaries, while other SGD processes, including seepage from the surficial aquifer and seawater recirculation through salt marsh sediments, contributed to the total SGD in these estuaries.

Study Site: Geologic and Hydrogeologic Characteristics

The Onslow Bay region of the southeastern North Carolina coastal plain lies between Cape Fear and Cape Lookout. The potential for land-sea groundwater exchange is high in this region; a number of studies of the coastal hydrology and geology have recognized groundwater with intermediate salinity discharging on the inner and mid-shelf regions of Onslow Bay, suggesting the possibility of a strong onshore-offshore hydraulic connection (Sherwani 1980; Lloyd and Daniel 1988).

North Carolina coastal plain geology consists of Upper Cretaceous and Cenozoic formations of interbedded sands, silts, clays, and limestones that dip and thicken eastward, extending beneath the continental shelf (Riggs et al. 1995; Winner and Coble

1996; Harris 1996) (**Figure 1**). In the Cape Fear region, the highly productive Eocene Castle Hayne aquifer (consisting primarily of shell limestone, dolomitic limestone, sandy limestone, and fine to medium sand) immediately underlies the unconsolidated sands and clays of the surficial aquifer (Winner and Coble, 1996; Giese et al, 1997). The Castle Hayne confining unit is thin (~ 3 m), and contains enough sand to allow some vertical leakage between the Castle Hayne and the overlying aquifers (Winner and Coble, 1996; Giese et al, 1997). The underlying Cretaceous units (the Peedee, Black Creek, and Cape Fear formations) contain interbedded sand, clay, and silt, which become calcareous in the Peedee (Sohl and Owens 1991).

Organization of Dissertation

This dissertation is organized into two primary parts: Chapters I and II involve the development of $\Delta^{14}C$ as a tracer of the fresh, confined component of SGD, while Chapters III and IV focus on placing the $\Delta^{14}C$-determined fluxes in the context of total SGD measurements using other geochemical SGD tracers, specifically ^{222}Rn and the four radium isotopes. The data in each of these chapters was collected from within the same study area in southeastern North Carolina during six different sampling expeditions from July 1997 to April 2002.

Chapter II, which was published in the May 2003 issue of *Limnology and Oceanography*, describes in detail the development of the $\Delta^{14}C$ method within a single estuary. The chapter presents a mixing model that uses the distinct DIC-$\Delta^{14}C$ values in confined aquifer discharge to the estuary via springs to distinguish these inputs from the other potential sources of DIC-$\Delta^{14}C$ to the estuary (including seawater, fresh water stream inputs, and salt marsh respiration DIC additions). Results from these mixing models show that artesian discharge dominated fresh water input to the estuary during sampling in November 1999 and April 2001, while stream flow dominated the fresh water input to the estuary during July 2000.

Chapter III presents radiocarbon data collected subsequent to Chapter II, during sampling periods in April 2001, November 2001, and April 2002. In this chapter, the development of the $\Delta^{14}C$ method is continued by examining further the variability of DIC-$\Delta^{14}C$ values in the non-spring input sources, particularly the respiration DIC inputs and fresh water streams. Pore water DIC and DIC isotopic analyses confirm the assumption, made in the previous chapter, that salt marsh respiration would add DIC with relatively high ^{14}C, so that artesian sources remain the only low-$\Delta^{14}C$ input to the estuaries. Variation in stream composition documents the variability of spring discharge to stream flow in these watersheds, and provides an estimation of the uncertainty of $\Delta^{14}C$-derived confined groundwater flux estimates. This chapter also tests the generality of the $\Delta^{14}C$ method of estimating artesian inputs by expanding to include a neighboring estuary. DIC-$\Delta^{14}C$ mixing model results from these sampling periods confirm that artesian inputs dominate the total fresh water input to both estuaries during most sampling periods.

Chapter IV focuses on radium and radon data collected concurrently with the $\Delta^{14}C$ data in Chapter III, and examines the different processes controlling the fluxes of radium and radon from these two estuaries.

Chapter V uses the data compiled in Chapters III and IV to make an intercomparison of flux estimates derived from $\Delta^{14}C$, ^{222}Rn, and radium isotopes. This intercomparison highlights how these different tracers describe different components of the total flux. While the flux of low-$\Delta^{14}C$ DIC and ^{222}Rn were dominated by artesian discharge, ^{228}Ra reflected seepage from the terrestrial surficial aquifer as well as salt water recirculation through estuarine sediments. ^{224}Ra and ^{223}Ra were dominated by salt water recirculation through salt marsh sediments. ^{226}Ra showed strong artesian influence, but was also modified by the salty SGD processes that dominated the other three radium isotopes.

The appendices include a brief discussion of nutrient data collected in November 2001 and April 2002 from both estuaries. A second appendix describes $\Delta^{14}C$ measurements made in two wells on the continental shelf off the coast of North Carolina, to test the effectiveness of the method when the salinity constraint is absent. A third appendix presents well head data from the wells closest to the estuaries from November 1999 through April 2002.

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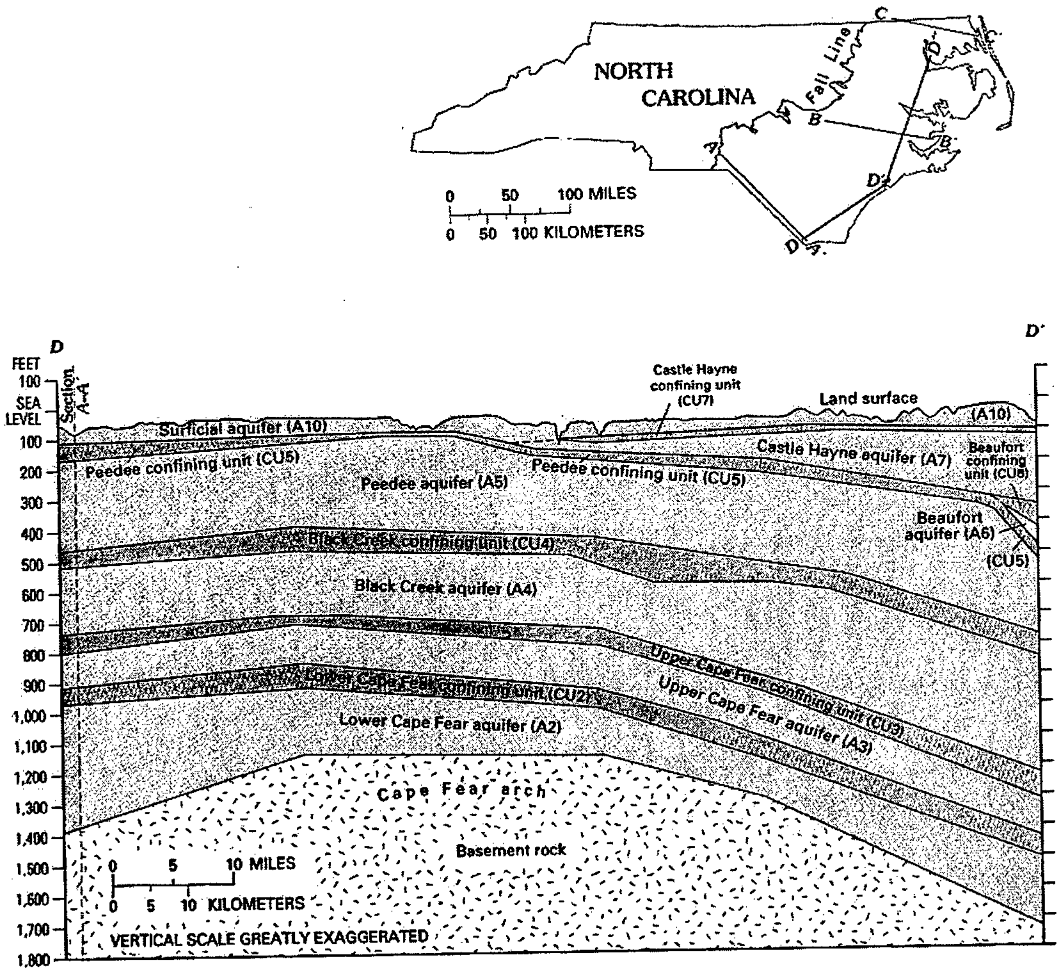

Figure I-1. Hydrogeologic section D-D', across the Cape Fear region of North Carolina (reproduced from Giese et al 1997). In the northeast half of the section, the limestone Castle Hayne aquifer immediately underlies the unconfined, sandy surficial aquifer.

Chapter II

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A carbon isotope method to quantify groundwater discharge at the land-sea interface

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Abstract

We present a new method to characterize and quantify groundwater discharge to estuaries and the coastal ocean. Using data from the Pages Creek estuary in the Cape Fear region of southeastern North Carolina, we show that the concentration and carbon isotopic composition ($\Delta^{14}C$ and $\delta^{13}C$ values) of dissolved inorganic carbon (DIC) can provide a tracer of a single, well-defined component of the surface water-groundwater system in coastal regions—the integrated freshwater discharge to an estuary from confined aquifers. Groundwater from the two shallowest confined aquifers in the Cape Fear region (the Castle Hayne and the Peedee) has DIC $\Delta^{14}C$ values ranging from $-282‰$ to $-829‰$, significantly lower than the radiocarbon content of surficial (water table) groundwater, rivers and streams, and seawater in the area ($\Delta^{14}C = -38‰$ to $+97‰$). DIC additions from salt marsh decomposition and DIC removal via photosynthesis and gas evasion can influence estuarine DIC concentrations and DIC $\delta^{13}C$ values. However, none of these processes results in strongly depleted DIC $\Delta^{14}C$ values. Because artesian springs are the only significant low-$\Delta^{14}C$ DIC input to the Pages Creek estuary, flood-ebb ^{14}C budgets provide a direct measure of the fraction of the total freshwater inputs to the Pages Creek estuary that is derived from artesian discharge. With this method, we have observed a striking range in the relative contribution of artesian flow to the Pages Creek estuary freshwater budget. During November 1999 and April 2001 (both periods of low precipitation in southeastern North Carolina), artesian groundwater discharge could account for essentially all of the Pages Creek freshwater inputs. In contrast, during July 2000 (a period of high precipitation in this region), artesian groundwater made a negligible contribution to the creek's freshwater budget.

Fresh groundwater can discharge into the coastal ocean wherever there is a land-sea hydraulic connection with a seaward head gradient (Johannes 1980), and it is widely recognized that groundwater-borne nutrients and pollutants can have a substantial impact on the chemistry and biology of estuaries and the coastal ocean (e.g., Capone and Bautista 1985; Giblin and Gaines 1990; Valiela et al. 1990; Simmons 1992). The potential importance of submarine groundwater discharge is enhanced by the fact that many dissolved chemical species have groundwater concentrations orders of magnitude higher than typical river concentrations. The term "submarine groundwater discharge" (SGD) has been used to describe various land-sea groundwater fluxes, from diffuse seepage of groundwater where the water table intersects the coast to focused artesian flow from seafloor springs (Stringfield 1966; Manheim 1967; Rosenau et al. 1977; Johannes 1980) (Fig. 1). This term can also include localized artesian flow from small springs discharging directly into estuaries.

There is some ambiguity associated with the SGD concept, because the discharging water can have salinities that range from fresh- to seawater values. This can result from entrainment of saltwater as seaward-flowing fresh groundwater overrides a landward-penetrating saltwater wedge or from wave- or tide-driven infiltration of salt water into coastal sediments (beaches, mud flats, and salt marshes) that contain some fresh groundwater (Bollinger and Moore 1984; Moore 1999). Recently, the term "subterranean estuary" has been applied to the entire suite of sea-/groundwater interactions along the coast (Moore 1999).

Hydrologic methods, including direct seepage meter measurements of benthic water fluxes and flow calculations us-

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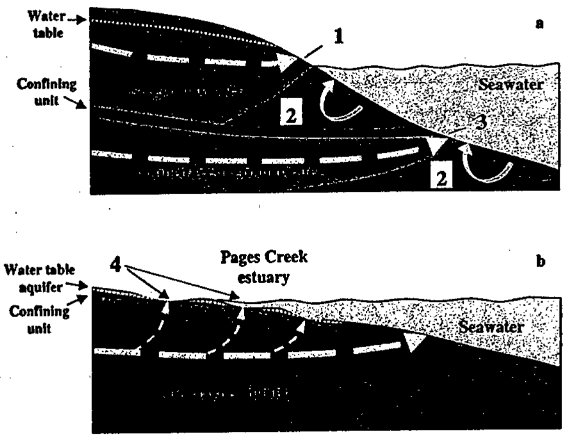

Fig. 1. (a) Simplified cross-section of a coastal groundwater system, with principal transport features: (1) surficial groundwater discharge at seepage face (dashed arrows represent schematic regional flow lines); (2) seawater recirculation/intrusion; and (3) freshwater discharge from confined aquifer. (b) Larger-scale schematic of Pages Creek estuary groundwater system. The shallowest confined aquifer, the Castle Hayne, discharges offshore, but some local springs discharge into the estuary (4).

ing piezometer data, yield point estimates of SGD (Valiela et al. 1990; Bokuniewicz 1992; Simmons 1992; Robinson et al. 1998). However, the spatial and temporal heterogeneity of SGD along a shoreline makes it difficult to extrapolate seepage meter and piezometer estimates. This has resulted in a growing interest in the use of geochemical tracers to assess the cumulative impact of SGD from numerous small, widely dispersed, and perhaps ephemeral sources such as springs, seeps, and diffuse discharge. The use of geochemical tracers of SGD is complicated by the fact that each tracer has different fate and transport properties so that estimates obtained using different tracers are not always easy to compare.

Recently, several workers have used coastal radium isotope budgets to conclude that submarine groundwater discharge may be more widespread and more important than has been thought (Burnett et al. 1990; Moore 1996, 1999; Krest et al. 2000; Charette et al. 2001). However, there is an acknowledged ambiguity in the radium-based estimates of groundwater flux into coastal waters—the groundwater radium flux is almost certainly elevated as radium is desorbed from aquifer sediments by salt water intrusion (Burnett et al. 1990; Moore 1996). This intrusion can occur because of natural processes (tidal pumping or natural changes in aquifer recharge) or anthropogenic effects (increased groundwater extraction or breaching of confining units by channel dredging). This desorption-driven enhancement of groundwater radium due to seawater intrusion is analogous to the enhanced radium release observed in estuaries, where radium-bearing riverine particles first encounter saltwater and where seawater seeps through tidal salt marsh sediments (e.g., Elsinger and Moore 1980; Rama and Moore 1996). As a result, it is recognized that radium may be a more sensitive indicator of the total subsurface water flux, including processes such as seawater intrusion and the recirculation of seawater through surface sediments and subbottom rock units on continental shelves, than of the land-sea freshwater flux alone (Moore 1999).

Trace gases such as radon and methane are not sensitive to salinity-linked desorption reactions and may thus more closely reflect actual groundwater fluxes. Radon-222, like radium, is often highly enriched in groundwater because its parent, ^{226}Ra, is present in most rocks and sediments. As a consequence, elevated concentrations of ^{222}Rn can document groundwater discharge (Cable et al. 1997; Corbett et al. 1999; Swarzenski et al. 2001). Methane is also often strongly enriched in groundwater relative to surface waters, as a result of anaerobic organic matter decomposition within some aquifers. Both of these gases are relatively insoluble in water and have low atmospheric concentrations, so that both are quickly lost via gas exchange once groundwater is exposed at the earth's surface. Methane can also be lost via oxidation or microbial consumption. As a result, observed coastal ^{222}Rn and CH_4 concentrations may provide only a minimum estimate of the total groundwater flux (Corbett et al. 1999; Swarzenski et al. 2001).

In the present study, we show that coupled analyses of dissolved inorganic carbon concentrations (DIC) and carbon isotopic compositions ($\Delta^{14}C$ and $\delta^{13}C$ values) provide a tracer of one component of the total SGD flux—fresh groundwater discharge from confined aquifers. To estimate the confined groundwater input to an estuary, we first determine the total freshwater input using flood tide and ebb tide salinity values. This freshwater input is then partitioned between surface sources (including the water table aquifer) and artesian groundwater using a carbon isotope mass balance based on DIC concentrations and $\Delta^{14}C$ values. Artesian groundwater and springs are expected to have lower $\Delta^{14}C$ values than surface waters and surficial groundwater (Fig. 2). As a test of this carbon-based method for estimating groundwater discharge as a fraction of the total freshwater discharge, we describe a study at Pages Creek, an estuary in Onslow Bay, North Carolina.

$\Delta^{14}C$ systematics—Although the DIC and $\delta^{13}C$-DIC values can be significantly modified by estuarine carbon cycle processes, the very large difference between input end-member $\Delta^{14}C$ values and the natural double label provided by paired ^{13}C and ^{14}C analyses (Spiker 1980) ensure that groundwater flux estimates based on estuarine DIC $\Delta^{14}C$ values will be largely unaffected by processes such as gas exchange, photosynthesis, and respiration of fresh organic matter.

$\delta^{13}C$ values are defined as

$$\delta^{13}C(‰) = \left\{\left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}}\right] - 1\right\} \times 1000 \qquad (1)$$

$\delta^{14}C$ is similarly defined as

$$\delta^{14}C(‰) = \left\{\left[\frac{(^{14}C/^{12}C)_{sample}}{(^{14}C/^{12}C)_{standard}}\right] - 1\right\} \times 1000 \qquad (2)$$

The $\delta^{14}C$ values are typically normalized to $\delta^{13}C = -25‰$ to remove fractionation effects that can result from processes such as CO_2 gas evasion or photosynthesis (Stuiver and Robinson 1974). This normalized $\delta^{14}C$ value is reported as $\Delta^{14}C$ (‰), which is defined as

$$\Delta^{14}C(‰) = 1000 \times \left\{1 + \left(\frac{\delta^{14}C}{1000}\right) \times \left[\frac{0.975^2}{\left(1 + \frac{\delta^{13}C}{1000}\right)^2}\right] - 1\right\} \quad (3)$$

This calculation assumes that the ^{14}C fractionation factor is approximately equal to the square of the ^{13}C fractionation factor, which results in a change in the $\delta^{14}C$ value that is almost twice that of $\delta^{13}C$ per fraction of DIC used (Stuiver and Robinson 1974).

As a result of this normalization, $\Delta^{14}C$ values are unchanged by DIC removal processes that fractionate carbon isotopes. As a consequence, despite the fact that photosynthetic CO_2 uptake and CO_2 gas evasion can exert a strong influence on estuarine DIC (Cai and Wang 1998; Cai et al. 1999), estuarine $\Delta^{14}C$ values will be determined by mixing between the DIC sources. $\Delta^{14}C$ values can therefore be used as a quasi conservative tracer of DIC inputs.

Site characteristics—The Onslow Bay region of the southeastern North Carolina coastal plain lies between Cape Fear and Cape Lookout. The potential for land-sea groundwater exchange is high in this region; a number of studies of the coastal hydrology and geology have recognized groundwater with intermediate salinity discharging on the inner and midshelf regions of Onslow Bay, which suggests the possibility of a strong onshore-offshore hydraulic connection (Sherwani 1980; Lloyd and Daniel 1988).

North Carolina coastal plain geology consists of Upper Cretaceous and Cenozoic formations of interbedded sands, silts, clays, and limestones that dip and thicken eastward, extending beneath the continental shelf (Riggs et al. 1995; Harris 1996; Winner and Coble 1996). In the Cape Fear region, the highly productive Eocene Castle Hayne aquifer (consisting primarily of shell limestone, dolomitic limestone, sandy limestone, and fine to medium sand) immediately underlies the unconsolidated sands and clays of the surficial aquifer (Giese et al. 1991; Winner and Coble 1996) (Fig. 1b). The Castle Hayne confining unit is thin (~3 m) and contains enough sand to allow some vertical leakage between the Castle Hayne and the overlying aquifers (Winner and Coble 1996; Giese et al. 1997). The underlying Cretaceous units (the Peedee, Black Creek, and Cape Fear formations) contain interbedded sand, clay, and silt, which become calcareous in the Peedee (Sohl and Owens 1991).

The Pages Creek estuary is a small, well-mixed tidal creek located on the Intracoastal Waterway (ICW), northeast of Wilmington (Fig. 3a,b). Two inlets, Rich Inlet to the north and Mason Inlet to the south, cut through the barrier islands and salt marshes that separate the ICW and Onslow Bay. The entire Pages Creek watershed has an area of $\sim 1.2 \times 10^7$ m². The Pages Creek estuary, including its salt marshes, has an area of $\sim 6.7 \times 10^5$ m². The tidal range is ~1.1 m at the mouth of the creek (Fig. 3b: E2); 2 km upstream, the range is ~0.6 m (Fig. 3b: E3). The closest major river is the

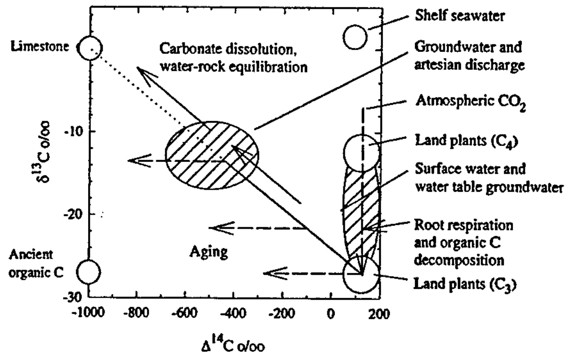

Fig. 2. Reservoir compositions and process trends. Today, atmospheric $\Delta^{14}C$ and $\delta^{13}C$ values are about +125‰ and −7.5‰, respectively. Surface seawater $\Delta^{14}C$ is about +90‰–100‰; seawater $\delta^{13}C$ is 0‰–1‰. Living vegetation incorporates the high atmospheric $\Delta^{14}C$ values and will have $\delta^{13}C$ values reflective of the photosynthetic pathway used (−10‰ to −15‰ for C_4 plants; −25‰ to −30‰ for C_3 plants). Root respiration CO_2 will have a $\delta^{13}C$ composition similar to that of the total plant material (Deines 1980) and a high $\Delta^{14}C$ value. CO_2 produced by microbial decomposition of soil/sediment organic matter will reflect the $\Delta^{14}C$ and $\delta^{13}C$ values of the source material (Keller and Bacon 1998). Carbonate rocks have high $\delta^{13}C$ values, reflecting the seawater $\delta^{13}C$ values of formation (0‰–1‰) and are radiocarbon-free ($\Delta^{14}C$ = −1000‰), so that groundwater flowing through carbonate rock will develop low $\Delta^{14}C$ and high $\delta^{13}C$ values through dissolution and ion exchange. Ancient organic material, such as peat, will also be radiocarbon-free but will have $\delta^{13}C$ values similar to the plant material of origin (−25‰ to −30‰).

Northeast Cape Fear River, which feeds into the Cape Fear River below Wilmington and drains into Long Bay south of Cape Fear (Fig. 3a). Freshwater inputs to the Pages Creek estuary consist of a few small streams (recharged by local precipitation and by groundwater), a number of artesian springs, and most likely diffuse seepage of unconfined groundwater directly into the creek.

Methods

Sample collection—Our isotopic mass balance approach requires the quantification of the DIC concentration, DIC isotopic values ($\delta^{13}C$ and $\Delta^{14}C$), and salinity of the primary water inputs to the estuary system. The primary DIC inputs to the Pages Creek estuary are (1) confined groundwater (as artesian springs), (2) fresh surficial waters (including both freshwater streams and discharge from the water table aquifer), (3) seawater entering the Pages Creek estuary through the ICW, and (4) salt marsh DIC input; the primary output is water flowing out to the ICW at low tide (5) (Fig. 4). Our sampling plan in Pages Creek was designed to constrain these end-member input compositions and to monitor changes in DIC, DIC isotopes, and salinity within the estuary through a tidal cycle.

River, estuary, and spring $\Delta^{14}C$, $\delta^{13}C$, DIC, titration alkalinity (TA), and salinity samples were collected by sub-

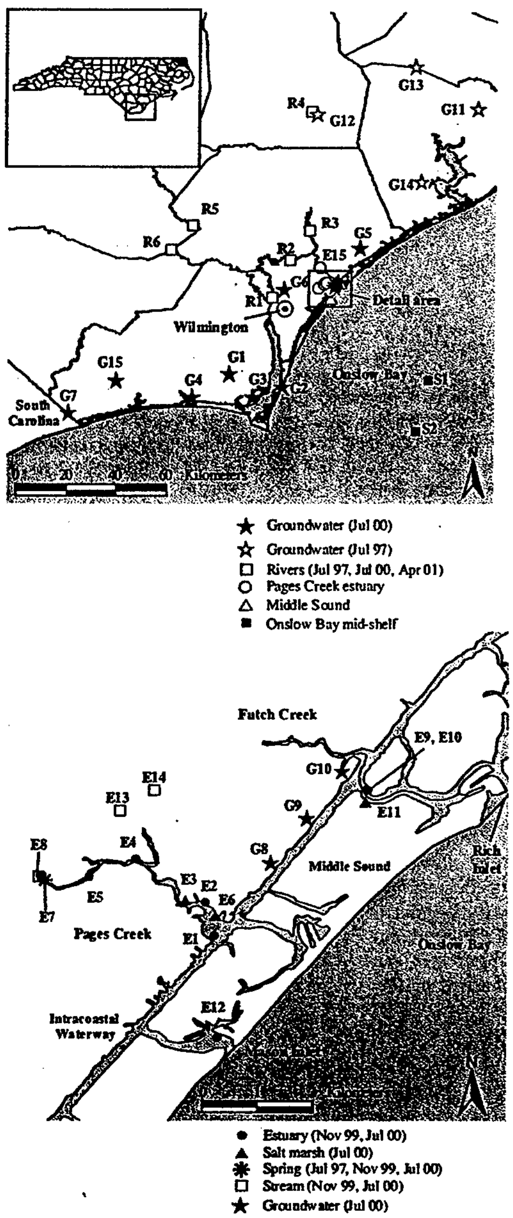

Fig. 3. Wilmington/Cape Fear region with sample locations, with detail of Pages Creek and Middle Sound sample locations.

merging and manually tripping a 5-liter Niskin bottle; where the water column was deep enough (all river, inlet, high-tide ICW, and high tide Pages Creek mouth samples), the Niskin was held vertically with its top at 0.25–0.5 cm below the water surface. Shallow-water column samples were collected by holding the Niskin horizontally under the water surface.

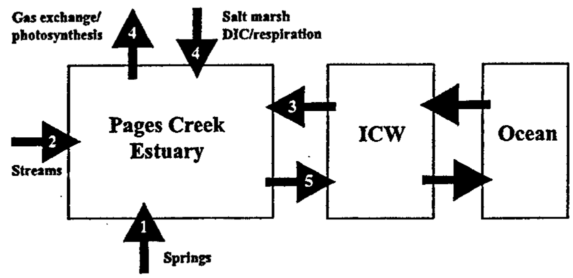

Fig. 4. Conceptual model of DIC inputs and outputs to the Pages Creek estuary. As discussed in the text, DIC inputs to Pages Creek are springs (1), streams (2), inflowing ICW water (3), and net exchange with salt marsh (4). The primary DIC output is water flowing out of the estuary at low tide (5). Gas evasion and photosynthesis do not affect the DIC $\Delta^{14}C$ of the outflow.

April 2001 stream samples were collected with a manual bilge pump.

Fifteen stations within Pages Creek, Mason Inlet, and Rich Inlet were sampled in July 1997, November 1999, July 2000, and April 2001 (Fig. 3b; Table 1). Sta. E2, near the mouth of the creek, was sampled to monitor the change in chemical composition of the water before low tide and before high tide in November 1999, July 2000, and April 2001. Stations from the inlets connecting the ICW with Onslow Bay were sampled to assess the isotopic composition of DIC derived from salt marsh decomposition processes.

Spring samples were collected at Sta. E7 in July 1997, November 1999, and July 2000. This spring discharges in a 0.5-m diameter pockmark that is fully exposed at low tide and is swept free of fine sediment by the artesian flow. Freshwater stream samples were collected at Sta. 8a in November 1999 and Sta. 8b in July 2000 and April 2001.

Groundwater samples from the coastal Cape Fear region were collected to document the spatial variability of groundwater DIC and DIC isotopic values. Samples from monitoring wells screened in the surficial, Castle Hayne, and the underlying Peedee aquifers were collected in July 1997 and July 2000 using a submersible pump, after first pumping out three well volumes to flush the wells (Table 2, Fig. 3a,b).

We sampled several rivers in southeastern North Carolina to provide a regional estimate of surface freshwater DIC composition (Table 3, Fig. 3a). Surface (<0.25 m) and bottom waters (30 m) in Onslow Bay were collected by divers in July 1997 at two sites located 20 km offshore (Table 3; Fig. 3a).

Sample analysis—Water samples for carbon isotopic analyses (DIC, $\delta^{13}C$, and $\Delta^{14}C$) were collected, unfiltered, in 500-ml glass bottles with greased ground-glass stoppers and poisoned with 100 μl of saturated $HgCl_2$, except as noted in Tables 1–3. Carbon isotopic and DIC analyses were conducted at the National Ocean Sciences Accelerator Mass Spectrometer facility in Woods Hole, Massachusetts. The precision for the $\Delta^{14}C$ analyses is ±5‰; for $\delta^{13}C$, ±0.1‰, and for DIC, ±3%.

April 2001 alkalinity samples were titrated using a poten-

Table 1. Pages Creek estuary salinity, dissolved inorganic carbon (DIC), $\Delta^{14}C$, $\delta^{13}C$, and titration alkalinity (TA) values.

Pages Creek estuary samples	Map legend	Date	Salinity	DIC (mmol kg^{-1})	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	TA* (meq L^{-1})
Pages Creek mouth: high tide	E2	Nov 99	31.200	2.237	+0.3	−1.43	†
Pages Creek mouth: high tide	E1	Jul 00	32.985	2.175	+38.3	−1.08	2.30
Pages Creek mouth: high tide	E2	Apr 01	34.728	2.368	+39.1	−0.78	2.49
Pages Creek mouth: high tide	E2	Apr 01	34.778	2.363	+40.0	−0.84	2.49
Pages Creek mouth: low tide	E2	Nov 99	27.900	2.562	−78.4	−2.18	†
Pages Creek mouth: low tide	E2	Jul 00	21.299	1.899	+9.3	−3.77	1.82
Pages Creek mouth: low tide	E2	Apr 01	32.401	2.463	−10.0	−1.89	2.56
Pages Creek mouth: low tide	E2	Apr 01	33.870	2.439	+27.9	−1.30	2.51
2.1 km upstream, high tide	E3	Jul 00	30.278	2.066	+54.4	−1.30	2.12
2.1 km upstream, low tide	E3	Jul 00	14.616	1.671	−12.7	−5.92	1.58
3.2 km upstream, rising tide	E4	Jul 00	16.544	1.661	+16.5	−4.77	1.52
Salt marsh	E5	Jul 00	33.133	2.146	+47.1	−0.79	2.20
Salt marsh	E5	Jul 00	21.818	1.933	+20.5	−3.56	1.88
Salt marsh	E6	Jul 00	30.574	2.103	+43.3	−1.32	2.20
Pages Creek spring	E7	Jul 97	†	4.470	−396.7	−11.53	3.79
Pages Creek spring 1	E7	Nov 99	0.200	4.464	−385.5	−11.36	†
Pages Creek spring 2	E7	Nov 99	0.200	4.485	−406.4	−11.16	†
Pages Creek spring 1	E7	Jul 00	1.189	4.192	−376.6	−11.17	3.48
Pages Creek spring 2	E7	Jul 00	0.526	4.432	−403.2	−11.23	3.66
P.C.‡ stream: Bayshore Rd	E8a	Nov 99	0.000	0.866	−79.4	−13.19	†
P.C. stream: Bayshore Rd	E8b	Jul 00	0.189	1.645	−162.3	−12.22	1.44
P.C. stream: Bayshore Rd§	E8b	Apr 01	0.164	1.452	−126.6	−12.63	1.14
P.C. stream: Furtado Rd§	E13	Apr 01	0.177	2.860	−176.5	−11.25	2.43
P.C. stream: Porters Neck Rd§	E14	Apr 01	0.142	1.271	−191.8	−12.56	1.07
Non-P.C. stream: Sidebury Rd§	E15	Apr 01	0.067	0.746	−109.5	−14.08	0.47
Inlet samples							
Mason Inlet: HT	E12	Nov 99	34.400	2.043	+59.3	+0.17	†
Rich Inlet: HT	E10	Jul 00	31.121	2.067	+39.5	−0.78	2.12
Mason Inlet: LT	E12	Nov 99	34.300	2.073	+57.9	+0.03	†
Rich Inlet: LT	E9	Jul 00	31.329	2.011	+38.6	−0.67	†
Middle Sound salt marsh	E11	Jul 00	32.625	2.182	+64.8	−0.89	2.40

* All estuary alkalinity samples were unfiltered.
† No measurement taken.
‡ P.C. = Pages Creek: indicates streams draining into the Pages Creek estuary.
§ April 2001 streams were sampled with a manual bilge pump into 500-ml glass bottles and were poisoned with 100 μl of saturated $HgCl_2$.

tiometric closed-cell titration system with a precision of 0.2%. July 2000 alkalinity samples were analyzed immediately in the field using a manual titration method (Wood 1976), with a precision of 1%. November 1999 and July 1997 alkalinity was determined by the Gran function titration method, to a precision of 0.5%.

Salinity samples for July 2000 and April 2001 groundwater, river, and estuary stations were analyzed by the hydrographic facility in the Physical Oceanography department at Woods Hole Oceanographic Institution with a precision better than ±0.01 ppt. November 1999 salinity values were estimated using a hand-held salinometer.

Results

The primary water sources to the Pages Creek estuary include groundwater inputs from the three shallowest aquifers in the region (the surficial, Castle Hayne, and Peedee aquifers), freshwater streams and rivers, and shelf waters that enter the estuary through the ICW.

Groundwater and springs—In general, surficial groundwater samples have much higher $\Delta^{14}C$ values than the Castle Hayne and Peedee groundwater samples (Table 2; Fig. 5). The $\delta^{13}C$ values of the Castle Hayne and Peedee aquifers are similar to each other and are higher than those of the surficial aquifer samples. DIC and TA values also tend to increase with increasing depth. Salinity for most groundwater samples was <1, with the exception of two of the deepest wells.

Surficial groundwater—Surficial groundwater $\Delta^{14}C$ values are generally higher than deeper groundwater $\Delta^{14}C$, ranging from about +18‰ to about +88‰ (Table 2; Fig. 5). The range in $\delta^{13}C$ values (−15‰ to −27‰) for surficial groundwater is large, and these values tend to be lower than the $\delta^{13}C$ values from deeper aquifers. DIC values for surficial groundwater samples (~1.3–1.6 mmol kg^{-1}) are generally low relative to deeper groundwater samples. Titration alkalinity is low for all surficial samples (~0.04 meq L^{-1} to ~1.0 meq L^{-1}). Two wells screened in the surficial aquifer, Cal-

Table 2. Groundwater salinity, dissolved inorganic carbon (DIC), $\Delta^{14}C$, $\delta^{13}C$, and titration alkalinity (TA) values.

Well sample*	Date	Map legend	Aquifer†	Screened interval (m below surface)	Salinity	DIC (mmol kg^{-1})	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	TA‡ (meq L^{-1})
Boiling Spring	Jul 00	G1	S	3–4	0.069	3.256	+88.4	−22.84	0.24
Fort Fisher State Park	Jul 00	G2	S	2–3	0.280	§	+36.6	−19.36	1.08
Southport RS4	Jul 00	G3	S	3–6	0.100	1.465	+77.1	−23.03	0.24
Sunset Harbor	Jul 00	G4	S	3–5	0.067	0.922	+41.1	−26.89	0.04
Topsail Beach	Jul 00	G5	S	3–5	0.107	1.631	−407.9	−15.82	0.99
Wilmington Airport	Jul 00	G6	S	2–4	0.076	1.338	+18.4	−15.12	0.28
Calabash	Jul 00	G7	S/L†	14–17	0.309	§	−396.9	−12.99	4.22
NENHC S1	Jul 00	G8	CH¶	9–12	0.294	2.138	−281.8	−15.36	1.52
NENHC S2	Jul 00	G9	CH¶	13–17	0.249	2.974	−413.8	−12.86	2.68
NENHC S3	Jul 00	G10	CH¶	9–11	0.895	5.104	−330.9	−13.61	4.54
Deppe	Jul 97	G11	S/L†	27–31	§	7.990	−556.8	−12.30	6.63
Chinqapin	Jul 97	G12	CH	31–49	§	5.030	−520.9	−12.31	3.88
Comfort	Jul 97	G13	CH	8–18	§	3.850	−498.7	−11.78	3.43
Dixon Tower/Folkstone	Jul 97	G14	CH	46–73	§	4.380	−748.1	−11.97	4.06
Southport RS4	Jul 00	G3	CH	20–23	0.235	4.864	−472.6	−11.59	3.42
Sunset Harbor	Jul 00	G4	S/L†	26–31	0.108	1.796	−576.8	−11.80	1.35
Boiling Spring	Jul 00	G1	S/PD‖	20–46	0.317	7.110	−653.3	−11.25	4.86
NENHC D1	Jul 00	G8	PD	50–55	0.410	6.426	−770.2	−10.95	5.64
NENHC D2	Jul 00	G9	PD	50–58	1.461	6.991	−821.9	−12.03	5.90
NENHC D3	Jul 00	G10	PD	47–52	0.777	6.439	−829.2	−12.67	5.52
Shallotte	Jul 00	G15	PD	18–21	0.243	§	−548.0	−9.85	3.76
Southport RS4	Jul 00	G3	PD	29–61	0.293	§	−786.9	−11.88	3.44
Sunset Harbor	Jul 00	G4	S/PD**	95–98	3.757	§	−998.1	−4.65	7.68

* All monitoring wells installed and maintained by the North Carolina Department of Environment and Natural Resources (NC-DENR) (http://www.dwr.ehnr.state.nc.us/), except the NENHC wells, installed and maintained by the Northeast New Hanover Conservancy (NENHC).
† NC-DENR aquifer assignment (unless otherwise noted): S, surficial; CH, Castle Hayne; PD, Peedee. Our S/L designation indicates wells listed as surficial by NC-DNER (based on absence of a confining unit) but where well lithology shows the presence of a limestone unit. At Deppe this may be the Castle Hayne.
‡ All groundwater alkalinity samples were filtered, except the Wilmington Airport surficial aquifer sample.
§ No measurement taken.
¶ Roberts 2002.
‖ Screened interval crosses the Peedee confining unit.
** Peedee lithostratigraphy in deep surficial aquifer.

abash and Topsail Beach, have much lower $\Delta^{14}C$ values (−396.9‰ and −407.9‰, respectively) than the other surficial wells. However, the relatively high $\delta^{13}C$ values, as well as the presence of shell fragments and carbonaceous sand, respectively (as described in NC-DENR borehole logs for these two wells) suggest the possibility of carbonate dissolution or isotopic exchange with shell material.

Castle Hayne groundwater—Groundwater samples labeled Castle Hayne in Table 2 were collected from wells screened only in the Castle Hayne aquifer, where NC-DENR borehole logs indicate the presence of a confining layer separating it from the surficial aquifer. These wells are generally low in $\Delta^{14}C$, but the values are spatially variable (−473‰ to −748‰) (Table 2; Fig. 5). The range in $\delta^{13}C$ values is small, from −11.6‰ to −12.3‰. DIC and TA values for most Castle Hayne wells are high, with DIC values ranging from ~3.8 to 8.0 mmol kg^{-1}, and TA values ranging from 3.4 to 6.6 meq L^{-1}.

The groundwater samples closest to the Pages Creek estuary are the NENHC Porters Neck wells (Fig. 3b). The three shallow wells from these sites are screened in a carbonate unit that has been designated as the Castle Hayne (Roberts 2002). However, these wells have higher $\Delta^{14}C$ and lower $\delta^{13}C$ values (−282‰ to −414‰ and −12.7‰ to −15.8‰, respectively) than other Cape Fear region Castle Hayne samples (Fig. 5). We suspect that this reflects local leakage of surficial groundwater down through the Castle Hayne confining unit.

Peedee groundwater—Wells screened in the Peedee aquifer have low $\Delta^{14}C$ values—generally lower than Castle Hayne wells but with some overlap (−548‰ to −998‰) (Table 2; Fig. 5). The $\delta^{13}C$ values of the Peedee wells are similar to the Castle Hayne wells (−9.9‰ to −12.7‰), with one higher value (−4.7‰). Peedee wells generally had the highest DIC values (6.4–7.1 mmol kg^{-1}) and the highest TA values (3.4–7.7 meq L^{-1}) of all groundwater samples.

Pages Creek spring—The Pages Creek spring samples have essentially constant $\Delta^{14}C$ and $\delta^{13}C$ values over a 3-yr sampling period (Table 1; Fig. 5). There is also a strong chemical and isotopic similarity between the spring samples and the Castle Hayne wells.

Surface freshwaters—We used two sets of samples to define the likely range of chemical and isotopic values for sur-

Table 3. $\Delta^{14}C$, $\delta^{13}C$, DIC, TA, and salinity values for river and Onslow Bay mid-shelf samples.

Surface water samples	Map legend	Date	Salinity	DIC (mmol kg^{-1})	$\Delta^{14}C$ (‰)	$\delta^{13}C$ (‰)	TA* (meq L^{-1})
Onslow Bay shelf waters							
Chapel bottom water 1†	S2	Jul 97	‡	2.19	+83.9	+1.13	‡
Chapel bottom water 2	S2	Jul 97	‡	2.15	+90.5	+1.15	‡
Chapel bottom water 3	S2	Jul 97	‡	2.06	+96.8	+1.20	2.52
Chapel bottom water 4	S2	Jul 97	‡	2.07	+80.1	+1.21	2.56
Chapel surface water 1	S2	Jul 97	‡	2.02	+92.5	+1.03	2.59
Chapel surface water 2	S2	Jul 97	‡	2.03	+95.2	+1.03	2.58
Rass bottom water 1	S1	Jul 97	‡	2.22	+90.3	+1.17	‡
Rass bottom water 2	S1	Jul 97	‡	2.25	+91.1	+1.22	‡
River samples							
NECFR§ Sta. 1	R1	Jul 00	11.923	1.279	+27.3	−8.34	1.12
NECFR Sta. 1	R1	Apr 01	5.758	0.804	+39.5	−8.39	0.64
NECFR Sta. 2	R2	Jul 00	0.154	0.651	−37.6	−15.10	0.56
NECFR Sta. 2	R2	Apr 01	0.075	0.512	+1.4	−16.66	0.27
NECFR Sta. 3	R3	Jul 00	0.092	0.603	‡	−16.35	0.42
NECFR Sta. 3	R3	Apr 01	0.067	0.532	+28.3	−16.70	0.27
NECFR Sta. 4	R4	Jul 97	‡	0.82	−9.2	−14.06	1.23
NECFR Sta. 4	R4	Jul 00	0.082	‡	‡	‡	0.32
NECFR Sta. 4	R4	Apr 01	0.078	0.641	−0.1	−13.73	0.45
Black River	R5	Apr 01	0.047	0.361	+83.5	−17.17	0.15
Cape Fear River	R6	Apr 01	0.072	0.537	+99.7	−11.64	0.37

* All mid-shelf and river alkalinity samples were unfiltered.
† Mid-shelf $\Delta^{14}C$ samples were collected by hand in 140-ml syringes and filtered through a 0.45-μm filter into a 125-ml glass bottle, then poisoned with 100 μl of saturated $HgCl_2$. Mid-shelf $\delta^{13}C$ and DIC samples were collected by hand in 4–6 10-ml syringes and filtered through a 0.45-μm filter, then flame-sealed in glass ampules for CO_2 stripping and DIC analysis.
‡ No measurement taken.
§ Northeast Cape Fear River.

face freshwaters in the region—river samples (including the Northeast Cape Fear, the Cape Fear, and the Black rivers) and streams that flow directly into the Pages Creek estuary.

Rivers—We sampled both piedmont rivers (the Northeast Cape Fear and the Cape Fear) and blackwater coastal plain rivers (the Black River) (Table 3). All three rivers have $\Delta^{14}C$ values comparable to most surficial groundwater samples and much higher than the Castle Hayne and Peedee groundwater $\Delta^{14}C$ values.

Pages Creek stream—The primary freshwater stream feeding into Pages Creek was measured at two slightly different locations. The July 2000 and April 2001 site was ~20 m above a culvert and elevation drop that sets the upstream limit to saltwater influence in Pages Creek, whereas the November 1999 sample was collected at a site a few hundred meters farther upstream. The July 2000 $\Delta^{14}C$ value was considerably lower than the November 1999 value (−162‰ vs. −79‰, respectively), and the $\delta^{13}C$ value was slightly higher (−12.2‰ vs. −13.2‰). DIC was also elevated in the July 2000 stream sample relative to November 1999 (1.6 mmol kg^{-1} and 0.9 mmol kg^{-1}). The April 2001 stream sample was intermediate between the other two stream samples in $\Delta^{14}C$, $\delta^{13}C$, and DIC values (−126.6‰, −12.63‰, and 1.5 mmol kg^{-1}) (Table 1; Fig. 6). Three other streams draining into Pages Creek (sampled only in April 2001) had even lower $\Delta^{14}C$ values (−176.5‰ to −191.8‰).

Seawater inputs—Onslow Bay shelf waters: The carbon isotopic values of the Onslow Bay midshelf bottom and surficial waters, measured in July 1997, plot in a tight cluster of high $\Delta^{14}C$ values (+80‰ to +97‰) and high $\delta^{13}C$ values (+1.03‰ to +1.22‰) (Table 3; Fig. 6). The DIC and TA values of these waters are also tightly clustered, ranging

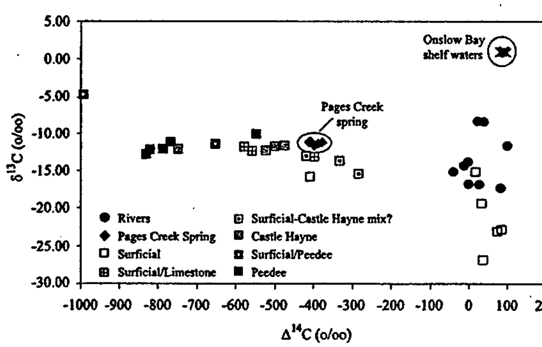

Fig. 5. $\Delta^{14}C$ and $\delta^{13}C$ values of groundwater, artesian spring, and river samples from the Cape Fear region of North Carolina. Peedee and Castle Hayne groundwaters have much lower $\Delta^{14}C$ than surficial groundwaters, rivers, and Onslow Bay shelf waters. Wells with carbon isotopic compositions between Castle Hayne and surficial aquifer ("Castle Hayne-surficial mix") values may indicate places where the Castle Hayne confining unit is leaky or absent.

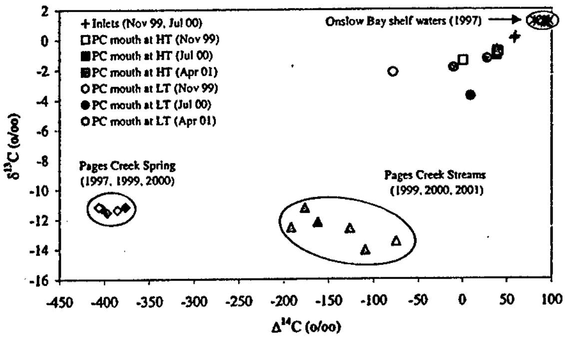

Fig. 6. $\Delta^{14}C$ and $\delta^{13}C$ values of Pages Creek estuary samples at low and high tide. Onslow Bay shelf waters, Mason Inlet (high and low tide), and Rich Inlet (high and low tide) have high $\Delta^{14}C$ and $\delta^{13}C$ values. Samples collected at the mouth of Pages Creek at low tide in November 1999, July 2000, and April 2001 show the addition of low-$\Delta^{14}C$ DIC relative to their high tide values.

from 2.0 to 2.3 mmol kg^{-1} and 2.5 to 2.6 meq L^{-1}, respectively.

Middle Sound and inlets: The Middle Sound samples at both high and low tide are chemically similar to Pages Creek estuary waters on the incoming tide (Table 1; Fig. 6). All Middle Sound samples have slightly lower $\Delta^{14}C$ and $\delta^{13}C$ values than the Onslow Bay shelf waters. Mason Inlet and Rich Inlet do not show large changes in isotopic composition, DIC, TA, or salinity within a tidal cycle. Tidal variations in $\Delta^{14}C$, $\delta^{13}C$, DIC, and TA at Mason Inlet (November 1999) and Rich Inlet (July 2000) were all within analytical precision. Variations in $\Delta^{14}C$, $\delta^{13}C$, DIC, TA, and salinity through a tidal cycle at Rich Inlet in July 2000 were equally small.

Inflow/outflow estuary samples: In November 1999 the outflow (low tide) salinity at the mouth of Pages Creek was about 10% lower than the high tide inflow (27.9 vs. 31.2) (Table 1; Fig. 6). The outflow $\Delta^{14}C$ (−78‰) was substantially lower than the inflow value (+0.3‰) and the outflow $\delta^{13}C$ value (−2.2‰) was lower than the inflow value (−1.4‰). From high to low tide, the DIC at the mouth of the creek increased from 2.2 mmol kg^{-1} to 2.6 mmol kg^{-1}.

In July 2000, the change in salinity from high tide to low tide was larger (a drop from 33 to 21), but the difference in $\Delta^{14}C$ values between high and low tide at the mouth was smaller, with $\Delta^{14}C$ = +38.3‰ at high tide compared with +9.3‰ at low tide (Table 1; Fig. 6). $\delta^{13}C$ values dropped from −1.1‰ at high tide to −3.8‰ at low tide, and, in contrast to the increases seen in November 1999 and April 2001, DIC values at the mouth of Pages Creek decreased from high (2.2 mmol kg^{-1}) to low tide (1.9 mmol kg^{-1}).

In April 2001, inflowing and outflowing waters were measured at the mouth of Pages Creek on two successive days. High tide salinity was similar on both days (34.7 and 34.8). However, low-tide salinity was lower on the first day (32.4) than the second (33.9), which presumably reflects a sampling time closer to full low tide on the first day. Both $\Delta^{14}C$ values at high tide are nearly identical (+39.1‰ and +40.0‰), but the day showing greater change in salinity has a much lower $\Delta^{14}C$ value at low tide (−10‰ compared with +27.9‰). The low-tide samples also show corresponding drops in $\delta^{13}C$ and increases in DIC on both days (Table 1; Fig. 6).

Discussion

Castle Hayne and Peedee groundwaters have much lower $\Delta^{14}C$ values than the other sources of DIC to the Pages Creek estuary: surface seawater (including shelf water, the ICW, and inflow to Pages Creek at high tide), surficial groundwater, and freshwater streams (Figs. 5, 6). Earlier, we showed that DIC removal processes such as gas evasion and photosynthesis do not influence DIC $\Delta^{14}C$ values. If we can be confident that there are no other sources of low-$\Delta^{14}C$ DIC to the system, then the DIC and DIC carbon isotopic values of the primary water input end members (inflowing ICW water, artesian springs, and freshwater streams) (Fig. 4) can be used to construct three-component mixing models to determine the relative importance of low-$\Delta^{14}C$ artesian discharge to the freshwater budget of the Pages Creek estuary.

Estuary DIC inputs—Salt marsh DIC inputs: Plant respiration and microbial decomposition of organic matter in salt marshes can be a significant part of estuarine carbon budgets (Hopkinson 1985; Cai and Wang 1998). However, respiration and decomposition in salt marsh sediments is likely to be dominated by relatively recent organic matter. If so, DIC inputs due to decomposition will have high $\Delta^{14}C$ values, similar to those of surface seawater and surficial groundwater, and they will not lead to overestimates of the artesian contribution to freshwater inputs.

We collected several low-tide samples from salt marshes within Pages Creek (Table 1). However, the low salinities of these samples show that they contain a significant freshwater component derived from streams and/or springs and thus do not reflect salt marsh decomposition processes alone.

We have only one set of samples from a salt marsh unaffected by known freshwater inputs: the E9–E11 samples from Middle Sound, just east (offshore) of the ICW. The tidal creek outflow (low tide) salinity is slightly higher than the inflow (high tide) salinity, perhaps because of evapotranspiration in the marsh. The outflowing tidal creek sample has a higher DIC, lower $\delta^{13}C$, and higher $\Delta^{14}C$ than the inflowing water from Rich Inlet at high tide. Thus there is DIC and $\delta^{13}C$ evidence of a DIC input from salt marsh decomposition but no indication of a low-$\Delta^{14}C$ DIC signature associated with this input. This is encouraging, although we note that the magnitude of any salt marsh DIC impact on the initial spring-stream-seawater mixture will be dependent on both the initial composition of the estuarine DIC (concentration and $\Delta^{14}C$) and on the amount and $\Delta^{14}C$ of the salt marsh DIC additions. For now we will assume that salt marsh decomposition adds high-$\Delta^{14}C$ DIC to Pages Creek, but this assumption still awaits a definitive test.

Artesian inflow: We use the observed Pages Creek spring DIC concentration and DIC isotopic values in our mixing calculations (below). The 4-yr consistency of DIC, $\delta^{13}C$, and

$\Delta^{14}C$ values in the Pages Creek spring suggests that its source composition is not highly variable. This lack of temporal variability further implies little mixing of the spring source with surficial groundwater, because such mixing is unlikely to be constant. Well head data from the Porters Neck limestone-screened wells suggest that the potentiometric surface of the shallowest confined aquifer is close to sea level, and borehole data from these wells suggest that the confining unit is very close (within a few meters) to the land surface. Therefore, this artesian spring may be the result of either a localized fault through the confining unit, or, perhaps more likely, the creek may have incised through the confining unit to the underlying aquifer.

Tidal creeks cutting through to this confined aquifer may not be an unusual occurrence in this area: there are several known springs in a neighboring creek, Futch Creek (Fig. 3b), and preliminary data from Futch Creek suggest that artesian inputs are significant to its freshwater budget. If so, such incised channels (cut through the exposed shelf at times of low sea level) may serve not only as high-conductivity offshore conduits for surficial groundwater but as foci for submarine groundwater discharge (A. Mulligan unpubl.).

Freshwater stream inflow: The carbon isotopic composition of the freshwater stream varies, but in November 1999, July 2000, and April 2001 the stream had lower $\Delta^{14}C$ values than surficial groundwater. These low $\Delta^{14}C$ values suggest that the stream is fed by some combination of artesian and surficial groundwater. For our mixing models, we will distinguish artesian inputs that discharge directly into the estuary from those that discharge elsewhere in the watershed and will therefore use the measured carbon isotopic composition of the stream as an end member in our mixing calculations. Because we expect surficial groundwater to have high $\Delta^{14}C$ and low $\delta^{13}C$ (Fig. 5; Table 2), our calculations of the artesian fraction of the total freshwater inputs will therefore be minimum estimates.

Mixing models—We show three–end-member mixing models for three sampling periods—November 1999, July 2000, and April 2001—plotted with the Pages Creek outflow composition in each season (Figs. 7a,b, 8a–f, 9a–c). The mixing models are constructed based on the measured DIC concentrations and DIC isotopic compositions of the three input end members, using the following equation (for seawater-spring-stream $\Delta^{14}C$- and $\delta^{13}C$-DIC mixing, where SW denotes seawater and *X, Y,* and *Z* are assumed fractions for each end member):

$$\begin{aligned}\Delta^{14}C_{mix} = {} & [(X_{SW} \times TCO_{2,SW} \times \Delta^{14}C_{SW}) \\ & + (Y_{spring} \times TCO_{2,spring} \times \Delta^{14}C_{spring}) \\ & + (Z_{stream} \times TCO_{2,stream} \times \Delta^{14}C_{stream})] \\ & \div [(X_{SW} \times TCO_{2,SW}) + (Y_{spring} \times TCO_{2,spring}) \\ & + (Z_{stream} \times TCO_{2,stream})] \end{aligned} \tag{4}$$

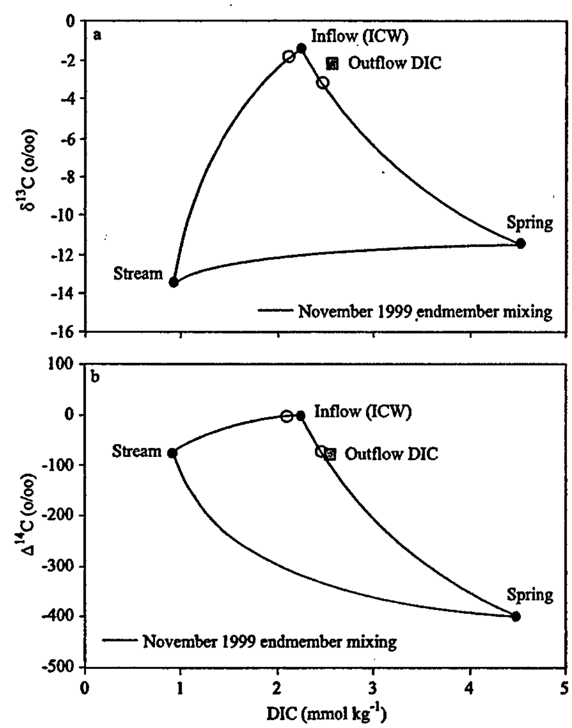

Fig. 7. November 1999 DIC concentration-isotope mixing curves among three Pages Creek estuary input sources: inflow from the ICW at high tide, freshwater stream input, and artesian groundwater/spring input. (a) DIC-$\delta^{13}C$ end-member mixing. (b) DIC-$\Delta^{14}C$ end-member mixing. Analytical precision for each graph is approximated by symbol size. The observed outflow DIC concentration and isotopic compositions are also shown (open squares). The open circles show the two–end member–only mixtures (inflow-stream and inflow-spring) predicted by the observed inflow-outflow salinity difference. As discussed in the text, these salinity-based predictions confirm the results of our DIC concentration-isotope mixing model.

$$\begin{aligned}\delta^{13}C_{mix} = {} & [(X_{SW} \times TCO_{2,SW} \times \delta^{13}C_{SW}) \\ & + (Y_{spring} \times TCO_{2,spring} \times \delta^{13}C_{spring}) \\ & + (Z_{stream} \times TCO_{2,stream} \times \delta^{13}C_{stream})] \\ & \div [(X_{SW} \times TCO_{2,SW}) + (Y_{spring} \times TCO_{2,spring}) \\ & + (Z_{stream} \times TCO_{2,stream})] \end{aligned} \tag{5}$$

We use salinity to determine the seawater input fraction to the Pages Creek estuary and the observed $\Delta^{14}C$ value of the outflow to partition between stream and spring freshwater inputs. Finally, we assess the impact of DIC inputs from salt marsh decomposition on our $\Delta^{14}C$-based SGD estimates.

End-member mixing model, November 1999: Two-component mixtures of waters having different DIC concentrations yield curved mixing lines on isotope-concentration plots (Fig. 7a,b). The spring and stream $\delta^{13}C$ values are similar (Fig. 7a) and would not permit us to distinguish between

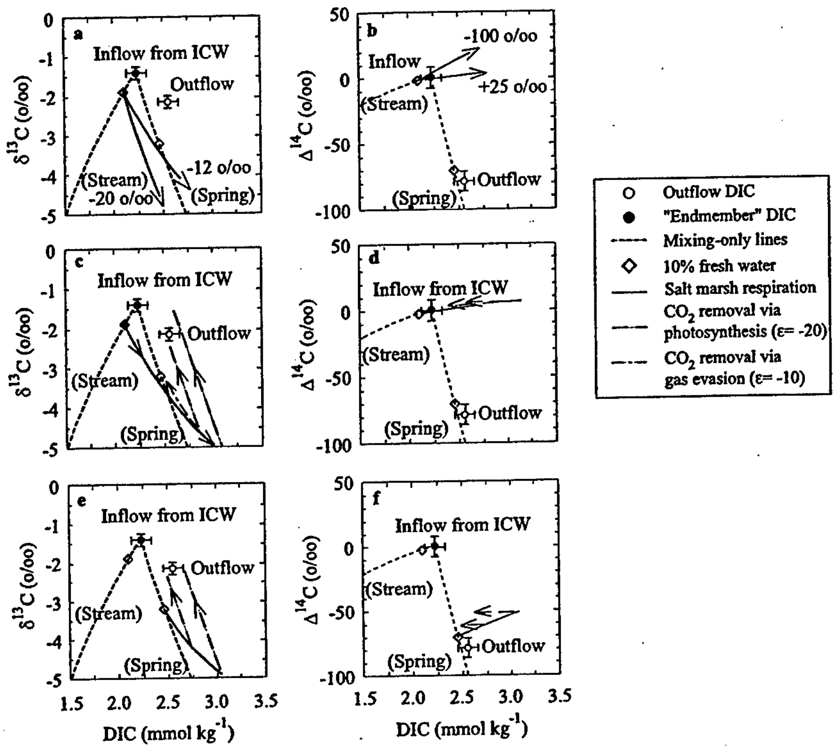

Fig. 8. (a,b) Salt marsh DIC additions ($\delta^{13}C = -12‰$ to $-20‰$; $\Delta^{14}C = +25‰$ to $+100‰$) to an inflow-stream mixture cannot match the outflow composition. (c,d) Salt marsh DIC input to an inflow-stream mixture plus DIC loss via photosynthesis (ε = 20‰) and gas evasion (ε = 10‰) still cannot match Outflow $\Delta^{14}C$. (e,f) Only salt marsh inputs to and DIC loss (via photosynthesis and gas evasion) from an inflow-spring mixture can approach the observed outflow $\Delta^{14}C$.

artesian and surficial groundwater even if there were no $\delta^{13}C$ fractionation effects due to photosynthesis, respiration, or CO_2 gas evasion. The $\Delta^{14}C$ value of the spring is, however, distinct from both the ICW inflow $\Delta^{14}C$ and the stream $\Delta^{14}C$ (Fig. 7b). The composition of water flowing out of the Pages Creek estuary at low tide, also plotted on these graphs ("Outflow DIC"), is most closely matched by a mixture of inflowing water from the ICW and spring-derived freshwater, with little or no stream contribution.

The outflowing water at the mouth of the Pages Creek estuary in November 1999 was 10% fresher than the inflow from the ICW. If we calculate a mixture of 10% freshwater (all from artesian springs) and 90% ICW water, the $\Delta^{14}C$ and DIC values of the calculated result plot very close to the $\Delta^{14}C$ and DIC values of the actual outflow from Pages Creek (Fig. 7b). Thus, our salinity measurements provide a useful cross-check of the estimates of artesian input to the Pages Creek estuary determined by the $\Delta^{14}C$-DIC mixing model and give support to the premise that biological carbon cycling is not a major controlling factor in the $\Delta^{14}C$ budget of this estuary.

Regardless, it is important to assess the potential impact of respiration, photosynthesis, and gas evasion on this interpretation of the data, because the composition of the November 1999 outflow falls outside the mixing triangles, indicating that other processes may be influencing outflow DIC isotopic composition. We first consider the possibility of matching the November 1999 outflow chemistry through some combination of respiration, photosynthesis, and gas evasion, applied to an inflow/stream mixture with no spring input (Fig. 8a,b). The solid arrows show the predicted DIC concentrations and carbon isotopic compositions for DIC additions to the 10% freshwater point on the inflow-stream mixing line, for respiration CO_2 with $\delta^{13}C$ values of $-12‰$ and $-20‰$ and respiration $\Delta^{14}C$ values of $+25‰$ and $+100‰$. The range of respiration $\delta^{13}C$ values is chosen to represent the types of vegetation in the estuary, from *Spartina* marsh grass ($\delta^{13}C = -12‰$) to marine organic matter ($\delta^{13}C = -20‰$). As discussed above, we believe that relatively high $\Delta^{14}C$ values are appropriate for salt marsh–derived DIC, because the $\Delta^{14}C$ values of atmospheric CO_2 have been higher than $+100‰$ since the 1950s, as a result of atmospheric testing of nuclear weapons in the 1950s and 1960s.

An acceptable fit to the outflow $\delta^{13}C$ value can be obtained if salt marsh respiration CO_2 ($\delta^{13}C = -12‰$ and $\Delta^{14}C =$

+25‰) is added to a 10% freshwater mixture along the inflow-stream mixing line and DIC is then removed via photosynthesis or gas evasion (under the assumption of an enrichment factor (ε) greater than or equal to -20 for photosynthesis and greater than or equal to -10 for gas evasion) (Fig. 8c,d). However, removal of CO_2 via photosynthesis or gas evasion from this mixture leaves the $\Delta^{14}C$ value essentially unchanged at +5‰; it does not improve the match to the low outflow $\Delta^{14}C$ value. We note that these DIC addition and loss calculations are not based on measured fluxes. They simply show that it is possible to match the observed DIC and $\delta^{13}C$ values without an artesian contribution to the freshwater budget. However, no combination of inputs and removal of modern (high $\Delta^{14}C$) DIC alone can match the observed outflow $\Delta^{14}C$ values. Only if the 10% freshwater is derived entirely from the spring is it possible to approach the observed outflow $\Delta^{14}C$ (Fig. 8e,f).

The mismatch between the model predictions and the observed outflow composition may be merely a function of end-member choice. If additional springs with higher DIC concentrations or higher $\Delta^{14}C$ values discharge into the Pages Creek estuary or if the high tide inflow composition had higher DIC or $\Delta^{14}C$ values than our ICW inflow sample, the mixing triangle would stretch to encompass the outflow DIC composition. In either case, though, the freshwater component of the outflow DIC composition at low tide in November 1999 would still be dominated by artesian spring input.

End-member mixing model, July 2000: A similar end-member mixing triangle for Pages Creek in July 2000 is shown in Fig. 9a. The data suggest that nearly all freshwater input to the Pages Creek estuary in July 2000 was from stream flow rather than spring discharge.

The DIC $\Delta^{14}C$ value of the July 2000 inflow stream sample is quite low. We suspect that this reflects spring discharge in the stream watershed. Using the observed July 2000 stream composition therefore gives us a minimum estimate of the fractional contribution of artesian flow to the Pages Creek estuary freshwater budget. However, even if we used the November 1999 stream composition to interpret the July 2000 outflow data, we would conclude that in July 2000 the freshwater inputs were predominantly stream-derived, with artesian inputs <10% of the total freshwater input. This result stands in sharp contrast to the situation in November 1999 (Fig. 9b).

End-member mixing model, April 2001: In April 2001, we sampled inflow and outflow at the mouth of Pages Creek on two successive days. These are plotted with the end-member mixing triangles (Fig. 9c). We use the July 2000 spring composition to construct the mixing model because no spring sample was collected in April 2001; the high consistency of the chemical composition of the spring samples in previous sampling periods makes this a realistic assumption. The stream end-member DIC composition is the average composition of the measured stream inputs into Pages Creek in April 2001.

As in November 1999, these data suggest that in April 2001 nearly all the freshwater input to Pages Creek was from spring discharge. The salinity decrease from high to low tide

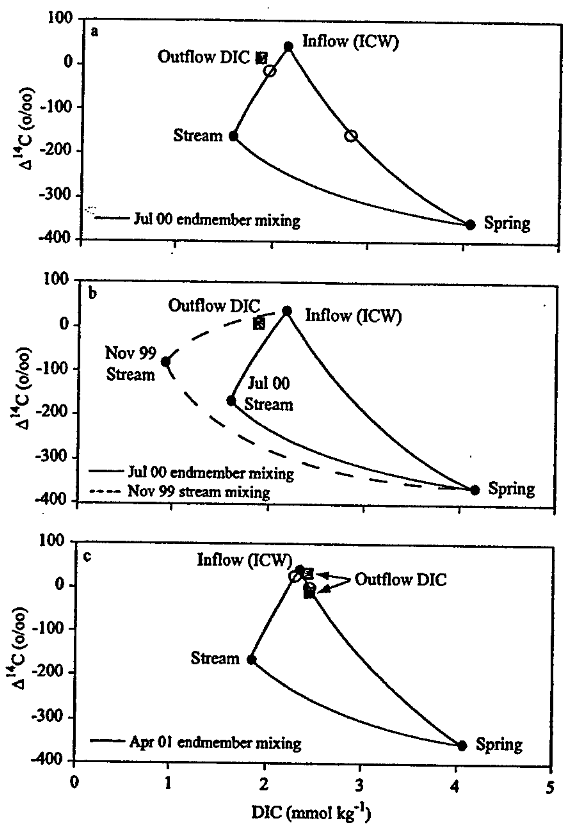

Fig. 9. DIC-DIC isotope mixing curves: (a) July 2000 DIC-$\Delta^{14}C$ mixing, suggesting that stream inputs were the dominant source of freshwater to Pages Creek at low tide in July 2000. (b) July 2000 end-member mixing triangle with November 1999 stream composition (higher $\Delta^{14}C$ and lower $\delta^{13}C$ values than July 2000 stream). When we used the November 1999 stream composition to interpret the July 2000 outflow data, the freshwater inputs in July 2000 still appeared to be predominantly stream-derived. (c) April 2001 DIC-$\Delta^{14}C$ mixing, suggesting that artesian spring inputs were the dominant source of freshwater to Pages Creek at low tide in April 2001.

was <10% on both days, as represented by the open circles in the graph. In each case, the calculated salt mass balance, under the assumption of only artesian freshwater input, produces a DIC composition similar to the outflow composition.

Sensitivity analysis—Even if respiration-derived CO_2 does not add low-$\Delta^{14}C$ DIC to the estuary, such DIC additions will increase the uncertainty in our SGD estimates. To evaluate this effect, we calculate changes in the November 1999 $\Delta^{14}C$ and TCO_2 values as a result of successive salt marsh DIC additions (Fig. 10). Salt marsh DIC is here assumed to have a $\Delta^{14}C$ value of +100‰, representing the respiration of young organic matter, and a $\delta^{13}C = -12‰$, the $\delta^{13}C$ value of the dominant vegetation in the marsh, *Spartina alterniflora*. Additions of high-$\Delta^{14}C$ DIC produce an upward slope in the DIC addition lines. This slope, combined with the ana-

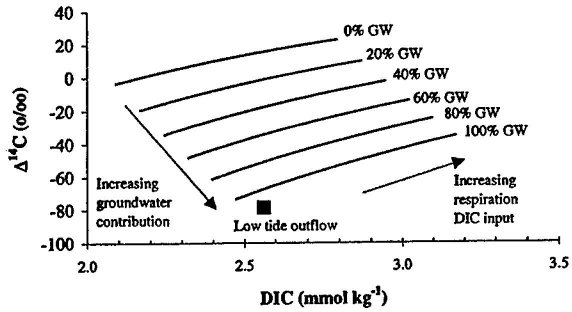

Fig. 10. Sensitivity calculations of the impact of salt marsh DIC additions to the DIC isotopic composition of Pages Creek at low tide in November 1999, for varying percentage contributions of artesian groundwater to the total freshwater input. Total freshwater input is 10%, based on a salt balance at the mouth of Pages Creek between high and low tides. The starting point for each line is a given percentage artesian groundwater contribution to the freshwater budget, with increasing additions of respiration DIC trending to the right. $\Delta^{14}C$ from respiration is assumed to be 100‰. Three-component mixing model estimates of artesian groundwater contribution to the outflowing water (as discussed in the text) suggest that artesian groundwater makes up 100% of the total freshwater input. Because of the change in $\Delta^{14}C$ as a result of respiration DIC inputs, the uncertainty of this estimate is about ±20%.

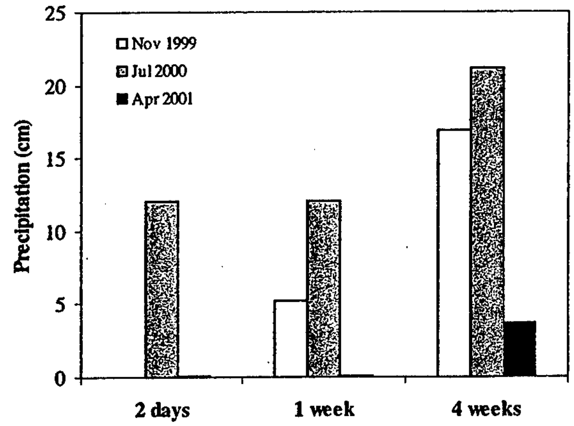

Fig. 11. Precipitation measured at the Wilmington airport (20 km northwest of Pages Creek; precipitation data provided by the State Climate Office of North Carolina at NC State University) for several time periods prior to sampling in November 1999, July 2000, and April 2001. Changes in the relative amount of stream flow may be the result of either seasonal or event-driven changes in precipitation. There was little difference between total precipitation for the 4 weeks prior to our November 1999 Pages Creek estuary sampling period (spring-dominated) and precipitation for the 4 weeks prior to July 2000 sampling (stream-dominated). However, rainfall occurred within 2 days of sampling in July 2000; in November 1999 the last rainfall occurred a week prior to sampling. Precipitation events on a scale of days prior to sampling in the Pages Creek estuary may determine the change in the relative contributions of artesian inputs and stream inputs to the Pages Creek freshwater budget.

lytical uncertainty in the $\Delta^{14}C$ values, yields an uncertainty in the groundwater fraction of total freshwater of about ±20%. This uncertainty will vary as a function of both the initial composition of the estuarine water (its DIC concentration and $\Delta^{14}C$) and the $\Delta^{14}C$ of the added DIC. The greater the ^{14}C difference between DIC and added carbon, the steeper the $\Delta^{14}C$-DIC addition lines and the greater the uncertainty in the final SGD estimate. This highlights the importance of determining the $\Delta^{14}C$ signature of salt marsh decomposition.

Seasonal change in relative artesian ground-/streamwater contributions to Pages Creek—On the basis of the mixing models described above, nearly all the freshwater input into the Pages Creek estuary during our sampling in November 1999 and in April 2001 was low-$\Delta^{14}C$ artesian groundwater. In July 2000, nearly all freshwater was streamwater. This change in the relative contributions of ground- and surface water to the Pages Creek freshwater budget among November 1999, July 2000, and April 2001 may be driven by factors affecting groundwater flow rates from the springs and/or by factors affecting total stream input to the estuary.

Changes in the flow rate from springs into the estuary presumably reflect changes in the hydraulic head of the source aquifers. Hydraulic head data from the surficial and the Castle Hayne aquifers at Topsail Beach showed a drop of ~1 m in head for both aquifers between November 1999 and July 2000. This summer drawdown, possibly a consequence of groundwater pumping in the Castle Hayne aquifer and of both high summertime evapotranspiration and pumping in the surficial aquifer, may affect the groundwater flow rate from springs. However, a correlation of Pages Creek spring flow to Topsail Beach well-head data was less apparent for April 2001 (spring-dominated), when head levels were not much higher than they were in July 2000 (stream-dominated). In addition, although head levels at Topsail Beach dropped to a 2-yr minimum in November 2001 (after a long regional drought), the flow rate from the Pages Creek spring was not visibly decreased. The apparently steady flow observed from this spring suggests that artesian input into the Pages Creek estuary is not highly variable.

We suspect the most likely explanation for changes in the relative contribution of groundwater to the Pages Creek estuary is precipitation-related variations in stream flow superimposed on background levels of artesian discharge. Stream input can be affected both by precipitation, on a seasonal or on an event scale, and by seasonal changes in evapotranspiration rates. Although rainfall in Wilmington is on average higher in July than in November and April, higher rates of evapotranspiration in the summer may prevent increased precipitation from infiltrating to the surficial aquifer. In the Pages Creek estuary, changes in stream inputs appear to be more strongly correlated with rainfall events on short timescales prior to sampling (Fig. 11). There was little difference in total precipitation between the 4 weeks prior to the November 1999 sampling period (spring-dominated) and July 2000 sampling (stream-dominated). However, >12 cm of rain fell within 2 days prior to sampling in July 2000, whereas in November 1999 the last rainfall (5 cm) occurred a week prior to our sampling. This suggests that precipitation events on a scale of days prior to sampling may control stream inputs to the Pages Creek estuary, even though the low $\Delta^{14}C$ value of the Pages Creek stream in July 2000 (relative to November 1999 and April 2001) indicates that this stream, at least, is not fed solely by runoff.

We have developed a carbon isotope–based method for quantifying the artesian component of freshwater inputs to estuaries and the coastal ocean. Using this method, we observed striking variability in the relative contributions of stream flow and artesian SGD to the freshwater budget of a small estuary in coastal North Carolina. Artesian flow dominated the freshwater budget in November 1999 and April 2001, whereas stream flow accounted for all the freshwater inputs in July 2000. We suspect that this reflects short-term (1–3 day) increases in stream flow as a result of precipitation events, superimposed on a more constant artesian discharge. The chemical consistency (and apparently steady discharge) of the artesian flow implies that tidal creek channels in this region have penetrated through the shallowest confining unit to the underlying aquifer. This suggests that creek channels (both modern and relict) may act as high-conductivity zones of direct connection between confined aquifers and coastal waters.

This carbon isotope–based method offers the advantage of distinguishing artesian groundwater inputs from surface and shallow subsurface runoff and thereby complements other tracer approaches such as the salinity mass balance. The simultaneous study of multiple tracers, each responding to a different suite of processes, will provide a more comprehensive picture of groundwater discharge into estuaries and the coastal ocean than can be obtained from any single approach.

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Chapter III. DEVELOPMENT OF THE $\Delta^{14}C$ METHOD: DIC-$\Delta^{14}C$ INPUT VARIABILITY AND CONSTRAINTS

Abstract

In coastal North Carolina, fresh water artesian discharge is characterized by a low $\Delta^{14}C$ signature acquired from the carbonate aquifer rock, and thus can be used to estimate the artesian contribution to estuarine freshwater budgets (Gramling et al 2003). In this chapter, the $\Delta^{14}C$-based method for estimating the artesian component of the fresh water input to an estuary is expanded; the generality of the method is tested by applying it to both the Pages Creek estuary and the Futch Creek estuary, and include new data from April 2001, November 2001, and April 2002. Application of the $\Delta^{14}C$ method to two inlets connecting the Intracoastal Waterway near these estuaries with the Atlantic Ocean suggests that the SGD-derived $\Delta^{14}C$ signal is not strong enough to be recognized in the inlets, where deviations from seawater composition are small. Additionally, measurements of salt marsh pore waters demonstrated that organic matter decomposition in salt marshes does not appear to be a source of low $\Delta^{14}C$ DIC, confirming an assumption made by Gramling et al (2003).

New spring and stream data from April 2001, November 2001, and April 2002 enable us to make a more rigorous assessment of the variability of the DIC and DIC isotopic compositions of these inputs to the estuaries. While spring chemistry was highly consistent through time at each of two spring sites sampled over three years, and spring $\Delta^{14}C$ values were highly consistent both spatially and temporally, spring DIC concentrations were variable within a single estuary. In contrast, substantial variability in stream chemistry was observed with respect to both DIC and $\Delta^{14}C$ values. Spring inputs dominated the fresh water budgets of both estuaries during April 2001 and April 2002, and dominated the fresh water budget of the Futch Creek estuary in November 2001. The $\Delta^{14}C$ data suggest that spring inputs provided only 10-50% of the fresh water inputs to the Pages Creek estuary in November 2001.

Introduction

$\Delta^{14}C$-based estimates of artesian inputs into the Pages Creek estuary during three sampling periods (November 1999, July 2000, and April 2001) were presented in Chapter II. Here, new data is presented to develop the $\Delta^{14}C$ method, and is expanded to include new data from the Pages Creek estuary (from November 2001 and April 2002) and from a neighboring estuary, the Futch Creek estuary (from April 2001, November 2001, and April 2002). Additionally, spring and stream data from these sampling periods is presented, groundwater data from the wells closest to Pages and Futch Creeks, and data from two inlets connecting the Intracoastal Waterway near these estuaries with the Atlantic Ocean. Two new aspects of the study are the addition of salt marsh pore water data and hourly time series in both the Pages and Futch Creek estuaries.

Respiration DIC additions were not measured in Chapter II, but were assumed to contribute DIC with high $\Delta^{14}C$, originating from modern organic matter. However, respiration of older organic matter is a potential source of low-$\Delta^{14}C$ DIC to the estuaries, which could introduce significant error into estimations of spring inputs. Therefore, this study includes analyses of marsh pore waters to determine the $\Delta^{14}C$ value of DIC added from respiration in these estuaries.

Methods

Study site

The study site information presented here primarily includes information not provided in the previous chapter. The geologic and hydrogeologic characteristics of the Onslow Bay region of southeastern North Carolina are described in Chapter II.

Pages Creek and Futch Creek are small, well-mixed tidal creeks located on the Intracoastal Waterway (ICW) northeast of Wilmington, NC (**Figure 1**). The closest hydraulic connection between this section of the ICW and Onslow Bay are two inlets that cut through the salt marsh barrier islands, Rich Inlet to the north and Mason Inlet to the south.

The Pages Creek estuary, including fringing salt marshes that are inundated at high tide, has an area of about 6.7×10^5 m^2. The Futch Creek estuary is about two-thirds the size of the Pages Creek estuary, with an area of about 4.4×10^5 m^2. The Pages Creek tide range averages about 0.9 meters, while the Futch Creek tide range averages about 0.6 meters. At low tide, the upper creekbeds of both Pages and Futch Creeks are exposed, even during neap tide.

Fresh water inputs into each creek consist of several small, intermittent streams (recharged by local precipitation and by groundwater), artesian springs, and diffuse groundwater seepage from an unconfined aquifer. In the Pages Creek estuary, one large spring at the upstream end of the estuary is the most visible and temporally consistent source of confined groundwater (Figure 1, Table 1), though other smaller and more temporally variable springs have been observed in the immediate vicinity. In the Futch Creek estuary at least three large springs have been observed to last for the duration of the study (Roberts 2002) (Figure 1, Table 1).

Sample collection and analysis

The dissolved inorganic carbon (DIC), titration alkalinity (TA), DIC isotopic, and salinity samples presented here were collected in April 2001, November 2001, and April 2002. April 2001 samples were collected about one week prior to the spring tide. November 2001 samples were collected before, during, and after the spring tide. April 2002 samples were collected during neap tide. Estuary samples were collected in two ways: in high tide/low tide pairs (just prior to full high or full low tide), and in time series: every hour for a full 12-hour tidal cycle. The primary goal of time series sampling was to determine whether sampling twice during a tidal cycle (in high tide/low tide pairs) is sufficient to capture the full range of tidal variations in DIC chemistry observed in the estuaries. High tide/low tide pairs were collected from the Pages and Futch Creek estuaries in April 2001, November 2001, and April 2002. Time series data were collected from the Pages Creek estuary in November 2001 and April 2002, and from the Futch Creek estuary in April 2002. All estuary samples were collected just inside the mouth of each creek (Figure 1, Table 1).

To consider how estuarine tracer fluxes might impact the coastal ocean, and to determine how strongly our $\Delta^{14}C$ tracer signals persist when integrated with signals from other neighboring creeks and salt marshes, samples were collected in high tide/low tide pairs from Rich Inlet and Mason Inlet (Figure 1). High and low tide samples were collected both at the mouth of each inlet (where the inlet connects to Onslow Bay), and also where the inlet connects to the ICW (Table 1).

Samples were also collected from the primary fresh water inputs to each creek: a large spring discharging directly into the Pages Creek estuary (also sampled during the November 1999, July 2000, and April 2001 collection periods discussed by Gramling et al (2003)), a spring discharging directly into the Futch Creek estuary, and fresh water streams flowing into each estuary (Figure 1, Table 1).

Groundwater samples from monitoring wells screened in the surficial, Castle Hayne and the underlying Peedee aquifers were collected in July 2000 and April 2002. July 2000 wells (including both surficial and Northeast New Hanover Conservancy (NENHC) wells) were sampled as described in Chapter II. April 2002 groundwater samples were collected only from the six Porters Neck Road NENHC wells closest to Pages and Futch Creeks, including three Castle Hayne-screened wells and three Peedee-screened wells (Figure 1, Table 1).

$\Delta^{14}C$ and salinity sampling and analysis

Estuary and inlet DIC, DIC isotopic, and salinity samples, and the November 1999 and July 2000 stream samples, were collected by submerging and manually tripping a 5-liter Niskin bottle; where the water column was deep enough (all high tide estuary samples, and Pages Creek estuary low tide samples), the Niskin was held vertically with its top at 0.25 cm to 0.5 cm below the water surface. Shallow water column samples were collected by holding the Niskin horizontally under the water surface.

April 2001, November 2001, and April 2002 stream and spring $\Delta^{14}C$ and salinity samples were collected with a manual bilge pump, holding the top of the hose 0.25 cm to 0.5 cm below the water surface, with the exception of the November 2001 Pages Creek spring sample, collected by holding the Niskin horizontally under the water surface. All samples were unfiltered, except the April 2002 spring and stream samples, which were filtered through a 1-µm filter. July 2000 and April 2002 groundwater samples were collected by submersible pump, after pumping three well volumes to flush the wells.

Water samples for all $\delta^{13}C$ and $\Delta^{14}C$ values, as well as the July 2000 DIC concentrations, were collected in 500 ml glass bottles with greased ground-glass stoppers and poisoned with 100 μl of saturated $HgCl_2$. $\Delta^{14}C$ analyses were conducted at the National Ocean Sciences Accelerator Mass Spectrometer (NOS-AMS) facility in Woods Hole, Massachusetts. The precision for the NOS-AMS $\Delta^{14}C$ analyses is ± 5 ‰, precision for $\delta^{13}C$ is ± 0.1‰, and for DIC is ± 3%.

April 2001, November 2001, and April 2002 DIC and alkalinity samples were titrated using a potentiometric closed-cell titration system, where DIC and alkalinity values were determined for 100 ml of sample based on a modified Gran function method (Bradshaw et al 1981). Analyses were standardized to a certified reference material with alkalinity known to a precision better than 0.01%. For samples with salinity > 5 ppt, alkalinity was determined to a precision of 0.5%, while alkalinity for samples with salinity < 5 ppt was calculated to a precision of 2% (both precisions based on seawater standard replicate analyses). July 2000 alkalinity values were determined by the Gran function titration method, where 1 ml of sample was titrated to a precision of 0.5%.

All salinity samples, with the exception of samples from November 1999, were collected in 100-ml glass bottles and analyzed by the hydrographic facility in the Physical Oceanography department at Woods Hole Oceanographic Institution, with a precision better than ± 0.01 ppt. November 1999 salinity values were estimated using a hand-held salinometer to a precision of ± 0.1 ppt.

November 2001 sediment pore water samples were collected by hand from the top 0-6 cm of two sites within the Middle Sound marsh just below Rich Inlet (Figure 1). The mud was collected into centrifuge tubes, of which half were stored on ice prior to centrifuging, and half were kept at room temperature to determine the changes in carbon isotopic composition of the water resulting from post-sampling respiration CO_2 additions. Samples were spun for five minutes at 5000 rpm to separate pore waters; the pore water was drawn into a syringe and filtered through a 0.45-μm Gelman Acrodisc syringe filter into N_2-flushed glass ampules containing $HgCl_2$ (McCorkle et al 1985). The ampules were immediately flame-sealed for later DIC extraction and DIC isotopic analysis. CO_2 for isotopic analyses was stripped from seawater as described in McCorkle et al (1985). Pore water radiocarbon samples were prepared by pooling CO_2 stripped from individual pore water samples within each of the two sampling sites until at least 0.5 mg C was collected to ensure high-precision AMS analyses. Pore water $\delta^{13}C$ and $\Delta^{14}C$ measurements were also made at the NOS-AMS facility.

As described in Chapter II, $\Delta^{14}C$ values are determined by the normalization of $\delta^{14}C$ values to $\delta^{13}C = -25‰$, to remove fractionation effects that can result from CO_2 evasion or photosynthesis (Stuiver and Robinson 1974). However, Torn and Southon (2001) have suggested that in cases where isotopic fractionation effects are minimal and mixing of CO_2 from sources with very different isotopic compositions predominates, this normalization may result in an error in estimation of the ^{14}C content of the sample. In this study, both mixing and isotopic fractionation effects may be important, and $\delta^{13}C$-normalized radiocarbon concentrations ($\Delta^{14}C$ values) were chosen.

Results

Estuary high/low tide pairs

The Futch Creek estuary high tide - low tide salinity difference (ΔSal) was always larger than the ΔSal in the Pages Creek estuary (Tables 2-3). For both estuaries, ΔSal was much smaller in November 2001 than in either April 2001 or April 2002. November 2001 ΔSal averaged 0.2 ppt in the Pages Creek estuary and 1.7 ppt in the Futch Creek estuary (Figures 2a, b).

Pages Creek estuary high tide salinity values in April 2001 were, on average, more than 1 ppt lower than high tide salinities from later sampling dates (34.8 ppt in April 2001 compared to 36.4 ppt in November 2001 and 36.2 ppt in April 2002). Futch Creek estuary high tide sample salinity was more consistent between sampling periods, averaging 36 ± 0.4 ppt.

$\Delta^{14}C$ values in both estuaries decreased from high to low tide (Figures 3a-b). The $\Delta^{14}C$ change between high and low tide was invariably larger at Futch than at Pages. Additionally, at Futch Creek the change in $\Delta^{14}C$ from high to low tide ($\Delta\ \Delta^{14}C$), when normalized to the high/low tide change in salinity ΔSal, was highly consistent among most sampling days in April 2001, November 2001 and April 2002 (Figure 4a). $\Delta\ \Delta^{14}C/\Delta$Sal was much more variable in the Pages Creek estuary (Figure 4b).

DIC concentrations increased from high to low tide during all sampling times at Futch, averaging 2.2 $\pm$0.05 mmol/kg at high tide and 2.4 $\pm$0.16 mmol/kg at low tide (Figures 5a, b). At Pages, DIC increased from high to low tide in April 2001 and April 2002, but in November 2001, the DIC concentrations showed no consistent trend.

$\delta^{13}C$ values generally decreased from high to low tide in the Futch Creek estuary, with the exception of the high/low tide pairs in April 2001 (Figures 6a, b). Pages Creek estuary $\delta^{13}C$ values showed no consistent trend from high to low tide in April 2001 or November 2002, while in April 2002, $\delta^{13}C$ values decreased from high to low tide. As in Futch, the April 22, 2001 high/low tide pair both showed unusually low $\delta^{13}C$ values.

Unlike the DIC concentrations, TA values showed no consistent high/low tide trend at the Futch Creek estuary in April 2001 and November 2001, though TA increased from high to low tide in April 2002. There was also no consistent trend at the Pages Creek estuary in April 2001 and November 2001, but TA also increased from high to low tide during April 2002 (Figures 7a, b).

Time series

Hourly time series samples were collected in November 2001 and April 2002 at the mouth of the Pages Creek estuary, and in April 2002 at the mouth of the Futch Creek estuary (Table 4). Although only a few points within each time series were analyzed for $\Delta^{14}C$, the lowest $\Delta^{14}C$ values occurred at the lowest tide stage, with a general increase in $\Delta^{14}C$ with higher tide stage (Figures 8a-c). A similar trend was observed in all time series for $\delta^{13}C$ values, with the lowest $\delta^{13}C$ at the lowest tide stage (Figures 9a-c).

DIC and TA values from the Pages Creek estuary November 2001 time series showed some scatter; both DIC and TA had a maximum value at low tide, but the rising and falling tide data showed no clear trend. In both the Pages and Futch April 2002 time series, however, the DIC and TA values were closely linked to the tidal cycle, with the highest DIC and TA at low tide, and the lowest values at high tide (Figures 10 and 11).

Rich Inlet and Mason Inlet – High tide/Low tide pairs

April 2002 high tide/low tide inlet measurements were taken at the mouths of each inlet, where they connected to the Atlantic Ocean, and also where they intersected the Intracoastal Waterway (ICW) (Figure 1). Salinity values were not highly variable as a function of sampling location within the inlet, or from inlet to inlet (Table 5). ΔSal was always small and decreased from high tide to low tide, averaging -0.12 ppt in Rich Inlet and -0.09 ppt in Mason Inlet (Figure 12a). The single November 2001 inlet measurement, made at low tide, showed a higher salinity (36.5 ppt) than was observed at high or low tide in the inlets in April 2002. For the inlet high/low tide pairs, the difference in $\Delta^{14}C$ value was always small, and generally within the ± 5‰ measurement error (Figure 12b). High/low tide DIC, $\delta^{13}C$, and TA differences tended to be small as well (Table 5).

Fresh water samples

Springs

The Pages Creek Bayshore spring $\Delta^{14}C$, $\delta^{13}C$, DIC, and TA values were highly consistent throughout sampling (-406 ± 3 ‰, -11 ± 0.1 ‰, 4.3 ± 0.2 mmol/kg, and 3.7 ± 0.0 meq/L, respectively) (Table 6, Figures 13 and 14). Futch Creek estuary springs were also relatively consistent with respect to $\Delta^{14}C$ values (-441 ± 14 ‰) and $\delta^{13}C$ values (-12 ± 0.7 ‰).

Futch Creek spring DIC and TA concentrations fell into two distinct groups (Table 6). The Saltwood Lane spring (sampled every season) had DIC values that were consistently lower (2.8 ± 0.0 mmol/kg) than the DIC in other springs within either estuary

(4.6 ± 0.4 mmol/kg). TA values followed a similar pattern. In April 2001, two additional Futch springs were sampled, but the DIC and TA values of the Saltwood Lane April 2001 sample remained consistent with the other Saltwood spring samples (from July 2000, November 2001, and April 2002) rather than the other April 2001 Futch spring samples.

Streams

Stream DIC and DIC isotopic compositions varied not only by location, but also by sampling time. Although most of the Pages Creek Bayshore stream samples had salinity < 0.2 ppt, the November 2001 Bayshore stream sample had a salinity of 31 ppt. The Bayshore stream $\Delta^{14}C$ values varied from –79 ‰ to –200 ‰ over three sampling periods (including only Bayshore stream samples with salinity < 1 ppt) (Table 6, Figure 13). Bayshore stream DIC concentrations were also highly variable, ranging from 0.9 to 2.1 mmol/kg. $\delta^{13}C$ and TA values for the different stream samples also reflected this variability (-12 ± 1 ‰ and 1.5 ± 0.4 meq/L, respectively) (Figure 14). Two other streams entering the Pages Creek estuary had $\Delta^{14}C$ values from +86 ‰ to –192 ‰, and a wide range of $\delta^{13}C$, DIC, and TA values as well.

Only one stream was observed to enter the Futch Creek estuary (Scotts Hill Loop). The April 2001 Scotts Hill Loop sample had high $\Delta^{14}C$ (+87 ‰), low $\delta^{13}C$ (-19 ‰), and low DIC and TA values, while the November 2001 and April 2002 samples showed the reverse, with low $\Delta^{14}C$ (-173 ± 18 ‰), high $\delta^{13}C$ (-11 ± 2 ‰), and high DIC and TA values.

Groundwater

All NENHC wells screened in the Castle Hayne aquifer, and most screened in the Peedee, had salinity less than 1 ppt in both July 2000 and April 2002 (Table 7). The Porters Neck Castle Hayne-screened wells had $\Delta^{14}C$ values ranging from –282‰ to –461‰, while Peedee-screened wells had lower $\Delta^{14}C$ values, ranging from –770‰ to –832‰ (Figure 13). Peedee wells had higher DIC (6.4 to 7.0 mmol/kg) and TA values (5.6 to 6.0 meq/L) than the Castle Hayne wells (2.2 to 5.1 mmol/kg and 1.5 to 4.5 meq/L, respectively). $\delta^{13}C$ values overlapped between aquifers, with a larger range of $\delta^{13}C$ values measured in the Castle Hayne wells (–11‰ to –13 ‰ in the Peedee wells, and $\delta^{13}C$ = –11‰ to –15‰ in the Castle Hayne) (Figure 14). The $\Delta^{14}C$ values within each Porters Neck well were highly consistent from July 2000 to April 2002, as were the $\delta^{13}C$, DIC, and TA values.

A summary of the relative $\Delta^{14}C$ values of the different DIC input sources to both estuaries is shown in Figure 13. The Peedee aquifer had the lowest $\Delta^{14}C$ values, at < –700‰; the Castle Hayne aquifer and the spring $\Delta^{14}C$ values were similar, at around –400‰, and the stream $\Delta^{14}C$ values showed a range from about +85‰ to –200‰. Estuarine high tide $\Delta^{14}C$ values were between +80‰ and +40‰, while low tide values ranged from about +50‰ to –140‰. Inlet $\Delta^{14}C$ values were generally > +50‰.

Salt marsh DIC additions

Surface waters overlying the marsh at Rich Inlet had $\Delta^{14}C$ values averaging +79 ± 7 ‰ for the samples kept on ice prior to analysis, and $\Delta^{14}C$ values averaging +57 ± 0.6 ‰ for the samples kept at room temperature (Figure 1, Tables 8-9). The pore waters from Site 1 had $\Delta^{14}C$ values averaging = +25.0 ± 20 ‰ (samples on ice) and +42.0 ± 4 ‰ (samples at room temperature). $\delta^{13}C$ values averaged –3.4 ± 0.2 ‰ (samples on ice) and –4.6 ± 0.3 ‰ (room temperature). At Site 2, the average $\Delta^{14}C$ of the pore waters was +18 ± 17 ‰ (samples on ice) and +24.3 ‰ (room temperature; only one pooled $\Delta^{14}C$ value was measured). The average $\delta^{13}C$ values were –3.0 ± 0.3‰ (samples on ice) and –4.6 ± 0.8 ‰ (room temperature).

Discussion

In this section, a comparison between time series and high/low tide data is discussed, as well as inlet high/low tide data. Additionally, the DIC and DIC isotopic values of the salt marsh, spring, and stream inputs to the Pages and Futch Creek estuaries are assessed. These inputs are then included in mixing models to estimate artesian inputs to the estuaries as a fraction of the total fresh water input.

Estuarine time series / high and low tide pair comparison

The DIC and DIC isotopic data from the three Pages and Futch estuarine time series were compared with the high/low tide pairs from each estuary within the same collection period, to determine whether sampling twice during a tidal cycle (before high tide and before low tide) is sufficient to capture the full range of tidal variations in DIC chemistry observed in the estuaries. When the salinity and $\Delta^{14}C$ values of the time series data are plotted together with the high/low tide pairs from each estuary, it is apparent that the data from each time series fell along similar salinity-related trends to their estuarine tide pairs (Figures 15a-b). This was particularly clear for the Futch April 2002 time series; the Pages April 2002 time series showed more scatter but followed the general trend (in Figure 15b, the lowest-salinity high and low tide pair represent April 2001 data, for which there was no corresponding time series). The range of salinity values in the November 2001 times series was so small that the time series data plotted within the range of high tide samples.

A similar time series – high/low tide pair comparison for $\delta^{13}C$ and salinity values shows that at Futch, the April 2002 time series $\delta^{13}C$ values again plot exactly within the range of the tide pair data, while at Pages, there is again more scatter (Figures 16a-b). Here, the two time series (November 2001 and April 2002) follow different salinity trends corresponding with their respective high and low tide pair trends. A comparison of the DIC and TA time series and high/low tide values at both estuaries shows similar patterns (Figures 17 and 18). From these data, the HT-LT pairs do provide a realistic picture of the overall trends through the full tidal cycle.

Inlet high tide / low tide pairs

Although the inlet high/low tide pairs were sampled to make estimates of artesian input on the ocean side of the ICW, the differences in both $\Delta^{14}C$ (<10‰) and salinity (~0.1 ppt) were too small to construct effective mixing models to determine spring inputs

(Figure 12). Additionally, of the four high/low tide pairs, two had higher $\Delta^{14}C$ values at low tide than at high tide, suggesting that, at least in April 2002, the artesian $\Delta^{14}C$ signal did not persist outside of the estuaries.

$\Delta^{14}C$ content of DIC from decomposition in salt marsh sediments

Pore waters from the Rich Inlet salt marsh were analyzed to assess the possible DIC-$\Delta^{14}C$ values that could be contributed to estuarine surface waters via salt marsh respiration. Marsh pore water DIC $\Delta^{14}C$ values are assumed to be the result of the addition of respiration DIC to the overlying seawater DIC. To determine the $\Delta^{14}C$ values of the added DIC from respiration, a mass balance calculation was used:

$$\left(TCO_{2,PW} \times \Delta^{14}C_{PW}\right) = \left(TCO_{2,SW} \times \Delta^{14}C_{SW}\right) + \left(TCO_{2,resp} \times \Delta^{14}C_{resp}\right) \tag{1}$$

where PW = pore water, SW = overlying seawater, and $TCO_{2,resp}$ = DIC added by respiration. A similar calculation was used to determine the $\delta^{13}C$ value of the respiration-added DIC. Using equation (1), the average respiration DIC $\Delta^{14}C$ value was -21 ± 26 ‰ ($\delta^{13}C = -6.7 \pm 0.5$ ‰) at Site 1, and average $\Delta^{14}C = -64 \pm 20$ ‰ ($\delta^{13}C = -7.6 \pm 0.6$ ‰) at Site 2 (Figures 19a-b). The measured pore waters were not replicate samples; they contained variable amounts of respiration CO_2, and the added DIC has a range of $\Delta^{14}C$ and $\delta^{13}C$ values. However, none of the added DIC had a $\Delta^{14}C$ value lower than -80‰, still much higher than any of the spring $\Delta^{14}C$ values, and at the high end of the stream $\Delta^{14}C$ values (Figure 13). This confirms the assumption made in Gramling et al (2003) that decomposition of organic matter in the salt marshes does not appear to be a source of very low $\Delta^{14}C$ DIC to these estuaries.

The average $\delta^{13}C$ values of the added DIC (-7 ‰) are high relative to the primary organic matter source present in the salt marshes, the marsh grass *Spartina alterniflora* ($\delta^{13}C$ = -12‰) (Craft et al 1988). This suggests that the added DIC is not the simple result of respiration CO_2 additions, but reflects both respiration and other processes that would add high-$\delta^{13}C$ DIC, such as dissolution of shell fragments ($\delta^{13}C \sim +1$ ‰) in the marsh soils. A DIC $\delta^{13}C$ value of –7‰ resulting from these two processes alone would require that about 60% of the DIC be contributed by respiration of *Spartina* organic matter, and 40% of the DIC be contributed by dissolution.

Spring, stream, and groundwater variability – endmember selection for mixing models

All spring inputs to these estuaries were highly consistent through time with respect to $\Delta^{14}C$ values, and some springs (such as the Pages Bayshore spring and the Futch Saltwood spring) also showed high consistency in DIC concentration through time. Because the DIC and $\Delta^{14}C$ values of the Pages Bayshore spring are so consistent (Table 6, Figure 13), we use the July 2000 Bayshore spring sample to construct the Pages April 2001 mixing models, discussed below (when no Pages spring sample was collected). Although the $\Delta^{14}C$ values of all Pages and Futch springs were similar, the DIC concentrations in the springs were variable spatially, even within a single estuary.

Stream inputs were also variable, spatially and temporally, with respect to both DIC concentration and $\Delta^{14}C$ value. One likely source of the variability is the observed presence of springs in some streambeds, suggesting that these streams were likely to have contained artesian inputs.

In Figure 20, all the spring and stream DIC and $\Delta^{14}C$ values are plotted against the July 2000 and April 2002 NENHC surficial, Castle Hayne, and Peedee groundwater values. Though all NENHC wells are only about two kilometers apart (Figure 1), the NENHC Castle Hayne-screened wells (S1 – S3) have a large range of DIC and even $\Delta^{14}C$ values. The surficial wells are variable with respect to DIC, but most have $\Delta^{14}C$ values that are > 0‰ (exceptions to this are discussed in Chapter II, and not shown in Figure 20). Of the streams, the Futch Scotts Hill Loop stream sample from April 2001 has the highest $\Delta^{14}C$ value and the lowest DIC concentration, and may therefore represent the least spring-influenced stream endmember.

While the DIC values of the Saltwood Lane spring are similar to the NENHC well S2, the Pages Creek Bayshore and Futch Creek Creekside springs have intermediate DIC values between wells S2 and S3, although these springs are also only a few hundred meters apart (Figure 1, Figure 20). Spatial variability of both Castle Hayne groundwater and Futch Creek spring nutrient levels has also been observed in previous studies; one Castle Hayne-screened well demonstrated nitrate levels four times as high as another Castle Hayne well only a few hundred meters away (Roberts 2002). Roberts (2002) also found that the Futch Saltwood spring in the upper marsh had nitrate levels ten times as high as the two Creekside springs. Mallin et al (1996) stated that observed spikes in spring nutrient levels in the Porters Neck region were likely to be the result of periodic introductions of fertilizer just updip of the area, and the variability in nutrient levels from spring to spring may be representative of different flow paths within the aquifer, and perhaps of spatially variable recharge areas where the confining unit is missing (Roberts 2002). This range of Castle Hayne DIC and even $\Delta^{14}C$ aquifer values highlights the necessity of measuring the composition of local inputs for geochemical estimates of SGD.

DIC-$\Delta^{14}C$ mixing lines between the low-DIC, high-$\Delta^{14}C$ April 2001 Scotts Hill Loop stream and the NENHC Castle Hayne wells S2 and S3 encompass most of the observed stream DIC and $\Delta^{14}C$ compositions (Figure 20). Although the Pages Creek Bayshore stream DIC-$\Delta^{14}C$ values fall along the Scotts Hill Loop – NENHC well S3 mixing line, the DIC-$\delta^{13}C$ values of these streams are high relative a mixing line between these samples (Figure 21). However, the $\delta^{13}C$ values of a stream-groundwater mix may be significantly modified by CO_2 removal processes: photosynthetic removal of 1 mmol of CO_2 from a mix of 35% groundwater and 65% stream would increase the $\delta^{13}C$ value of the mix by 13‰ (Figure 21). A combination of CO_2 removal (via photosynthesis and/or gas evasion) and CO_2 additions (via respiration) could therefore result in the observed stream DIC-$\delta^{13}C$ values as well as the DIC-$\Delta^{14}C$ values.

In Figure 20, the DIC and $\Delta^{14}C$ values of all spring and stream samples are plotted with the surficial and Castle Hayne groundwater data. The fresh Bayshore stream samples fall within this mixing triangle, and the temporal variability in the Bayshore composition seems to suggest a mixing trend, possibly reflecting varying degrees of mixing between low-DIC, high-$\Delta^{14}C$ stream water and high-DIC, low-$\Delta^{14}C$ Castle Hayne water. It is important to note that the stream compositions, if the result of two-endmember mixing between Scotts Hill Loop and Castle Hayne water, are still no more than 15% - 30% groundwater. It is also worth noting that as the streams entering the Pages and Futch Creek estuaries are not true endmembers and generally contain varying degrees of spring input themselves, the mixing model estimates of relative spring input to the estuaries using these streams as endmembers will be necessarily minimum estimates.

Figure 20 also shows that the spring samples fall into two distinct groups. The Futch Creek estuary Saltwood Lane samples are lower in DIC concentration but have similar $\Delta^{14}C$ values to the Pages Bayshore and other Futch springs. The difference in DIC concentration can have a significant impact on the estimation of spring inputs, depending on which spring composition is used as the endmember in the mixing models. Therefore, both spring compositions are considered in the mixing models for the Futch Creek estuary (discussed below).

The single stream observed flowing into the Futch Creek estuary, the Scotts Hill Loop Road stream, was sampled in April 2001, November 2001, and April 2002. The discharge of this stream was not measured, but appeared to be extremely low during all sampling periods, and seemed quite small compared to the volume of water observed entering Futch Creek estuary from springs. Because of the observed low stream flow, and the absence of any other observed stream inputs, it is possible that the outflow composition of the Futch Creek estuary is the result of mixing between inflow and spring alone. This possibility is supported by the generally constant change in $\Delta^{14}C$ relative to the change in salinity from high to low tide in this estuary (Figure 4a), which suggests that the $\Delta^{14}C$ tracer of artesian discharge is essentially linearly related to the fresh water input, and that the $\Delta^{14}C$ additions are coming from a fresh water source with a highly consistent $\Delta^{14}C$ value through time, such as the springs (whereas the Scotts Hill Loop stream $\Delta^{14}C$ value is quite variable from April 2001 to November 2001). Two-endmember (inflow-spring) and three-endmember (inflow-spring-stream) mixing in the Futch Creek estuary are discussed further below.

Non-fresh (> 1 ppt) stream and spring samples

Several spring and stream samples, including the November 2001 Bayshore stream, the November 2001 Saltwood spring, and the November 2001 and April 2002 Scotts Hill Loop stream samples, had salinity > 1 ppt (Table 6, Figure 20). The November 2001 Futch spring sample (Saltwood Lane, ~ 4 ppt) was collected on the day of the spring tide stage, and the salinity data suggest that the depression around the spring was never fully flushed of high tide seawater during that sampling day. The slightly elevated $\Delta^{14}C$ and $\delta^{13}C$ values from this spring sample, therefore, likely represent mixing with seawater rather than real variability in spring composition.

Similarly, the November 2001 Bayshore stream sample, with salinity ~ 31 ppt, was collected during the spring tide stage. During this sampling period, the streambed was inundated with inflowing ICW water at high tide but the streamflow was too low to completely flush the seawater on the falling tide. The elevated $\Delta^{14}C$, $\delta^{13}C$, and DIC values in this stream sample relative to the other Bayshore stream samples are consistent with the suggestion that this stream sample consists of mixing between seawater and spring inputs. As a result, the November 2001 Bayshore stream sample was not used in the Pages Creek November mixing models. Instead, an average Bayshore stream composition from November 1999 to April 2002 was used. In several of the mixing models shown below, the Bayshore streams with the maximum and minimum observed $\Delta^{14}C$ values were also included as constraints on a possible range of relative stream and spring contributions to the fresh water budget.

Mixing models for outflow DIC

A salinity mass balance is used to constrain the maximum possible fresh water flux to each estuary, while the observed $\Delta^{14}C$ value of the outflow is used to assess the relative inputs of spring and stream to the fresh water budget. Then, three-component mixing models are used to calculate the relative inputs of spring and stream to the total fresh water budget of the Pages and Futch Creek estuaries during April 2001, November 2001, and April 2002. As described in Chapter II, the models were based on the measured DIC concentrations and DIC isotopic compositions of the three input components.

For seawater-spring-stream endmembers, the Δ^{14}C- and δ^{13}C-DIC values are given by:

$\Delta^{14}C_{mix} =$ **(2)**

$$\frac{\left[\left(X_{SW} \times TCO_{2,SW} \times \Delta^{14}C_{SW}\right) + \left(Y_{spring} \times TCO_{2,spring} \times \Delta^{14}C_{spring}\right) + \left(Z_{stream} \times TCO_{2,stream} \times \Delta^{14}C_{stream}\right)\right]}{\left[\left(X_{SW} \times TCO_{2,SW}\right) + \left(Y_{spring} \times TCO_{2,spring}\right) + \left(Z_{stream} \times TCO_{2,stream}\right)\right]}$$

and $\delta^{13}C_{mix} =$ **(3)**

$$\frac{\left[\left(X_{SW} \times TCO_{2,SW} \times \delta^{13}C_{SW}\right) + \left(Y_{spring} \times TCO_{2,spring} \times \delta^{13}C_{spring}\right) + \left(Z_{stream} \times TCO_{2,stream} \times \delta^{13}C_{stream}\right)\right]}{\left[\left(X_{SW} \times TCO_{2,SW}\right) + \left(Y_{spring} \times TCO_{2,spring}\right) + \left(Z_{stream} \times TCO_{2,stream}\right)\right]}$$

where SW = seawater and X, Y, Z = volume fractions of each component.

April 2001 mixing models

Pages and Futch Creek estuaries

On both sampling days in April 2001, the outflow compositions of both the Pages and Futch Creek estuaries plot on or near the inflow-spring mixing line, suggesting that essentially all of the fresh water input to both estuaries during this sampling period was from springs (Figures 22-23).

In the Futch Creek estuary, the outflow composition plots near the inflow-spring mixing line, but outside of the three-component mixing triangle (Figure 23). As discussed in the fresh water endmember section above, Figures 23a-b include an additional three-component mixing line, using an average April 2001 spring Δ^{14}C-DIC composition. When plotted with this average spring composition, the outflow DIC falls along the inflow-spring mixing line.

November 2001 mixing models

Pages Creek estuary

Five inflow/outflow pairs were used to construct mixing models in the Pages Creek estuary in November 2001 (Figures 24-26). The inflow-outflow salinity differences were very small on all five November 2001 sampling days (Figure 2a). On two of the sampling days (Nov. 12 and Nov. 13) the outflow $\Delta^{14}C$-DIC falls along a mixing line between inflow and spring, suggesting that all fresh water contribution to the estuary on these days consisted of spring input (Figures 24a-d). However, on the remaining three sampling days (Nov. 15, 16, and 18), the outflow DIC suggested a mix between spring, stream, and inflow compositions (Figures 25-26). Mixing with the highest-$\Delta^{14}C$ stream (Nov-99) and the lowest-$\Delta^{14}C$ stream (Apr-02) shows that the percent spring contribution to the total fresh water input on these days varies between about 45-50% using the November 1999 stream composition to as little as 10-20% using the April 2002 stream composition (Figures 25-26). However, these estimates consider only the DIC and $\Delta^{14}C$ data; none of these mixing scenarios is able to simultaneously satisfy $\Delta^{14}C$ and salinity constraints.

The high/low tide ΔSal on these three days was small, only ~0.1 ppt, but a spring-stream-inflow mix resulting in the observed DIC and $\Delta^{14}C$ values of the outflow composition would require a ΔSal of 2 - 4 ppt. For the November 15th mixing model, to lower the salinity-constrained $\Delta^{14}C$ to the observed outflow value via respiration, nearly 1 mmol of DIC (at the lowest calculated $\Delta^{14}C$ value of -64‰) would need to be added (and would then require CO_2 removal via photosynthesis or gas evasion to bring the DIC values back to the observed outflow DIC) (Figure 27). Therefore, during these three sampling days in the Pages Creek estuary, the $\Delta^{14}C$ and salinity tracer signals provide inconsistent spring input estimates, suggesting that there may be other processes impacting the $\Delta^{14}C$ or salinity budgets of the estuary on these days.

Futch Creek estuary

Five inflow/outflow pairs were also used to construct mixing models in the Futch Creek estuary in November 2001 (Figures 28-30). Mixing with both the Saltwood spring (low-DIC) and the average of the Futch April 2001 springs (high-DIC) are shown. Although the Saltwood spring appeared to be discharging at the highest rate of the Futch springs, the outflow DIC does not plot along the inflow-Saltwood spring mixing line during any of these sampling days, suggesting that one or more additional inputs or processes were impacting the outflow composition. Although stream inputs may have affected the outflow, as described above, stream flow in the Scotts Hill Loop stream appeared to be negligible. However, the outflow composition could be the result of mixing between inflow and other springs with higher DIC, followed by respiration DIC additions and/or CO_2 removal via gas exchange or photosynthesis (which would not alter the $\Delta^{14}C$ value but would change the DIC) (Figure 31).

For the November 12th mixing model, this is most reasonable if the spring endmember used is the average Futch spring composition (as shown in the Futch Creek April 2001 mixing models), rather than the low-DIC Saltwood Lane spring. The November 12th outflow DIC was 7% fresh relative to the inflow. Using this inflow-spring mix as a starting point, respiration additions at the lowest calculated $\Delta^{14}C$ value (-64‰) do not approach the outflow DIC from the inflow-Saltwood spring mixing line (Figure 31a). However, from the inflow-average spring mixing line, it is possible to approach the outflow DIC composition using any of the calculated respiration $\Delta^{14}C$ values (Figure 31b).

For the November 15th mixing model, however, the outflow DIC is less than the DIC of either inflow-spring mixing line (Figure 32). The outflow on this day was 4% fresh relative to the inflow; taking the inflow-average spring at 4% fresh as the starting point, it is possible to approach the outflow DIC composition by removal of DIC via photosynthesis (and/or gas exchange). Again, because the outflow $\Delta^{14}C$ value would be unchanged by CO_2 removal, this scenario is most reasonable from the inflow-average spring 4% fresh starting point. Mixing between inflow, springs, and inputs from a high-$\Delta^{14}C$ source, such as the April 2001 Scotts Hill Loop stream (possibly representative of surficial groundwater $\Delta^{14}C$ values) would not provide a match to the outflow DIC (Figure 32).

April 2002 mixing models

Pages and Futch Creek estuaries

In April 2002, the Pages Creek estuary outflow $\Delta^{14}C$-DIC fall near the inflow-spring mixing line, suggesting that fresh water inputs to Pages during these sampling days consist only of spring inputs (Figure 33). In the Futch Creek estuary, mixing lines between both the Saltwood spring and the average spring compositions are included. As described for the November 2001 Futch Creek estuary mixing models, stream inputs may have impacted the outflow DIC, but observations of streamflow from this time suggested that is was very low. The outflow DIC on both April 2002 sampling days plotted along the inflow-average spring mixing line rather than the inflow-Saltwood spring mixing line (Figure 34).

Results from these mixing models suggest that the spring flux dominated the fresh water budget to both estuaries in April 2001 and April 2002, and to the Futch Creek estuary in November 2001 (Table 10). In the Futch Creek estuary, it is likely that spring inputs, whether from the Saltwood spring or from other springs within the estuary, dominated fresh water inputs. The November 2001 ΔSal was very small in Pages Creek, and as a result the relative spring and stream inputs are difficult to resolve. This difficulty is compounded by the variability of stream chemistry, and the possibility of multiple springs with a range of DIC concentrations and isotopic compositions.

Conclusions

In this chapter, the $\Delta^{14}C$-based method described in Chapter II for estimating the artesian component of the fresh water input to an estuary was expanded in several ways:

the generality of the method was tested by its application to an additional estuary. The small changes in $\Delta^{14}C$ from high to low tide in the inlets suggests that spring $\Delta^{14}C$ signals did not persist on the ocean side of the ICW, at least during the sampling in April 2002; as a result, effective mixing models could not be constructed for the inlets. Hourly sampling through a tidal cycle, when compared with sampling high and low tide pairs, shows that sampling only twice during a tidal cycle was generally sufficient to capture the range of DIC and DIC isotopic variation.

Spring inputs appeared to dominate the fresh water budgets of both estuaries during April 2001 and April 2002. In November 2001, spring inputs may still have provided all of the fresh water to the Futch Creek estuary, but only 10-50 % of the fresh water input to the Pages Creek estuary (although the dual constraints of salinity and $\Delta^{14}C$ could not be satisfied by a combination of the measured inputs).

Spring chemistry was highly consistent throughout sampling within the two spring sites that were measured over several collection efforts. Although the $\Delta^{14}C$ values of all the springs were similar, some spatial variability in spring DIC concentration was observed within the Futch Creek estuary. In contrast, we observed substantial variability in stream $\Delta^{14}C$ values, at least in part reflecting variable contributions of artesian groundwater to the streams. Finally, organic matter decomposition in salt marshes does not appear to be a source of low $\Delta^{14}C$ DIC, confirming an assumption made by Gramling et al (2003).

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Table III-1: Sample locations and map identification (Figure 1).

Sample name	Latitude	Longitude	Map ID (Figure 1)
Pages Creek estuary			
Estuary mouth station (HT/LT pairs, time series)	34.27000	-77.77063	E1
Streams			
Bayshore	34.27784	-77.80270	E2
Furtado	34.29033	-77.78715	E3
Porters Neck	34.29422	-77.78065	E4
Springs			
Bayshore	34.27705	-77.80173	E5
Futch Creek estuary			
Estuary mouth station (HT/LT pairs, time series)	34.30072	-77.74383	E6
Streams			
Scotts Hill Loop	34.31368	-77.75668	E7
Springs			
Spring upstream of 1021 Creekside	34.30325	-77.75945	E8
Spring at 1021 Creekside	34.30260	-77.75798	E9
Saltwood Lane spring	34.30384	-77.76485	E10
Inlets			
Mason Inlet - mouth	34.24502	-77.77130	I1
Mason Inlet - ICW	34.24847	-77.78045	I2
Rich Inlet - mouth	34.29790	-77.71653	I3
Rich Inlet - ICW	34.29467	-77.74080	I4
Groundwater			
NENHC wells S1, D1	34.28056	-77.75847	G1
NENHC wells S2, D2	34.28882	-77.75157	G2
NENHC wells S3, D3	34.29783	-77.74498	G3
Rich Inlet pore water Site 1	34.29022	-77.73595	PW
Rich Inlet pore water Site 2	34.28965	-77.73573	PW*

* Pore water sites 1 and 2 are not distinguishable at map scale.

Table III-2: Pages Creek estuary DIC, TA, and DIC isotopic values.

	Date	Salinity ppt	DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo	TAlk meq/L
Pages Creek-High Tide	4/21/01	34.728	2.368	39.1	-0.78	2.489
Pages Creek-High Tide	4/22/01	34.778	2.363	40.0	-1.89	2.560
Average 4/01 PC HT		**34.753**	**2.365**	**39.6**	**-1.34**	**2.525**
Pages Creek-Low Tide	4/21/01	33.238	2.463	-10.0	-0.84	2.488
Pages Creek-Low Tide	4/22/01	33.870	2.439	27.9	-1.30	2.514
Average 4/01 PC LT		**33.554**	**2.451**	**9.0**	**-1.07**	**2.501**
Pages Creek-High Tide	11/12/01	36.262	2.339	46.3	-0.41	2.563
Pages Creek-High Tide	11/13/01	36.414	2.337	61.8	-0.27	2.559
Pages Creek-High Tide	11/15/01	36.428	2.301	65.9	-0.08	2.534
Pages Creek-High Tide	11/16/01	36.406	2.289	71.8	0.03	2.525
Pages Creek-High Tide	11/18/01	36.424	2.289	63.4	0.02	2.525
Average 11/01 PC HT		**36.387**	**2.311**	**61.8**	**-0.14**	**2.541**
Pages Creek-Low Tide	11/12/01	36.106	2.343	46.0	-0.51	2.557
Pages Creek-Low Tide	11/13/01	36.128	2.355	52.8	-0.46	2.571
Pages Creek-Low Tide	11/15/01	36.333	2.301	34.2	0.00	2.539
Pages Creek-Low Tide	11/16/01	36.328	2.279	53.0	0.06	2.523
Pages Creek-Low Tide	11/18/01	36.285	2.188	54.9	0.03	2.444
Average 11/01 PC LT		**36.236**	**2.293**	**48.2**	**-0.18**	**2.527**
Pages Creek-High Tide	4/13/02	36.147	2.175			2.415
Pages Creek-High Tide	4/14/02	36.160	2.171	55.3	0.29	2.413
Pages Creek-High Tide	4/16/02	36.153	2.191	52.1	0.14	2.416
Average 4/02 PC HT		**36.153**	**2.179**	**53.7**	**0.22**	**2.415**
Pages Creek-Low Tide	4/13/02	35.124	2.268			2.466
Pages Creek-Low Tide	4/14/02	35.167	2.246	35.3	-0.55	2.462
Pages Creek-Low Tide	4/16/02	35.327	2.239	40.7	-0.58	2.478
Average 4/02 PC LT		**35.206**	**2.251**	**38.0**	**-0.57**	**2.469**

Table III-3: Futch Creek estuary DIC, TA, and DIC isotopic values.

	Date	Salinity ppt	DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo	TAlk meq/L
Futch Creek-High Tide	4/21/01	35.587	2.288	59.9	-0.23	2.456
Futch Creek-High Tide	4/22/01	35.429	2.328	43.7	-4.59	2.790
Average 4/01 FC HT		**35.508**	**2.308**	**51.8**	**-2.41**	**2.623**
Futch Creek-Low Tide	4/21/01	23.693	2.700	-139.5	-0.23	2.449
Futch Creek-Low Tide	4/22/01	26.936	2.591	-100.4	-3.74	2.698
Average 4/01 FC LT		**25.314**	**2.645**	**-120.0**	**-1.99**	**2.574**
Futch Creek-High Tide	11/12/01	36.348	2.207	67.8	0.44	2.492
Futch Creek-High Tide	11/13/01	36.427	2.182	69.5	0.54	2.481
Futch Creek-High Tide	11/15/01	36.434	2.204	75.8	0.49	2.481
Futch Creek-High Tide	11/16/01	35.427	2.225	76.6	0.48	2.520
Futch Creek-High Tide	11/18/01	36.481	2.207	62.4	0.53	2.492
Average 11/01 FC HT		**36.223**	**2.205**	**70.4**	**0.50**	**2.493**
Futch Creek-Low Tide	11/12/01	33.783	2.358	6.1	-1.49	2.539
Futch Creek-Low Tide	11/13/01	34.392	2.311	12.5	-1.09	2.512
Futch Creek-Low Tide	11/15/01	34.964	2.214	36.0	-0.59	2.482
Futch Creek-Low Tide	11/16/01	34.908	2.248	29.8	-0.64	2.467
Futch Creek-Low Tide	11/18/01	34.560	2.264	20.9	-0.71	2.489
Average 11/01 FC LT		**34.521**	**2.279**	**21.1**	**-0.90**	**2.498**
Futch Creek-High Tide	4/13/02	35.911	2.175			2.419
Futch Creek-High Tide	4/14/02	35.917	2.176	55.8	0.14	2.416
Futch Creek-High Tide	4/16/02	35.991	2.214	41.9	-0.02	2.430
Average 4/02 FC HT		**35.939**	**2.188**	**48.9**	**0.06**	**2.422**
Futch Creek-Low Tide	4/13/02	32.446	2.268			2.537
Futch Creek-Low Tide	4/14/02	32.934	2.315	-3.2	-1.38	2.528
Futch Creek-Low Tide	4/16/02	30.843	2.392	-44.7	-2.22	2.620
Average 4/02 FC LT		**32.074**	**2.325**	**-24.0**	**-1.80**	**2.562**

Table III-4: Time series DIC, TA, and DIC isotopic values.

	Date	Time	Salinity ppt	DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo	TAlk meq/L
Pages Creek							
Nov-01							
	11/13/01	5:32	36.414	2.337	61.8	-0.27	2.559
	11/13/01	7:27	36.404	2.320			2.547
	11/13/01	8:32	36.415	2.352			2.570
	11/13/01	9:33	36.399	2.335			2.556
	11/13/01	10:22	36.382	2.325			2.564
	11/13/01	11:25	36.300	2.324	57.5	-0.33	2.559
	11/13/01	12:50	36.128	2.355	52.8	-0.46	2.571
	11/13/01	13:32	36.069	2.359	52.5	-0.51	2.575
	11/13/01	14:33	36.368	2.280			2.553
	11/13/01	15:24	36.465	2.290			2.537
	11/13/01	16:25	36.406	2.305			2.547
	11/13/01	17:25	36.424	2.258			2.557
	11/13/01	18:27	36.415	2.294			2.541
	11/13/01	19:25	36.403	2.320			2.552
Apr-02							
	4/14/02	8:38	36.136	2.183			2.421
	4/14/02	9:37	36.160	2.171	55.3	0.29	2.413
	4/14/02	10:50	36.140	2.176			2.416
	4/14/02	11:50	36.105	2.171			2.416
	4/14/02	12:53	35.939	2.196			2.431
	4/14/02	13:48	35.811	2.205	42	-0.1	2.437
	4/14/02	14:30	35.597	2.223	38.9	-0.28	2.447
	4/14/02	16:01	35.167	2.246	35.3	-0.55	2.462
	4/14/02	16:32	35.220	2.242	19.7	-0.51	2.463
	4/14/02	17:35	35.734	2.216	35.4	-0.18	2.443
	4/14/02	18:30	35.999	2.201			2.432
	4/14/02	19:30	36.082	2.188			2.425
Futch Creek							
Apr-02							
	4/16/02	9:02	35.915	2.228			2.437
	4/16/02	10:01	35.991	2.214	41.9	-0.02	2.430
	4/16/02	11:20	35.907	2.212			2.430
	4/16/02	12:00	35.937	2.208			2.430
	4/16/02	13:03	35.837	2.207			2.435
	4/16/02	14:00	35.513	2.208			2.446
	4/16/02	15:04	34.408	2.253			2.483
	4/16/02	16:03	33.202	2.310	-1.3	-1.34	2.531
	4/16/02	17:12	30.843	2.392	-44.7	-2.22	2.620
	4/16/02	18:01	32.055	2.351	-27.6	-1.78	2.563
	4/16/02	19:01	35.527	2.193	39.6	-0.09	2.457
	4/16/02	20:00	35.898	2.191			2.437

Table III-5: Rich and Mason Inlet DIC, TA, and DIC isotopie values.

	Date	Salinity ppt	DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo	TAlk meq/L
Rich Inlet-Low Tide	11/17/01	36.541	2.197	50.9	0.54	2.500
Rich Inlet Mouth-High Tide	4/15/02	36.236	2.129	59.6	0.52	2.392
Rich Inlet Mouth-High Tide	4/17/02	36.286	2.132	63.8	0.65	2.383
Rich Inlet @ ICW-High Tide	4/17/02	36.292	2.150	67.6	0.48	2.401
Average 4/02 Rich Inlet-High Tide		**36.271**	**2.137**	**63.7**	**0.55**	**2.392**
Rich Inlet Mouth-Low Tide	4/15/02	36.138	2.166	67.6	0.68	2.422
Rich Inlet Mouth-Low Tide	4/17/02	36.223	2.162	61.8	0.36	2.415
Rich Inlet @ ICW-Low Tide	4/17/02	36.113	2.166	58.1	0.24	2.431
Average 4/02 Rich Inlet-Low Tide		**36.158**	**2.165**	**62.5**	**0.43**	**2.423**
Mason Inlet Mouth-High Tide	4/15/02	36.290	2.113	47.7	0.37	2.387
Mason Inlet @ ICW-High Tide	4/17/02	36.216	2.138			2.394
Average 4/02 Mason Inlet-High Tide		**36.253**	**2.126**	**47.7**	**0.37**	**2.391**
Mason Inlet Mouth-Low Tide	4/15/02	36.169	2.183	53.4	0.21	2.417
Mason Inlet @ ICW-Low Tide	4/17/02	36.153	2.171			2.412
Average 4/02 Mason Inlet-Low Tide		**36.161**	**2.177**	**53.4**	**0.21**	**2.415**

Table III-6: Spring and stream DIC, TA, and DIC isotopic values.

	Date	Salinity ppt	DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo	Talk meq/L
Springs						
Pages Creek						
Bayshore spring	11/7/99	0.0	4.485	-406.4	-11.16	*
Bayshore spring	7/28/00	0.526	4.432	-403.2	-11.23	3.657
Bayshore spring	11/15/01	0.239	4.118	-404.8	-11.28	3.696
Bayshore spring	4/11/02	0.232	4.157	-410.3	-11.10	3.741
Futch Creek						
Spring upstream of 1021 Creekside	4/20/01	0.404	4.863	-445.0	-12.16	4.558
Spring at 1021 Creekside	4/20/01	0.483	4.287	-440.4	-12.06	4.037
Saltwood Lane spring	4/23/01	0.283	2.805	-453.8	-11.51	2.799
Average 2001 FC springs		*0.390*	*3.985*	*-446.4*	*-11.91*	*3.798*
Saltwood Lane spring	7/28/00	0.585	3.062	-431.7	-11.34	2.892
Saltwood Lane spring	11/16/01	4.032	2.837	-418.1	-10.50	2.724
Saltwood Lane spring	4/18/02	1.115	2.850	-449.3	-11.09	2.750
Streams						
Pages Creek						
Stream at Bayshore	11/7/99	0.0	0.866	-79.4	-13.19	*
Stream at Bayshore	7/28/00	0.189	1.645	-162.3	-12.22	1.440
Stream at Bayshore	4/23/01	0.164	1.311	-126.6	-12.63	1.139
Stream at Bayshore	4/11/02	0.261	2.092	-199.7	-10.75	1.876
Average Bayshore stream (< 1 ppt)		*0.154*	*1.478*	*-142.0*	*-12.20*	*1.485*
Stream at Bayshore	11/15/01	30.963	2.593	-67.6	-3.97	2.549
Stream at Porters Neck Road	4/19/01	0.142	1.218	-191.8	-12.56	1.067
Stream at Furtado Road	4/19/01	0.177	2.530	-176.5	-11.25	2.434
Stream at Furtado Road	11/15/01	3.662	3.806	86.4	-9.30	3.570
Stream at Furtado Road	4/13/02	0.201	2.859	*	*	2.656
Futch Creek						
Stream at Scotts Hill Loop Road	4/23/01	0.080	0.677	86.5	-18.86	0.461
Stream at Scotts Hill Loop Road	11/15/01	9.919	3.188	-160.5	-9.43	3.064
Stream at Scotts Hill Loop Road	4/15/02	3.057	3.248	-186.0	-12.49	3.005
Other streams						
Sidebury Road	4/1/01	0.746	0.742	-109.5	-14.08	0.474
Sidebury Road	11/15/01	0.141	2.850	*	*	2.280

*** No analysis performed.**

Table III-7: Groundwater DIC, TA, and DIC isotopic values.

Well Sample*	Date	Aquifer**	Salinity ppt	DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo	Talk meq/L
Boiling Spring	Jul-00	S	0.069	3.256	88.4	-22.84	0.24
Fort Fisher State Park	Jul-00	S	0.280		36.6	-19.36	1.08
Southport	Jul-00	S	0.100	1.465	77.1	-23.03	0.24
Sunset Harbor	Jul-00	S	0.067	0.922	41.1	-26.89	0.04
Topsail Beach	Jul-00	S	0.107	1.631	-407.9	-15.82	0.99
Wilmington Airport	Jul-00	S	0.076	1.338	18.4	-15.12	0.28
Calabash	Jul-00	S/L[@]	0.309		-396.9	-12.99	4.22
NENHC S1	Jul-00	CH	0.294	2.138	-281.8	-15.36	1.52
NENHC S2	Jul-00	CH	0.249	2.974	-413.8	-12.86	2.68
NENHC S3	Jul-00	CH	0.895	5.104	-330.9	-13.61	4.54
NENHC D1	Jul-00	PD	0.410	6.426	-770.2	-10.95	5.64
NENHC D2	Jul-00	PD	1.461	6.991	-821.9	-12.03	5.90
NENHC D3	Jul-00	PD	0.777	6.439	-829.2	-12.67	5.52
NENHC S1	Apr-02	CH	0.257	2.319	-332.4	-15.03	2.034
NENHC S2	Apr-02	CH	0.281	3.050	-461.4	-11.39	2.675
NENHC S3	Apr-02	CH	0.818	4.881	-289.4	-14.37	4.282
NENHC D1	Apr-02	PD	0.379	6.404	-774.3	-10.85	5.618
NENHC D2	Apr-02	PD	0.667	6.839	-794.3	-11.20	5.999
NENHC D3	Apr-02	PD	0.512	6.531	-831.9	-12.56	5.729

* Surficial aquifer-screened monitoring wells installed and maintained by the North Carolina Department of Environment and Natural Resources (NC-DENR). NENHC wells installed and maintained by the Northeast New Hanover Conservancy.

** S = Surficial (water table) aquifer, CH = Castle Hayne aquifer; PD = Peedee aquifer

[@] Listed as surficial by NC-DENR (based on absence of a confining unit); well lithology shows the presence of a limestone unit

Table III-8: Rich Inlet marsh pore water (cold) and surface water DIC and DIC isotopic values.

	DIC mmol/kg	Std Dev	$\delta^{13}C$ o/oo	Std Dev	Pooled for $\Delta^{14}C$ analysis	$\Delta^{14}C$ o/oo	Std Dev
Pore water: Site 1 #1	4.299		-3.45		1, 5, 9, 15	8.6	
Pore water: Site 1 #5	4.324		-3.42				
Pore water: Site 1 #9	5.142		-3.46				
Pore water: Site 1 #15	4.277		-3.47				
Pore water: Site 1 #3	4.139		-3.50		3, 11, 13, 19	18.7	
Pore water: Site 1 #11	4.590		-3.52				
Pore water: Site 1 #17	4.049		-2.98				
Pore water: Site 1 #19	4.867		-3.46				
Pore water: Site 1 #7	5.181		-3.46		7	47.7	
Average pore water: Site 1	**4.541**	**0.427**	**-3.41**	**0.16**		**25.0**	**20.3**
Pore water: Site 2 #21	4.296		-3.51		21, 23, 29, 37	6.2	
Pore water: Site 2 #23	4.049		-3.21				
Pore water: Site 2 #29	3.347		-2.59				
Pore water: Site 2 #37	3.644		-2.93				
Pore water: Site 2 #27	3.225		-2.57		27, 31, 33, 35, 39	30.3	
Pore water: Site 2 #31	3.801		-3.12				
Pore water: Site 2 #33	3.205		-2.91				
Pore water: Site 2 #35	3.500		-2.83				
Pore water: Site 2 #39	3.568		-3.26				
Average pore water: Site 2	**3.626**	**0.370**	**-2.99**	**0.31**		**18.3**	**17.0**
Inlet surface water	2.102		0.42				
Inlet surface water	2.093		0.47				
Inlet surface water	2.065		0.43				
Inlet surface water	2.081		0.39			84.1	
Inlet surface water	2.021		0.43				
Inlet surface water	2.105		0.49				
Inlet surface water	2.038		0.43				
Inlet surface water	2.069		0.49				
Inlet surface water	2.110		0.49				
Inlet surface water	2.051		0.47			74.5	
Inlet surface water	2.100		0.44				
Average surface water	**2.076**	**0.030**	**0.45**	**0.03**		**79.3**	**6.8**

Table III-9: Rich Inlet marsh pore water (warm) and surface water DIC and DIC isotopic values.

	DIC mmol/kg	Std Dev	$\delta^{13}C$ o/oo	Std Dev	Pooled for $\Delta^{14}C$ analysis	$\Delta^{14}C$ o/oo	Std Dev
Pore water: Site 1 #2	5.368		-4.78		2, 18, 20	38.4	
Pore water: Site 1 #18	5.701		-4.48				
Pore water: Site 1 #20	5.399		-4.25				
Pore water: Site 1 #4	5.911		-4.99		4, 8, 10	41.9	
Pore water: Site 1 #8	6.956		-4.39				
Pore water: Site 1 #10	6.390		-4.86				
Pore water: Site 1 #6 and #14	5.698		-4.26		6, 14, 12, 16	45.8	
Pore water: Site 1 #12	5.570		-4.91				
Pore water: Site 1 #16	5.598		-4.32				
Average pore water: Site 1	**5.843**	**0.517**	**-4.58**	**0.30**		**42.0**	**3.7**
Pore water: Site 2 #28	5.105		-4.30				
Pore water: Site 2 #40	4.706		-4.49				
Pore water: Site 2 #26 and #36	11.206		-6.33				
Pore water: Site 2 #32	5.144		-4.28				
Pore water: Site 2 #34	4.971		-4.25		32, 34, 38	24.3	
Pore water: Site 2 #38	5.453		-4.14				
Average pore water: Site 2	**6.098**	**2.514**	**-4.63**	**0.84**		**24.3**	
Inlet surface water	2.039		0.45				
Inlet surface water	2.046		0.45				
Inlet surface water	2.114		0.47				
Inlet surface water	2.027		0.41			57.5	
Inlet surface water	2.047		0.51				
Inlet surface water	2.065		0.43				
Inlet surface water	2.070		0.43				
Inlet surface water	2.082		0.39			56.6	
Average surface water	**2.061**	**0.028**	**0.44**	**0.04**		**57.1**	**0.6**

Table III-10: Fresh water inputs as percent of outflow, and spring inputs as percent of fresh inputs.

		% fresh in outflow	% of fresh input = spring	HT-LT salinity (ΔSal)
Pages Creek	11/7/99	11	100	3.3
	7/26/00	35	0	11.687
	4/21/01	6.7	100	1.490
	4/22/01	2.6	100	0.908
	11/12/01	0.43	100	0.157
	11/13/01	0.79	100	0.286
	11/15/01	0.26	10-44*	0.095
	11/16/01	0.21	16-48*	0.079
	11/18/01	0.38	18-50*	0.138
	4/13/02	2.8	@	1.023
Futch Creek**	4/14/02	2.7	100	0.993
	4/16/02	2.3	100	0.826
	4/21/01	33	100	11.894
	4/22/01	24	100	8.493
	11/12/01	7.1	100	2.565
	11/13/01	5.6	100	2.035
	11/15/01	4.0	100	1.470
	11/16/01	1.5	100	0.519
	11/18/01	5.3	100	1.921
	4/13/02	9.6	@	3.465
	4/14/02	8.3	100	2.983
	4/16/02	14	100	5.148

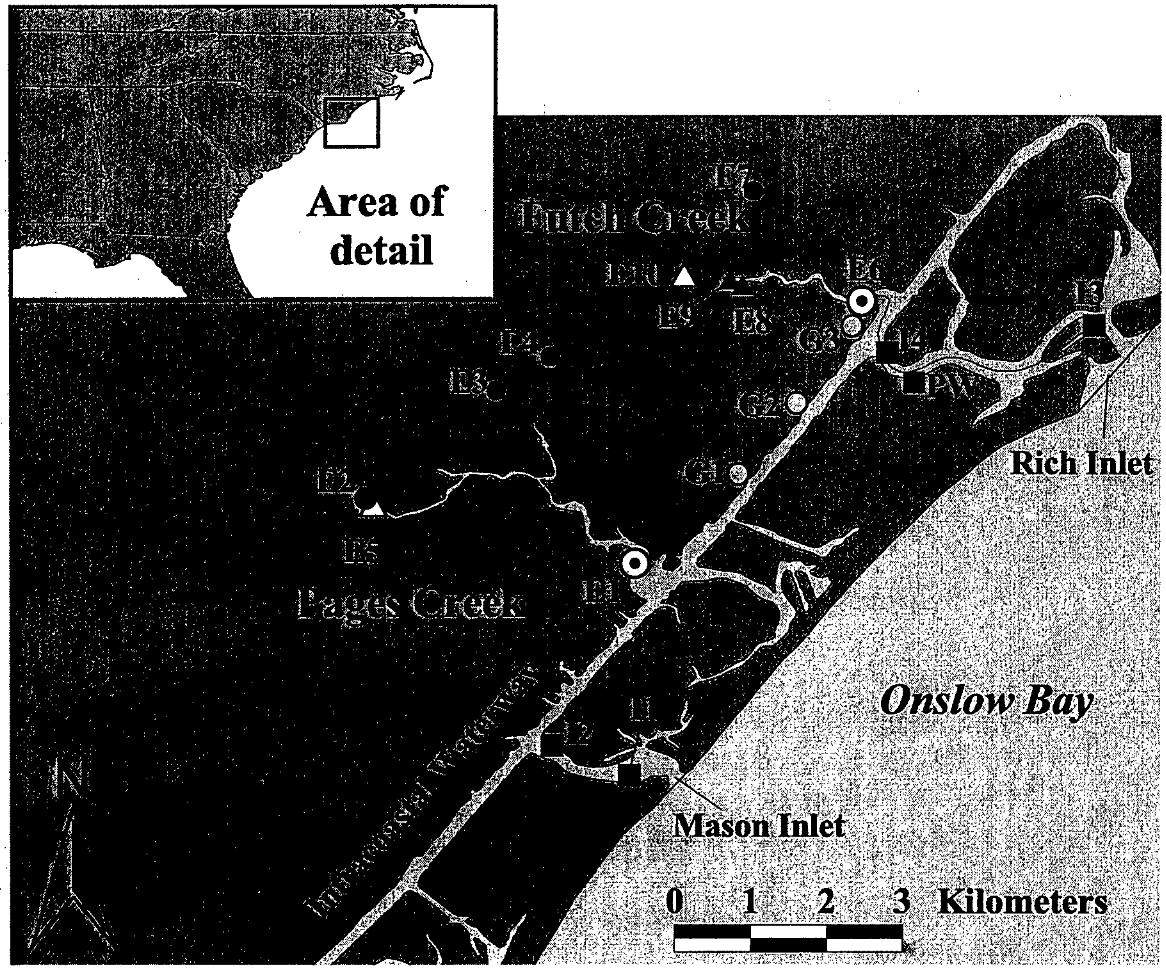
* Varies with stream endmember

** Stream input may be negligible

@ Δ^{14}C not analyzed.

Figure III-1

Detail of Pages Creek, Futch Creek, Rich Inlet, and Mason Inlet sample locations.

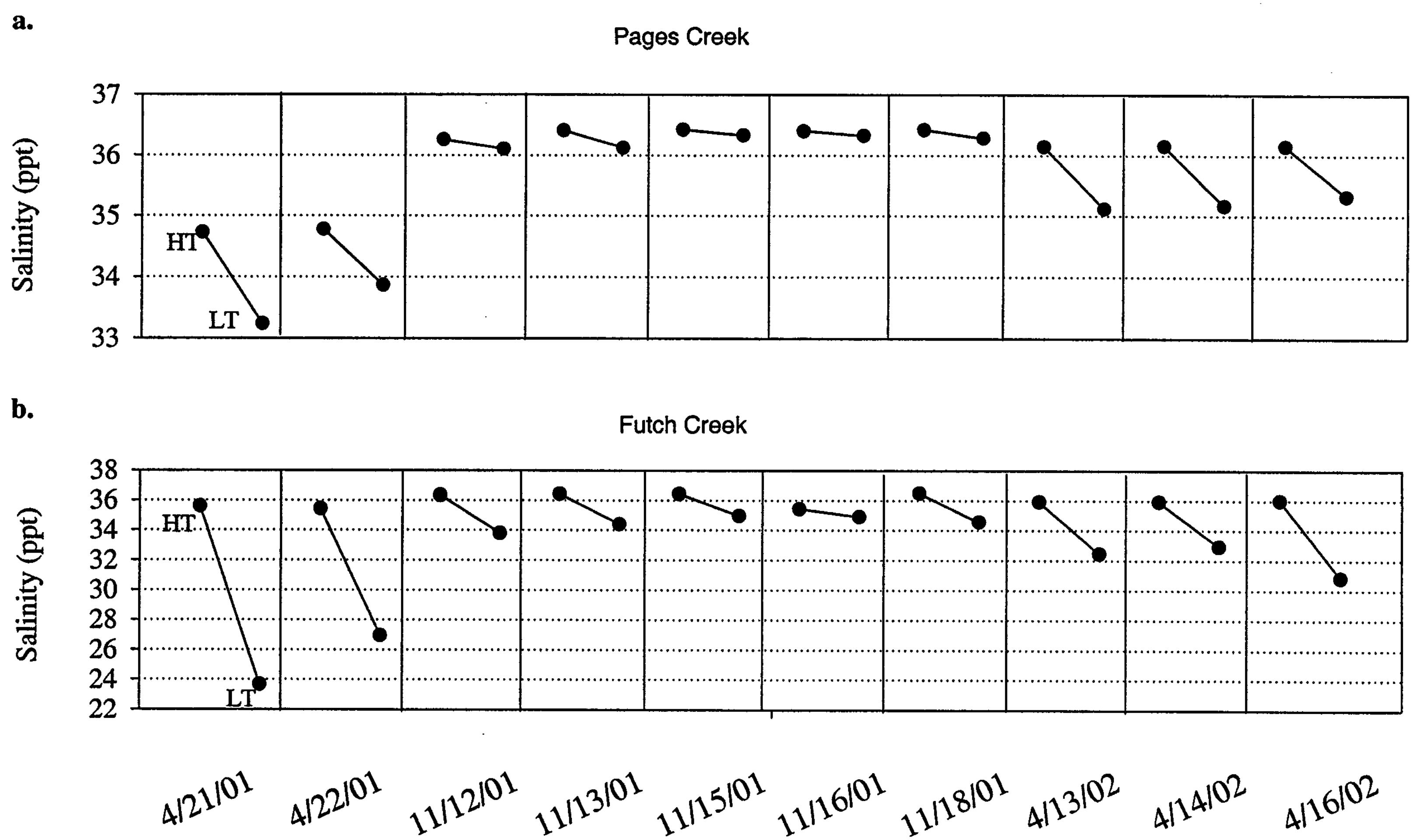


◉ Estuary stations (April 2001, November 2001, April 2002)
● Streams (November 1999, July 2000, April 2001, November 2001, April 2002)
△ Largest springs (November 1999, July 2000, April 2001, November 2001, April 2002)
▲ Other springs (April 2001)
■ Rich Inlet (November 2001)
■ Rich and Mason Inlets (April 2002)
◍ NENHC wells (July 2000, April 2002)

Figure III-1

Figure III-2

April 2001, November 2001, and April 2002 high and low tide salinity values for a) Pages Creek. b) Futch Creek. Within each box, the left dot represents the high tide value (HT) and the right dot the low tide value (LT). Note the scale change between a and b. High/low tide salinity gradients were higher during all sampling times in Futch Creek than in Pages Creek.



a.
Pages Creek
Salinity (ppt)
37
36
35
34
33
HT
LT
b.
Futch Creek
Salinity (ppt)
38
36
34
32
30
28
26
24
22
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure III-2

Figure III-3

April 2001, November 2001, and April 2002 high and low tide $\Delta^{14}C$ values for a) Pages Creek. b) Futch Creek. Within each box, the left dot represents the high tide value (HT) and the right dot the low tide value (LT). Note the scale change between a and b. High/low tide $\Delta^{14}C$ gradients were higher during all sampling times in Futch Creek than in Pages Creek.

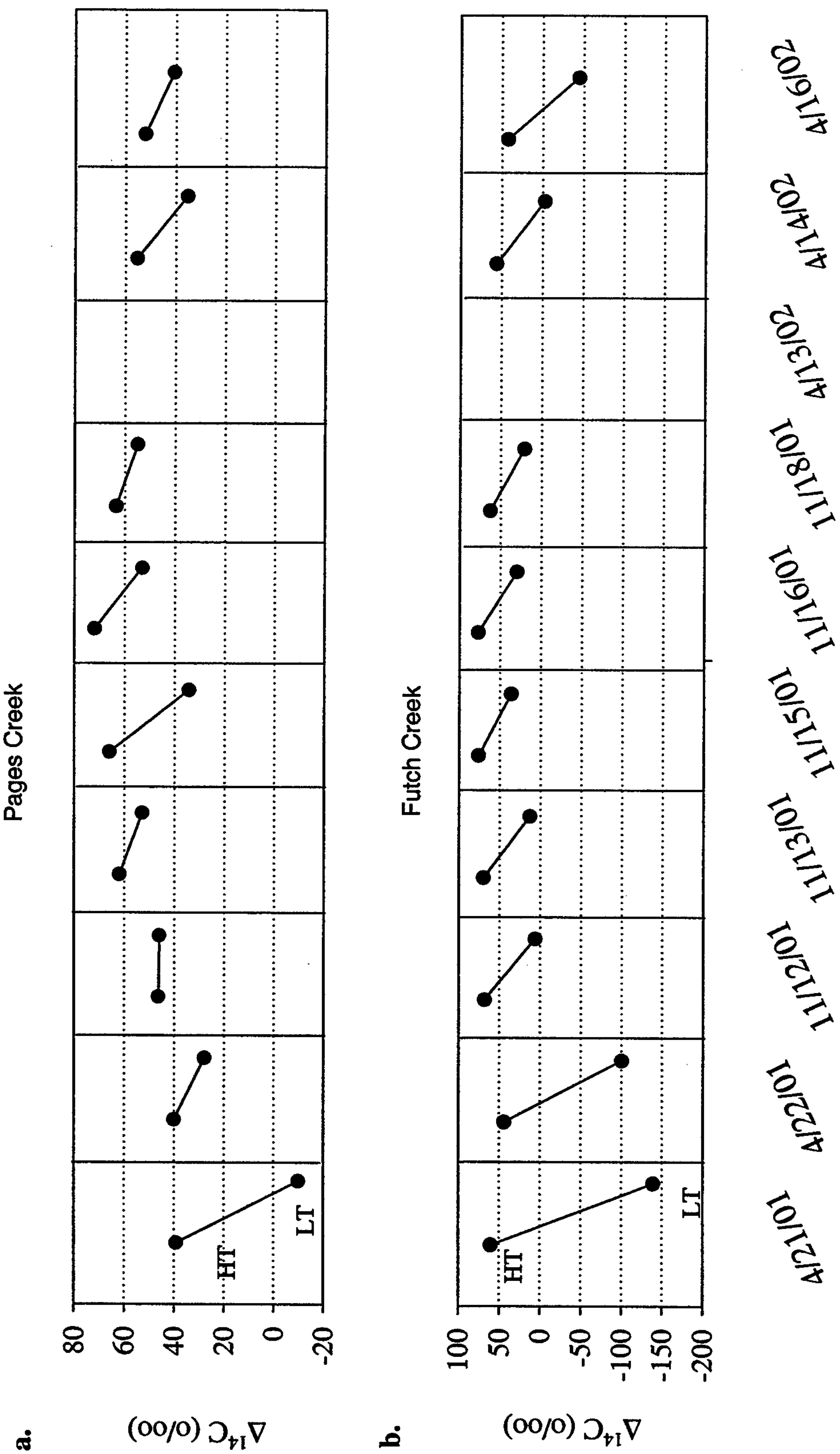
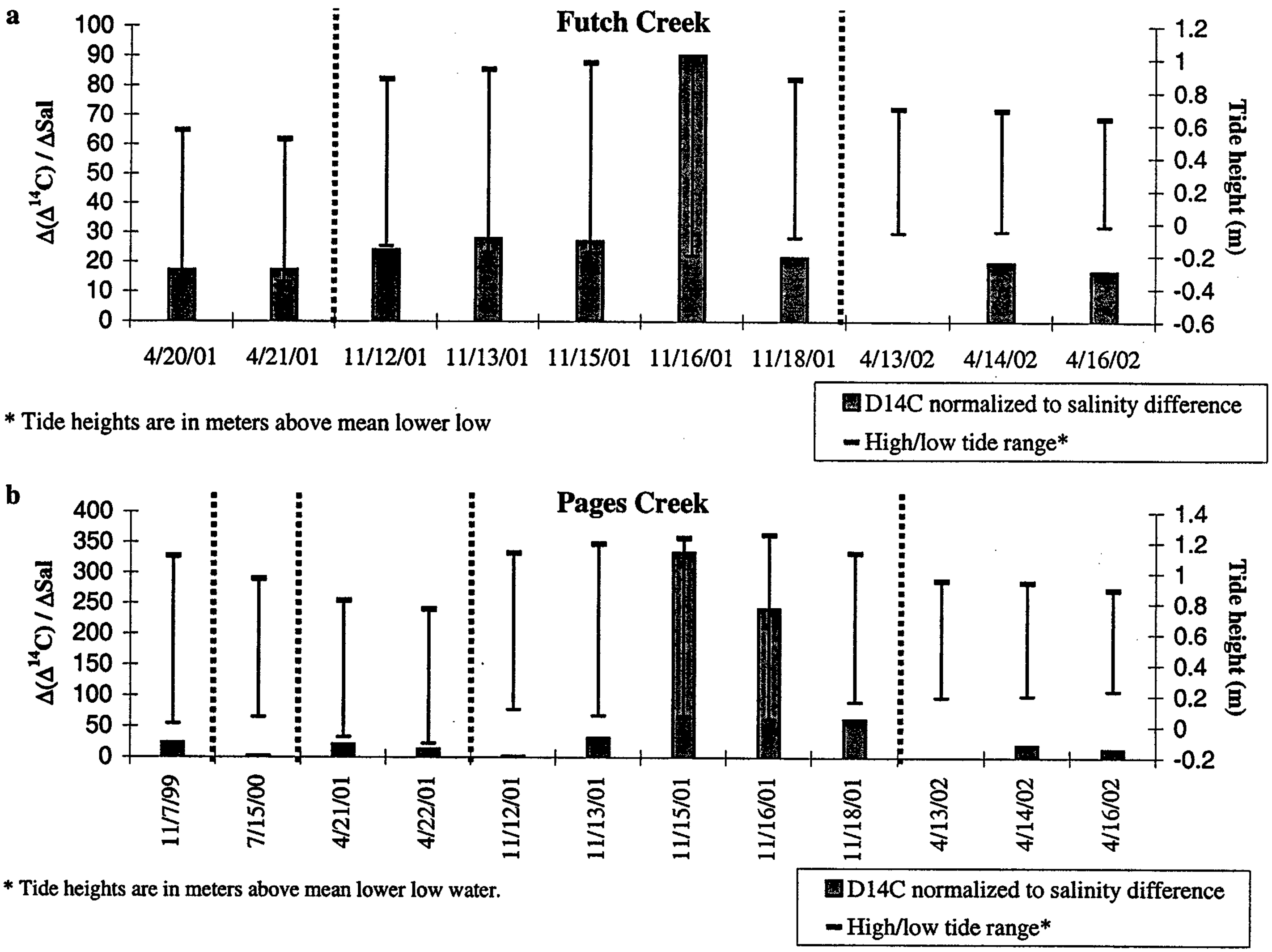

a.
Pages Creek
$\Delta^{14}C$ (o/oo)
80
60
40
20
0
-20
HT
LT
b.
Futch Creek
$\Delta^{14}C$ (o/oo)
100
50
0
-50
-100
-150
-200
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure III-3

Figure III-4

The high/low tide change in $\Delta^{14}C$ ($\Delta\,\Delta^{14}C$) normalized to the high/low tide change in salinity (ΔSal) at Futch and Pages Creeks. Bars represent $\Delta\,\Delta^{14}C/\Delta Sal$ for each sampling day in April 2001, November 2001 and April 2002. Lines represent the tide range between high and low tide for each creek (secondary y-axis). a) Futch Creek. On most sampling days (with the exception of November 16, 2001), the change in $\Delta^{14}C$ was linearly related to the change in salinity. b) Pages Creek $\Delta\,\Delta^{14}C/\,\Delta Sal$. While the change in $\Delta^{14}C$ value normalized to the change in salinity was generally consistent in April 2001 and April 2002, the differences in $\Delta^{14}C$ values on three of the sampling days in November 2001 were high relative to the salinity difference.

Figure III-4



* Tide heights are in meters above mean lower low

* Tide heights are in meters above mean lower low water.

Figure III-5

April 2001, November 2001, and April 2002 high and low tide dissolved inorganic carbon (DIC) concentrations for a) Pages Creek. b) Futch Creek. Within each box, the left dot represents the high tide value (HT) and the right dot the low tide value (LT). Note the scale change between a and b. While DIC increased from high to low tide at all times in the Futch Creek estuary (though the changes were relatively small in November 2001), DIC only increased at the Pages Creek estuary from high to low tide during April 2001 and April 2002, while November DIC showed no pattern between high and low tide.

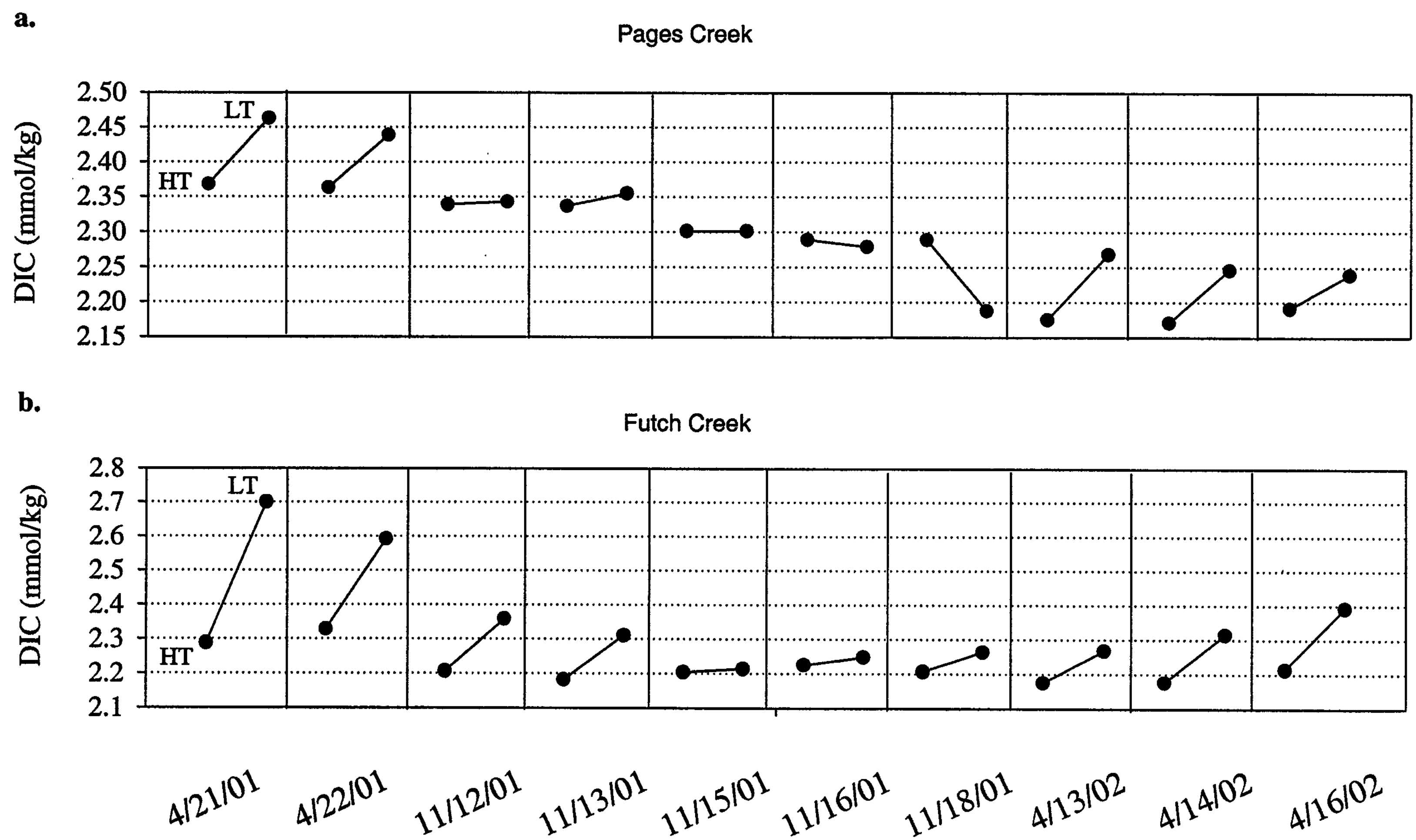

a.
Pages Creek
DIC (mmol/kg)
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
LT
HT
b.
Futch Creek
DIC (mmol/kg)
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure III-5

Figure III-6

April 2001, November 2001, and April 2002 high and low tide $\delta^{13}C$ values for a) Pages Creek. b) Futch Creek. Within each box, the left dot represents the high tide value (HT) and the right dot the low tide value (LT). Note the scale change between a and b. $\delta^{13}C$ values decreased from high to low tide in the Futch Creek estuary during November 2001 and April 2002, and in the Pages Creek estuary in April 2002, while April 2001 showed little change on one sampling day, and unusually low high and low tide values on the second day, in both estuaries. November 2001 $\delta^{13}C$ values showed little change from high to low tide in the Pages Creek estuary.

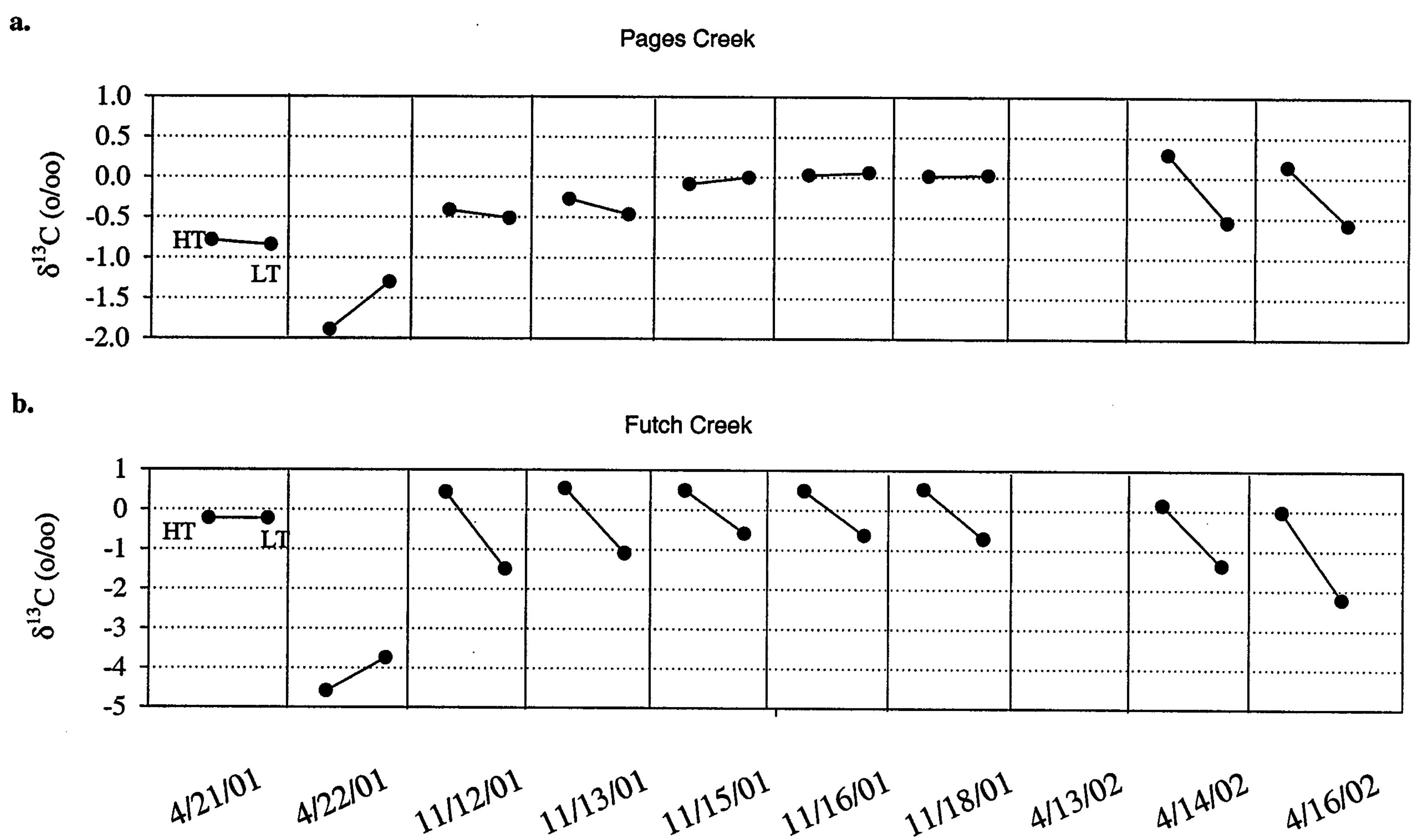

a.
Pages Creek
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
δ13C (o/oo)
HT
LT
b.
Futch Creek
1
0
-1
-2
-3
-4
-5
δ13C (o/oo)
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure III-6

Figure III-7

April 2001, November 2001, and April 2002 high and low tide total alkalinity (TAlk) concentrations for a) Pages Creek. b) Futch Creek. Within each box, the left dot represents the high tide value (HT) and the right dot the low tide value (LT). Note the scale change between a and b. While both estuaries showed an increase in alkalinity from high to low tide in April 2002, April 2001 and November 2001 alkalinity concentrations showed no consistent pattern between high and low tide in either estuary.

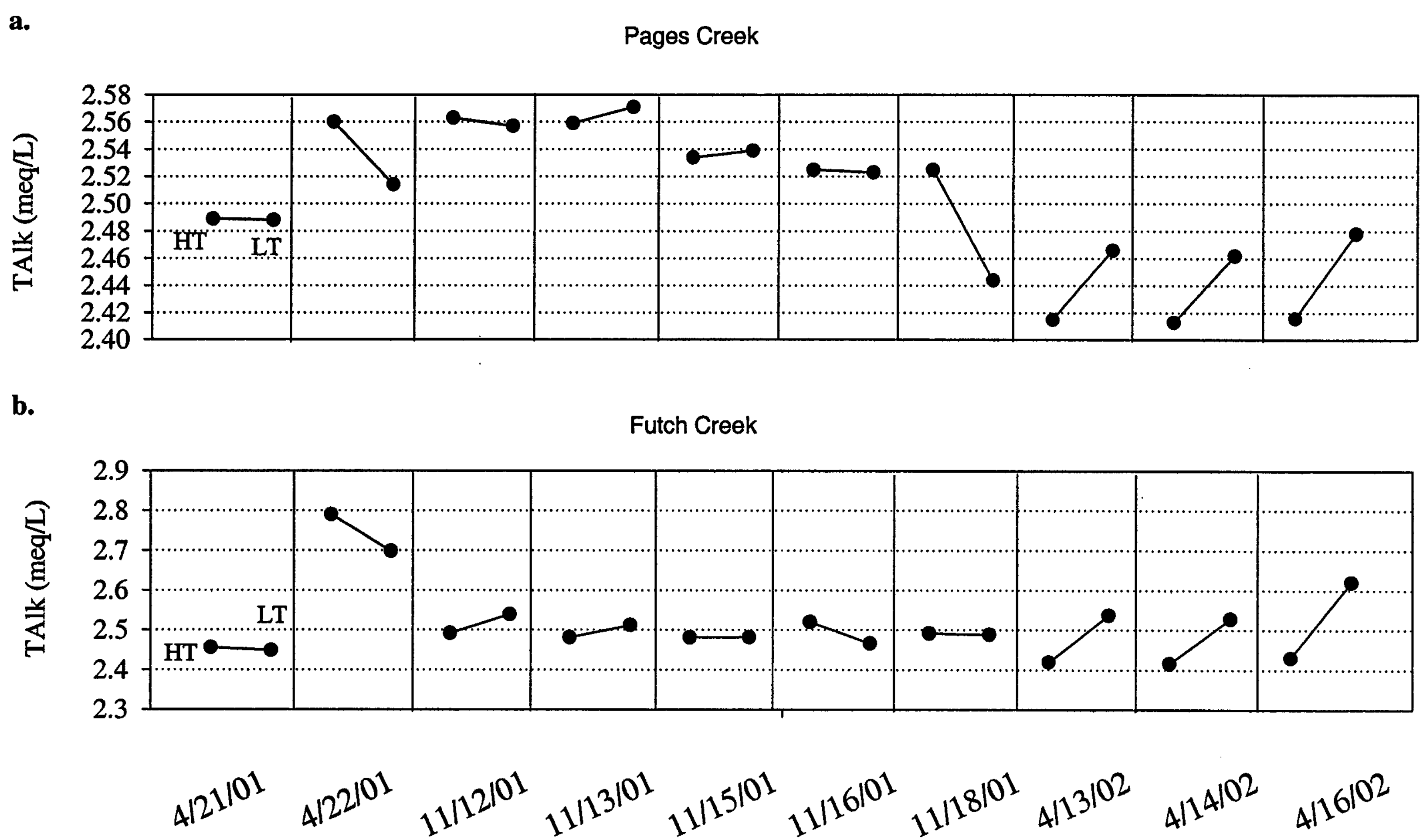

a.
Pages Creek
TAlk (meq/L)
2.58
2.56
2.54
2.52
2.50
2.48
2.46
2.44
2.42
2.40
HT
LT
b.
Futch Creek
TAlk (meq/L)
2.9
2.8
2.7
2.6
2.5
2.4
2.3
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure III-7

Figure III-8

Time series $\Delta^{14}C$ and water depth data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Lines represent the water depth throughout the tidal cycle. Error bars represent ± 5‰ precision error on $\Delta^{14}C$ values. $\Delta^{14}C$ values are lowest at low tide for all three time series and highest at high tide.

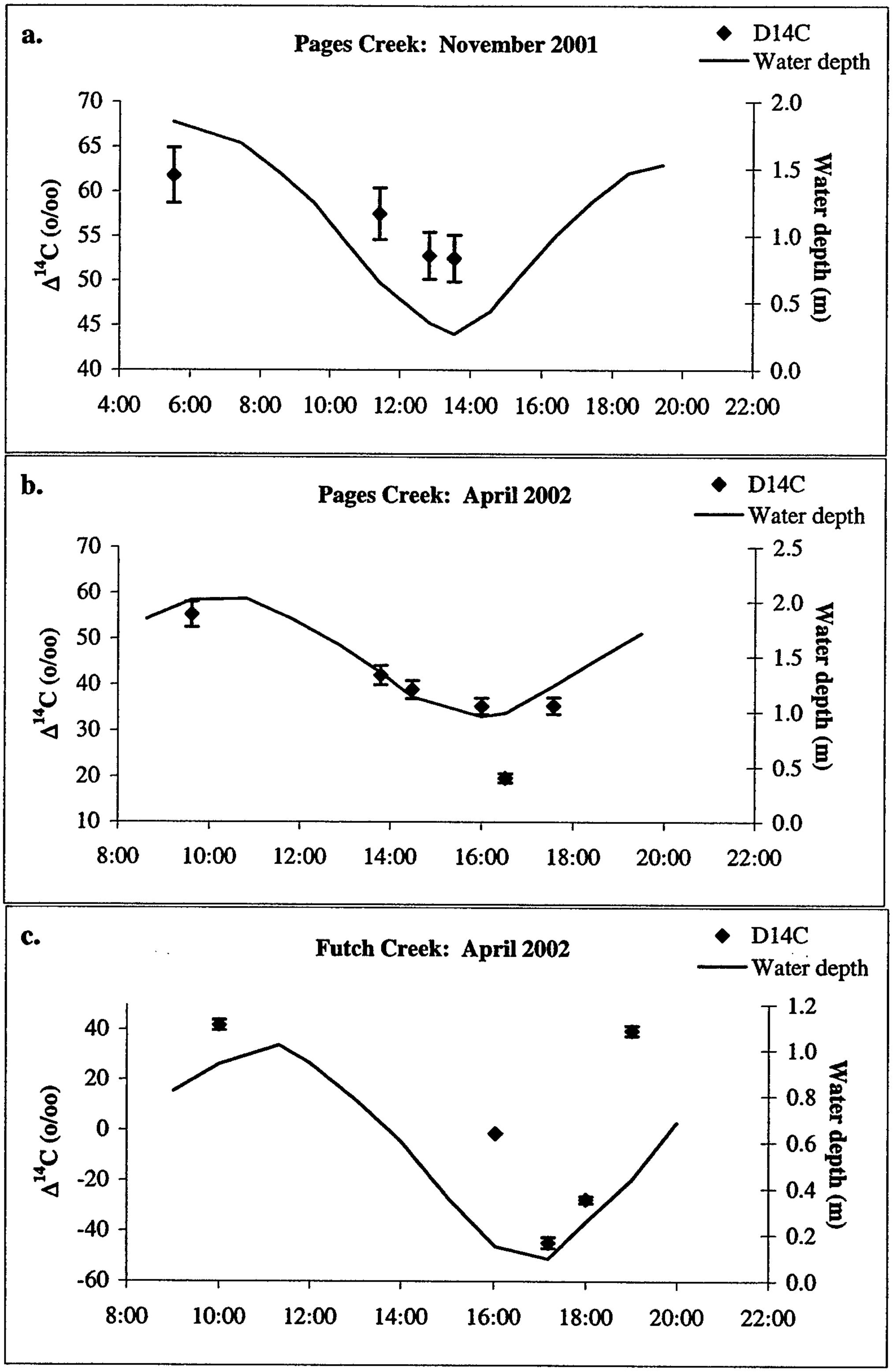

a.
Pages Creek: November 2001
D14C
Water depth
Δ14C (o/oo)
Water depth (m)
70
65
60
55
50
45
40
2.0
1.5
1.0
0.5
0.0
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
b.
Pages Creek: April 2002
D14C
Water depth
Δ14C (o/oo)
Water depth (m)
70
60
50
40
30
20
10
2.5
2.0
1.5
1.0
0.5
0.0
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
c.
Futch Creek: April 2002
D14C
Water depth
Δ14C (o/oo)
Water depth (m)
40
20
0
-20
-40
-60
1.2
1.0
0.8
0.6
0.4
0.2
0.0
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00

Figure III-8

Figure III-9

Time series $\delta^{13}C$ and water depth data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Lines represent the water depth throughout the tidal cycle. Error bars represent ± 0.1 ‰ precision error on $\delta^{13}C$ values. $\delta^{13}C$ values are lowest at low tide for all three time series and highest at high tide.

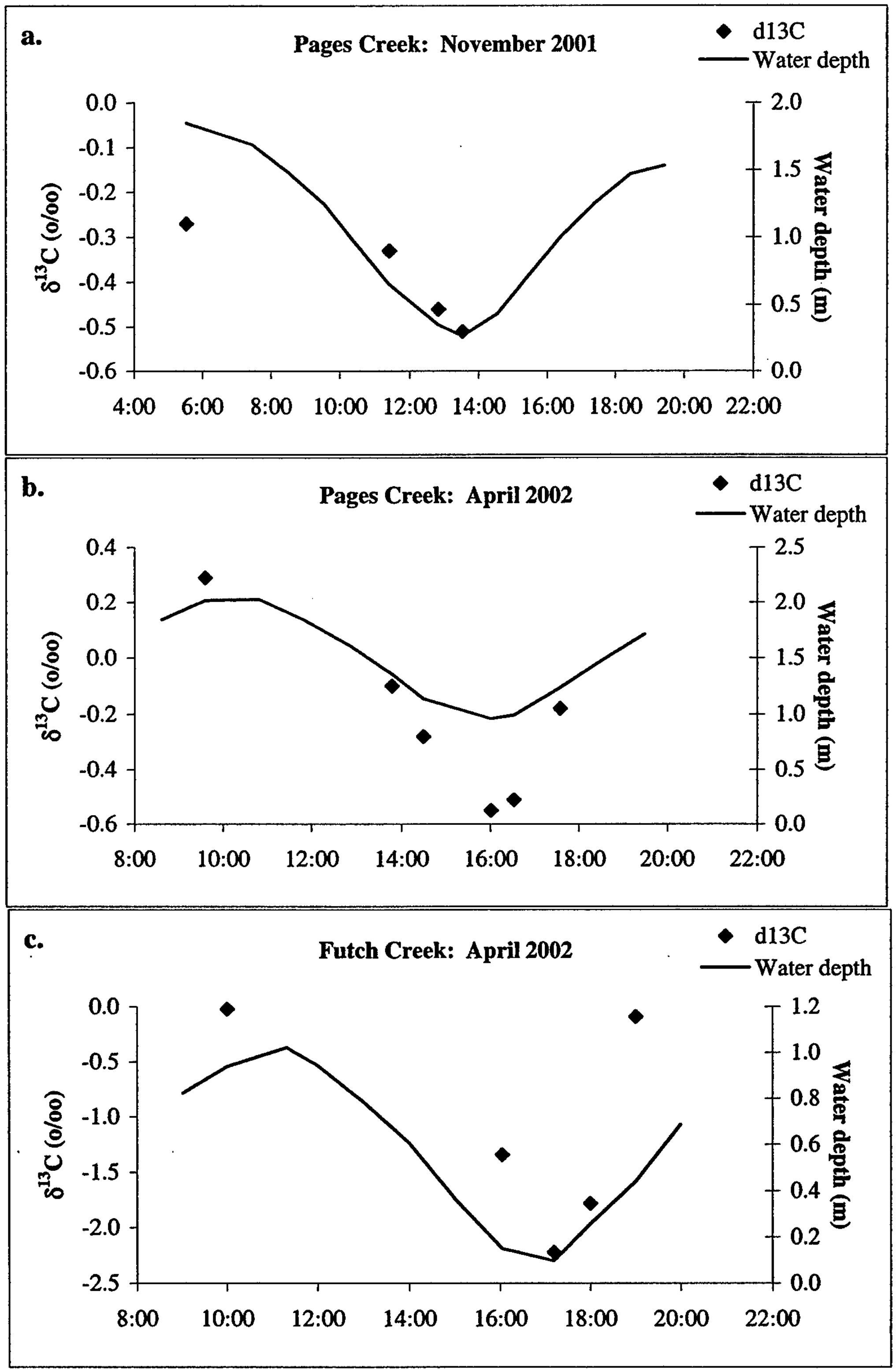

a.
Pages Creek: November 2001
d13C
Water depth
δ13C (o/oo)
Water depth (m)
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
2.0
1.5
1.0
0.5
0.0
4:00 6:00 8:00 10:00 12:00 14:00 16:00 18:00 20:00 22:00
b.
Pages Creek: April 2002
d13C
Water depth
δ13C (o/oo)
Water depth (m)
0.4
0.2
0.0
-0.2
-0.4
-0.6
2.5
2.0
1.5
1.0
0.5
0.0
8:00 10:00 12:00 14:00 16:00 18:00 20:00 22:00
c.
Futch Creek: April 2002
d13C
Water depth
δ13C (o/oo)
Water depth (m)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
1.2
1.0
0.8
0.6
0.4
0.2
0.0
8:00 10:00 12:00 14:00 16:00 18:00 20:00 22:00

Figure III-9

Figure III-10

Time series DIC and water depth data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Lines represent the water depth throughout the tidal cycle. Error bars represent ± 0.5 % precision error. November DIC concentrations show scatter throughout the time series; although a maximum value occurs near low tide. April 2002 Pages and Futch Creek time series, however, show clear maxima at low tide in DIC concentration, while the high tide values are low.

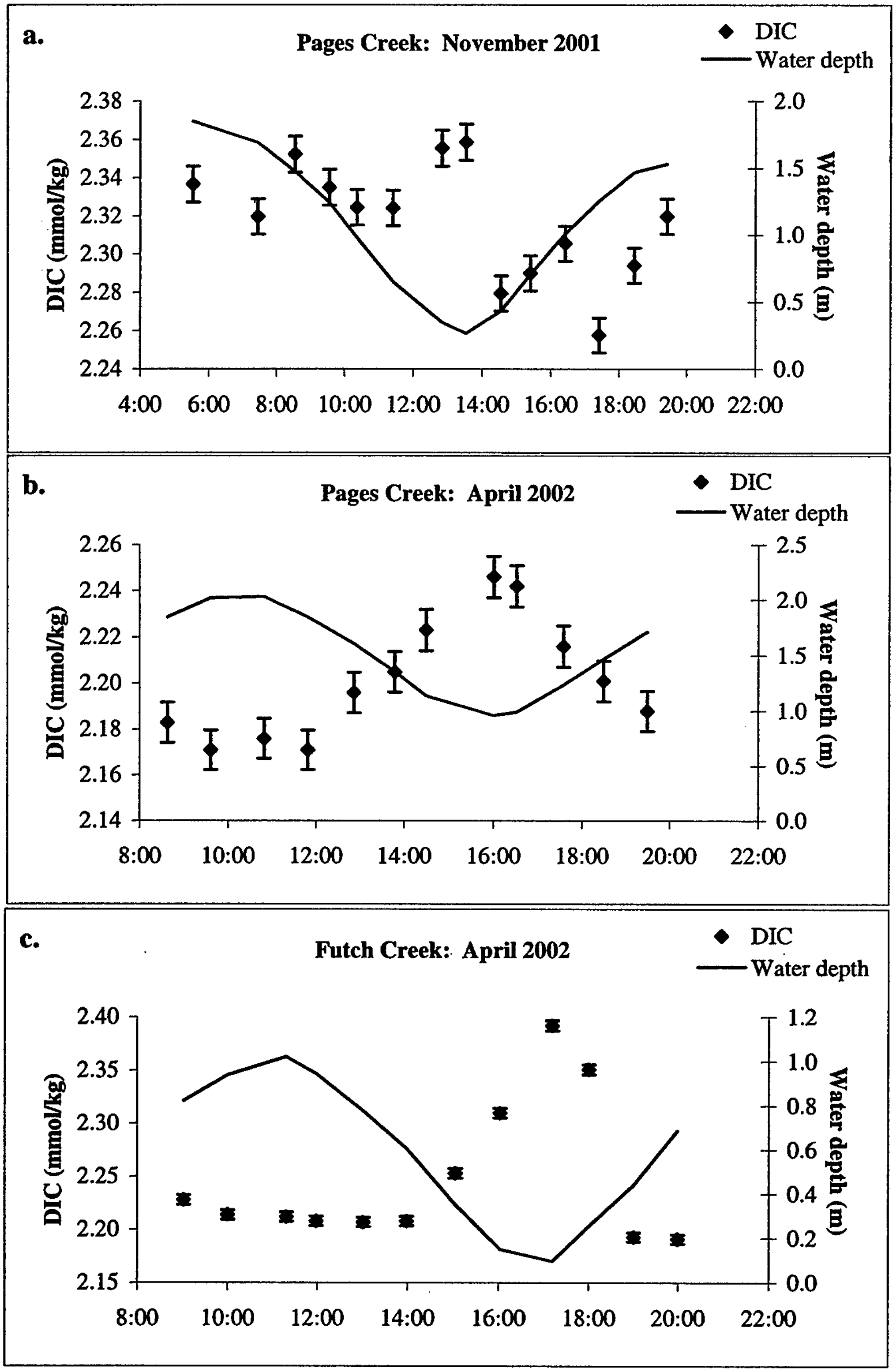


Figure III-10

Figure III-11

Time series TAlk and water depth data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Lines represent the water depth throughout the tidal cycle. Error bars represent ± 0.5 % precision error. November TAlk concentrations show scatter throughout the time series; although a maximum value occurs near low tide. As with DIC concentrations, April 2002 Pages and Futch Creek time series, however, show clear maxima at low tide in alkalinity, while the high tide values are low.

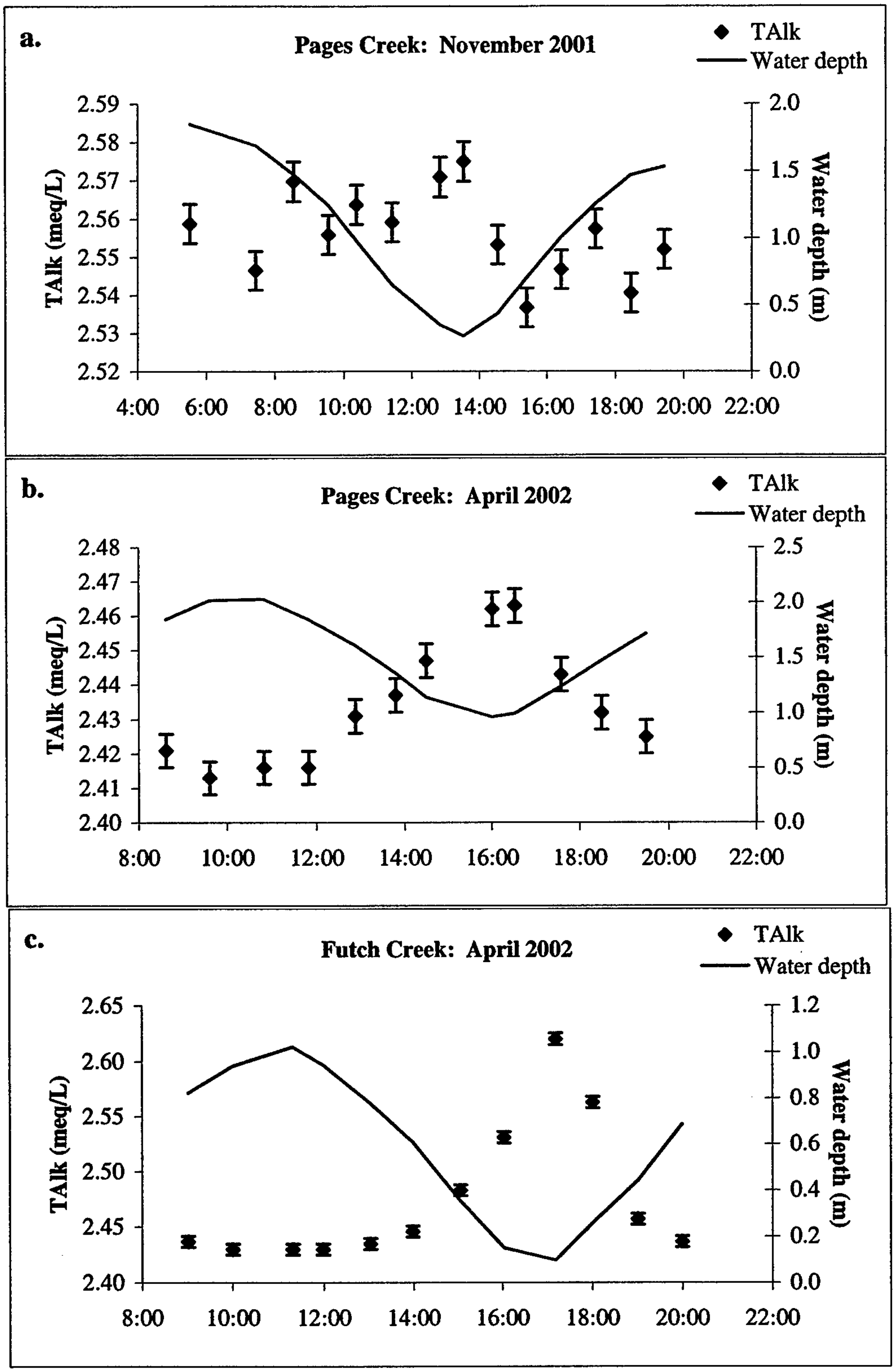


Figure III-11

Figure III-12

Rich and Mason Inlet November 2001 low tide and April 2002 high and low tide a) salinity values, b) $\Delta^{14}C$ values, and c) DIC concentrations. Within each box, the left dot represents the high tide value (HT) and the right dot the low tide value (LT). Note the scale change between a and b. Salinity decreased from high to low tide at all times in April 2002, with the change in salinity </= 0.2 ppt. November 2001 low tide salinity was higher than any of the April 2002 values. $\Delta^{14}C$ values showed no clear high/low tide trend in the inlets, and tidal differences in $\Delta^{14}C$ were generally within the ± 5‰ precision error. DIC concentrations increased from high to low tide during April 2002.

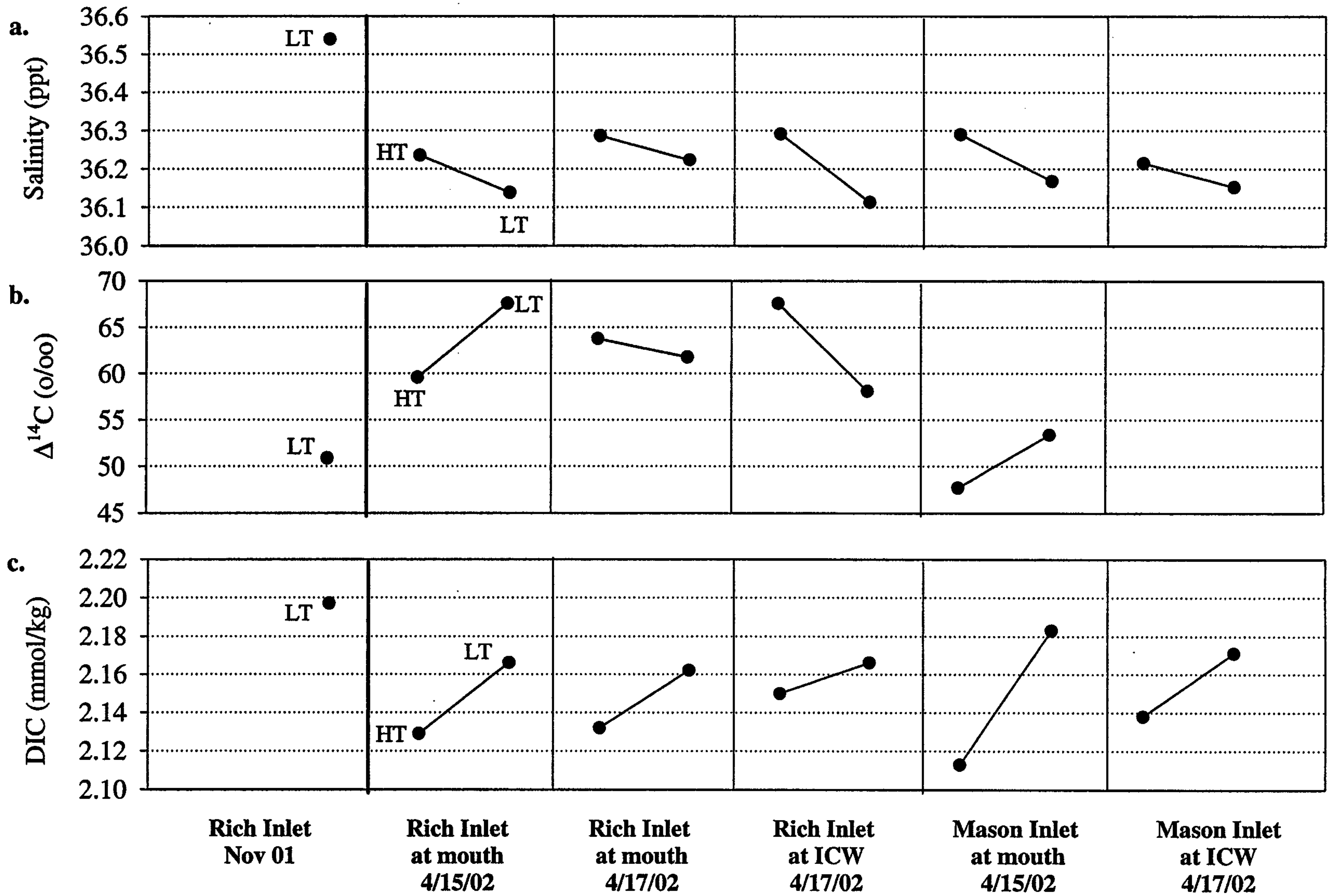


Figure III-12

Figure III-13

$\Delta^{14}C$ values of possible DIC sources to the Pages and Futch Creek estuaries. Inlet and inflow $\Delta^{14}C$ values tend to be > +40‰, stream $\Delta^{14}C$ ranges from +90‰ to –200‰, and spring $\Delta^{14}C$ values are ~ –400‰. Castle Hayne groundwater $\Delta^{14}C$ values are similar to spring values, ranging from –300‰ to –500‰, while Peedee groundwater $\Delta^{14}C$ values are the lowest, ranging from –750‰ to –850‰.

Figure III-13

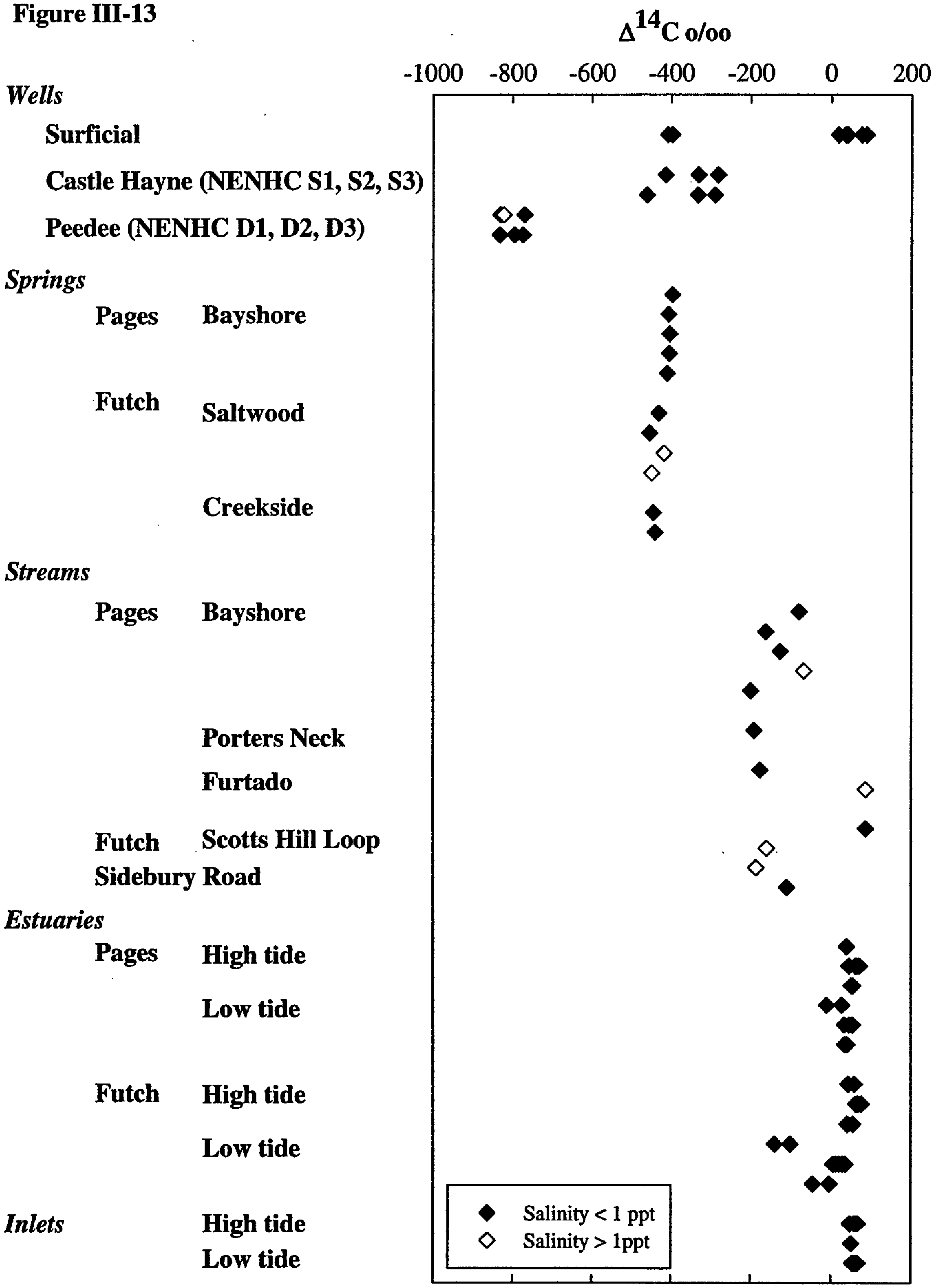


Figure III-14

$\delta^{13}C$ values of possible DIC sources to the Pages and Futch Creek estuaries. Inlet and inflow $\delta^{13}C$ values tend to be > 0‰, stream $\delta^{13}C$ ranges from –5‰ to –20‰, and spring $\delta^{13}C$ values were highly consistent through time and from spring to spring, ranging from –11‰ to –12‰ for all spring samples. Castle Hayne groundwater $\delta^{13}C$ values ranged from –11‰ to –15‰; Peedee groundwater $\delta^{13}C$ values ranged from –11‰ to –13‰. Surficial aquifer $\delta^{13}C$ values varied from –13‰ to –27‰.

Figure III-14

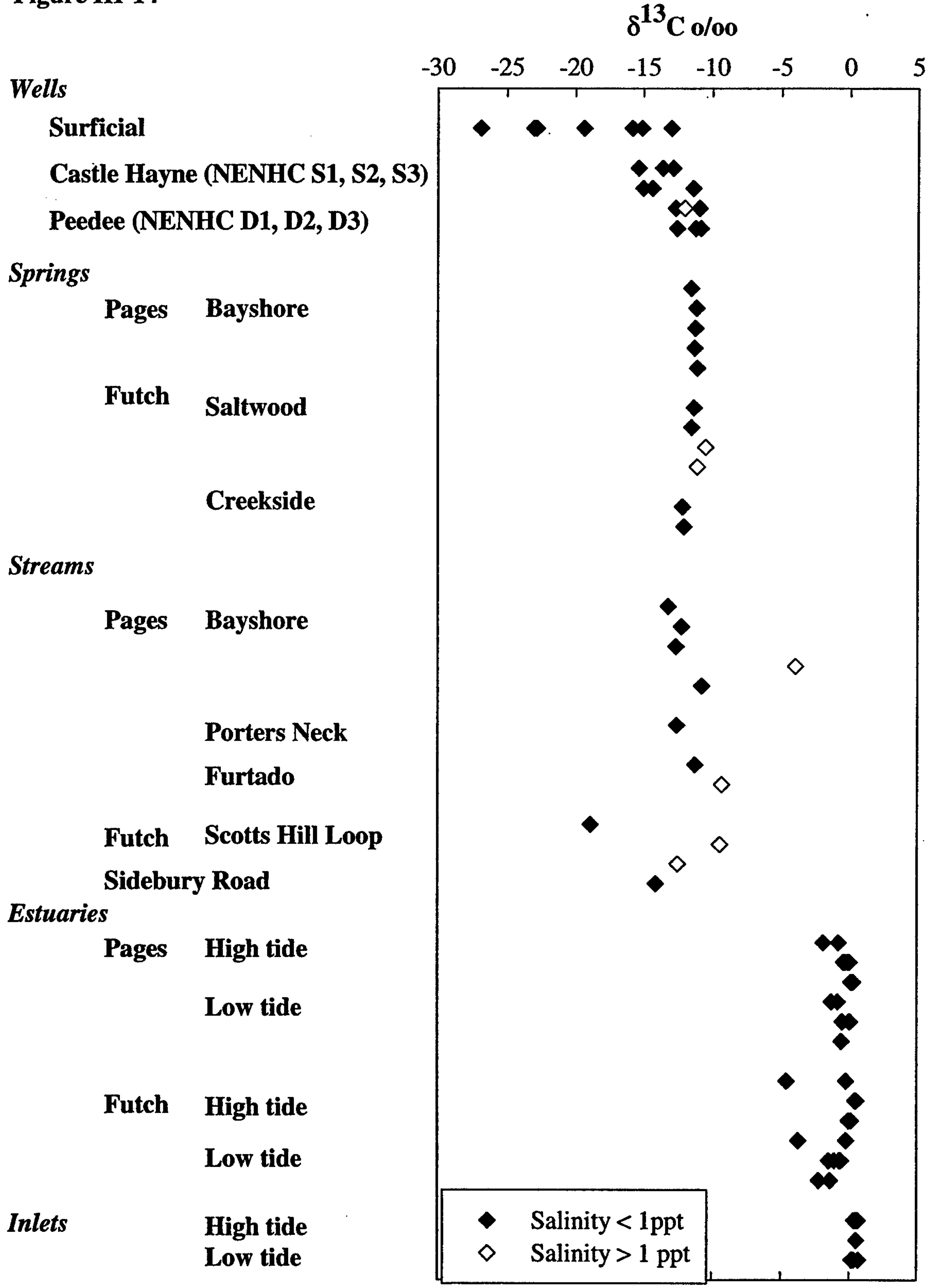


Figure III-15

November 2001 and April 2002 time series $\Delta^{14}C$ and salinity data with high and low tide $\Delta^{14}C$ and salinity data. Error bars represent ± 5‰ precision error in $\Delta^{14}C$ value and ± 0.01 ppt error in salinity value. a) Futch Creek estuary (April 2002 time series only). b) Pages Creek estuary (November 2001 and April 2002 time series). The trend of the change in $\Delta^{14}C$-salinity from high to low tide corresponds to the trend shown by each time series.

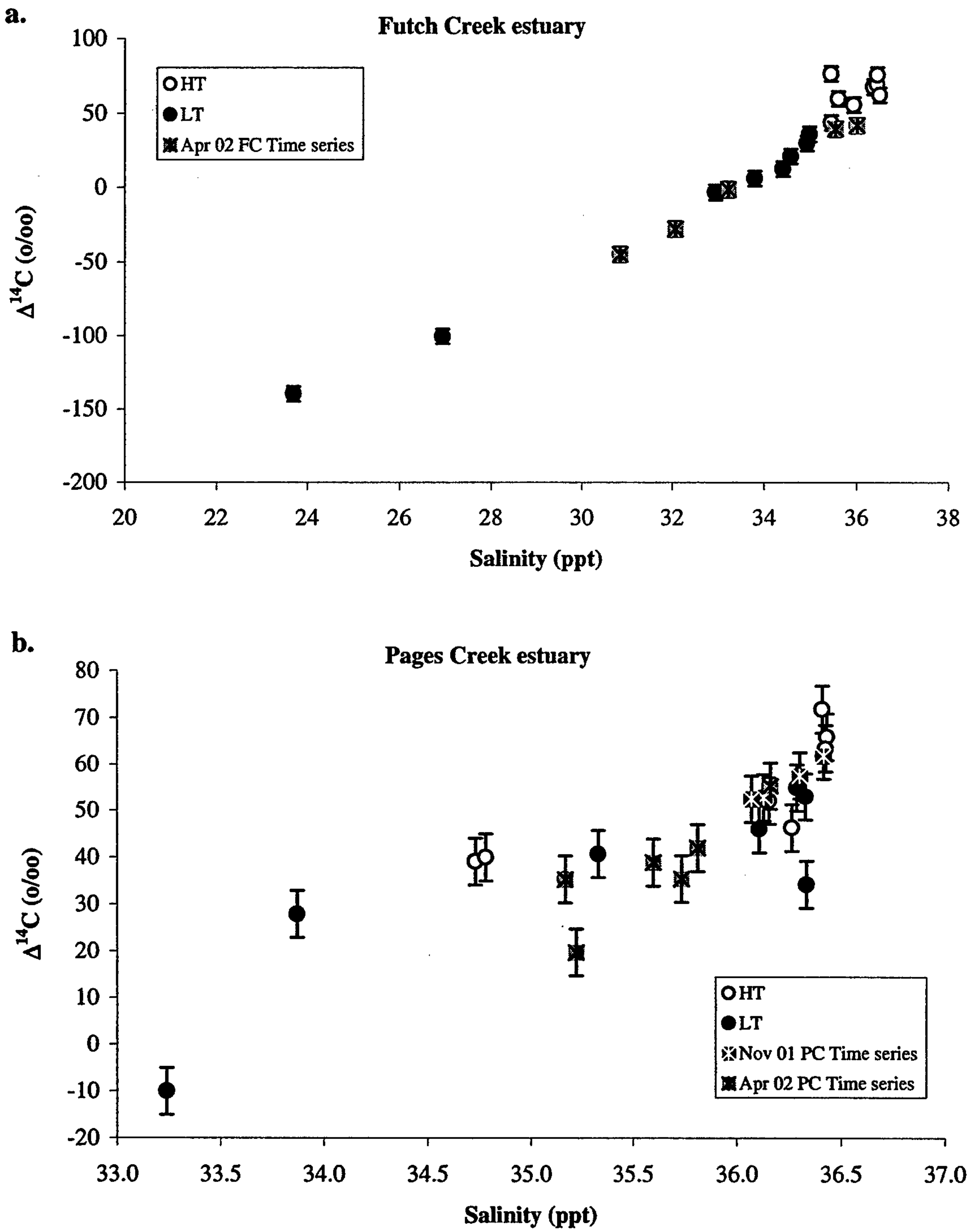
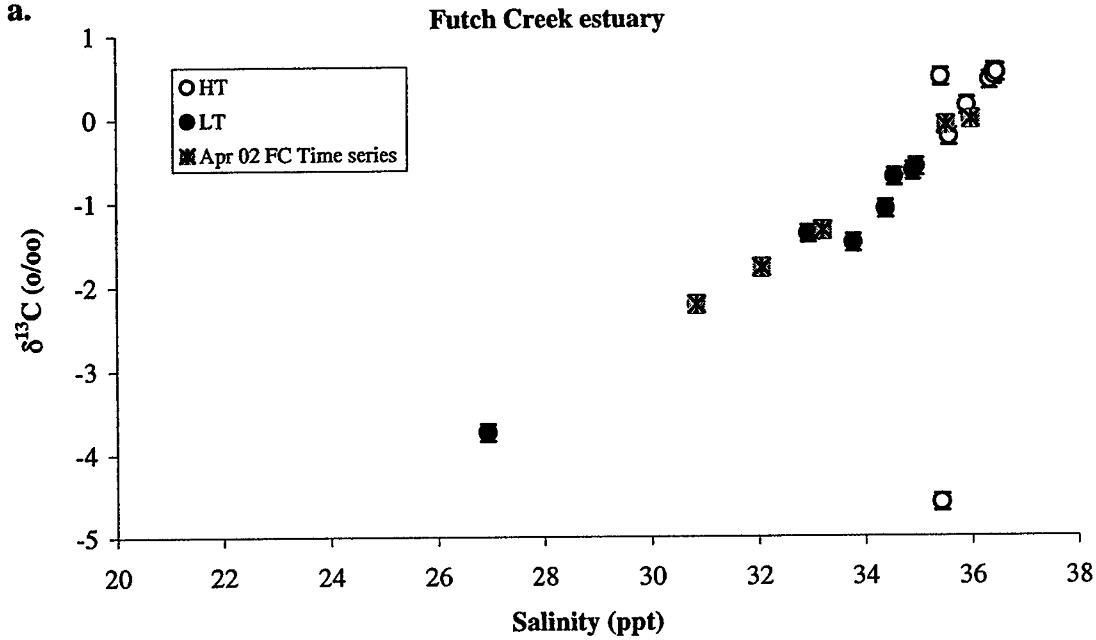


Figure III-15

Figure III-16

November 2001 and April 2002 time series $\delta^{13}C$ and salinity data with high and low tide $\delta^{13}C$ and salinity data. Error bars represent ± 0.1‰ precision error in $\delta^{13}C$ value and ± 0.01 ppt error in salinity value. a) Futch Creek estuary (April 2002 time series only). b) Pages Creek estuary (November 2001 and April 2002 time series).

a.



b.

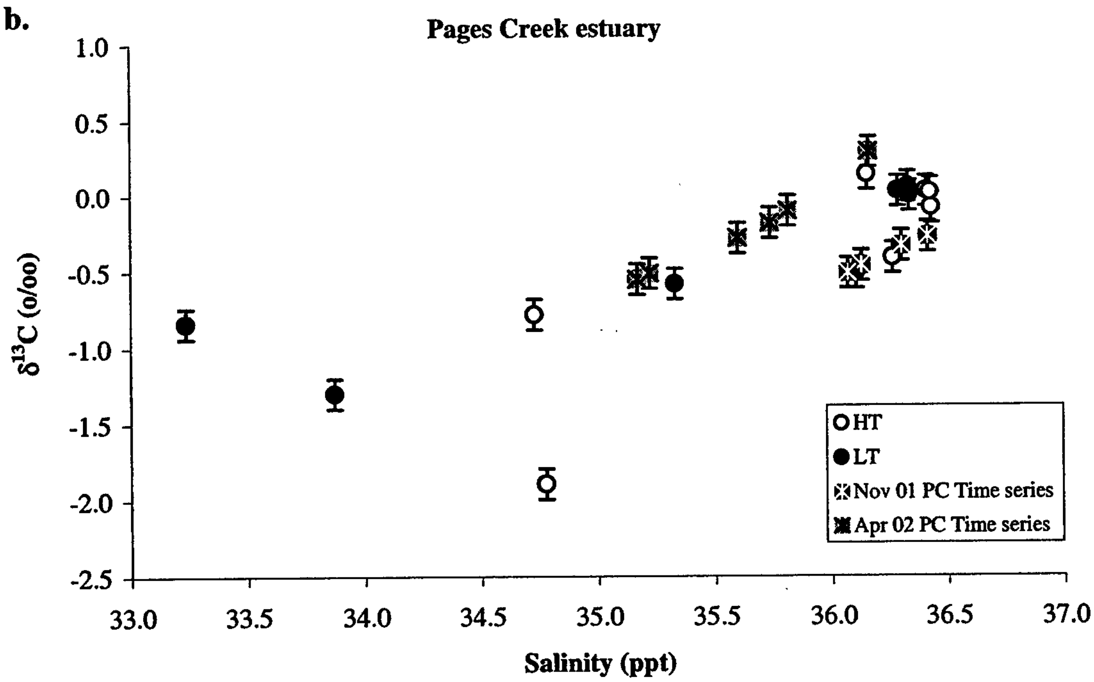


Figure III-16

Figure III-17

November 2001 and April 2002 time series DIC and salinity data with high and low tide DIC and salinity data. Error bars represent ± 0.5 % precision error in DIC value and ± 0.01 ppt error in salinity value. a) Futch Creek estuary (April 2002 time series only). b) Pages Creek estuary (November 2001 and April 2002 time series).

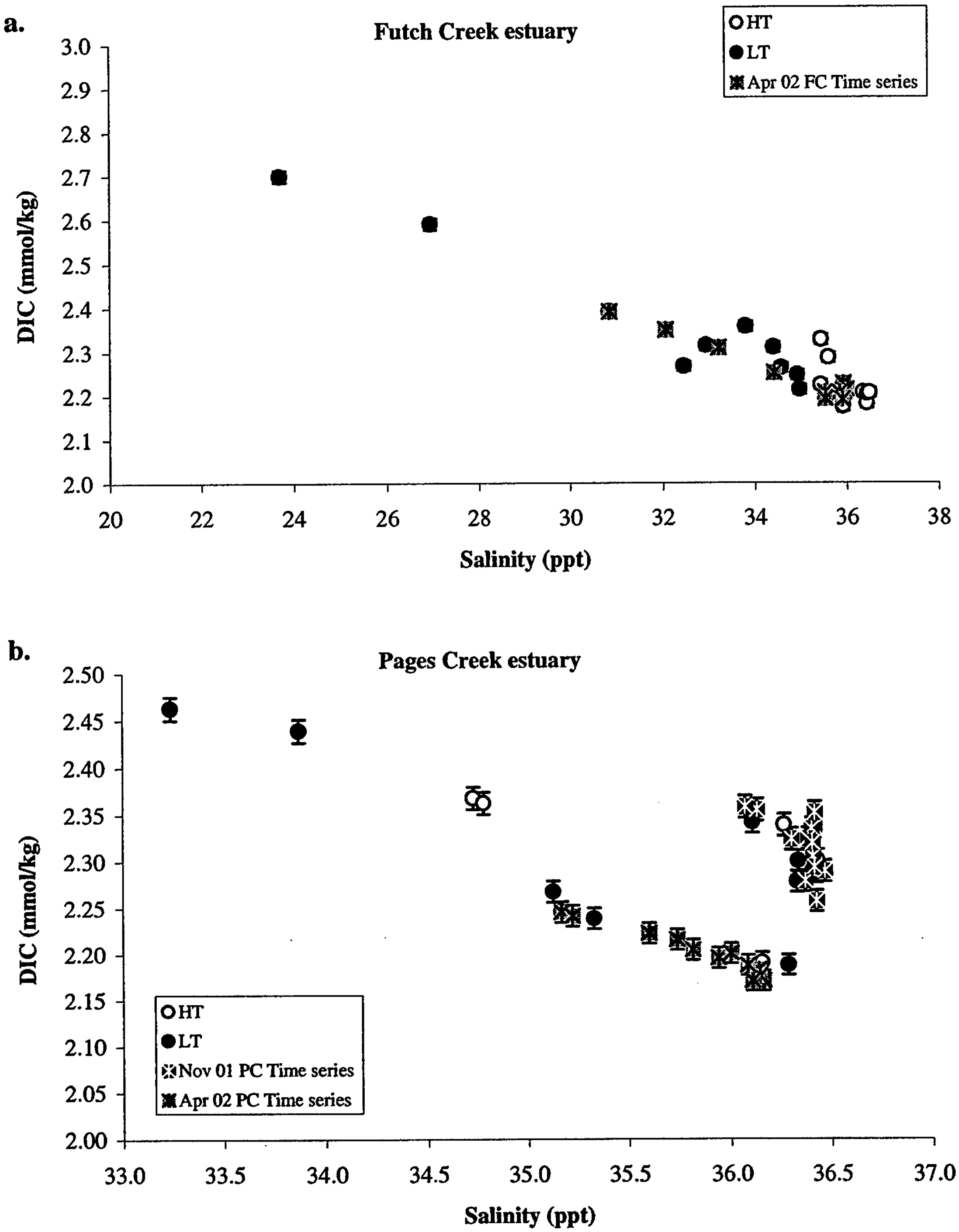


Figure III-17

Figure III-18

November 2001 and April 2002 time series TAlk and salinity data with high and low tide alkalinity and salinity data. Error bars represent ± 0.1‰ precision error in alkalinity value and ± 0.01 error in salinity value. a) Futch Creek estuary (April 2002 time series only). b) Pages Creek estuary (November 2001 and April 2002 time series).

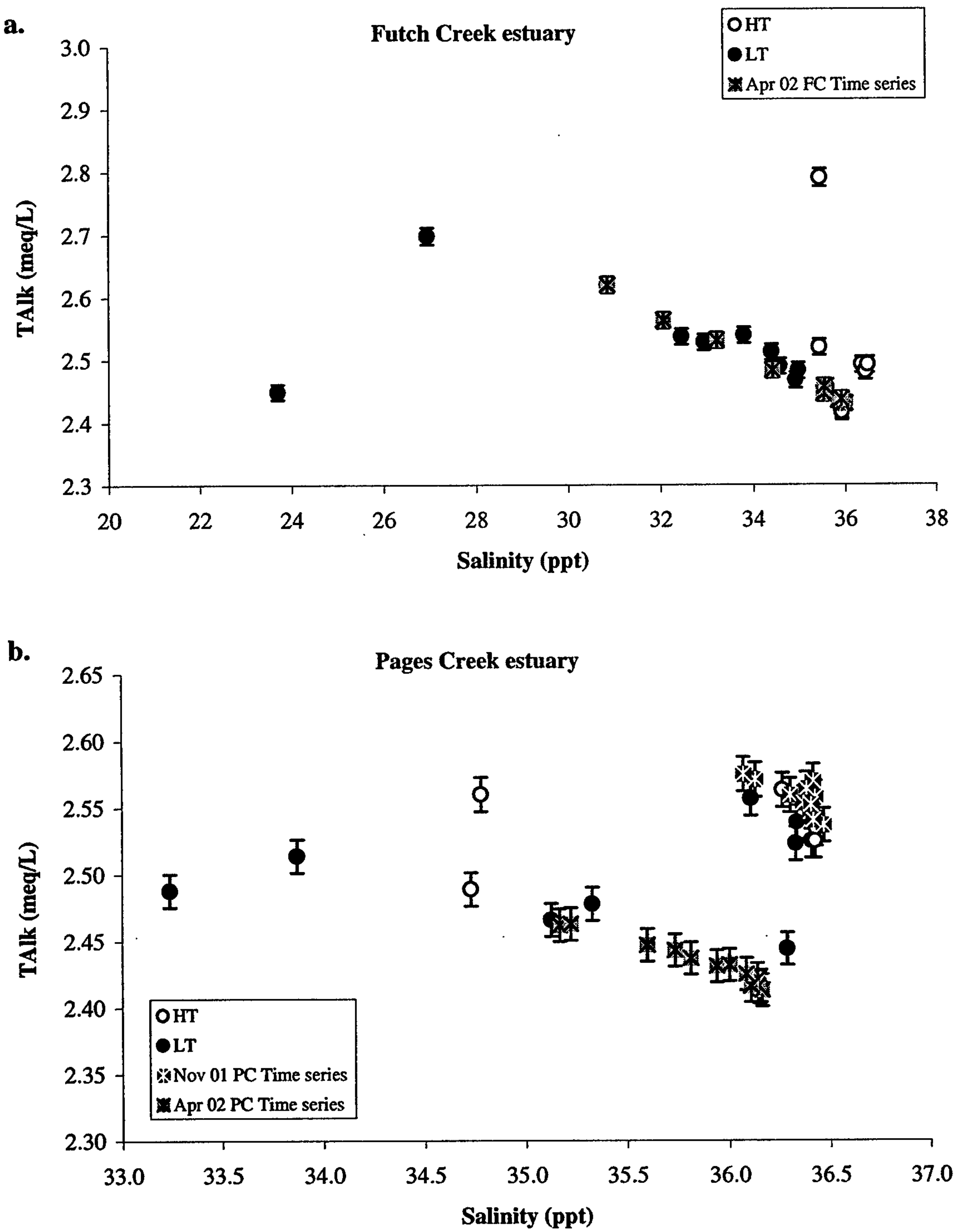


Figure III-18

Figure III-19

Pore water DIC and DIC isotopic values from two sites within the salt marsh next to Rich Inlet, with calculated average isotopic values of DIC added to surface waters flooding the marsh at high tide. a) $\Delta^{14}C$ values. b) $\delta^{13}C$ values. Average $\Delta^{14}C$ values of the DIC added to the surface waters were –21‰ at Site 1 and –64‰ at Site 2. Average $\delta^{13}C$ values of the DIC added to the surface waters were –6.7‰ at Site 1, and –7.6‰ at Site 2.

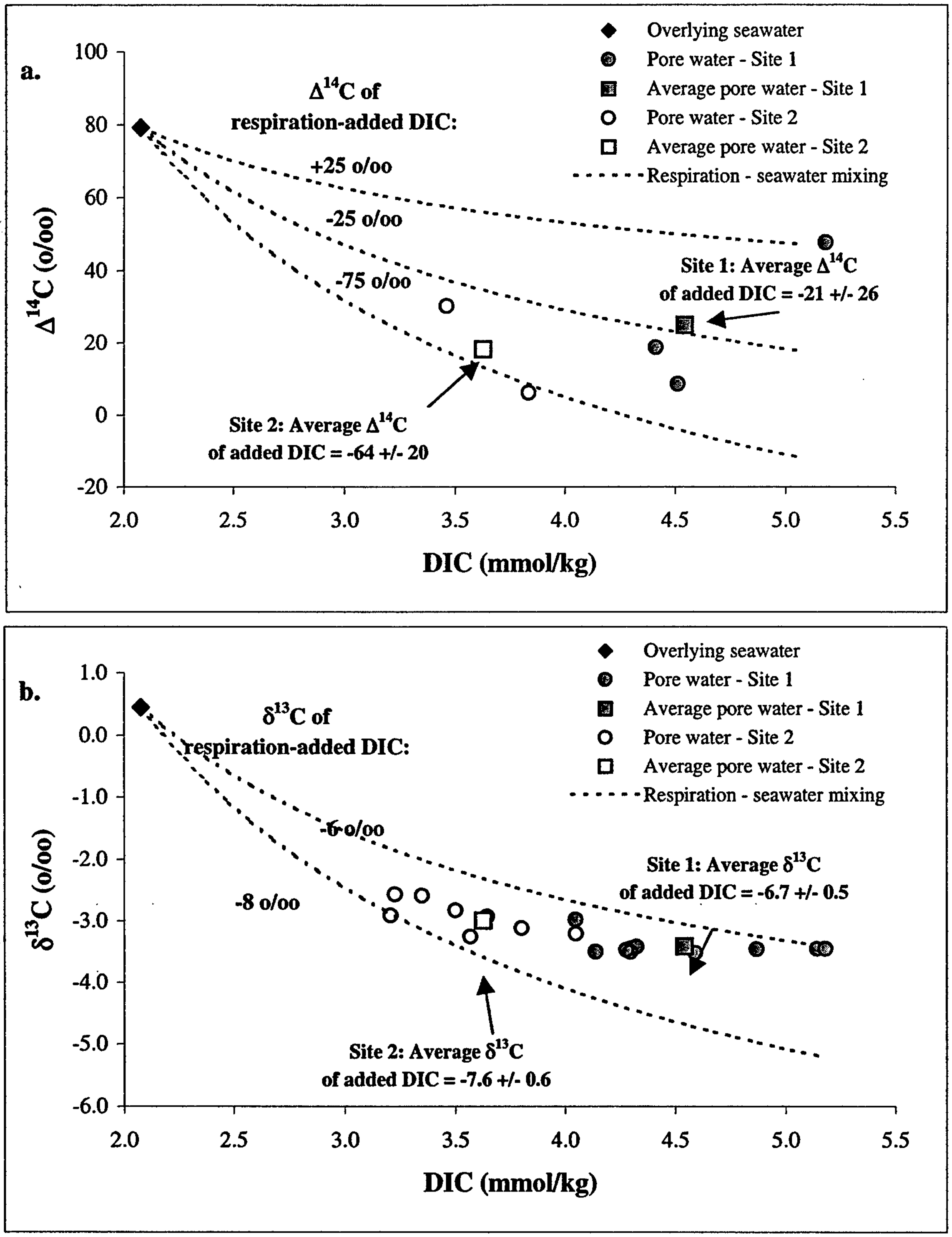


Figure III-19

Figure III-20

Pages and Futch Creek estuary spring and stream DIC and $\Delta^{14}C$ values, with surficial, Castle Hayne, and Peedee groundwater DIC and $\Delta^{14}C$ values. Black lines represent mixing lines between Scotts Hill Loop stream and NENHC wells S2 (dotted) and S3 (solid). While the $\Delta^{14}C$ values of all springs are similar, the Futch Creek springs fall into two groups with respect to DIC concentration: Saltwood Lane spring (low-DIC) and other Futch Creek springs (high-DIC, similar to Bayshore spring). The Futch Creek Saltwood Lane spring samples are similar in composition to the NENHC well S2, screened in the Castle Hayne. The Pages Creek Bayshore spring samples, and the other Futch Creek spring samples, had DIC values intermediate between NENHC Castle Hayne-screened wells S2 and S3. The $\Delta^{14}C$ and DIC values of the Bayshore stream samples (diamonds) may result from mixing between Castle Hayne water (of a well S3 composition) and surficial groundwater, as represented by the low-DIC, high-$\Delta^{14}C$ Scotts Hill Loop stream sample (April 2001).

The salty November 2001 Bayshore stream (~30 ppt) is likely to be a mix of inflow and spring only. The average Bayshore stream sample (used in mixing calculations) is represented by a grey diamond. The average April 2001 Futch spring sample (used in mixing calculations) is represented by a white cross on a black box. Black boxes on the stream/groundwater mixing lines represent a mix of 50% stream and 50% groundwater; stream samples, if a mix between the two, are always less than 50% Castle Hayne water.

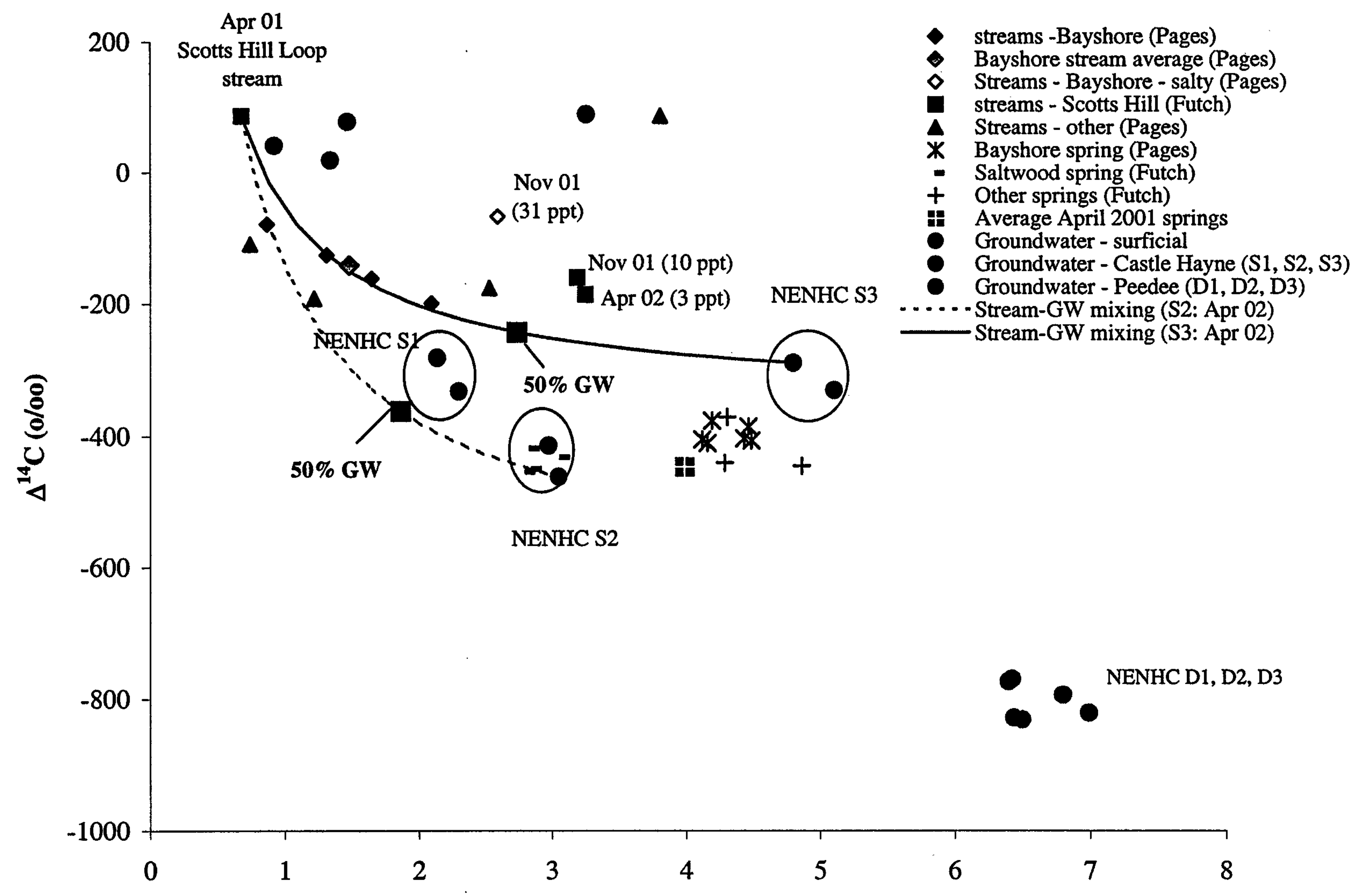


Figure III-20

Figure III-21.

Pages and Futch Creek estuary spring and stream DIC and $\delta^{13}C$ values, with surficial, Castle Hayne, and Peedee groundwater DIC and $\delta^{13}C$ values. Although the Pages Bayshore stream samples fell along a DIC-$\Delta^{14}C$ mixing line between the Futch Creek Scotts Hill Loop stream and NENHC well S3, the Bayshore streams have high $\delta^{13}C$ values relative to the Scotts Hill Loop – well S3 DIC-$\delta^{13}C$ mixing line. However, isotopic fractionation effects resulting from CO_2 removal via photosynthesis or gas evasion can significantly affect the $\delta^{13}C$ value of the mix. Photosynthetic removal of 1 mmol of CO_2 from a mix of 35% groundwater (well S3) and 65% Scotts Hill Loop stream water – as suggested by the position of the April 2002 Bayshore stream sample along the DIC-$\Delta^{14}C$ mixing line – increases the $\delta^{13}C$ value of the mix by 13‰. A combination of CO_2 removal and respiration CO_2 additions can thus alter the $\delta^{13}C$ value of the mix to match the observed April 2002 stream composition.

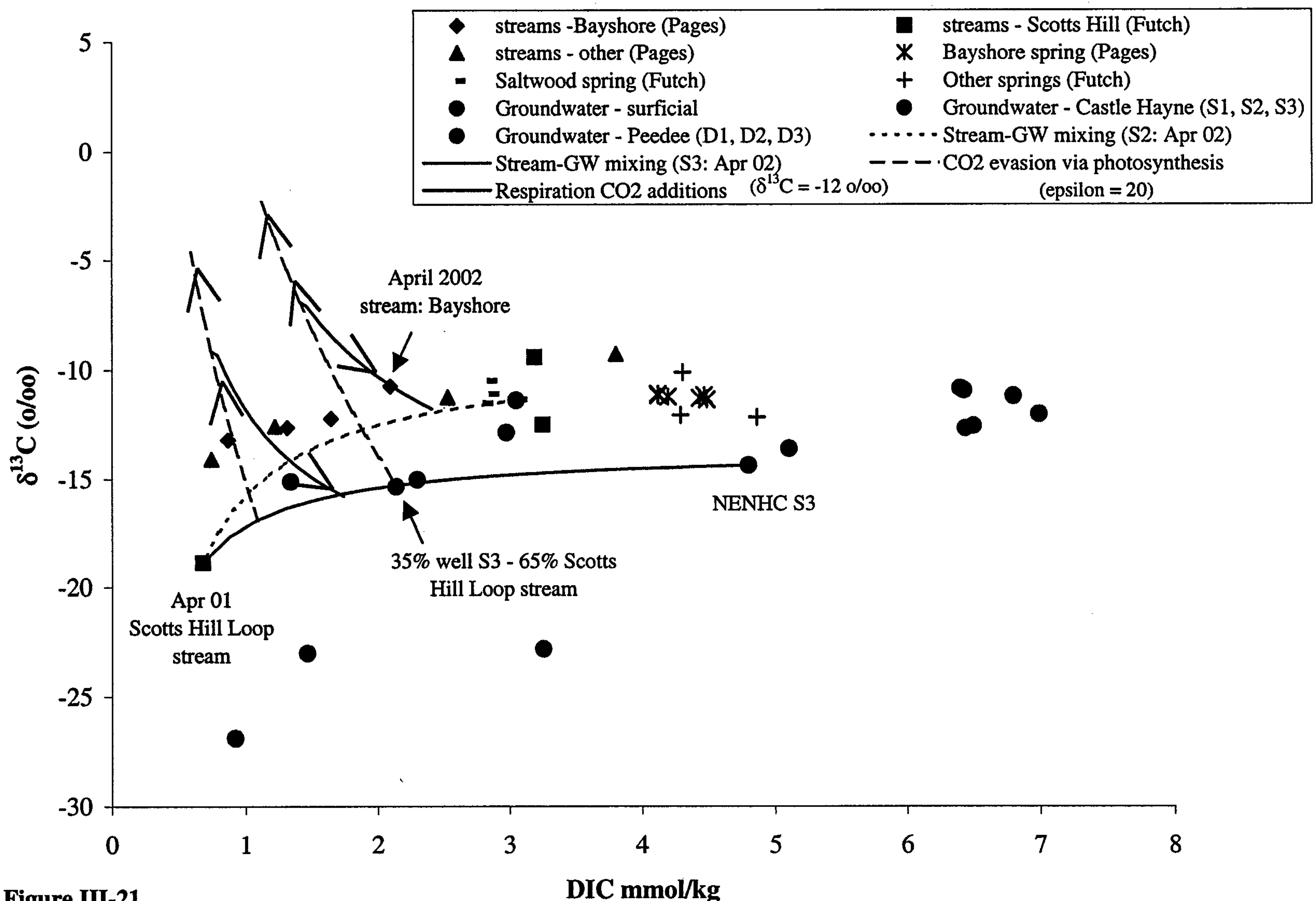


Figure III-21

Figure III-22

April 2001 Pages Creek estuary DIC concentration–$\Delta^{14}C$ mixing curves between three components: inflow from Intracoastal Waterway (ICW), fresh stream input, and artesian groundwater/spring input. The low tide outflow DIC and DIC isotope values are also shown (grey square). Analytical precision for each graph is approximated by symbol size. a) April 21, 2001. b) April 22, 2001. On both days, the low tide outflow DIC-$\Delta^{14}C$ composition falls along the inflow-spring mixing line, suggesting that in April 2001, artesian spring inputs contributed ~ 100% of the total fresh water input to Pages Creek at low tide.

Figure III-22 **Pages Creek**

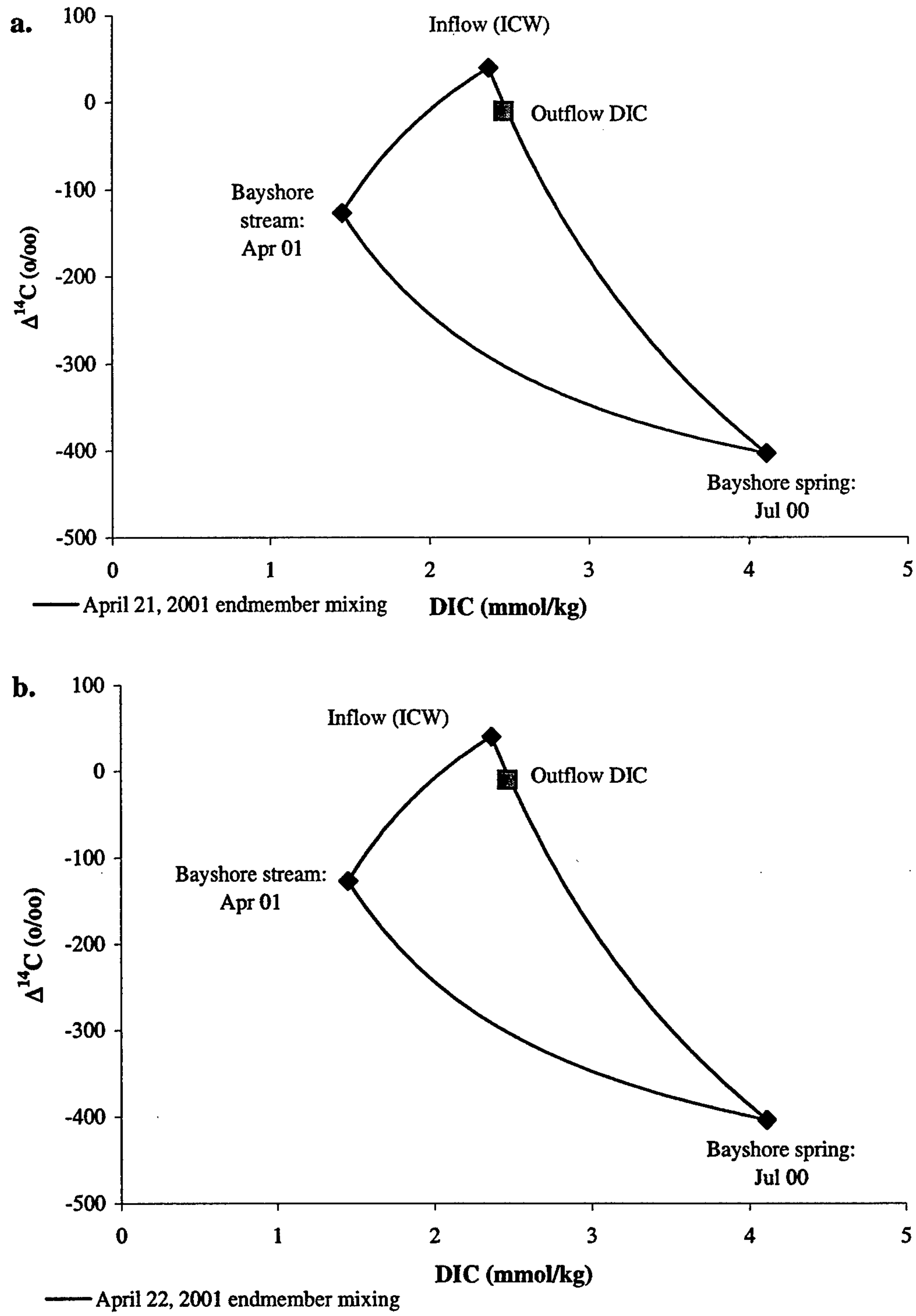
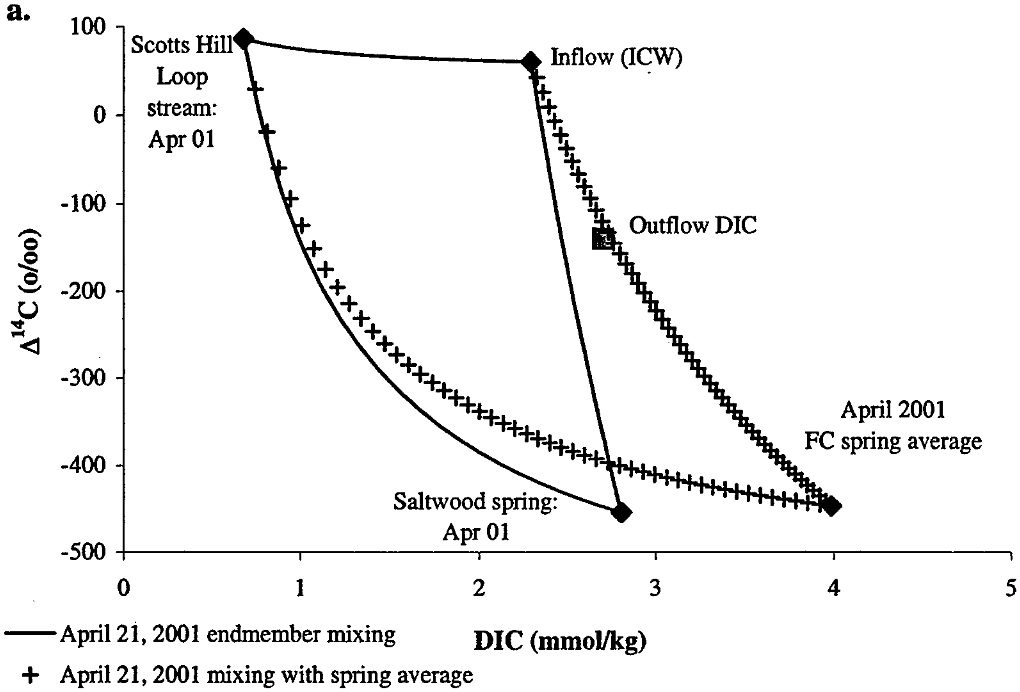


Figure III-23

April 2001 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. Two mixing triangles are shown: the solid lines represent inflow and stream mixing with the largest observed Futch Creek spring (Saltwood Lane). The '+' symbols represent inflow and stream mixing with an average of April 2001 Futch Creek spring compositions (similar $\Delta^{14}C$ values but higher DIC concentrations than at Saltwood). The low tide outflow DIC and DIC isotope values are also shown (grey square). Analytical precision for each graph is approximated by symbol size. a) April 21, 2001. b) April 22, 2001. The outflow falls outside of the Saltwood spring triangle but along the inflow-spring average mixing line. These mixing curves suggest that the artesian spring inputs contributed all of the fresh water input to the Futch Creek estuary at low tide in April 2001.

Figure III-23 **Futch Creek**

a.



b.

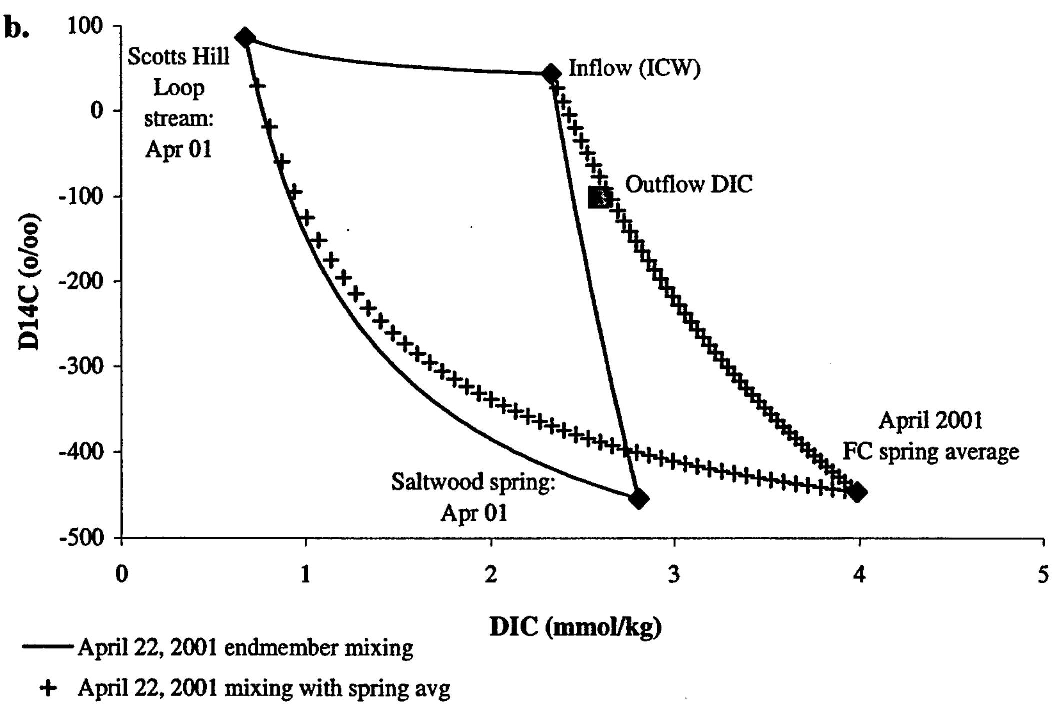


Figure III-24

November 2001 Pages Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. Because no November 2001 fresh stream sample was collected, an average Pages Creek stream composition is used to construct the mixing triangle. The low tide outflow DIC and DIC isotope values are also shown (grey square). a) November 12, 2001, with b) close-up of outflow DIC. c) November 13, 2001, with d) close-up of outflow DIC. Analytical precision for graphs a and c are approximated by symbol size, while for b and d, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. On both days, the low tide outflow DIC-$\Delta^{14}C$ compositions fall along the inflow-spring mixing line, suggesting that on these days artesian spring inputs contributed ~ 100% of the total fresh water input to Pages Creek at low tide.

Figure III-24

Pages Creek

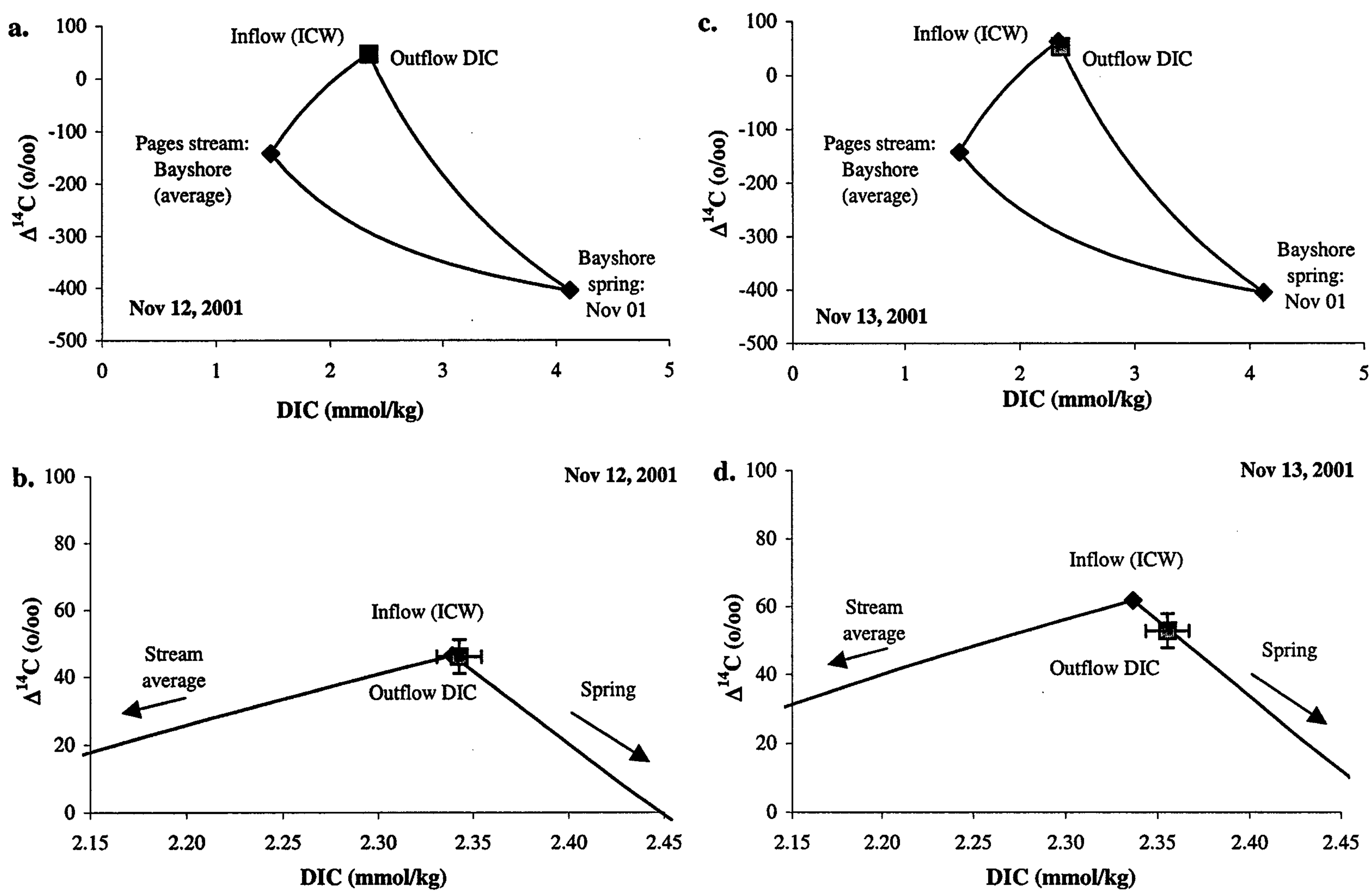


Figure III-25

November 2001 Pages Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. In addition to the average Pages Creek stream composition, mixing triangles using the range of observed stream $\Delta^{14}C$ values are also shown, to provide maximum and minimum estimates of relative spring input. The low tide outflow DIC and DIC isotope values are also shown (grey square). a) November 15, 2001, with b) close-up of outflow DIC. c) November 16, 2001, with d) close-up of outflow DIC. Analytical precision for graphs a and c are approximated by symbol size, while for b and d, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. On both days, the outflow DIC-$\Delta^{14}C$ composition is within the mixing triangle, suggesting a mix of inflow, stream, and spring inputs. Calculation of the relative spring contribution is dependent on choice of stream endmember. However, as discussed in the text, the measured outflow $\Delta^{14}C$ and salinity values cannot be matched by any combination of observed spring, stream and inflow inputs.

Figure III-25

Pages Creek

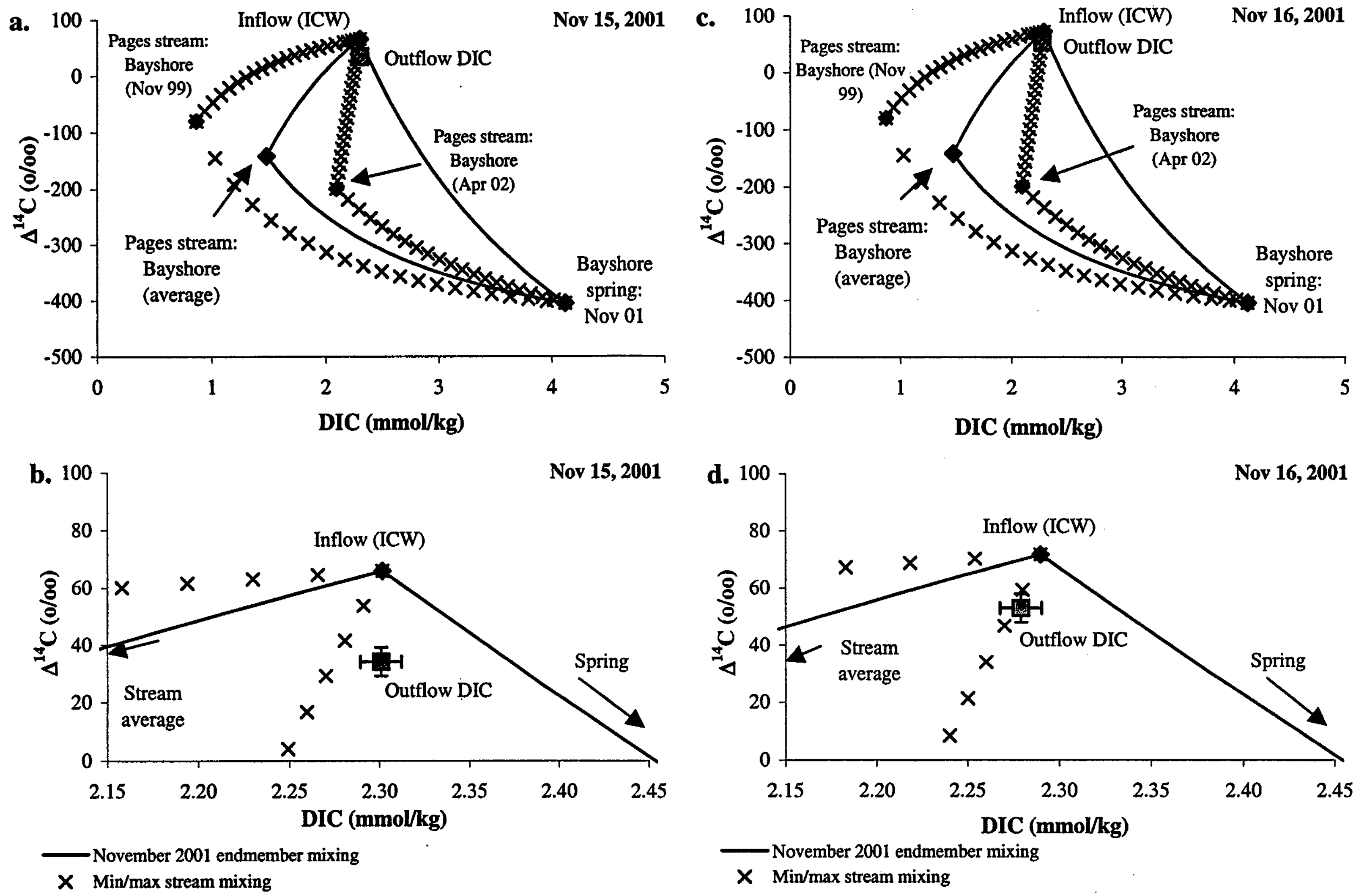


Figure III-26

November 2001 Pages Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. In addition to the average Pages Creek stream composition, mixing triangles using the range of observed stream $\Delta^{14}C$ values are also shown, to provide maximum and minimum estimates of relative spring input. The low tide outflow DIC and DIC isotope values are also shown (grey square). a) November 18, 2001, with b) close-up of outflow DIC. Analytical precision for graph a is approximated by symbol size, while for b, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. The placement of the outflow DIC-$\Delta^{14}C$ values, between the inflow-average stream mixing line and the inflow-minimum $\Delta^{14}C$ stream mixing line, suggests that stream inputs dominated the fresh water budget to Pages Creek on this sampling day. However, as discussed in the text, the measured outflow $\Delta^{14}C$ and salinity values cannot be matched by any combination of observed spring, stream and inflow inputs.

Figure III-26

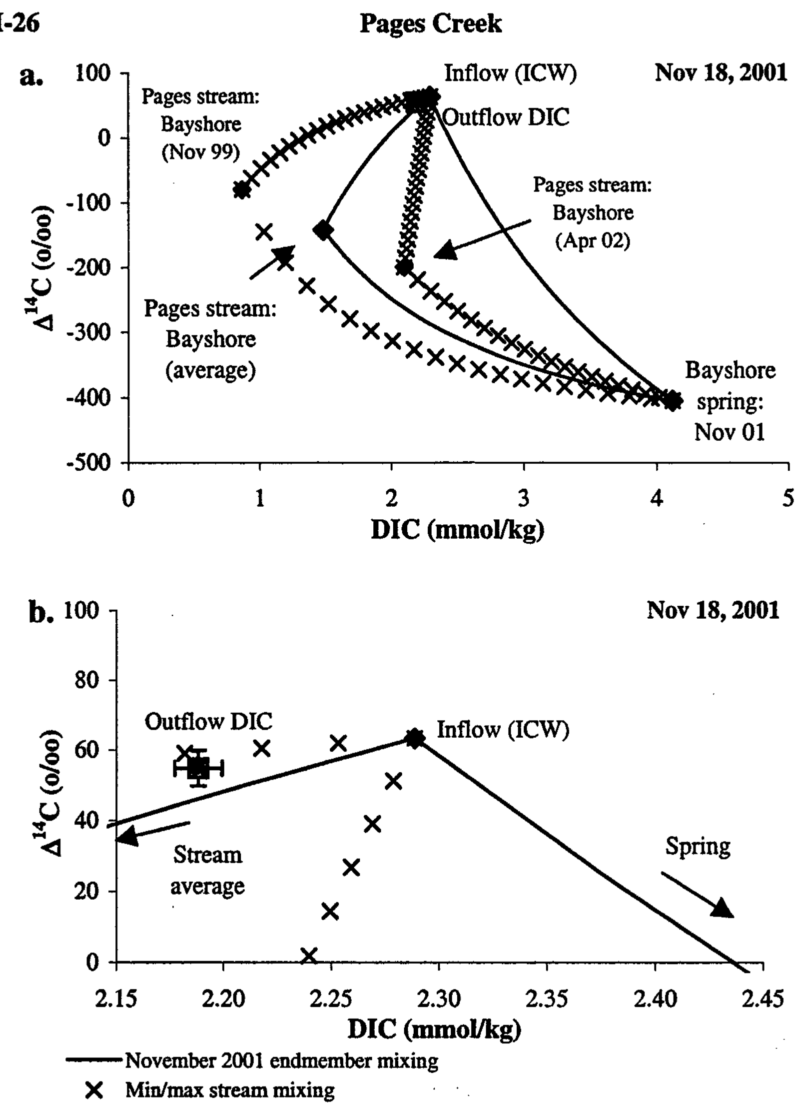


Figure III-27

Closeup of Pages Creek estuary November 15, 2001 inflow-spring-stream mixing triangle. The low tide outflow DIC and DIC isotope values are represented by the grey square, with error bars representing ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. Outflow salinity was only 0.3% fresh (mixing line falls within the high tide symbol size); as discussed in the text, the low tide outflow $\Delta^{14}C$ value cannot be matched by any salinity-constrained combination of the measured inflow and fresh water inputs. Respiration DIC additions (at $\Delta^{14}C$ value = –64‰) also cannot approach the outflow DIC.

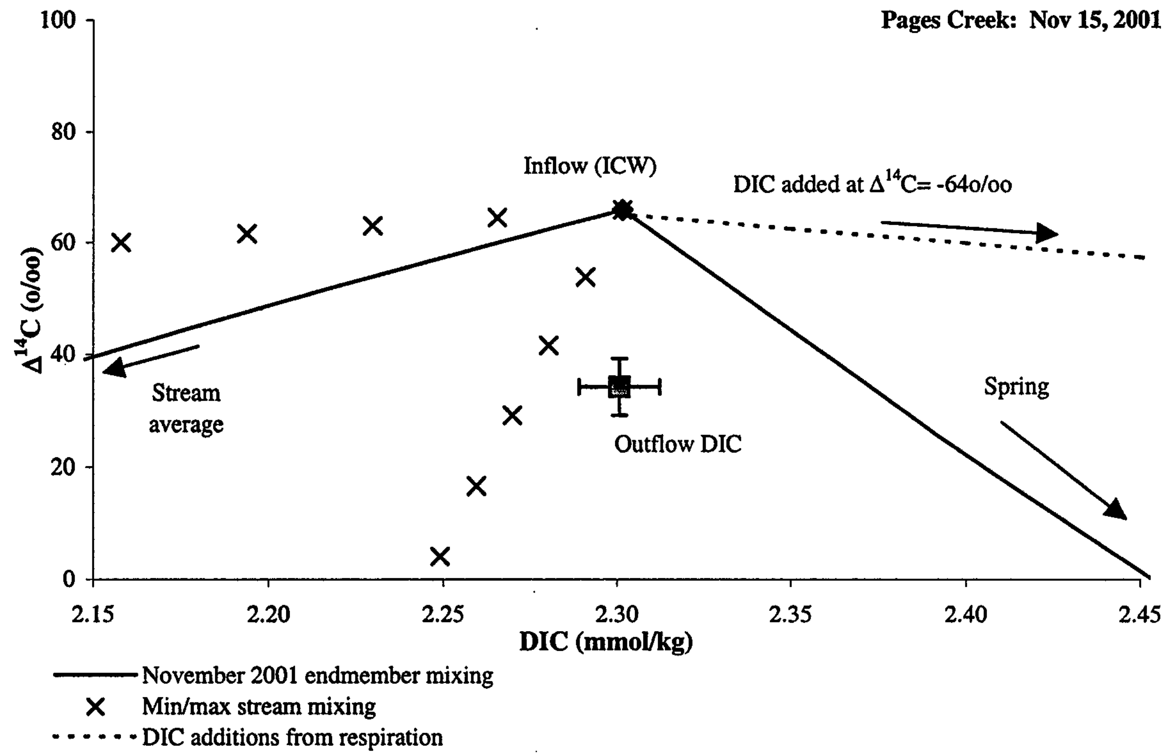


Figure III-27

Figure III-28

November 2001 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. Although the Scotts Hill Loop stream is included as a mixing endmember, field observations of very low streamflow during sampling suggest that the outflow is more likely a mix of inflow and spring only. Two mixing triangles are shown: the solid lines represent inflow and stream mixing with the largest observed Futch Creek spring (Saltwood Lane). The '+' symbols represent inflow and stream mixing with an average of April 2001 Futch Creek spring compositions (similar $\Delta^{14}C$ values but higher DIC concentrations than at Saltwood). The low tide outflow DIC and DIC isotope values are also shown (grey square). a) November 12, 2001, with b) close-up of outflow DIC. c) November 13, 2001, with d) close-up of outflow DIC. Analytical precision for graphs a and c are approximated by symbol size, while for b and d, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values.

Figure III-28

Futch Creek

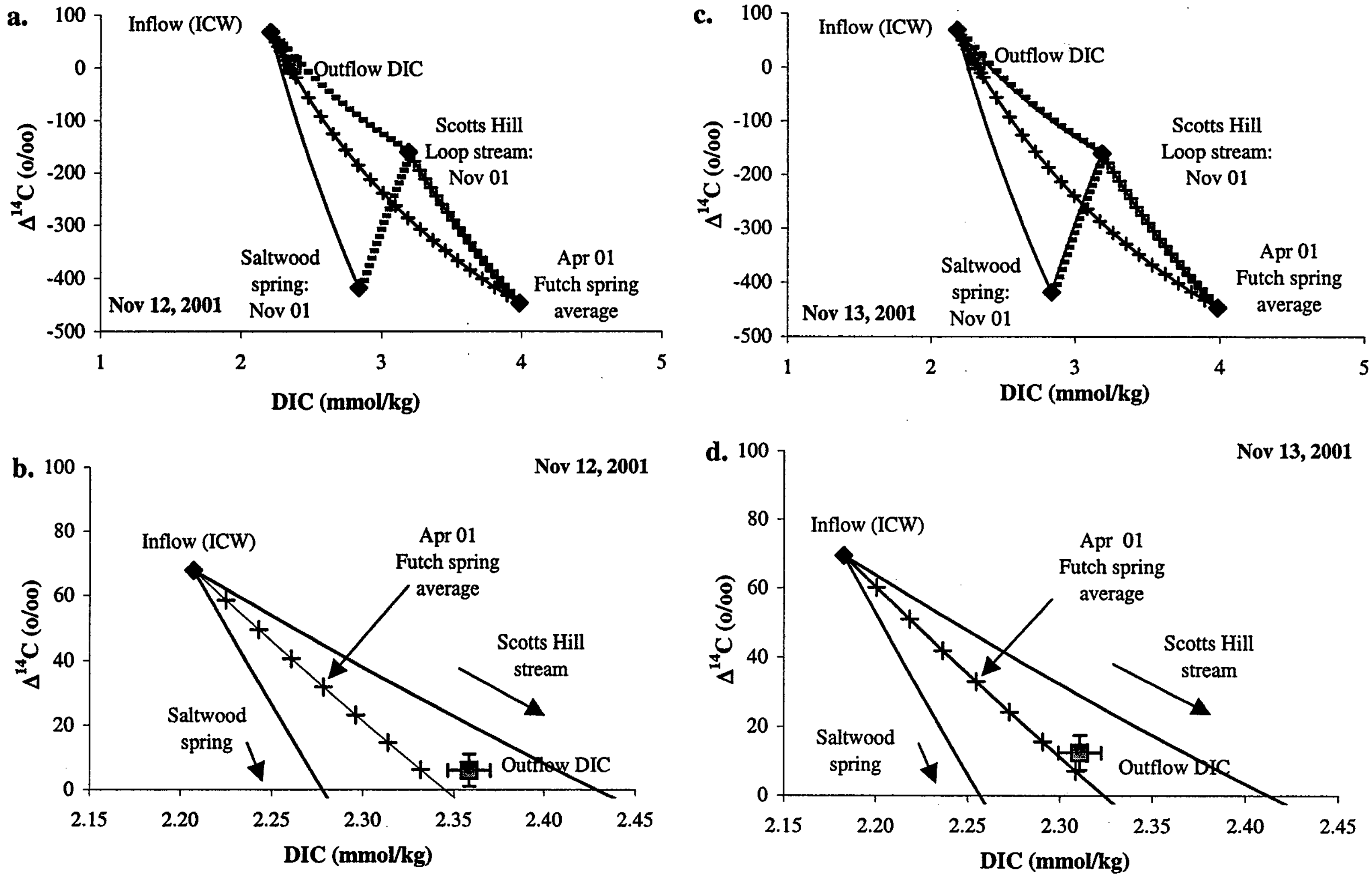


Figure III-29

November 2001 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. Although the Scotts Hill Loop stream is included as a mixing endmember, field observations of very low streamflow during sampling suggest that the outflow is more likely a mix of inflow and spring only. Two mixing triangles are shown: the solid lines represent inflow and stream mixing with the largest observed Futch Creek spring (Saltwood Lane). The '+' symbols represent inflow and stream mixing with an average of April 2001 Futch Creek spring compositions (similar $\Delta^{14}C$ values but higher DIC concentrations than at Saltwood). The low tide outflow DIC and DIC isotope values are also shown (grey square). a) November 15, 2001, with b) close-up of outflow DIC. c) November 16, 2001, with d) close-up of outflow DIC. Analytical precision for graphs a and c are approximated by symbol size, while for b and d, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values.

Figure III-29

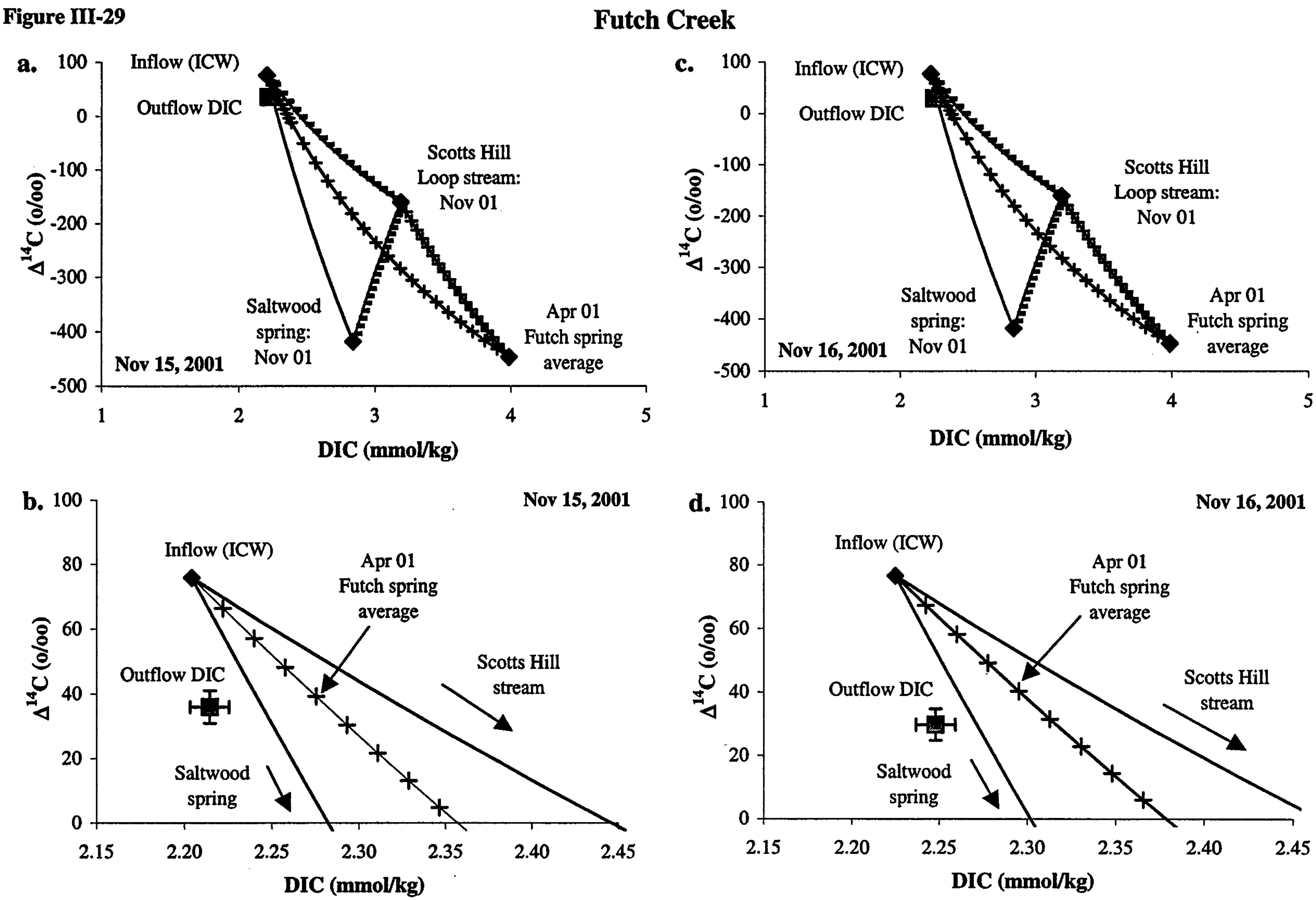


Figure III-30

November 2001 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. Although the Scotts Hill Loop stream is included as a mixing endmember, field observations of very low streamflow during sampling suggest that the outflow is more likely a mix of inflow and spring only. Two mixing triangles are shown: the solid lines represent inflow and stream mixing with the largest observed Futch Creek spring (Saltwood Lane). The '+' symbols represent inflow and stream mixing with an average of April 2001 Futch Creek spring compositions (similar $\Delta^{14}C$ values but higher DIC concentrations than at Saltwood). The low tide outflow DIC and DIC isotope values are also shown (grey square). a) November 18, 2001, with b) close-up of outflow DIC. Analytical precision for graph a is approximated by symbol size, while for b, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values.

Figure III-30

Futch Creek

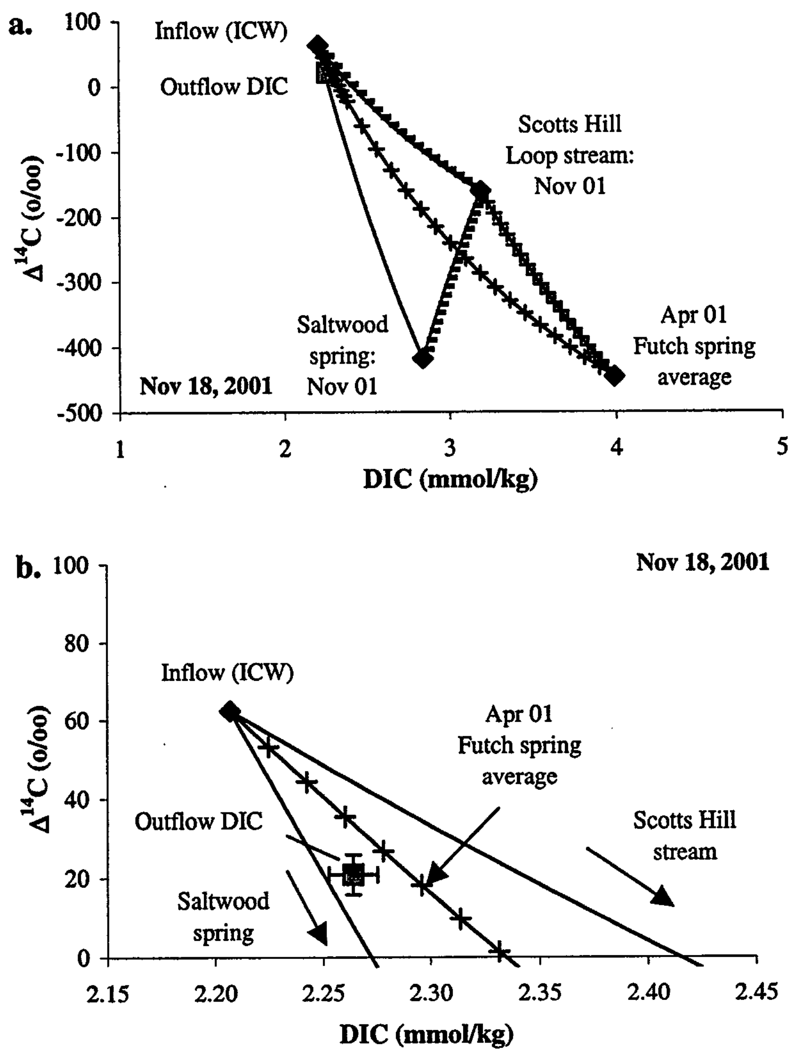


Figure III-31

Closeup of November 12, 2001 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves, with respiration DIC additions. The outflow sample on this day was 7% fresh relative to the inflow sample. The low tide outflow DIC and DIC isotope values are shown (grey square), with error bars representing ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. a) Starting at the 7% fresh point on the inflow-Saltwood spring mixing line, respiration DIC added at $\Delta^{14}C$ = –64‰ does not approach the outflow DIC composition. b) From the 7% fresh point on the inflow-spring average mixing line, additions of DIC at both –64‰ and –21‰ approach the outflow DIC.

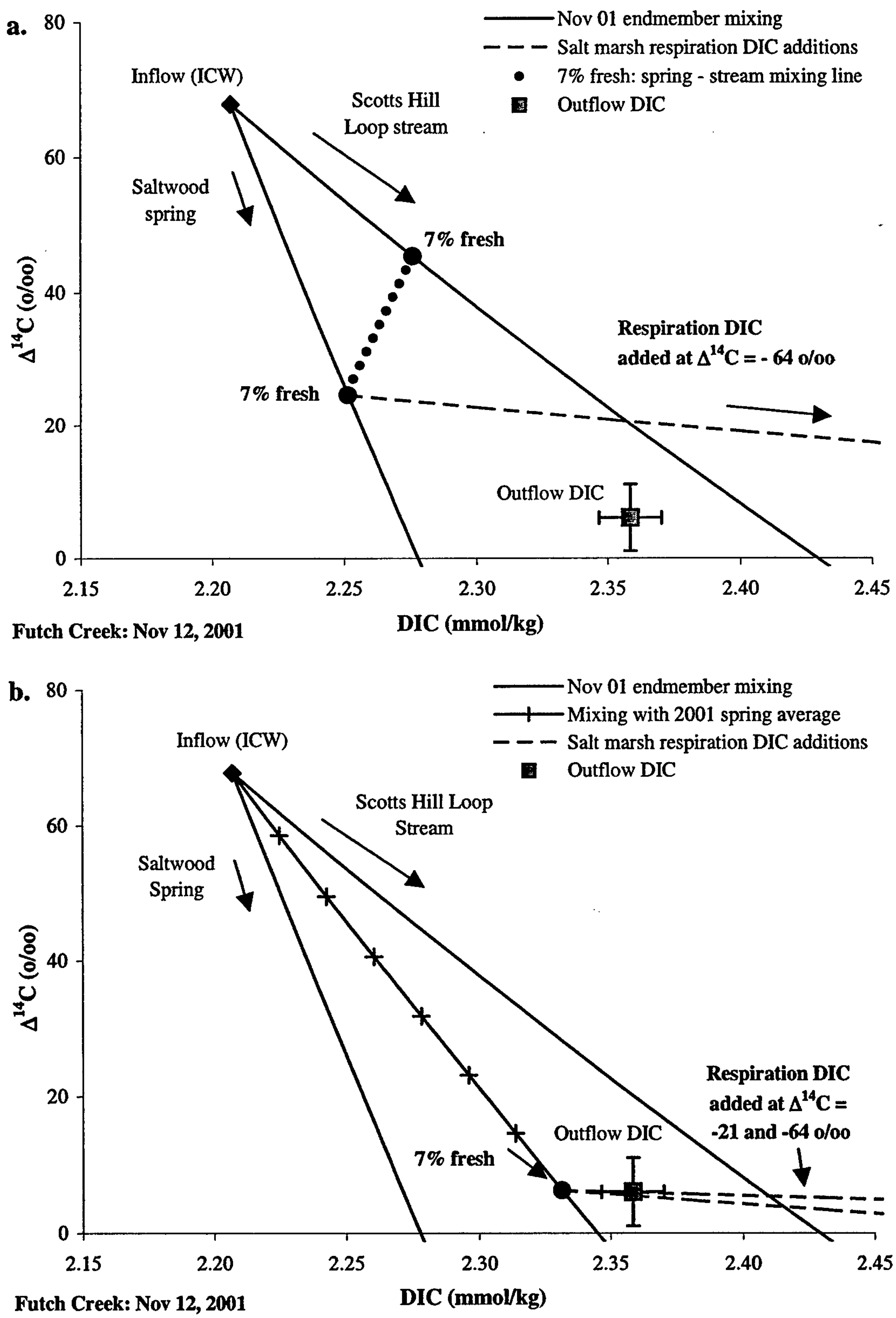


Figure III-31

Figure III-32

Closeup of November 15, 2001 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves, with CO_2 removal due to photosynthesis. The outflow sample on this day was 4% fresh relative to the inflow sample. The '+' symbols represent inflow and stream mixing with an average of April 2001 Futch Creek spring compositions. The 'x' symbols represent inflow mixing with the April 2001 Scotts Hill Loop stream sample (high $\Delta^{14}C$ and low DIC). The low tide outflow DIC and DIC isotope values are shown (grey square), with error bars representing ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. The dotted line represents The outflow DIC is lower than the inflow-spring mixing line, and cannot be matched by a mix between any inflow-spring 4% fresh point and the April 2001 Scotts Hill Loop stream sample. However, from the 4% fresh point on the inflow-spring average mixing line, photosynthetic removal of CO2 allows the inflow-spring mix composition to approach the outflow composition.

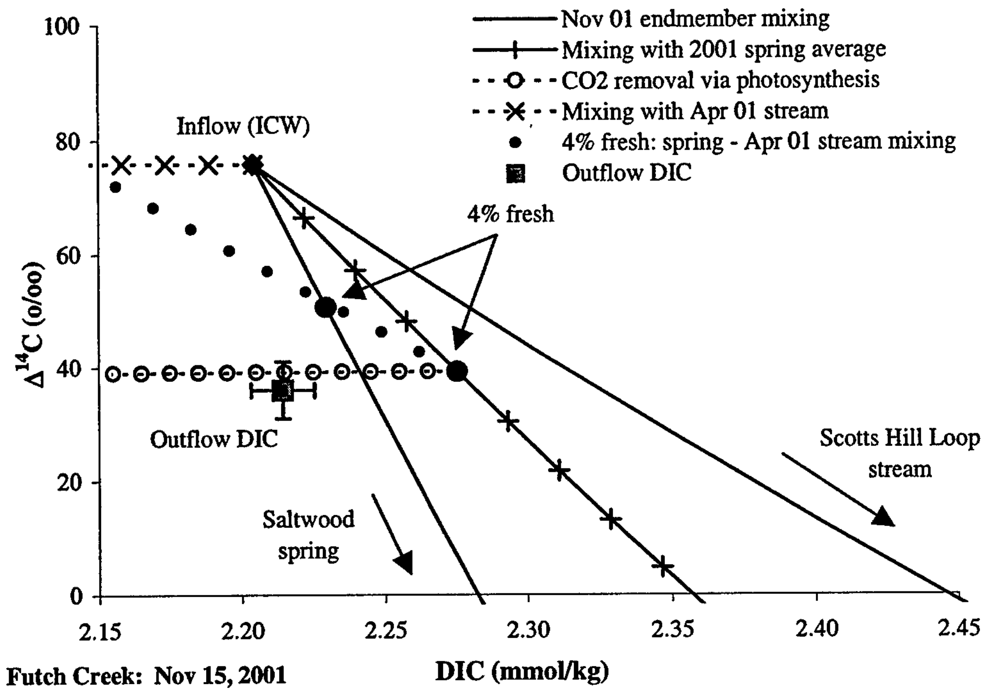


Figure III-32

Figure III-33

April 2002 Pages Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. The low tide outflow DIC and DIC isotope values are also shown (grey square). a) April 14, 2002, with b) close-up of outflow DIC. c) April 16, 2002, with d) close-up of outflow DIC. Analytical precision for graphs a and c are approximated by symbol size, while for b and d, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. Outflow DIC-$\Delta^{14}C$ values are near the inflow-spring mixing line, suggesting that on these sampling days, spring inputs were ~ 100% of the fresh water input to Pages Creek at low tide.

Figure III-33

Pages Creek

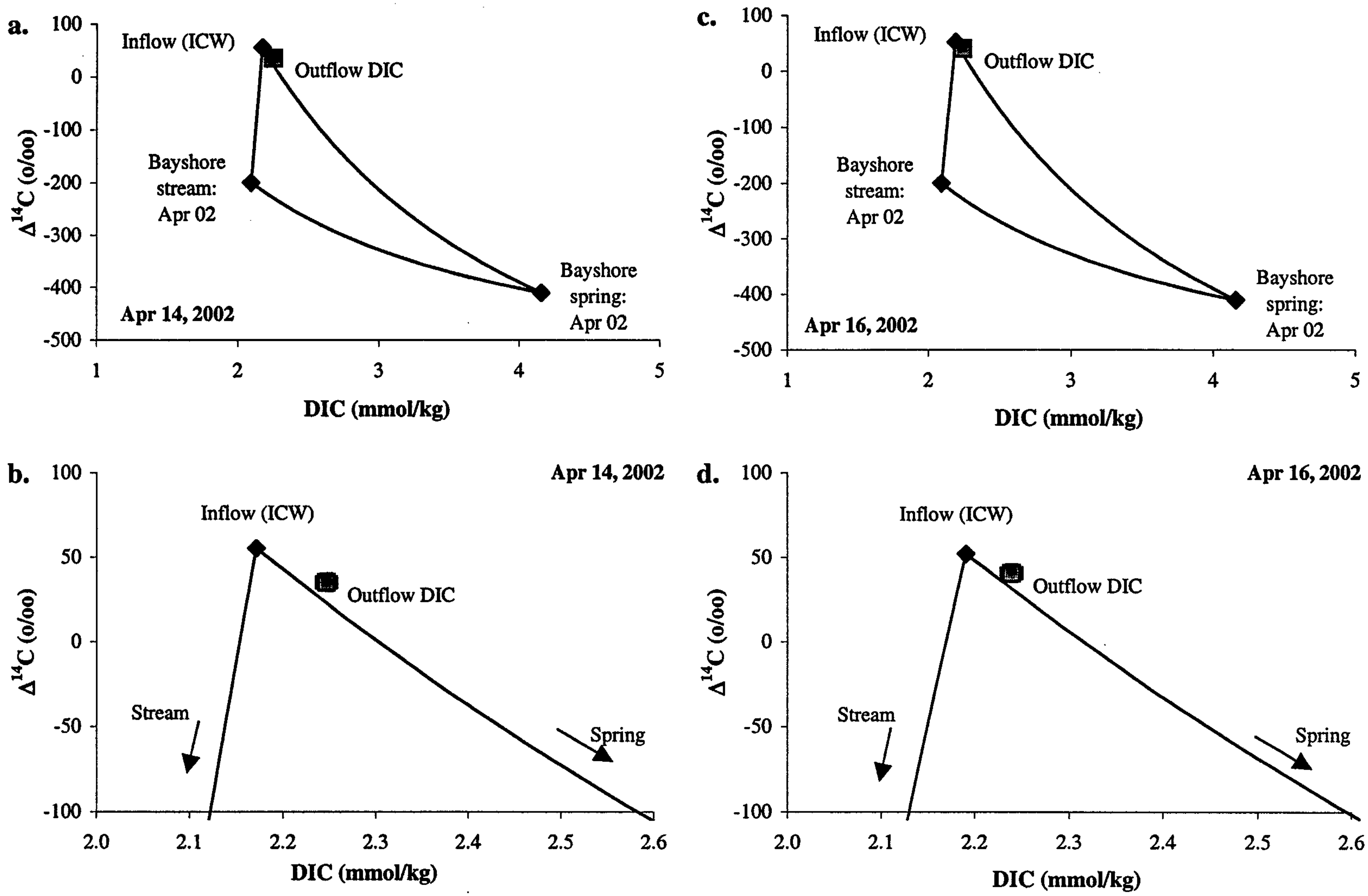
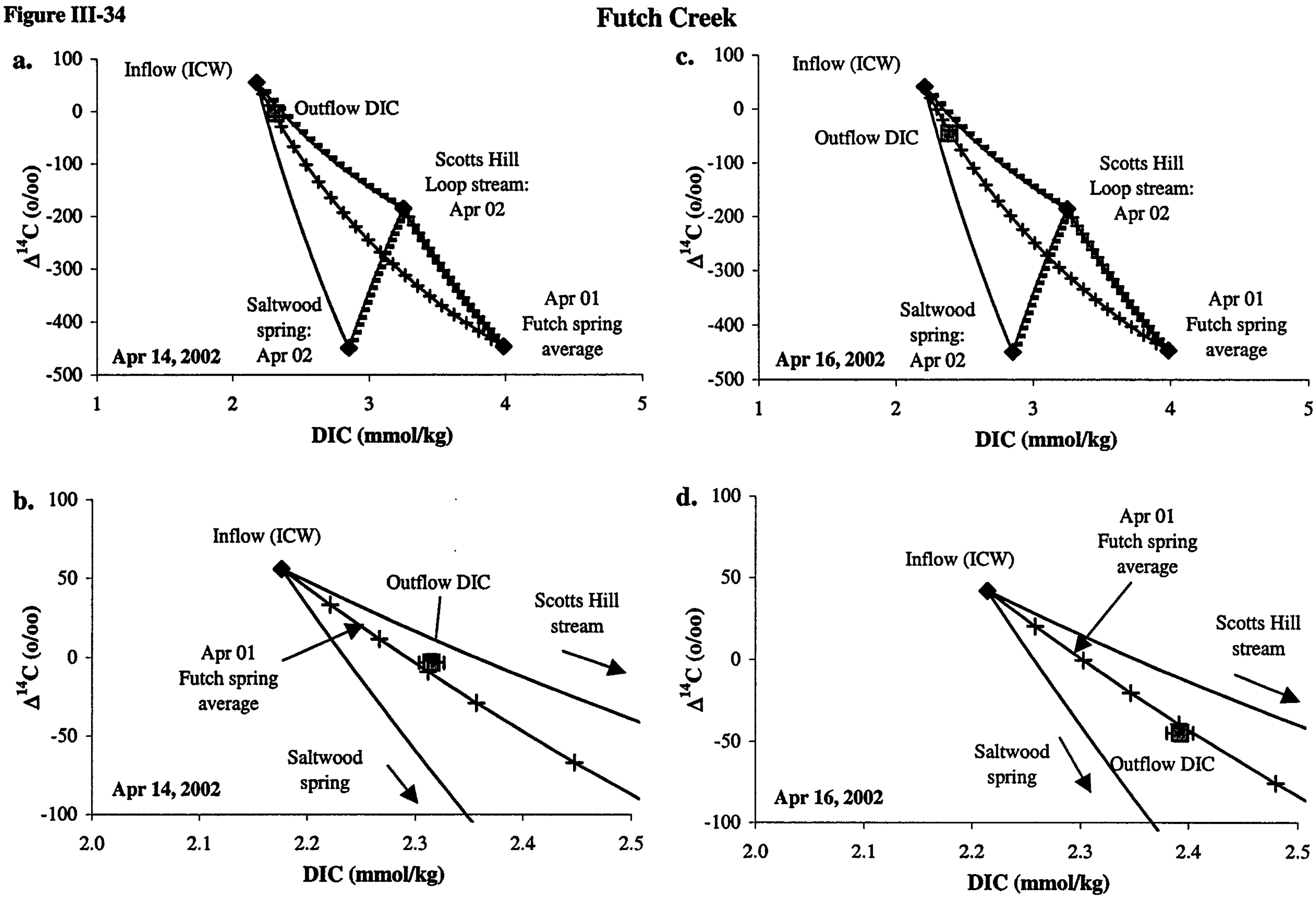


Figure III-34

April 2002 Futch Creek estuary DIC concentration–$\Delta^{14}C$ inflow-stream-spring mixing curves. The '+' symbols represent inflow and stream mixing with an average of April 2001 Futch Creek spring compositions. The low tide outflow DIC and DIC isotope values are also shown (grey square). a) April 14, 2002, with b) close-up of outflow DIC. c) April 16, 2002, with d) close-up of outflow DIC. Analytical precision for graphs a and c are approximated by symbol size, while for b and d, error bars represent ± 5‰ precision error in $\Delta^{14}C$ values and ± 0.5‰ in DIC values. As for November 2001, the Scotts Hill Loop stream is included as a mixing endmember, but field observations of very low streamflow during sampling suggest that the outflow is more likely a mix of inflow and spring only.

Figure III-34



Chapter IV. PROCESSES CONTROLLING ESTUARINE RADIUM AND RADON FLUXES

Abstract

The mass balances of ^{226}Ra, ^{228}Ra, ^{223}Ra, ^{224}Ra, and ^{222}Rn were evaluated within two North Carolina estuaries in April 2001, November 2001, and April 2002. Radiocarbon data, collected concurrently, suggest that fresh water input to Pages and Futch Creeks was primarily controlled by fresh artesian inputs from the confined aquifer. ^{222}Rn activities were very high in the springs, and hourly time series data from the Futch Creek estuary showed a strong inverse correlation between salinity and ^{222}Rn, suggesting that the springs also supported most of the excess ^{222}Rn budget in both estuaries.

Outflow radium and radon activities were almost always higher than inflow activities in the Futch Creek estuary, but export was less consistent in the Pages Creek estuary, particularly during the November 2001 season. In the Futch Creek estuary in April 2001, all of the excess ^{226}Ra in the low tide outflow relative to the inflow at high tide was also derived from the springs. During the other sampling seasons the springs were a significant source of excess ^{226}Ra to both estuaries. In the Futch Creek estuary in April 2001, most of the excess ^{228}Ra was derived from spring inputs, but during other sampling periods (and at all times in the Pages Creek estuary), less than 25% of the observed excess ^{228}Ra was contributed by springs. The maximum spring contribution to the excess ^{223}Ra and ^{224}Ra was generally less than 10%.

A source in addition to springs, streams, and inflow from the ICW is required to support most of the observed excess ^{228}Ra, ^{223}Ra, and ^{224}Ra at Futch, and to support excess ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra at Pages. Residual (non-spring, stream, or inflow) excess radium activity ratios show that the additional input was generally high in ^{228}Ra relative to ^{226}Ra, and was probably also elevated in ^{224}Ra relative to ^{228}Ra. The source of the ^{226}Ra and ^{228}Ra may be seepage through the estuarine bottom sediments, driven by both advection of surficial groundwater and tidal pumping.

1. Introduction

Radium and radon isotopes have been used as geochemical tracers of submarine groundwater discharge (SGD) because they tend to be highly enriched in groundwater relative to seawater, behave conservatively with respect to biological processes, and decay over a range of half-lives that make them useful for measuring mixing of water masses over different time scales (e.g. Bollinger and Moore 1993; Rama and Moore 1996; Cable et al 1996; Krest et al 2000; Corbett et al 1999, 2000). The total discharge of groundwater at the coast can encompass both land-sea fluxes from coastal aquifers and seawater cycling through coastal sediments; recently, several studies have suggested that estimates of SGD based on fluxes of radium and radon are likely to measure both terrestrially-driven groundwater flux and flux due to the recirculation of seawater (e.g. Moore 1999; Burnett et al 2002; Cable et al 2003).

Seawater recirculation often represents a majority of the total discharge of groundwater at the coast, and the chemical constituents transported by recirculating salt water can have a significant impact on the receiving waters. Moore (1999) defined the underground coastal mixing zone where fresh groundwater interacts with circulating seawater as a "subterranean estuary". Recirculation of seawater through bottom sediments can lead to the oxidation and release of buried organic matter and can thereby have a significant impact on coastal nutrient budgets. Additionally, the fluid composition of the water in this "subterranean estuary" is often highly chemically altered relative to either of its original sources, and can be instrumental in altering the redox state in sediments, in dolomitization of coastal limestone, or in calcite dissolution (Moore 1999).

Both radium and radon isotopes are generated in sediments and can subsequently be transported to the water column by a variety of mechanisms. Dissolved species in interstitial waters can be added to the water column by diffusion across the sediment-water interface. Pore water exchange with surface waters can occur by repeated draining and refilling of sediments due to the rise and fall of the tide, or as a result of wind-driven tidal pumping of overlying water through bottom sediments; additionally, diffusive fluxes may be enhanced by bioturbation and bioirrigation of the sediments (e.g. Bollinger and Moore 1993; Webster et al 1994, 1995; Hancock and Murray 1996; Rama and Moore 1996).

In addition to transport to coastal waters from sediment pore waters, radium and radon may also be transported by land-sea fresh groundwater fluxes (from confined or surficial aquifers). These radium inputs may not be easy to distinguish: in tidal marsh zones, seepage from an unconfined coastal aquifer may not be limited to the head of the estuary, but may be more diffuse, channeled farther into the marsh as a result of the development of muddy, low-permeability layers adjacent to the creeks, and of spatial heterogeneities in the hydraulic conductivity of the creek bed (Schultz and Ruppel 2002).

To better interpret the flux estimates derived from isotopes of radium and radon at a given site, it is important to determine the processes that control the budgets of each tracer within the site.

In this study, radon-222, the four isotopes of radium, and salinity in two small North Carolina estuaries were simultaneously measured. DIC and DIC isotopes were also measured (Chapter III). Tracer isotopic ratios and relationships were observed to determine their source(s) (e.g. advective and diffusive fluxes via estuarine bottom sediments, tidal flushing of estuarine sediments, or discharge from springs), as well as their major pathways and systems of transport.

During nearly all sampling periods, the radon budget in both estuaries could be accounted for by discharge from artesian sources. Spring discharge, as reflected in $\Delta^{14}C$, provided nearly all the fresh water to both estuaries during the sampling times (as described in Chapter III). The four isotopes of radium, however, were not linearly related to salinity during our sampling, and were more strongly related to seepage from saline bottom sediments than to fresh groundwater discharge. The radium data also did not show a strong correlation to the tidally-driven draining and refilling of marsh sediment pore water.

1.1 Radium Systematics

The uranium and thorium decay series produce four radium isotopes: ^{226}Ra ($t_{1/2}$ = 1600 yr), ^{228}Ra ($t_{1/2}$ = 5.75 yr), ^{223}Ra ($t_{1/2}$ = 11.4 d), and ^{224}Ra ($t_{1/2}$ = 3.66 d) (Figure 1). Each radium isotope is the decay product of a thorium parent. While thorium isotopes are highly particle-reactive in both fresh and salt water (K_d, the ratio of adsorbed to dissolved species, is ~10^7), radium isotopes adsorb to particles in fresh water (K_d ~10^3 to 10^5) but become mobilized in waters of increasing ionic strength (e.g. Li et al 1977). In a closed system, secular equilibrium between parent and daughter isotopes is reached when the rate of decay of the daughter is balanced by its rate of formation by the parent.

The difference in their sorptive properties can create parent-daughter disequilibrium: upon interaction with seawater, radium is released by sediments preferentially to thorium and is transported away from its parent. As a result, the radium is no longer supported by thorium decay and decreases as a function of its own radioactive decay. The decay of unsupported radium within the water column can be used to estimate the time since removal from the sediments (Rama and Moore 1996; Krest 1999).

Although the rate of desorption of radium from particles in waters of increasing ionic strength does not significantly vary among the four isotopes, sediments that experience frequent inundation by salt water, such as in tidal marshes, can become depleted in the longer-lived radium isotopes relative to the shorter-lived radium isotopes (Webster et al 1995). Webster et al (1994) experimentally determined that when clay-sized sediments (with a higher proportion of surface-bound Ra relative to sand-sized grains) were flushed with a 50% seawater solution, only 1% of the total bound radium was lost to the pore water in a single flushing. For tidal sediments flushed every 12 hours, weeks are required to remove all the surface-bound radium from a single pool (if not replaced by its Th parent). Repeated flushing of sediments on such time scales (long relative to the half-lives of ^{224}Ra and ^{223}Ra but short relative to the half-lives of ^{228}Ra and ^{226}Ra) will result in a smaller decrease in the steady-state concentration of short-lived Ra isotopes in bottom sediments but a depletion of the long-lived isotopes, assuming no additional source of radium to the sediments (Hancock and Murray 1996).

Dissolved or particulate activity ratios of the four radium isotopes can vary as a result of differences in the source material. Although the average crustal abundance of thorium is about three times that of uranium, carbonates tend to be enriched in uranium (which can replace calcium in the limestone mineralogical structure, or can be adsorbed to phosphate minerals) relative to thorium (which is highly particle-reactive and is depleted in seawater). The average relative abundance of uranium to thorium in limestones is ~ 1.3, while in beach sandstones the U:Th ratio is closer to 0.5 (Clark et al 1966; NCRP 1987). Consequently, groundwater from a limestone aquifer can become enriched in the ^{238}U- and ^{235}U-series daughters ^{226}Ra and ^{223}Ra relative to the ^{232}Th-series daughters ^{228}Ra and ^{224}Ra (Figure 1).

1.2 Radon Geochemistry

Radon is highly enriched in groundwater relative to seawater (Cable et al 1996a,b; Corbett et al 1999; Corbett et al 2000; Top et al 2001). ^{222}Rn, with a half-life of 3.8 days, is the radioactive decay product of ^{226}Ra (Figure 1), and is ultimately a decay product of ^{238}U. ^{222}Rn is released to groundwater by production and alpha-recoil from ^{226}Ra within the aquifer material (Rama and Moore 1984; Ellins et al 1990). Because it is a noble gas, therefore not subject to chemical transformation, and has a short half-life, radon is well suited to measuring groundwater discharge to a tidally flushed estuarine system. However, radon is quickly lost to the atmosphere once groundwater is exposed at the land surface. As a result, coastal ^{222}Rn activities may provide only a minimum estimate of the total groundwater flux (Corbett et al 1999; Swarzenski et al 2001).

2. Methods

2.1 Study Site

Pages Creek and Futch Creek are two small, well-mixed tidal creeks located on the Intracoastal Waterway (ICW) northeast of Wilmington, NC (Figure 2). The closest hydraulic connection between this section of the ICW and the Atlantic Ocean are two inlets that cut through the salt marsh barrier islands, Rich Inlet to the north and Mason Inlet to the south (Figure 2).

The Pages Creek estuary, including fringing salt marshes that are inundated at high tide, has an area of about 6.7×10^5 m^2. The Futch Creek estuary is about two-thirds the size of the Pages Creek estuary, with an area of about 4.4×10^5 m^2. The Pages Creek tide range averages about 0.9 meters, while the Futch Creek tide range averages about 0.6 meters. At low tide, the upper creekbeds of both Pages and Futch Creeks are exposed, even during neap tide.

Neither creek receives discharge from a major river; fresh water inputs into each creek consist of several small, intermittent streams (recharged by local precipitation and by groundwater), artesian springs, and diffuse groundwater seepage from the unconfined surficial aquifer. In the Pages Creek estuary, one large spring at the upstream end of the estuary is the most visible and temporally consistent source of confined groundwater, though other smaller and more temporally variable springs have been observed. In the Futch Creek estuary at least three large springs have been observed to last for the duration of the study (Roberts 2002).

North Carolina coastal plain geology consists of interbedded sands, silts, clays, and limestones that dip and thicken eastward (Riggs et al 1995; Winner and Coble 1996; Harris 1996). Pages Creek and Futch Creek are located near the New Hanover County line, in the southern portion of Onslow Bay. In this region, the highly productive Castle Hayne aquifer, composed of shell limestone, dolomitic limestone, sandy limestone, and fine to medium sand underlies the unconsolidated sands and clays of the surficial aquifer (Winner and Coble 1996; Giese et al 1997). The Castle Hayne confining unit is thin, only about 3 meters throughout much of its area, and contains sand lenses that allow some vertical leakage between the Castle Hayne and overlying aquifers (Winner and Coble 1996; Giese et al 1997). The underlying Cretaceous units (the Peedee, Black Creek, and Cape Fear formations) contain interbedded sand, clay, and silt, which become calcareous in the Peedee (Sohl and Owens 1991).

2.2 Sample Collection and Analysis

2.2.1 Sample Collection

Radium, radon, nutrient, and salinity samples were collected in April 2001, November 2001, and April 2002. These periods were chosen to observe both seasonal and tidal effects on these tracers. April 2001 samples were collected about one week prior to the spring tide. November 2001 samples were collected before, during, and after the spring tide. April 2002 samples were collected during neap tide.

Estuary samples were collected in two ways: in high tide/low tide pairs (just prior to full high or full low tide), and in time series: every hour for a full 12-hour tidal cycle. The primary goal of time series sampling was to determine whether sampling twice during a tidal cycle (in high tide/low tide pairs) is sufficient to capture the full range of tidal variations in radium and radon chemistry observed in the estuaries. High tide/low tide pairs were collected from the Pages and Futch Creek estuaries in April 2001, November 2001, and April 2002. Time series data were collected from the Pages Creek estuary in November 2001 and April 2002, and from the Futch Creek estuary in April 2002. All estuary samples were collected inside the mouth of each creek (Figure 2).

To consider how estuarine tracer fluxes might impact the coastal ocean, and to determine how strongly our estuarine radium and radon tracer signatures persist when integrated with signals from other neighboring creeks and salt marshes, samples were collected in high tide/low tide pairs from Rich Inlet and Mason Inlet (Figure 2). High and low tide samples were collected both at the mouth of each inlet (where the inlet connects to Onslow Bay), and also where the inlet connects to the ICW.

Samples were also collected from the primary fresh water inputs to each creek: a large spring discharging directly into the Pages Creek estuary, a spring discharging directly into the Futch Creek estuary, and fresh water streams flowing into each estuary. In addition, groundwater samples from monitoring wells screened in the Castle Hayne and the underlying Peedee aquifers were collected in July 2000 and April 2002. These groundwater samples provide an upper limit on radon activity entering the estuaries via the springs (radon in the springs was likely to be subject to significant gas evasion during discharge) and also provide endmember radium activities for the limestone Castle Hayne and the sandy Peedee aquifers.

2.2.2 Dissolved/Particulate Radium Sampling and Analysis

Although all estuary samples were assumed to contain only dissolved radium, fresh water samples (springs, streams, and groundwater) may have contained both dissolved and particulate radium. Therefore, to assess total radium activities in fresh waters entering the estuaries, some spring and stream samples were filtered to collect particulates for sorbed radium analysis. April 2001 dissolved radium samples were collected, unfiltered, by manual bilge pump into 40-liter cubitainers (for estuary samples) or 20-liter cubitainers (for spring and stream samples). November 2001 dissolved radium samples were collected by manual bilge pump into 20-L cubitainers or by automatic bilge pump for 100+-L samples. All dissolved radium samples were collected unfiltered. Particulate radium samples were collected by automatic bilge pump and filtered through a 1-μm filter. April 2002 dissolved radium samples were collected by manual bilge pump into 20-L cubitainers or by automatic bilge pump for 100+-L samples, and by submersible pump for the groundwater samples. July 2000 groundwater samples were 20-L; April 2002 groundwater samples were 100-L. All April 2002 radium samples were filtered through at least a 1-μm filter; other samples were filtered as noted in Table 1.

Water-filled cubitainers were attached to columns loosely filled with MnO_2-coated acrylic fibers and then were gravity fed through the fibers to collect the radium for analysis. Samples collected by automatic bilge pump (100+-L) were pumped at < 1 L min^{-1} through columns filled with MnO_2 fibers to collect the radium (Moore and Reid 1973).

The Mn-fibers were partially dried in the lab and placed in a delayed coincidence scintillation counter for measurement of ^{223}Ra and ^{224}Ra (Moore and Arnold 1996). The Mn-fibers were then ashed at 820°C for 16 h and the ash was packed in counting vials to uniform density to minimize internal attenuation. The ash was placed in a well-type gamma spectrometer to measure ^{226}Ra and ^{228}Ra activities (Charette et al 2001). Propagated error in the reported radium measurements is <10%.

2.2.3 Radon Sampling and Analysis

All November 2001 radon samples from estuaries, springs, and streams were collected by hand in 4-liter evacuated bottles, which were immediately sealed to prevent gas loss. April 2002 radon samples from the Pages Creek estuary and high tide/low tide pairs from the Futch Creek estuary were collected by hand in 4-liter evacuated bottles, sealed to prevent gas loss. The radon in these samples was extracted in a Lucas cell and counted via alpha-scintillation (Mathieu et al 1988).

April 2002 radon samples from springs and streams were collected by manual bilge pump and filtered through a 1-μm filter (spring samples only) into 250-ml bottles. The Futch Creek estuary time series radon samples were subsampled into 250-ml bottles from a 5-liter Niskin bottle that was manually tripped while submerged in the water column. The radon in these samples was measured on a Durridge RAD7 solid state silicon alpha detector to a precision better than 10%.

April 2002 groundwater radon was sampled by submersible pump through a 1-μm filter into 250-ml bottles. The radon in these samples was measured on a Durridge RAD7 solid state silicon alpha detector to a precision better than 10%. Radon samples collected simultaneously and measured using both analysis techniques correlate well, and are generally within error (Figure 3).

2.2.4 Salinity and Water Depth Analyses

All salinity samples from April 2001, November 2001, and April 2002 were collected in 100-ml glass bottles and analyzed by the hydrographic facility in the Physical Oceanography department at Woods Hole Oceanographic Institution, with a precision better than ± 0.01. Additional November 2001 and April 2002 time series salinity and water depth measurements were made with a handheld YSI 600R Multiprobe System.

3. Results

Salinity, radium, and radon data from the Pages and Futch Creek estuaries are presented, including high tide/low tide, time series, inlet, and spring and stream data. Because it is expected that different processes might control ^{224}Ra and ^{223}Ra versus ^{228}Ra and ^{226}Ra, radium results are divided into short- and long-lived radium results.

3.1 Pages Creek estuary – High tide/Low tide pairs

3.1.1 Salinity

Of the three sampling times (April 2001, November 2001, and April 2002), the high tide (HT) - low tide (LT) salinity differences (ΔSal) in the Pages Creek estuary were smallest in November 2001, averaging -0.2 ppt (Table 2, Figure 4a). The average April 2001 ΔSal was -1.2 ppt, while the average April 2002 ΔSal was -0.9 ppt. High tide salinity values in April 2001 were, on average, more than 1 ppt lower than high tide salinities from later sampling dates (34.8 ppt in April 2001 compared to 36.4 ppt in November 2001 and 36.2 ppt in April 2002).

3.1.2 Short-lived radium isotopes: ^{224}Ra and ^{223}Ra

Overall, Pages Creek estuary high tide-low tide ^{224}Ra (Δ^{224}Ra) and ^{223}Ra (Δ^{223}Ra) generally showed similar patterns. In April 2001 and April 2002, the Pages Creek estuary exported both ^{224}Ra and ^{223}Ra (showing an increase in the activity of each isotope from high to low tide) with one exception (an exception not observed in the Futch Creek estuary) (Figures 4b and c, Table 2).

The November 2001 Δ^{224}Ra and Δ^{223}Ra showed no consistent pattern of export or import. The largest decrease in Δ^{224}Ra occurred at the spring tide on November 16, 2001 (Figure 4b). Δ^{223}Ra in November 2001 was marked by very little change; the differences between high tide ^{223}Ra and low tide ^{223}Ra were mostly within measurement error.

3.1.3 Long-lived radium isotopes: ^{226}Ra and ^{228}Ra

^{226}Ra and ^{228}Ra were also exported on three of the four sampling days in April 2001 and April 2002 (although the one day when this did not occur does not correspond to that of the short-lived isotopes). As with the short-lived isotopes, the long-lived isotopes did not show consistent export from the Pages Creek estuary in November 2001 (Table 2, Figures 5a-c). In general, Δ^{228}Ra and Δ^{226}Ra tended to track each other well, with the most notable exception on the day of full spring tide (November 16th): Δ^{226}Ra was exported, but Δ^{228}Ra showed almost no change from high to low tide. Overall, high tide ^{228}Ra values were much lower in April 2002 (average 14.2 ± 2.6 dpm 100L^{-1}) than during April 2001 and November 2001 (26.6 ± 2.7 dpm 100L^{-1} and 28.4 ± 4.7 dpm 100L^{-1}, respectively).

3.1.4 Radon-222

^{222}Rn generally increased from high to low tide in the Pages Creek estuary, although there were exceptions during both November 2001 and April 2002 (Table 2). There is no consistent pattern in Δ^{222}Rn relative to tidal stage during November 2001: Δ^{222}Rn fluctuates between positive and negative while the tide is increasing, then is highest two days after the spring tide (Figures 6a-b). The average November 2001 high tide ^{222}Rn activity was 5.1 ± 4.7 dpm L^{-1}, compared to 2.1 ± 1.7 dpm L^{-1} in April 2002. November 2001 average low tide ^{222}Rn was 11.3 ± 10.8 dpm L^{-1}, compared to 5.1 ± 2.5 in April 2002.

3.2 Futch Creek estuary – High tide/Low tide pairs

3.2.1 Salinity

HT-LT ΔSal in the Futch Creek estuary was always larger than in the Pages Creek estuary. As in Pages Creek, the smallest observed salinity differences between high and low tide occurred in November 2001, averaging about -1.7 ppt (Table 3, Figure 7a). The ΔSal averaged about -10 ppt in April 2001, and about -3.9 ppt in April 2002. Unlike the April 2001 high tide salinity in our Pages Creek samples, Futch Creek estuary high tide sample salinity was not highly variable among the three sampling periods, averaging 36 ± 0.42 ppt.

3.2.2 Short-lived radium isotopes: ^{224}Ra and ^{223}Ra

^{224}Ra and ^{223}Ra increased from high tide to low tide at all times in the Futch Creek estuary (with the exception of one sampling day in April 2001 where the Δ^{224}Ra was nearly zero) (Table 3, Figures 7b-c). Inflowing ^{224}Ra at high tide was considerably lower on average in November 2001 (14.7 ± 3.2 dpm $100L^{-1}$) than in April 2001 (25.7 ± 3.3dpm $100L^{-1}$) or April 2002 (26.7 ± 3.6 dpm $100L^{-1}$).

3.2.3 Long-lived radium isotopes: ^{226}Ra and ^{228}Ra

^{226}Ra increased from high to low tide at all times in the Futch Creek estuary (Table 3, Figures 8a-b). The high tide ^{226}Ra activities were elevated in November 2001 (18.0 ± 1.3 dpm $100L^{-1}$) relative to April 2002 (11.7 ± 0.4 dpm $100L^{-1}$), similar to a pattern observed in the Pages Creek estuary, though the April 2001 high tide values were different between the two estuaries. Low tide ^{226}Ra was much less variable from season to season, averaging 19.7 ± 2.9 dpm $100L^{-1}$ for all three seasons.

^{228}Ra generally increased from high to low tide in the Futch Creek estuary, with two exceptions, one in April 2001 and one in November 2001 (Table 3, Figure 8c). On these days, the high tide ^{228}Ra activity was unusually high, at 28.7 dpm/100L and 33.3 dpm $100L^{-1}$, respectively. Average high tide ^{228}Ra in November 2001 was 25.1 ± 4.7 dpm $100L^{-1}$, and 16.1 ± 1.7 dpm $100L^{-1}$ in April 2002. As with ^{226}Ra, low tide ^{228}Ra activities tended to be less variable than high tide ^{228}Ra activities, averaging 26.8 ± 4.3 dpm $100L^{-1}$ for all seasons.

3.2.4 Radon-222

^{222}Rn always increased from high to low tide in the Futch Creek estuary, and showed generally higher $\Delta^{222}Rn$ in the outflow than was observed in the Pages Creek estuary (Table 3, Figures 9a-b). Average inflowing ^{222}Rn values were highly consistent between November 2001 and April 2002 (3.5 ± 0.6 dpm L^{-1} and 3.2 ± 1.2 dpm L^{-1}, respectively). Low tide ^{222}Rn was, on average, higher in November 2001 (23.7 ± 7.2 dpm L^{-1}) than in April 2002 (15.7 ± 10.1 dpm L^{-1}). Though always positive, $\Delta^{222}Rn$ does not show any clear relationship to tidal stage in November 2001.

3.3 Pages Creek and Futch Creek estuary Time Series

3.3.1 Salinity

The salinity profile during the Pages Creek estuary November 2001 time series shows a fairly constant salinity (at ~36.41 ppt) for a few hours before and after high tide (Figure 10a). Just before low tide, the salinity dips to 36.30 ppt, then jumps up again to 36.46 ppt before falling to a low of 36.07 ppt at low tide. After low tide, the salinity rises quickly to 36.47 ppt, then returns again to ~ 36.41 ppt (Table 4). Water depth data fell into a sinusoidal curve, and did not show any pulses that correlate to the high salinities just before and just after low tide.

The April 2002 Pages Creek and Futch Creek time series did not show the same fluctuations in salinity around low tide (Table 4, Figures 10b and 10c). In Pages Creek, salinity varied between 36.16 ppt at high tide and 35.16 ppt at low tide. In Futch Creek, the salinity variation was larger (35.99 ppt at high tide and 30.84 ppt at low tide).

3.3.2 Short-lived radium isotopes: ^{224}Ra and ^{223}Ra

^{224}Ra from the November 2001 time series at Pages Creek and the April 2002 time series at Futch Creek showed little relationship to tide stage (Table 4, Figure 10a and 10c). In both of these series, the highest ^{224}Ra value was observed well before full low tide; in November the highest ^{224}Ra corresponded to the brief high salinity peak before low tide. A second high ^{224}Ra value was observed just at the second high tide (18:00-19:00 hrs). In the April 2002 Pages Creek time series, the lowest ^{224}Ra was observed just after high tide, with a peak in ^{224}Ra occurring at low tide, followed by more scattered values on the subsequent rising tide (Figure 10b).

^{223}Ra tended to be highest at low tide in all three time series (although a second maximum was observed in November 2001 at high tide, corresponding to the second peak in ^{224}Ra) (Figures 11a-c). High tide ^{223}Ra activities tended to be low, but were not necessarily the lowest within any series.

3.3.3 Long-lived radium isotopes: ^{228}Ra and ^{226}Ra

November 2001 time series ^{226}Ra and ^{228}Ra water column activities did not correlate well with salinity changes across the tidal cycle (Table 4, Figures 12a and 13a). However, most of the ^{226}Ra and ^{228}Ra values from this sampling period fell within the 10% error.

Pages Creek ^{226}Ra during the April 2002 time series, in contrast, correlated well with the tidal cycle, with the highest ^{226}Ra just after low tide, and the lowest ^{226}Ra just before high tide (Figure 12b). The pattern of ^{228}Ra activities was similar to that of ^{226}Ra, with one high ^{228}Ra value occurring on the falling tide at mid-tide (Figure 13b).

Futch Creek ^{226}Ra and ^{228}Ra in April 2002 showed the strongest correlation between salinity and long-lived radium isotopes, with the highest ^{226}Ra and ^{228}Ra activities observed just at low tide, and the lowest ^{226}Ra and ^{228}Ra activities observed just at high tide (Figures 12c and 13c).

3.3.4 ^{222}Rn

^{222}Rn water column activities from the Pages Creek time series in both November 2001 and April 2002 showed a strong correlation with the tidal cycle and with salinity (Table 4, Figures 14a-b). In both time series, the lowest ^{222}Rn activities were observed near full high tide, and the highest activities at or just after full low tide.

3.4 Rich Inlet and Mason Inlet – High tide/Low tide pairs

3.4.1 Salinity

April 2002 high tide/low tide inlet measurements were taken at the mouths of each inlet, where they connected to the Atlantic Ocean, and also where they intersected the Intracoastal Waterway (ICW) (Figure 2). Salinity values, however, were not highly variable as a function of sampling location within the inlet, or from inlet to inlet (Table 5, Figure 15a). ΔSal was always small and decreased from high tide to low tide, averaging -

0.12 ppt in Rich Inlet and -0.09 ppt in Mason Inlet. The single November 2001 inlet measurement, made at low tide, showed a higher salinity (36.5 ppt) than was observed at high or low tide in the inlets in April 2002.

3.4.2 Short-lived radium isotopes: ^{224}Ra and ^{223}Ra

In April 2002, the ^{224}Ra always increased in the inlets from high to low tide, and were similar from inlet to inlet (Table 5, Figure 15b). Average high tide ^{224}Ra was 12.3 ± 3.5 dpm $100L^{-1}$ at Rich Inlet and 9.4 ± 1.9 dpm $100L^{-1}$ at Mason Inlet; average low tide ^{224}Ra values were 24.1 ± 2.3 dpm $100L^{-1}$ and 26.9 ± 3.7 dpm $100L^{-1}$, respectively. While the Δ^{224}Ra in Mason Inlet was higher at the ICW than at the mouth, this was not true at Rich Inlet. However, the inflow ^{224}Ra in Rich Inlet at the ICW was elevated relative to the inflow ^{224}Ra in Rich Inlet at the mouth. ^{223}Ra showed similar trends to ^{224}Ra (Figure 15c). The November 2001 low tide ^{224}Ra and ^{223}Ra values in Rich Inlet were similar to the April 2002 low tide values.

3.4.3 Long-lived radium isotopes: ^{228}Ra and ^{226}Ra

In April 2002, ^{226}Ra and ^{228}Ra generally increased from high to low tide in the inlets, though the high tide-low tide ^{226}Ra differences in Rich Inlet fell mostly within a 10% measurement error (Table 5, Figures 16a-c). Δ^{228}Ra was also small in Rich Inlet, but the Δ^{228}Ra in Mason Inlet was larger than the estimated error. The lone November 2001 Rich Inlet low tide sample had considerably higher ^{226}Ra and ^{228}Ra activities than any of the April 2002 samples (Figure 17).

3.5 Fresh water: springs, streams, and groundwater

The Pages and Futch Creek springs show fairly consistent values from season to season, and are similar from site to site (Table 6). The springs were elevated in ^{222}Rn relative to the streams, and tended to be enriched in ^{226}Ra relative to ^{228}Ra (Figure 18). The exception to this is the November 2001 Pages Creek stream (Table 6, not plotted in Figure 18), which had a salinity of about 30 ppt. This sample was collected during the spring tide, and the streambed had been inundated with inflowing ICW water but had not yet been flushed out by fresh water. This stream sample is therefore not representative of zero-salinity endmember stream inputs to the estuary.

Particulate ^{226}Ra and ^{228}Ra activities were measured in November 2001 from the Pages Creek spring (salinity ~ 0.2 ppt) and the Futch Creek Scotts Hill Loop stream (salinity ~ 10 ppt). Particulate ^{226}Ra activities in both spring and stream were small, only about 3% and 1% of their dissolved ^{226}Ra activities, respectively (Table 6). Both spring and stream had negligible particulate ^{228}Ra activities.

Most groundwater samples had salinity less than 1 ppt (Table 7). Both Castle Hayne and Peedee groundwater tended to be low in ^{228}Ra relative to ^{226}Ra, though both ^{226}Ra and ^{228}Ra activities were generally higher in July 2000 than in April 2002 (Table 7, Figure 19).

^{222}Rn activities in groundwater were up to three orders of magnitude higher than activities in the estuaries, with the highest radon activities found in the Castle Hayne groundwater (3000 – 9000 dpm L^{-1}) (Table 7). Castle Hayne groundwater ^{222}Rn was also about an order of magnitude higher than the radon activities in the springs, which ranged from 184 – 600 dpm L^{-1}.

4. Discussion

A primary goal of this study is to determine whether the Pages and Futch Creek estuaries export radium and radon, and furthermore to determine the principal sources of these isotopes both to the estuaries and ultimately to the coastal ocean. An additional goal is to determine whether the chief inputs of each isotope are similar from estuary to estuary and whether they can be correlated to seasonal and temporal cycles (e.g. monthly tidal stage and daily tidal stage).

The mass balances of the four radium isotopes and of ^{222}Rn were evaluated within each estuary, and the potential sources of these isotopes to each estuary were considered. These potential sources included inflowing water from the ICW, stream inputs, discharge from springs originating from the confined Castle Hayne aquifer, discharge from the surficial aquifer, and regeneration within both the estuarine bottom sediments and within tidal marsh sediments.

Of these potential inputs, high tide inflow, spring, and stream radium and radon activities were measured directly. Surficial aquifer radium and radon activities were not directly measured and this input source cannot be easily distinguished from several other potential inputs with the existing data set. Both the sediment-derived fluxes and the stream inputs are likely to contain surficial aquifer discharge, but neither can be considered as representative of surficial aquifer endmember radium or radon activities. Fluxes from the estuarine bottom sediments must have included, in the case of the shorter-lived isotopes, regeneration from Th parents as well as aquifer discharge. Additionally, streams entering the estuaries are groundwater-fed, and the presence of springs in some streambeds suggests that these streams may contain inputs from both surficial and confined groundwater.

4.1 Expectations/predictions from previous radium- and radon-based groundwater studies

Previous work at North Inlet, South Carolina, a site with similar geologic terrain to southeastern North Carolina, has observed higher outflow activities than inflow activities for all four radium isotopes (Bollinger and Moore 1993, Rama and Moore 1996, Krest et al 2000). Additionally, several studies in coastal South Carolina determined that groundwater inputs (defined as the upward advection of pore water, driven by an inland hydraulic head) were required to explain not only the excess ^{226}Ra and ^{228}Ra (defined as the activity of each isotope in the low tide outflow after high tide inflow activity has been subtracted) in the outflow from the North Inlet salt marsh, but also, to a large extent, the excess ^{224}Ra and ^{223}Ra activities (Rama and Moore 1996; Crotwell 1998; Krest et al 2000).

Based on these South Carolina studies, groundwater discharge to the Pages and Futch Creek estuaries, rather than regeneration within the sediments, was predicted to be a principal source of observed excess ^{226}Ra, as well as ^{228}Ra and ^{222}Rn. The decay constant for ^{226}Ra is small ($\lambda = 4.3 \times 10^{-4}$ yr^{-1}) and the resulting small rate of regeneration within the estuarine or tidal sediments was not likely to be a significant source of excess ^{226}Ra to the estuaries during the time scale of interest. For ^{228}Ra, the decay constant is larger ($\lambda = 1.2 \times 10^{-1}$ yr^{-1}), possibly resulting in some regeneration within the sediments on the time scales in this study. However, the rate of supply of this sediment ^{228}Ra by diffusion across the sediment-water interface is likely to be much smaller than the rate of supply via groundwater-driven advection, so that sediment regeneration is not likely to be a significant source term.

In the case of ^{222}Rn, the decay constant is much larger ($\lambda = 6.7 \times 10^{1}$ yr^{-1}), suggesting that the sediments could be a significant source of ^{222}Rn to the estuaries during the time scales of interest. However, because ^{222}Rn activities tend to be highly enriched in groundwater from a uranium-enriched limestone aquifer, and have been found to be as much as three orders of magnitude greater than seawater ^{222}Rn activities, the springs were likely to be a dominant source of ^{222}Rn (Swarzenski et al 2001).

The radiocarbon data has shown that during the three sampling seasons considered in this study, the fresh water budgets of these estuaries were generally controlled by springs originating from a confined aquifer, rather than by stream inputs or by fresh discharge from the surficial aquifer (Chapter III). We therefore predicted that the springs would be the primary source of the long-lived radium isotopes ^{226}Ra and ^{228}Ra (dissolved and/or particulate), as well as ^{222}Rn, to the estuaries.

The ^{223}Ra and ^{224}Ra estuarine budgets, however, were expected to be controlled by some combination of groundwater discharge and regeneration, desorption, and decay within both bottom and tidal sediments. The decay constants for ^{224}Ra and ^{223}Ra ($\lambda = 6.8 \times 10^{1}$ yr^{-1} and $\lambda = 2.3 \times 10^{1}$ yr^{-1}, respectively) are large enough that the sediments could provide a significant source of these isotopes to the estuaries.

4.2 Estimating excess radium isotopes and ^{222}Rn derived from springs

While the Futch Creek estuary showed a low tide excess (low tide activity – high tide inflow activity) of the four isotopes of radium and ^{222}Rn relative to high tide inflow during all three sampling seasons, the Pages Creek estuary exported radium and radon during both April sampling seasons but not always during the November season.

To estimate the spring contribution to the excess of each radium isotope and to the excess of ^{222}Rn within each estuary, the activity of each of the tracers in the spring discharge is multiplied by the percent fresh (and by the percent of the fresh contributed by springs) in the outflow:

$$\% \text{ spring contribution} = \frac{\% \text{ fresh} * \% \text{ spring} * \text{spring activity}}{\text{excess tracer}} \tag{1}$$

The radiocarbon data suggest that spring inputs were 100% of the total fresh water input to each estuary during April 2001 and April 2002, and to the Futch Creek estuary during November 2001, and that spring inputs were 10-50% of the total fresh water input to the Pages Creek estuary during November 2001 (Chapter III). Therefore, % spring = 1 for all times except at Pages Creek in November 2001. To estimate a maximum spring contribution, spring inputs to the Pages Creek estuary in November 2001 are assumed to be 50% of the total fresh water input. Results from this calculation are shown in Table 8. A maximum and minimum range of the percent spring contribution is shown, where maximum spring contribution uses the highest observed spring radium or radon activity (April 2001 McMillan spring for radium and November 2001 Saltwood spring for ^{222}Rn), and minimum spring contribution uses the lowest observed spring radium or radon activity (April 2001 Saltwood spring for radium and April 2002 Bayshore spring for ^{222}Rn) (Table 6).

4.3 ^{222}Rn

4.3.1 Excess ^{222}Rn primarily supported by springs

The springs were an important source of ^{222}Rn to both estuaries, as predicted, and were the dominant source to the Futch Creek estuary during most sampling days (Table 8). Using the maximum observed ^{222}Rn in the springs (November 2001 Saltwood spring), the springs contributed more than enough ^{222}Rn to support the observed excess ^{222}Rn in the outflow during nearly all sampling periods. In April 2002, the maximum ^{222}Rn spring contribution is several times the observed excess; however, it should be noted that the ^{222}Rn in the springs was considerably lower in April 2002 than in November 2001, and the minimum percent contribution may be closer to the true spring input during this period (Table 6). It is also possible that ^{222}Rn evasion to the atmosphere accounts for the greater calculated spring contribution relative to observed excess ^{222}Rn (atmospheric fluxes of ^{222}Rn are evaluated in Chapter V). However, even using the maximum observed spring ^{222}Rn activity to estimate spring contributions, the springs did not provide all of the ^{222}Rn to the Pages Creek estuary during any sampling day in November 2001, or even to the Futch Creek estuary on the day of the highest spring tide (November 16, 2001).

4.3.2 Time series ^{222}Rn correlated with salinity

^{222}Rn water column activities from the Pages Creek estuary time series in November 2001 were strongly correlated with salinity as well as with the daily tidal cycle, although the relationship was not perfectly linear (Figure 20a). The Futch Creek estuary April 2002 time series showed an even more linear mixing relationship between salinity and ^{222}Rn (Figure 20b). When this April 2002 time series is extrapolated back to the zero-salinity point, it is apparent that the ^{222}Rn activities in most of the springs were enough to support all the observed excess ^{222}Rn in both estuaries (Figure 21).

It is also worth noting that the excess ^{222}Rn was always larger in the Futch Creek estuary than in the Pages Creek estuary, and, furthermore, that while radon was always higher in the outflow from Futch than in the inflow, this was not always true in Pages. Of the two times when radon appeared to be lower in the outflow at Pages, one (November 12, 2001) showed an unusually elevated inflow ^{222}Rn activity, and the other (April 13, 2002) showed a small HT-LT difference that was within error measurements. The overall stronger outflow ^{222}Rn signal in Futch is likely to be the result of the stronger spring influence in that estuary, further evidenced by the consistently larger (spring-dominated) salinity changes from high to low tide at Futch relative to Pages.

Although the time series ^{222}Rn activities fell close to a simple inflow-spring salinity mixing line, the Pages Creek estuary November 2001 time series ^{222}Rn showed deviations from simple mixing. These ^{222}Rn samples were collected only on the falling tide, and mid-tide ^{222}Rn activities fell above the mixing line.

Hourly salinity samples collected at Pages Creek in November 2001 showed a feature that did not appear in the hourly salinity data at Pages in April 2002: a peak in salinity two hours prior to full low tide that does not correspond to tidal changes in water depth (Figure 22a). However, increased April 2002 sampling resolution as provided by the YSI Multiprobe (measuring salinity every two minutes) demonstrated that this salinity fluctuation was a regular feature in the Pages Creek estuary, occurring about two hours prior to low tide on every tidal cycle (Figure 22b). This feature may represent drainage of marsh pore waters, possibly having salinity greater than seawater as a result of evapotranspiration within the marsh.

4.4 Long-lived radium isotopes: ^{226}Ra and ^{228}Ra

4.4.1 Excess ^{226}Ra: substantially supported by springs

Spring ^{226}Ra activities were only sufficient to support all of the low tide excess ^{226}Ra (when there was excess) in the April 2001 Futch Creek samples and in two of the November 2001 Futch Creek samples (Table 8). On other sampling days in November 2001 and in April 2002, the springs contributed a substantial percentage, but not all, of the excess ^{226}Ra to the Futch Creek estuary. In the Pages Creek estuary, April 2001 and November 2001 spring contributions to the ^{226}Ra budget were 1-20% of the excess ^{226}Ra in the water column, while April 2002 spring input corresponded to up to 50% of the total excess ^{226}Ra.

4.4.2 Excess ^{228}Rn: minimally supported by springs

For ^{228}Ra, spring inputs were never sufficient to supply the all of the observed excess ^{228}Ra in the outflow of either estuary (Table 8). Although the Futch Creek estuary April 2001 ^{228}Ra was more spring-influenced (spring contributions of 53-92% of the excess ^{228}Ra), during all other times, ^{228}Ra from the springs was responsible for less than 25% of the total excess ^{228}Ra observed in the outflow from either estuary.

4.4.3 $\Delta^{226}Ra$ and $\Delta^{228}Ra$ normalized to high tide/low tide salinity difference

Overall, in the Futch Creek estuary, spring contributions to the ^{226}Ra and ^{228}Ra budgets were strongest in April 2001 (corresponding to the largest ΔSal and the smallest Δ^{226}Ra), and weakest in April 2002 (which had intermediate ΔSal and the largest Δ^{226}Ra). When the Futch Creek estuary Δ^{226}Ra and Δ^{228}Ra values are normalized to their high tide-low tide salinity differences (ΔSal), the relative heights of the bars give an indication of the relative importance of outflow ^{226}Ra and ^{228}Ra additions that did not originate from the springs (Figure 23). In November 2001, the Δ^{226}Ra/ΔSal and Δ^{228}Ra/ΔSal show the highest relative contribution of both ^{226}Ra and ^{228}Ra from a non-fresh (therefore non-spring) source occurring on November 16, at the full spring tide. This suggests that the source(s) of the non-spring-derived excess ^{226}Ra and ^{228}Ra could be influenced by the tidal cycle, possibly resulting from enhanced flow due to tidal pumping through bottom sediments.

Although the change in radium relative to salinity differences in the Futch Creek estuary is largest in November 2001, this is largely due to the small high/low tide salinity differences during that season relative to the April sampling seasons. The absolute $\Delta^{226}Ra$ and $\Delta^{228}Ra$ values are higher in April 2002, and smaller in April 2001 (Figure 8, Table 8). In November 2001, Castle Hayne and surficial aquifer well head levels 15 km north of Futch Creek were at an 18-year low (Figure 24). The prolonged drought may have led to reduced supply of fresh water from the surficial aquifer, and therefore increased overall salinity in the marsh outflow. The drought continued through April 2002, but localized precipitation occurred during that sampling period, and there is some evidence that local precipitation events may have a greater effect on the salinity budget of these estuaries than seasonal changes in surface water flow (Gramling et al 2003).

In the Pages Creek estuary, spring contributions were generally responsible for only a small fraction of the excess ^{226}Ra and ^{228}Ra, with the highest relative spring ^{226}Ra signal (14-54%) occurring in April 2002 (which had the smallest average $\Delta^{226}Ra$ in Pages). Normalizing the Pages Creek estuary $\Delta^{226}Ra$ and $\Delta^{228}Ra$ values to their salinity differences demonstrates that again, November 2001 ^{226}Ra and ^{228}Ra additions from a non-spring, non-fresh source were highest relative to the excess ^{226}Ra and ^{228}Ra (Figures 25a-b). Additionally, as in the Futch Creek estuary, the largest relative non-spring ^{226}Ra additions occurred during the full spring tide on November 16, 2001 (although, unlike in the Futch Creek estuary, the absolute $\Delta^{226}Ra$ was also high on this day) (Figure 5). However, ^{228}Ra showed almost no change from high to low tide during the full spring tide on November 16, 2001, unlike ^{228}Ra in the Futch Creek estuary (Figure 5).

An additional point to note is that in both the Pages and the Futch Creek estuaries, negative high/low tide differences in ^{226}Ra and ^{228}Ra occurred on days with inflow ^{226}Ra

and ^{228}Ra values that were elevated relative to the average inflow values. This high tide variability is on the same scale as the overall high/low tide radium differences (whereas the low tide ^{226}Ra and ^{228}Ra values tend to be less variable). Inflowing waters to both estuaries may have been elevated in radium relative to ocean radium activities, possibly as a result of water cycling through the creeks (with a residence time of ~0.5 day) and re-entering the ICW at low tide. This effect is likely to be stronger in the Pages Creek estuary, located just downstream of Futch Creek along the ICW (Figure 2). Therefore, although the export of the short-lived isotopes is more consistent and generally higher in the Futch Creek estuary, when the variable November 2001 Pages Creek inflow radium activities are taken into account it is less clear whether the non-spring source of ^{226}Ra and ^{228}Ra was stronger in Futch, or whether additions from this source are similar in both estuaries but tended to be more masked in Pages.

4.5 Non-spring sources of ^{226}Ra and ^{228}Ra

As demonstrated by Table 8, in addition to the springs, there must have been one or more sources within the estuaries supplying ^{226}Ra and ^{228}Ra during most sampling times. This source would have to account for most of the excess ^{226}Ra and ^{228}Ra in the Pages Creek estuary, and it would also be an important source to the Futch Creek estuary, particularly of ^{228}Ra.

4.5.1 Stream ^{226}Ra and ^{228}Ra inputs

Radiocarbon data suggest that the other potential source of fresh water to the estuaries, the streams, contributed 0% of the total fresh water input to the Futch Creek estuary at all times and to the Pages Creek estuary during April 2001 and April 2002, but contributed 50% to 90% of the total fresh water input in November 2001. However, as indicated by the ΔSal, the total fresh water input was very small during that sampling period, and stream inputs (even using the highest radium and radon activities observed in any stream sample) contributed less than 5% of the observed excess of any tracer.

4.5.2 Other sources: surficial aquifer advection, regeneration in sediments

Other potential sources of ^{226}Ra and ^{228}Ra include advection from the surficial aquifer (driven by tidal pumping) and regeneration within the surficial aquifer sediments and the marsh sediments. As discussed above (section 4.1), regeneration of ^{226}Ra is not expected to be a significant source term (and may be only a minor source term for ^{228}Ra as well), suggesting that surficial aquifer advection may have supplied the additional excess ^{226}Ra and ^{228}Ra. This is discussed in more detail below (section 4.8).

4.6 Short-lived radium isotopes: ^{223}Ra and ^{224}Ra

4.6.1 Excess ^{223}Ra and ^{224}Ra: minimally supported by springs

As with ^{228}Ra, the springs (and streams) supply, in most cases, a negligible fraction of the total excess of each of the short-lived isotopes (Table 8). The ^{223}Ra and ^{224}Ra budgets were expected to be largely controlled by regeneration, desorption, and decay within the estuarine bottom or tidal marsh sediments.

4.6.2 Comparison of excess ^{223}Ra and ^{224}Ra with tide stage

A possible indicator of the magnitude of radium regeneration and release from the tidal marsh sediments (rather than from the estuarine bottom sediments) is to compare the degree of inundation of the tidal marshes in each estuary with excess ^{224}Ra and ^{223}Ra in the water column. The highest tide stage of our sampling seasons occurred during the spring tide of November 2001, with the highest high tide about half a meter higher than at any time during sampling in April 2001 (halfway to spring tide) or April 2002 (during neap tide). However, in the Pages Creek estuary, November 2001 showed the smallest average excess ^{224}Ra and ^{223}Ra of all the sampling periods, and in some cases the inflow was higher than the outflow. In the Futch Creek estuary, although ^{224}Ra and ^{223}Ra were exported at all times, the highest $\Delta^{224}Ra$ and $\Delta^{223}Ra$ occurred in April 2002, and not in November 2001. Thus, the observed excess ^{223}Ra and ^{224}Ra in November 2001 were not likely to be directly related to degree of inundation.

Although in November 2001 the Pages Creek estuary shows little high/low tide change in ^{223}Ra, and a decrease in ^{224}Ra on the outflow during and after the spring tide, there is no corresponding decrease in ^{224}Ra or ^{223}Ra activity in the outflow in Futch Creek. This more consistent export of the short-lived isotopes at Futch did not result from estuarine differences in spring input. With respect to the long-lived isotopes of radium, Futch Creek showed more spring influence than Pages, but even in Futch the springs rarely supplied more than 10% of the excess ^{224}Ra and ^{223}Ra (Table 8).

When the November 2001 Futch Creek estuary Δ^{224}Ra is normalized to the high tide-low tide salinity difference ΔSal, the highest Δ^{224}Ra/ΔSal occurs at the spring tide, or the highest monthly tide stage (Figure 26a). A similar pattern is observed for Δ^{223}Ra/ΔSal in November 2001 (Figure 26b). However, in the Pages Creek estuary, no such pattern is observed, and during the full spring tide of November 16th, both ^{224}Ra and ^{223}Ra were higher in the inflowing water than in the outflow (Figures 27a-b).

4.7 High tide/low tide pairs vs. time series sampling

To determine whether sampling twice per tidal cycle was a sufficient proxy for the full range of radium and radon tidal variations in these estuaries, data collected across a 12-hour time series were compared with data collected at high and low tide alone. Though this appeared to be a fair assumption for radon in both the November 2001 Pages Creek time series and the April 2002 Futch Creek time series (Figures 14, 20), the radium time series showed more scatter in both creeks and during both seasons (Figures 10-13).

In the November 2001 Pages Creek time series, there were fluctuations in all four radium isotope water column activities (as well as in salinity) that were not linearly related to tide stage, nor did the maximum and minimum radium values correspond to the low or high tide (Figures 10a, 11a, 12a, 13a). This suggests that for this season, at least, simple high tide/low tide sampling did not capture radium activity variability as a function of the tide.

The April 2002 Pages Creek radium isotope time series still showed scatter that deviated from a simple linear relationship to tide, but the high/low points within the tidal cycle tended to capture, respectively, the low/high radium values for all four isotopes (Figures 10b, 11b, 12b, 13b). The April 2002 Futch Creek time series longer-lived radium isotopes showed a close relationship to tide stage, but the short-lived isotopes showed no relationship at all, suggesting that the processes controlling the short-lived isotopes of radium are not strongly coupled to those controlling ^{222}Rn and the long-lived isotopes of radium within either estuary (Figures 10c, 11c, 12c, 13c).

4.8 Radium activity ratios

Inflow, spring, and stream inputs, therefore, are not sufficient to support most of the observed excess radium activities in either the Pages or Futch Creek estuaries. The remainder of the observed excess may have been supplied by seepage through estuarine bottom sediments, incorporating surficial aquifer fluxes as well as regeneration and release of radium (for ^{228}Ra, ^{223}Ra, and ^{224}Ra).

4.8.1 $^{228}Ra/^{226}Ra$

In the absence of direct measurements of surficial aquifer activities or of regeneration within the sediments, one method of isolating these inputs is to consider the activity ratios of the radium isotopes. The ratio of ^{228}Ra to ^{226}Ra activity, as described above, gives an indication of the relative influence of the springs, originating in a uranium-enriched limestone aquifer. The average ^{226}Ra:^{228}Ra:^{223}Ra:^{224}Ra activity ratio in the springs was 1:0.42:0.05:0.55, suggesting that spring-dominated discharge should have a ^{228}Ra/^{226}Ra AR ~ 0.42, possibly as low as 0.25 (Tables 9-10) (Figures 18-19, Figure 28). In the open ocean, the activity ratio of ^{228}Ra to ^{226}Ra is close to 0.5, though this AR can increase to > 1 near the coast (with lower overall Ra activities) (Moore 1996, Crotwell 1998, Moore 2000). However, the outflow ^{228}Ra/^{226}Ra AR in both creeks was close to 1.45, and generally increased from high to low tide (Tables 11-13), suggesting that the source of the additional excess radium has a ^{228}Ra/^{226}Ra AR higher than either springs or inflowing ICW water.

Pages Creek estuary high tide ^{228}Ra/^{226}Ra activity ratios were much more variable among (and within) the different sampling periods than were the low tide activity ratios (Table 11, Figures 29a-b). April 2001 high tide ^{228}Ra/^{226}Ra AR's were the highest, averaging 1.66 ± 0.17, compared to 1.45 ± 0.12 and 1.03 ± 0.31(November 2001 and April 2002, respectively). In contrast, low tide ^{228}Ra/^{226}Ra AR were highly consistent among the sampling periods, averaging 1.48 ± 0.11 for all low tide values (Figure 30). In the Futch Creek estuary, the ^{228}Ra/^{226}Ra was also more variable at high tide (1.38 ± 0.23) than at low tide (1.36 ± 0.14) (Table 13, Figures 31-32).

The low tide damping of the variable high tide values suggests that a source carrying a high $^{228}Ra/^{226}Ra$ AR is mixing with low $^{228}Ra/^{226}Ra$ spring inputs. April 2001 showed the most spring influence at the Futch Creek estuary, as well as the smallest excess ^{226}Ra and ^{228}Ra, and any additional inputs from a high $^{228}Ra/^{226}Ra$ source must have been small.

Additionally, the excess ^{226}Ra at Pages was smallest and most spring-influenced in April 2002, but the overall $^{228}Ra/^{226}Ra$ increased from high to low tide. Mass balance calculations of the residual excess ^{226}Ra and ^{228}Ra in the Futch Creek estuary in April 2002 (the excess after subtracting inputs from springs and streams) suggest that the AR ranged from 5:1 to 8:1. Pore water and estuarine sediment analyses would be required to define additional constraints on the input sources.

The high residual (non-spring-derived) $^{228}Ra/^{226}Ra$ AR in the outflow is similar to estuarine pore water radium $^{228}Ra/^{226}Ra$ activity ratios from North Inlet, SC, which range from about 5:1 to 11:1 (Rama and Moore 1996; Krest et al 2000). Because the concentration of radium in the estuaries is small relative to potential pore water concentration, a small volume addition from pore waters with elevated concentrations such as those at North Inlet could have a disproportionately large impact on the surface water activities.

4.8.2 $^{224}Ra/^{228}Ra$

The difference between the high tide $^{224}Ra/^{228}Ra$ AR and the low tide $^{224}Ra/^{228}Ra$ AR in each estuary can also provide information about the input sources. Although $^{224}Ra/^{228}Ra$ is equal to one at secular equilibrium, the average spring $^{224}Ra/^{228}Ra$ was enriched in ^{224}Ra relative to ^{228}Ra, with an AR ~ 1.3. It is important to note that, as is apparent from the maximum potential spring contributions to the estuarine radium budgets, the springs were depleted in both ^{224}Ra and ^{228}Ra relative to ^{226}Ra and were generally not a primary source of ^{224}Ra or ^{228}Ra (and that spring inputs would dilute the average ^{224}Ra and ^{228}Ra activities in the estuaries). Open ocean $^{224}Ra/^{228}Ra$ is essentially zero, but increases with proximity to the coast. Inflowing high tide $^{224}Ra/^{228}Ra$ to Rich and Mason Inlets ranged from 0.7-1.5, but averaged less than 1.0. Inlet $^{224}Ra/^{228}Ra$

always increased from high to low tide in April 2002, averaging about 1.5 at low tide (Table 14). The low tide $^{224}Ra/^{228}Ra$ AR in the November 2001 sample, however, was much lower (0.67).

Surface pore water ^{224}Ra activity may be enriched relative to ^{228}Ra activity if the parent of ^{224}Ra, ^{228}Th, becomes preferentially concentrated in surface sediments. One possible mechanism for this includes mixing of deep with surface sediments as a result of bioturbation, where ^{228}Ra, ^{228}Th, and ^{224}Ra are supplied to surface sediments and ^{228}Ra and ^{224}Ra are repeatedly removed by tidal exchange, thus increasing the $^{228}Th/^{228}Ra$ in the surface sediments to greater than one (Rama and Moore 1996). ^{224}Ra may also become enriched in pore water relative to ^{228}Ra as a result of alpha recoil from the decay of ^{228}Th bound within aquifer solids.

Pages Creek high tide-low tide changes in $^{224}Ra/^{228}Ra$ varied among the three sampling seasons (Table 11, Figures 33-34). Though during April 2001 and November 2001 the inflowing $^{224}Ra/^{228}Ra$ activity ratios were within 1.09 ± 0.08, April 2002 high tide $^{224}Ra/^{228}Ra$ activity ratios were elevated (1.83 ± 0.52), reflecting the low high tide ^{228}Ra values during that sampling period.

The Futch Creek estuary high/low tide changes in $^{224}Ra/^{228}Ra$ AR showed no pattern in April 2001 and April 2002, but the $^{224}Ra/^{228}Ra$ AR showed a consistent increase from high to low tide throughout the November 2001 sampling period (Table 12, Figures 35-36). When all sampling seasons are considered, high tide $^{224}Ra/^{228}Ra$ was much more variable (AR = 1.09 ± 0.61) than low tide $^{224}Ra/^{228}Ra$ (AR = 1.34 ± 0.15). The high tide values appeared to be grouped by season, with November at the low end and April (2001 and 2002) at the high end.

$^{224}Ra/^{228}Ra$ activity ratios in the Futch Creek estuary showed a similar pattern to $^{228}Ra/^{226}Ra$: highly variable in the inflow, and more constant in the outflow. Again, the difference in the high/low tide trends in $^{224}Ra/^{228}Ra$ between the two estuaries may be related to the much higher ^{224}Ra entering Pages Creek at high tide, relative to Futch Creek inflow ^{224}Ra activities, as a result of inflow from Rich Inlet.

4.8.3 $^{223}Ra/^{226}Ra$

As with $^{224}Ra/^{228}Ra$, an elevated $^{223}Ra/^{226}Ra$ AR (greater than ~0.05) also suggests additions of ^{223}Ra as a result of regeneration and release within sediments. The average $^{223}Ra/^{226}Ra$ AR in the Pages and Futch Creek springs is ~ 0.06.

$^{223}Ra/^{226}Ra$ was higher in Rich Inlet relative to Mason Inlet overall, and generally increased from high to low tide in the inlets, reflecting additions of ^{223}Ra from the marsh sediments. Both Pages and Futch Creek estuary $^{223}Ra/^{226}Ra$ AR's also increased from high to low tide during all sampling days in April 2001 and April 2002 (Tables 11-12, Figures 37-38). However, November 2001 Pages Creek estuary $^{223}Ra/^{226}Ra$ values mostly decreased from high to low tide, reflecting the positive change in $\Delta^{226}Ra$ on those days (as the $\Delta^{223}Ra$ was quite small).

4.8.4 $^{223}Ra/^{224}Ra$

As with $^{228}Ra/^{226}Ra$, $^{223}Ra/^{224}Ra$ activity ratios can reflect source ratios. ^{223}Ra and ^{226}Ra are both from uranium-series decay chains, and are consequently elevated in the carbonate aquifer relative to the thorium-series daughters ^{224}Ra and ^{228}Ra. April 2002 $^{223}Ra/^{224}Ra$ AR values tended to decrease in both Rich and Mason Inlets from high to low tide, suggesting that the primary source of the excess ^{223}Ra and ^{224}Ra to the inlets is relatively enriched in ^{224}Ra (Table 14).

In the Pages Creek estuary, high tide-low tide changes in the $^{223}Ra/^{224}Ra$ AR ($\Delta^{223}Ra/^{224}Ra$) reflected the differences between the April 2001/2002 short-lived radium isotopic patterns and the November 2001 short-lived radium isotopic patterns. In April 2001 and April 2002, the $^{223}Ra/^{224}Ra$ AR always increased from high tide to low tide, because the ^{223}Ra increased more than the ^{224}Ra (Figure 39, Table 11). In November 2001, however, the $\Delta^{223}Ra$ was generally small. Overall, the supply of the short-lived isotopes to the Pages Creek estuary in November 2001 was small. Although Futch Creek estuary ^{224}Ra and ^{223}Ra activities increased from high to low tide at all times, the $^{223}Ra/^{224}Ra$ AR showed no trend with respect to season, tide stage, or salinity difference (Table 12, Figure 40).

5. Conclusions

Outflow radium and radon activities were almost always higher than inflow activities in the Futch Creek estuary. The Pages Creek estuary was less consistent in exporting any of these tracers, particularly during the November 2001 season. During most sampling seasons, springs originating from a confined aquifer were the only significant fresh water input to both estuaries; the larger tidal salinity variations in the Futch Creek estuary suggest that it is more spring-dominated than Pages.

Because the spring activities of ^{222}Rn were so large, spring input of ^{222}Rn dominated the radon budget within both estuaries. Discharge from the artesian springs accounted for all of the excess ^{222}Rn during most sampling days in the Futch Creek estuary, and on all April 2002 sampling days in the Pages Creek estuary. Spring inputs also accounted for all of the excess ^{226}Ra at the Futch Creek estuary during sampling in April 2001, and 20 – 100% of the excess ^{226}Ra at the Futch Creek estuary during November 2001 and April 2002. In the Pages Creek estuary, spring inputs accounted for 1 – 54% of the observed excess ^{226}Ra during all sampling periods.

A source in addition to springs, streams, and inflow from the ICW is required to support most of the observed excess ^{228}Ra, ^{223}Ra, and ^{224}Ra at Futch, and to support excess ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra at Pages. Residual (non-spring, stream, or inflow) excess radium activity ratios show that the additional input was generally high in ^{228}Ra relative to ^{226}Ra, and was probably also elevated in ^{224}Ra relative to ^{228}Ra. The source of the ^{226}Ra and ^{228}Ra may be seepage through the estuarine bottom sediments, driven by both advection of surficial groundwater and tidal pumping. Additional elevated ^{224}Ra and ^{223}Ra in the outflow was most likely derived from regeneration within the tidal marsh sediments. Pore water radium activities have been observed to be orders of magnitude higher than surface water activities, so that a small flux would be sufficient to alter the surface water budgets considerably.

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Table IV-1: Radium and radon sampling data for Pages and Futch Creek estuaries

Sampling Location	Sampling Date	Volume (L)	Collection method A=manual bilge pump B=automatic bilge pump	Dissolved Ra filtration (uM)
Estuaries: HT/LT pairs				
Pages and Futch Creeks HT/LT p:	Apr-01	50.0	A	unfiltered
Pages Creek-High Tide	11/12/01	43.4	A	unfiltered
Pages Creek-Low Tide	11/12/01	43.9	A	unfiltered
Futch Creek-High Tide	11/12/01	41.0	A	unfiltered
Futch Creek-Low Tide	11/12/01	41.8	A	unfiltered
Pages Creek-High Tide	11/13/01	41.6	A	unfiltered
Pages Creek-Low Tide	11/13/01	44.6	A	unfiltered
Futch Creek-High Tide	11/13/01	41.3	A	unfiltered
Futch Creek-Low Tide	11/13/01	42.1	A	unfiltered
Pages Creek-High Tide	11/15/2001	41.8	A	unfiltered
Pages Creek - Low Tide	11/15/2001	43.2	A	unfiltered
Futch Creek-High Tide	11/15/2001	41.3	A	unfiltered
Futch Creek-Low Tide	11/15/2001	31.6	A	unfiltered
Pages Creek-High Tide	11/16/2001	42.4	A	unfiltered
Pages Creek-Low Tide	11/16/2001	41.5	A	unfiltered
Futch Creek-High Tide	11/16/2001	42.3	A	unfiltered
Futch Creek-Low Tide	11/16/2001	21.2	A	unfiltered
Pages Creek-High Tide	11/18/2001	41.6	A	unfiltered
Pages Creek-Low Tide	11/18/2001	42.2	A	unfiltered
Futch Creek-High Tide	11/18/2001	32.0	A	unfiltered
Futch Creek-Low Tide	11/18/2001	88.4	A	unfiltered
Pages Creek-High Tide	4/13/2002	40.0	A	5 then 1
Pages Creek-Low Tide	4/13/2002	40.0	A	5 then 1
Futch Creek-High Tide	4/13/2002	40.0	A	5 then 1
Futch Creek-Low Tide	4/13/2002	41.0	A	5 then 1
Futch Creek-High Tide	4/14/2002	40.0	A	5
Futch Creek-Low Tide	4/14/2002	40.0	A	5 then 1
Pages Creek-High Tide	4/16/2002	40.0	A	5 then 1
Pages Creek-Low Tide	4/16/2002	40.0	A	5 then 1
Time series				
Pages Creek	11/13/2001	123.9	B	unfiltered
Pages Creek	11/13/2001	126.8	B	unfiltered
Pages Creek	11/13/2001	125.0	B	unfiltered
Pages Creek	11/13/2001	130.5	B	unfiltered
Pages Creek	11/13/2001	145.9	B	unfiltered
Pages Creek	11/13/2001	114.7	B	unfiltered
Pages Creek	11/13/2001	139.6	B	unfiltered
Pages Creek	11/13/2001	142.1	B	unfiltered
Pages Creek	11/13/2001	100.8	B	unfiltered
Pages Creek	11/13/2001	145.0	B	unfiltered

Table IV-1 (con't)

Pages Creek	11/13/2001	100.7	B	unfiltered
Pages Creek	11/13/2001	136.9	B	unfiltered
Pages Creek	11/13/2001	91.4	B	unfiltered
Pages Creek	11/13/2001	87.7	B	unfiltered
Pages Creek	4/14/2002	110.2	B	5 then 1
Pages Creek	4/14/2002	113.6	B	5 then 1
Pages Creek	4/14/2002	112.8	B	5 then 1
Pages Creek	4/14/2002	113.6	B	5 then 1
Pages Creek	4/14/2002	116.8	B	5 then 1
Pages Creek	4/14/2002	140.2	B	5 then 1
Pages Creek	4/14/2002	118.7	B	5 then 1
Pages Creek	4/14/2002	119.3	B	5 then 1
Pages Creek	4/14/2002	113.9	B	5 then 1
Pages Creek	4/14/2002	114.1	B	5 then 1
Pages Creek	4/14/2002	114.1	B	5 then 1
Pages Creek	4/14/2002	114.7	B	5 then 1
Futch Creek	4/16/2002	113.6	B	5 then 1
Futch Creek	4/16/2002	112.8	B	5 then 1
Futch Creek	4/16/2002	114.0	B	5 then 1
Futch Creek	4/16/2002	110.9	B	5 then 1
Futch Creek	4/16/2002	113.6	B	5 then 1
Futch Creek	4/16/2002	113.7	B	5 then 1
Futch Creek	4/16/2002	113.6	B	5 then 1
Futch Creek	4/16/2002	113.6	B	5 then 1
Futch Creek	4/16/2002	117.7	B	5 then 1
Futch Creek	4/16/2002	113.6	B	5 then 1
Futch Creek	4/16/2002	113.6	B	5 then 1
Futch Creek	4/16/2002	82.2	B	5 then 1
Inlets				
Middle Sound, Low Tide	11/17/2001	21.5	A	unfiltered
Mouth of Rich Inlet at high tide	4/15/2002	40.0	A	5 then 1
Mouth of Rich Inlet at low tide	4/15/2002	40.0	A	5 then 1
Mouth of Mason Inlet at high tide	4/15/2002	40.0	A	5 then 1
Mouth of Mason Inlet at low tide	4/15/2002	40.0	A	5 then 1
Mouth of Rich Inlet at high tide	4/17/2002	40.0	A	1
Mouth of Rich Inlet at low tide	4/17/2002	40.0	A	1
Rich Inlet @ ICW HT	4/17/2002	40.0	A	1
Rich Inlet @ ICW LT	4/17/2002	40.0	A	1
Mason Inlet @ ICW HT	4/17/2002	40.0	A	1
Mason Inlet @ ICW LT	4/17/2002	40.0	A	1

Table IV-1 (con't)

Spring/Stream/Groundwater				
Pages Creek Stream-Furtado Rd	4/20/2001	25.0	A	unfiltered
Pages Creek stream at Furtado Rc	4/13/2002	170.5	B	5 then 1
Pages Creek Stream-Porters Neck	4/20/2001	25.0	A	unfiltered
Pages Creek Stream: Bayshore R	4/23/2001	25.0	A	unfiltered
Pages Creek Stream: Bayshore R	11/15/2001	137.8	B	unfiltered
Pages Creek Stream: Bayshore R	4/11/2002	40.9	A	1
FC stream: Scotts Hill Loop Rd	4/23/2001	25.0	A	unfiltered
FC stream: Scotts Hill Loop Rd	11/15/2001	102.0	B	1
FC stream: Scotts Hill Loop Rd	4/15/2002	136.3	B	5 then 1
Sidebury Rd Stream	4/20/2001	25.0	A	unfiltered
Futch Creek Spring	4/20/2001	25.0	A	unfiltered
Futch Creek Spring	4/22/2001	25.0	A	unfiltered
Futch Creek Spring	4/22/2001	25.0	A	unfiltered
Futch Creek spring at Saltwood L	4/23/2001	25.0	A	unfiltered
Futch Creek spring at Saltwood L	11/16/2001	125.1	B	unfiltered
Futch Creek spring at Saltwood L	4/18/2002	167.3	B	5
Bayshore Spring	11/15/2001	137.5	A	unfiltered
Bayshore spring - Pages Creek	4/11/2002	36.4	A	1
NENHC D1 (Peedee)	4/12/2002	100.0	B	1
NENHC S1 (Castle Hayne)	4/12/2002	100.0	B	1
NENHC D2 (Peedee)	4/12/2002	100.0	B	1
NENHC S2 (Castle Hayne)	4/12/2002	100.0	B	1
NENHC D3 (Peedee)	4/12/2002	100.0	B	1
NENHC S3 (Castle Hayne)	4/12/2002	100.0	B	1

Table IV-2: Pages Creek estuary high tide and low tide radium, radon, and salinity

		Salinity ppt	Std. Dev.	^{224}Ra dpm/100 L	Std. Dev.	^{223}Ra dpm/100 L	Std. Dev.	^{226}Ra dpm/100 L	Std. Dev.	^{228}Ra dpm/100 L	Std. Dev.	^{222}Rn dpm/L	Std. Dev.
Pages Creek													
Pages Creek-High Tide	4/21/01	34.728		28.3		5.5		18.5		28.5			
Pages Creek-High Tide	4/22/01	34.778		28.2		6.7		13.9		24.7			
Average 4/01 PC HT		**34.753**	**0.035**	**28.2**	**0.1**	**6.1**	**0.9**	**16.2**	**3.2**	**26.6**	**2.7**		
Pages Creek-Low Tide	4/21/01	33.238		53.3		11.3		16.5		25.6			
Pages Creek-Low Tide	4/22/01	33.870		45.3		11.9		19.4		28.6			
Average 4/01 PC LT		**33.554**	**0.447**	**49.3**	**5.6**	**11.6**	**0.4**	**18.0**	**2.0**	**27.1**	**2.1**		
Pages Creek-High Tide	11/12/01	36.262		35.9		6.7		21.8		33.6		7.5	
Pages Creek-High Tide	11/13/01	36.414		24.4		5.4		18.0		24.3		0.7	
Pages Creek-High Tide	11/15/01	36.428		7.3		1.7		21.4		30.3		3.4	
Pages Creek-High Tide	11/16/01	36.406		36.9		5.3		19.4		31.3		1.9	
Pages Creek-High Tide	11/18/01	36.424		25.7		5.7		17.1		22.7		12.1	
Average 11/01 PC HT		**36.387**	**0.070**	**26.0**	**11.9**	**5.0**	**1.9**	**19.5**	**2.1**	**28.4**	**4.7**	**5.1**	**4.7**
Pages Creek-Low Tide	11/12/01	36.106		36.0		6.9		19.8		31.0		2.1	
Pages Creek-Low Tide	11/13/01	36.128		36.5		5.3		22.5		34.6		7.9	
Pages Creek-Low Tide	11/15/01	36.333											
Pages Creek-Low Tide	11/16/01	36.328		17.0		4.9		24.9		31.2		8.0	
Pages Creek-Low Tide	11/18/01	36.285		24.0		4.5		18.9		29.1		27.0	
Average 11/01 PC LT		**36.236**	**0.111**	**28.4**	**9.6**	**5.4**	**1.0**	**21.5**	**2.7**	**31.5**	**2.3**	**11.3**	**10.8**
Pages Creek-High Tide	4/13/02	36.147		25.4		4.2						3.4	
Pages Creek-High Tide	4/14/02	36.160		21.0		4.4		12.9		16.1		2.7	
Pages Creek-High Tide	4/16/02	36.153		29.2		5.0		15.3		12.4		0.2	
Average 4/02 PC HT		**36.153**	**0.006**	**25.1**	**4.1**	**4.7**	**0.4**	**14.1**	**1.7**	**14.2**	**2.6**	**2.1**	**1.7**
Pages Creek-Low Tide	4/13/02	35.124		15.6		3.4		6.2		8.3		2.2	
Pages Creek-Low Tide	4/14/02	35.167		34.5		8.8		15.4		23.1		6.9	
Pages Creek-Low Tide	4/16/02	35.327		55.5		12.6		17.6		26.5		6.1	
Average 4/02 PC LT		**35.206**	**0.107**	**35.2**	**20.0**	**8.3**	**4.6**	**13.1**	**6.1**	**19.3**	**9.7**	**5.1**	**2.5**

Table IV-3: Futch Creek estuary high tide and low tide radium, radon, and salinity

		Salinity ppt	Std. Dev.	^{224}Ra dpm/100 L	Std. Dev.	^{223}Ra dpm/100 L	Std. Dev.	^{226}Ra dpm/100 L	Std. Dev.	^{228}Ra dpm/100 L	Std. Dev.	^{222}Rn dpm/L	Std. Dev.
Futch Creek-High Tide	4/21/01	35.587		23.4		3.7		11.9		12.0			
Futch Creek-High Tide	4/22/01	35.429		28.0		5.5		17.4		28.7			
Average 4/01 FC HT		**35.508**	**0.112**	**25.7**	**3.3**	**4.6**	**1.2**	**14.7**	**3.9**	**20.4**	**11.8**		
Futch Creek-Low Tide	4/21/01	23.693		23.0		5.4		13.2		16.4			
Futch Creek-Low Tide	4/22/01	26.936		40.4		6.6		18.6		26.3			
Average 4/01 FC LT		**25.314**	**2.293**	**31.7**	**12.3**	**6.0**	**0.9**	**15.9**	**3.8**	**21.4**	**7.0**		
Futch Creek-High Tide	11/12/01	36.348		17.1		3.5		18.4		33.3		4.3	
Futch Creek-High Tide	11/13/01	36.427		11.2		3.3		19.9		24.2		3.2	
Futch Creek-High Tide	11/15/01	36.434		14.7		2.5		18.0		22.4			
Futch Creek-High Tide	11/16/01	35.427		18.5		2.7		16.4		22.6		3.2	
Futch Creek-High Tide	11/18/01	36.481		11.7		4.1		17.4		22.8		3.2	
Average 11/01 FC HT		**36.223**	**0.448**	**14.7**	**3.2**	**3.2**	**0.6**	**18.0**	**1.3**	**25.1**	**4.7**	**3.5**	**0.6**
Futch Creek-Low Tide	11/12/01	33.783		39.6		7.4		20.3		29.1		22.8	
Futch Creek-Low Tide	11/13/01	34.392		35.4		6.2		21.4		27.0		17.5	
Futch Creek-Low Tide	11/15/01	34.964		37.8		4.2		23.7		27.8			
Futch Creek-Low Tide	11/16/01	34.908		33.1		7.0		20.1		25.2		20.5	
Futch Creek-Low Tide	11/18/01	34.560		31.7		6.4		21.2		28.7		34.0	
Average 11/01 FC LT		**34.521**	**0.477**	**35.5**	**3.3**	**6.3**	**1.2**	**21.3**	**1.4**	**27.6**	**1.5**	**23.7**	**7.2**
Futch Creek-High Tide	4/13/02	35.911		25.7		5.5		11.3		15.6		4.1	
Futch Creek-High Tide	4/14/02	35.917		23.7		4.1		12.0		18.0		1.9	
Futch Creek-High Tide	4/16/02	35.991		30.6		4.5		11.7		14.8		3.7	
Average 4/02 FC HT		**35.939**	**0.045**	**26.7**	**3.6**	**4.7**	**0.7**	**11.7**	**0.4**	**16.1**	**1.7**	**3.2**	**1.2**
Futch Creek-Low Tide	4/13/02	32.446		70.6		14.0						6.1	
Futch Creek-Low Tide	4/14/02	32.934		45.8		8.3		18.8		29.9		14.9	
Futch Creek-Low Tide	4/16/02	30.843		34.9		14.0		20.3		30.9		26.2	
Average 4/02 FC LT		**32.074**	**1.094**	**40.4**	**18.3**	**11.1**	**3.3**	**19.5**	**1.0**	**30.4**	**0.7**	**15.7**	**10.1**

Table IV-4: Pages and Futch Creek estuary time series: radium, radon, and salinity

Sampling Date	Sampling Time	Salinity ppt	Water depth (m)*	^{224}Ra dpm/100 L	^{223}Ra dpm/100 L	^{226}Ra dpm/100 L	^{228}Ra dpm/100 L	^{222}Rn dpm/L
Pages Creek time series								
11/13/01	5:25	36.414	**	24.4	5.4	18.0	24.3	0.7
11/13/01	7:23	36.404	1.693	18.4	5.8	21.5	25.8	**
11/13/01	8:24	36.415	1.476	13.8	5.2	21.7	34.6	**
11/13/01	9:28	36.399	1.245	21.6	4.6	18.4	25.3	6.6
11/13/01	10:18	36.382	0.981	25.3	5.0	20.5	33.7	**
11/13/01	11:20	36.300	0.691	36.5	5.3	22.5	34.6	7.9
11/13/01	11:27	36.460	0.651	29.0	4.1	18.5	23.8	**
11/13/01	12:03	36.360	0.477	29.0	4.2	20.5	34.0	**
11/13/01	12:42	36.128	0.351	27.6	7.5	21.8	31.4	**
11/13/01	13:25	36.069	0.267	20.6	6.0	21.9	32.6	12.0
11/13/01	14:25	36.368	0.433	26.9	5.1	20.1	33.1	**
11/13/01	15:20	36.465	0.703	23.6	4.3	20.2	30.1	**
11/13/01	16:21	36.406	1.009	18.9	3.8	15.9	22.6	**
11/13/01	17:20	36.424	1.256	19.3	4.2	18.6	27.9	**
11/13/01	18:22	36.415	1.471	37.6	7.9	19.6	33.5	**
11/13/01	19:20	36.403	1.532	39.4	6.8	20.1	31.0	**
Pages Creek time series								
4/14/02	8:42	36.136	1.846	24.2	4.4	12.1	18.2	**
4/14/02	9:50	36.160	2.018	21.0	4.4	12.9	16.1	**
4/14/02	10:57	36.140	2.029	18.4	3.0	14.4	14.4	**
4/14/02	11:57	36.105	1.846	21.9	5.0	14.4	18.7	**
4/14/02	12:57	35.939	1.609	26.7	5.8	15.6	29.6	**
4/14/02	13:57	35.811	1.357	28.8	7.5	16.1	22.4	**
4/14/02	14:37	35.597	1.138	33.2	7.4	15.5	21.8	**
4/14/02	15:57	35.167	0.960	34.5	8.8	15.4	23.1	**
4/14/02	16:32	35.220	0.990	35.3	6.4	19.0	28.6	**
4/14/02	17:40	35.734	1.235	26.9	3.8	16.7	24.0	**
4/14/02	18:36	35.999	1.469	35.5	6.8	13.9	17.6	**
4/14/02	19:39	36.082	1.714	27.3	5.3	11.0	16.9	**
Futch Creek time series								
4/16/02	9:07	35.915	0.824	21.3	5.7	17.0	22.8	**
4/16/02	10:00	35.991	0.940	35.8	7.8	16.1	21.4	**
4/16/02	11:10	35.907	1.022	30.6	4.5	11.7	14.8	4.3
4/16/02	12:10	35.937	0.946	27.1	4.4	16.1	19.0	4.0
4/16/02	13:13	35.837	0.778	44.2	9.9	15.4	19.3	4.8
4/16/02	14:00	35.513	0.607	35.5	8.2	14.8	21.4	11.9
4/16/02	15:16	34.408	0.353	29.2	6.6	17.0	23.9	19.2
4/16/02	16:13	33.202	0.151	23.2	7.5	18.6	27.5	33.9
4/16/02	17:18	30.843	0.098	34.9	14.0	20.3	30.9	48.0
4/16/02	18:17	32.055	0.256	21.7	7.5	19.0	26.2	52.1
4/16/02	19:00	35.527	0.440	35.3	5.3	15.3	20.4	**
4/16/02	20:00	35.898	0.687	40.4	8.9	15.6	20.0	7.3

*determined by YSI
**no data

Table IV-5: Inlet high tide and low tide radium and salinity

		Salinity ppt	Std. Dev.	^{224}Ra dpm/100 L	Std. Dev.	^{223}Ra dpm/100 L	Std. Dev.	^{226}Ra dpm/100 L	Std. Dev.	^{228}Ra dpm/100 L	Std. Dev.
Rich Inlet-Low Tide	11/17/01	36.541		29.3		3.8		29.5		43.9	
Rich Inlet Mouth-High Tide	4/15/02	36.236		9.6		2.3		13.2		13.8	
Rich Inlet Mouth-High Tide	4/17/02	36.286		11.2		3.1		12.5		11.8	
Rich Inlet @ ICW-High Tide	4/17/02	36.292		16.3		3.9		12.9		10.9	
Average 4/02 Rich Inlet-High Tide		**36.271**	**0.031**	**12.3**	**3.5**	**3.1**	**0.8**	**12.8**	**0.4**	**12.2**	**1.5**
Rich Inlet Mouth-Low Tide	4/15/02	36.138		21.6		3.8		12.1		12.3	
Rich Inlet Mouth-Low Tide	4/17/02	36.223		24.4		6.4		13.2		17.3	
Rich Inlet @ ICW-Low Tide	4/17/02	36.113		26.2		4.7		15.6		14.9	
Average 4/02 Rich Inlet-Low Tide		**36.158**	**0.058**	**24.1**	**2.3**	**5.0**	**1.3**	**13.6**	**1.8**	**14.9**	**2.5**
Mason Inlet Mouth-High Tide	4/15/02	36.290		10.7		1.7		12.6		13.1	
Mason Inlet @ ICW-High Tide	4/17/02	36.216		8.1		2.0		11.2		11.2	
Average 4/02 Mason Inlet-High Tide		**36.253**	**0.053**	**9.4**	**1.9**	**1.9**	**0.3**	**11.9**	**1.0**	**12.1**	**1.3**
Mason Inlet Mouth-Low Tide	4/15/02	36.169		24.3		3.2		16.1		21.7	
Mason Inlet @ ICW-Low Tide	4/17/02	36.153		29.5		6.2		14.6		19.3	
Average 4/02 Mason Inlet-Low Tide		**36.161**	**0.011**	**26.9**	**3.7**	**4.7**	**2.1**	**15.3**	**1.1**	**20.5**	**1.7**

Table IV-6: Spring and stream radium and radon activities

Springs		Salinity ppt	^{224}Ra dpm/100 L	^{223}Ra dpm/100 L	^{226}Ra dpm/100 L	^{228}Ra dpm/100 L	^{222}Rn dpm/L	Volume L
Pages Creek								
Bayshore spring	Nov-01	0.239	15.7	1.8	27.0	13.9	492.9	
Bayshore spring	Apr-02	0.232	20.5	2.8	31.3	14.0	183.6	
Bayshore spring - particulates	Nov-01				0.7	0**		138
Futch Creek								
Spring at McMillan house	Apr-01	7.074						
Spring at McMillan house	Apr-01	2.956	14.7	6.8	44.8	11.4		
Spring at McMillan house	Apr-01	2.886						
Spring at McMillan house	Apr-01	2.787	12.7	3.6	48.8	12.1		
Spring upstream of 1021 Creekside	Apr-01	0.404	5.7	1.0	10.4			
Saltwood Lane spring	Apr-01	0.283	3.3	0.2	8.1	6.9		
Saltwood Lane spring (start)	Nov-01	4.032	14.6	1.6	21.5	14.4	597.8	
Saltwood Lane spring (end)*	Nov-01	3.769						
Saltwood Lane spring	Apr-02	1.115	8.0	0.5	10.9	6.2	299.7	
Streams								
Pages Creek								
Stream at Bayshore	Apr-01	0.164	11.9	2.4	41.9	21.0		
Stream at Bayshore	Nov-01	30.963	25.1	8.4	39.8	49.1		
Stream at Bayshore	Apr-02	0.261	11.0	2.5	34.0	16.8	54.7	
Stream at Furtado Road	Apr-01	0.177	12.4	1.4	19.0	19.0		
Stream at Porters Neck Road	Apr-01	0.142	10.4	1.0	25.8	16.8		
Stream at Furtado Road	Nov-01	3.662						
Stream at Furtado Road	Apr-02	0.201	9.9	0.8	21.4	16.5	31.6	
Futch Creek								
Stream at Scotts Hill Loop Road	Apr-01	0.080	4.8	0.4	10.6	14.3		
Stream at Scotts Hill Loop Road	Nov-01	9.919	49.4	4.5	43.0	49.2		
Stream at Scotts Hill Loop Road	Apr-02	3.057	20.2	4.3	30.8	36.6	37.6	
Scotts Hill Loop- particulates	Nov-01				0.4	0.0		102
Other Streams								
Sidebury Road	Apr-01	0.067	4.8	0.4	12.4	7.6		

*salinity taken at the start and at the end of spring sampling
** ^{228}Ra in both particulate samples was negligible

Table IV-7: Groundwater radium and radon

Groundwater	Date	Salinity ppt	^{224}Ra dpm/100 L	^{223}Ra dpm/100 L	^{226}Ra dpm/100 L	^{228}Ra dpm/100 L	^{222}Rn dpm/L
Castle Hayne aquifer							
NENHC* S1	Jul-00	0.294			85.2	29.7	
NENHC S2	Jul-00	0.249			90.7	29.3	
NENHC S3	Jul-00	0.895			215.5	46.3	
NENHC S1	Apr-02	0.257	13.0	1.6	47.8	14.2	9216.5
NENHC S2	Apr-02	0.281	9.8	2.7	75.2	9.8	3051.3
NENHC S3	Apr-02	0.818	29.2	8.3	161.5	29.7	4524.3
Peedee Aquifer							
NENHC D1	Jul-00	0.410					
NENHC D2	Jul-00	1.461					
NENHC D3	Jul-00	0.777			34.6	21.7	
NENHC D1	Apr-02	0.379	10.3	1.1	8.9	5.7	96.0
NENHC D2	Apr-02	0.667	15.1	1.4	31.6	13.6	422.2
NENHC D3	Apr-02	0.512	8.4	0.7	25.9	8.6	179.4

* Northeast New Hanover Conservancy well

Table IV-8: Estimated contributions of spring inputs to the observed excess radium and radon activities in the Pages and Futch Creek estuaries.

	Sampling	Excess (low tide - high tide)*					Maximum percent spring contribution**					Minimum percent spring contribution***				
	Date	^{224}Ra	^{223}Ra	^{226}Ra	^{228}Ra	^{222}Rn	^{224}Ra	^{223}Ra	^{226}Ra	^{228}Ra	^{222}Rn	^{224}Ra	^{223}Ra	^{226}Ra	^{228}Ra	^{222}Rn
		dpm/100 L				dpm/L	dpm/100 L				dpm/L	dpm/100 L				dpm/L
Pages Creek	4/21/01	25.0	5.8	-1.9	-2.8		2.2	2.7				0.6	0.2			
Pages Creek	4/22/01	17.1	5.2	5.5	3.9		1.9	1.8	23	8.1		0.5	0.1	15	4.6	
Futch Creek	4/21/01	-0.4	1.6	1.3	4.4			74	1253	92			4.5	803	53	
Futch Creek	4/22/01	12.4	1.1	1.2	-2.4		25	77	943			6.4	4.7	605		
Pages Creek	11/12/01	0.1	0.2	-2.0	-2.6	-5.4	23	4.1				5.9	0.3			
Pages Creek	11/13/01	12.1	-0.1	4.5	10.3	7.2	0.4		4.3	0.5	32	0.1		2.7	0.3	10
Pages Creek	11/15/01															
Pages Creek	11/16/01	-19.9	-0.4	5.5	-0.1	6.1			1.0		11			0.6		3.2
Pages Creek	11/18/01	-1.7	-1.2	1.7	6.4	14.9			5.3	0.4	7.6			3.4	0.2	2.3
Futch Creek	11/12/01	22.5	3.9	2.0	-4.2	18.5	4.0	6.6	173		228	1.0	0.4	111		70
Futch Creek	11/13/01	24.2	3.0	1.5	2.8	14.4	2.9	6.8	181	24	233	0.8	0.4	116	14	71
Futch Creek	11/15/01	23.1	1.7	5.6	5.4		2.2	8.7	35	9.0		0.6	0.5	22	5.2	
Futch Creek	11/16/01	14.6	4.2	3.6	2.7	17.3	1.3	1.3	20	6.6	51	0.3	0.08	13	3.8	16
Futch Creek	11/18/01	19.9	2.3	3.8	5.9	30.8	3.4	8.2	69	10.8	102	0.9	0.5	44	6.2	31
Pages Creek	4/13/02	-9.8	-0.8	6.2	8.3	3.6			22	4.1				14	2.4	
Pages Creek	4/14/02	13.4	4.5	2.5	7.0	3.4	2.6	2.2	54	4.8	384	0.7	0.1	35	2.7	118
Pages Creek	4/16/02	26.3	7.6	2.4	14.2	4.9	1.1	1.1	47	2.0	233	0.3	0.1	30	1.1	71
Futch Creek	4/13/02	44.9	8.5	-11.3		10.8	2.7	4.1			2928	0.7	0.3			899
Futch Creek	4/14/02	22.1	4.2	6.8	11.8	24.3	4.8	7.3	59	8.5	381	1.2	0.4	38	4.9	117
Futch Creek	4/16/02	4.2	9.4	8.5	16.0	12.1	43	5.5	82	11	379	11	0.3	53	6.2	117

* Negative indicates low tide activity is less than high tide activity; percent spring contribution not calculated if no excess.
** See text for calculation. Assumes spring inputs = 100% of total fresh input at both Pages and Futch Creeks in April 2001 and April 2002, and at Futch Creek in November 2001. For Pages Creek in November 2001, assumes spring inputs = 50% of total fresh input (Chapter III).
*** Maximum spring contribution uses highest Ra and Rn activities observed in any spring. Minimum spring contribution uses lowest observed Ra and Rn.

Table IV-9: Spring and stream radium isotope activity ratios

		Salinity ppt	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	$^{223}Ra/^{224}Ra$
Springs						
Pages Creek						
Bayshore spring	Nov-01	0.239	0.52	1.13	0.07	0.11
Bayshore spring	Apr-02	0.232	0.45	1.46	0.09	0.13
Futch Creek						
Spring at McMillan house	Apr-01	7.074				
Spring at McMillan house	Apr-01	2.956	0.25	1.29	0.15	0.46
Spring at McMillan house	Apr-01	2.886				
Spring at McMillan house	Apr-01	2.787	0.25	1.05	0.07	0.29
Spring upstream of 1021 Creekside	Apr-01	0.404			0.10	0.18
Saltwood Lane spring	Apr-01	0.283	0.86	0.48	0.03	0.07
Saltwood Lane spring (start)	Nov-01	4.032	0.67	1.02	0.07	0.11
Saltwood Lane spring (end)*	Nov-01	3.769				
Saltwood Lane spring	Apr-02	1.115	0.57	1.29	0.04	0.06
Streams						
Pages Creek						
Stream at Bayshore	Apr-01	0.164	0.50	0.56	0.06	0.21
Stream at Bayshore	Nov-01	30.963	1.23	0.51	0.21	0.34
Stream at Bayshore	Apr-02	0.261	0.49	0.66	0.07	0.23
Stream at Furtado Road	Apr-01	0.177	1.00	0.65	0.07	0.11
Stream at Porters Neck Road	Apr-01	0.142	0.65	0.62	0.04	0.09
Stream at Furtado Road	Nov-01	3.662				
Stream at Furtado Road	Apr-02	0.201	0.77	0.60	0.04	0.09
Futch Creek						
Stream at Scotts Hill Loop Road	Apr-01	0.080	1.35	0.34	0.04	0.09
Stream at Scotts Hill Loop Road	Nov-01	9.919	1.14	1.01	0.11	0.09
Stream at Scotts Hill Loop Road	Apr-02	3.057	1.19	0.55	0.14	0.21
Other Streams						
Sidebury Road	Apr-01	0.067	0.61	0.63	0.03	0.07

*salinity taken at the start and at the end of spring sampling

Table IV-10: Groundwater isotope ratios

Groundwater	Date	Salinity ppt	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	$^{223}Ra/^{224}Ra$
Castle Hayne aquifer						
NENHC* S1	Jul-00	0.294	0.35			
NENHC S2	Jul-00	0.249	0.32			
NENHC S3	Jul-00	0.895	0.21			
NENHC S1	Apr-02	0.257	0.30	0.91	0.03	0.13
NENHC S2	Apr-02	0.281	0.13	1.00	0.04	0.28
NENHC S3	Apr-02	0.818	0.18	0.98	0.05	0.28
Peedee Aquifer						
NENHC D1	Jul-00	0.410				
NENHC D2	Jul-00	1.461				
NENHC D3	Jul-00	0.777	0.63			
NENHC D1	Apr-02	0.379	0.64	1.80	0.12	0.11
NENHC D2	Apr-02	0.667	0.43	1.11	0.05	0.10
NENHC D3	Apr-02	0.512	0.33	0.98	0.03	0.08

* Northeast New Hanover Conservancy well

Table IV-11: Pages Creek estuary high tide and low tide radium isotope ratios

		Salinity ppt	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	$^{223}Ra/^{224}Ra$
Pages Creek						
Pages Creek-High Tide	4/21/01	34.728	1.54	0.99	0.30	0.19
Pages Creek-High Tide	4/22/01	34.778	1.78	1.14	0.49	0.24
Average 4/01 PC HT		**34.753**	**1.66**	**1.07**	**0.39**	**0.22**
Pages Creek-Low Tide	4/21/01	33.238	1.55	2.08	0.69	0.21
Pages Creek-Low Tide	4/22/01	33.870	1.47	1.58	0.61	0.26
Average 4/01 PC LT		**33.554**	**1.51**	**1.83**	**0.65**	**0.24**
Pages Creek-High Tide	11/12/01	36.262	1.54	1.07	0.31	0.19
Pages Creek-High Tide	11/13/01	36.414	1.35	1.00	0.30	0.22
Pages Creek-High Tide	11/15/01	36.428	1.42			0.23
Pages Creek-High Tide	11/16/01	36.406	1.62	1.18	0.27	0.14
Pages Creek-High Tide	11/18/01	36.424	1.33	1.13	0.34	0.22
Average 11/01 PC HT		**36.387**	**1.45**	**1.10**	**0.30**	**0.20**
Pages Creek-Low Tide	11/12/01	36.106	1.56	1.16	0.35	0.19
Pages Creek-Low Tide	11/13/01	36.128	1.54	1.05	0.24	0.15
Pages Creek-Low Tide	11/15/01	36.333				
Pages Creek-Low Tide	11/16/01	36.328	1.25	0.54	0.20	0.29
Pages Creek-Low Tide	11/18/01	36.285	1.54	0.82	0.24	0.19
Average 11/01 PC LT		**36.236**	**1.48**	**0.90**	**0.25**	**0.20**
Pages Creek-High Tide	4/13/02	36.147				0.16
Pages Creek-High Tide	4/14/02	36.160	1.25	1.31	0.34	0.21
Pages Creek-High Tide	4/16/02	36.153	0.81	2.36	0.33	0.17
Average 4/02 PC HT		**36.153**	**1.03**	**1.83**	**0.33**	**0.19**
Pages Creek-Low Tide	4/13/02	35.124	1.35	1.88	0.55	0.22
Pages Creek-Low Tide	4/14/02	35.167	1.50	1.49	0.58	0.26
Pages Creek-Low Tide	4/16/02	35.327	1.51	2.09	0.71	0.23
Average 4/02 PC LT		**35.206**	**1.45**	**1.82**	**0.61**	**0.23**

Table IV-12: Futch Creek estuary high tide and low tide radium isotope ratios

		Salinity ppt	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	$^{223}Ra/^{224}Ra$
Futch Creek-High Tide	4/21/01	35.587	1.01	1.95	0.31	0.16
Futch Creek-High Tide	4/22/01	35.429	1.65	0.97	0.31	0.20
Average 4/01 FC HT		**35.508**	**1.33**	**1.46**	**0.31**	**0.18**
Futch Creek-Low Tide	4/21/01	23.693	1.24	1.40	0.41	0.23
Futch Creek-Low Tide	4/22/01	26.936	1.41	1.53	0.35	0.16
Average 4/01 FC LT		**25.314**	**1.33**	**1.47**	**0.38**	**0.20**
Futch Creek-High Tide	11/12/01	36.348	1.81	0.51	0.19	0.20
Futch Creek-High Tide	11/13/01	36.427	1.22	0.46	0.16	0.29
Futch Creek-High Tide	11/15/01	36.434	1.24	0.66	0.14	0.17
Futch Creek-High Tide	11/16/01	35.427	1.38	0.82	0.17	0.15
Futch Creek-High Tide	11/18/01	36.481	1.31	0.51	0.23	0.35
Average 11/01 FC HT		**36.223**	**1.39**	**0.59**	**0.18**	**0.23**
Futch Creek-Low Tide	11/12/01	33.783	1.43	1.36	0.36	0.19
Futch Creek-Low Tide	11/13/01	34.392	1.26	1.31	0.29	0.18
Futch Creek-Low Tide	11/15/01	34.964	1.18	1.36	0.18	0.11
Futch Creek-Low Tide	11/16/01	34.908	1.26	1.31	0.35	0.21
Futch Creek-Low Tide	11/18/01	34.560	1.36	1.10	0.30	0.20
Average 11/01 FC LT		**34.521**	**1.30**	**1.29**	**0.30**	**0.18**
Futch Creek-High Tide	4/13/02	35.911	1.38	1.65	0.49	0.21
Futch Creek-High Tide	4/14/02	35.917	1.50	1.32	0.34	0.17
Futch Creek-High Tide	4/16/02	35.991	1.26	2.07	0.39	0.15
Average 4/02 FC HT		**35.939**	**1.38**	**1.68**	**0.41**	**0.18**
Futch Creek-Low Tide	4/13/02	32.446				0.20
Futch Creek-Low Tide	4/14/02	32.934	1.59	1.53	0.44	0.18
Futch Creek-Low Tide	4/16/02	30.843	1.52	1.13	0.69	0.40
Average 4/02 FC LT		**32.074**	**1.56**	**1.33**	**0.57**	**0.29**

Table IV-13: Pages and Futch Creek estuary time series: radium isotope ratios

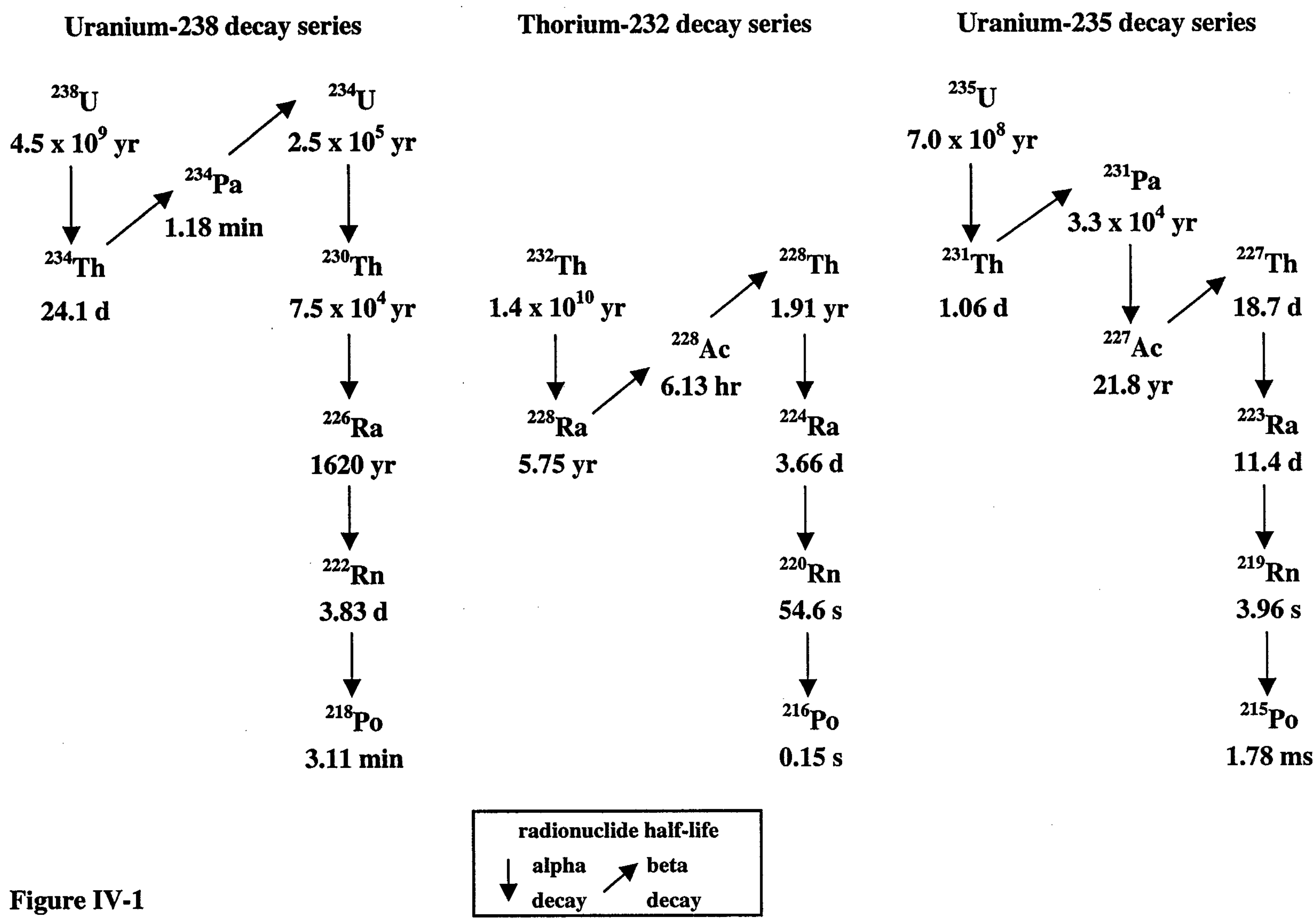
Sampling Date	Sampling Time	Salinity (ppt)	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	$^{223}Ra/^{224}Ra$
Pages Creek time series						
11/13/01	5:25	36.414	1.35	1.00	0.30	0.22
11/13/01	7:23	36.404	1.20	0.71	0.27	0.31
11/13/01	8:24	36.415	1.60	0.40	0.24	0.38
11/13/01	9:28	36.399	1.37	0.85	0.25	0.21
11/13/01	10:18	36.382	1.65	0.75	0.25	0.20
11/13/01	11:20	36.300	1.54	1.05	0.24	0.15
11/13/01	11:27	36.460	1.29	1.22	0.22	0.14
11/13/01	12:03	36.360	1.66	0.85	0.20	0.14
11/13/01	12:42	36.128	1.44	0.88	0.34	0.27
11/13/01	13:25	36.069	1.49	0.63	0.28	0.29
11/13/01	14:25	36.368	1.65	0.81	0.25	0.19
11/13/01	15:20	36.465	1.49	0.78	0.21	0.18
11/13/01	16:21	36.406	1.42	0.84	0.24	0.20
11/13/01	17:20	36.424	1.51	0.69	0.22	0.22
11/13/01	18:22	36.415	1.71	1.12	0.40	0.21
11/13/01	19:20	36.403	1.54	1.27	0.34	0.17
Pages Creek time series						
4/14/02	8:42	36.136	1.51	1.33	0.36	0.18
4/14/02	9:50	36.160	1.25	1.31	0.34	0.21
4/14/02	10:57	36.140	1.00	1.27	0.21	0.16
4/14/02	11:57	36.105	1.30	1.17	0.35	0.23
4/14/02	12:57	35.939	1.90	0.90	0.37	0.22
4/14/02	13:57	35.811	1.39	1.29	0.47	0.26
4/14/02	14:37	35.597	1.41	1.52	0.48	0.22
4/14/02	15:57	35.167	1.50	1.49	0.58	0.26
4/14/02	16:32	35.220	1.50	1.23	0.34	0.18
4/14/02	17:40	35.734	1.44	1.12	0.23	0.14
4/14/02	18:36	35.999	1.27	2.02	0.49	0.19
4/14/02	19:39	36.082	1.54	1.62	0.48	0.19
Futch Creek time series						
4/16/02	9:07	35.915	1.34	0.94	0.34	0.27
4/16/02	10:00	35.991	1.33	1.67	0.48	0.22
4/16/02	11:10	35.907	1.26	2.07	0.39	0.15
4/16/02	12:10	35.937	1.18	1.43	0.27	0.16
4/16/02	13:13	35.837	1.25	2.28	0.64	0.22
4/16/02	14:00	35.513	1.45	1.66	0.56	0.23
4/16/02	15:16	34.408	1.41	1.22	0.39	0.23
4/16/02	16:13	33.202	1.48	0.84	0.41	0.33
4/16/02	17:18	30.843	1.52	1.13	0.69	0.40
4/16/02	18:17	32.055	1.38	0.83	0.39	0.35
4/16/02	19:00	35.527	1.33	1.73	0.34	0.15
4/16/02	20:00	35.898	1.28	2.02	0.57	0.22

Table IV-14: Inlet high tide and low tide radium isotope ratios

		Salinity ppt	$^{228}Ra/^{226}Ra$	$^{224}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	$^{223}Ra/^{224}Ra$
Rich Inlet-Low Tide	11/17/01	36.5406	1.49	0.67	0.13	0.13
Rich Inlet Mouth-High Tide	4/15/02	36.2359	1.05	0.69	0.17	0.24
Rich Inlet Mouth-High Tide	4/17/02	36.2863	0.95	0.95	0.25	0.28
Rich Inlet @ ICW-High Tide	4/17/02	36.2919	0.85	1.49	0.31	0.24
Average 4/02 RI High Tide		**36.2714**	**0.95**	**1.04**	**0.24**	**0.25**
Rich Inlet Mouth-Low Tide	4/15/02	36.1384	1.02	1.75	0.31	0.17
Rich Inlet Mouth-Low Tide	4/17/02	36.2231	1.31	1.41	0.48	0.26
Rich Inlet @ ICW-Low Tide	4/17/02	36.1130	0.96	1.76	0.30	0.18
Average 4/02 RI-Low Tide		**36.1582**	**1.10**	**1.64**	**0.37**	**0.21**
Mason Inlet Mouth-High Tide	4/15/02	36.2899	1.04	0.82	0.13	0.16
Mason Inlet @ ICW-High Tide	4/17/02	36.2155	1.00	0.72	0.18	0.25
Average 4/02 MI-High Tide		**36.2527**	**1.02**	**0.77**	**0.16**	**0.20**
Mason Inlet Mouth-Low Tide	4/15/02	36.1686	1.35	1.12	0.20	0.13
Mason Inlet @ ICW-Low Tide	4/17/02	36.1526	1.32	1.53	0.42	0.21
Average 4/02 MI-Low Tide		**36.1606**	**1.33**	**1.33**	**0.31**	**0.17**

Figure IV-1

Uranuim-Thorium decay series.

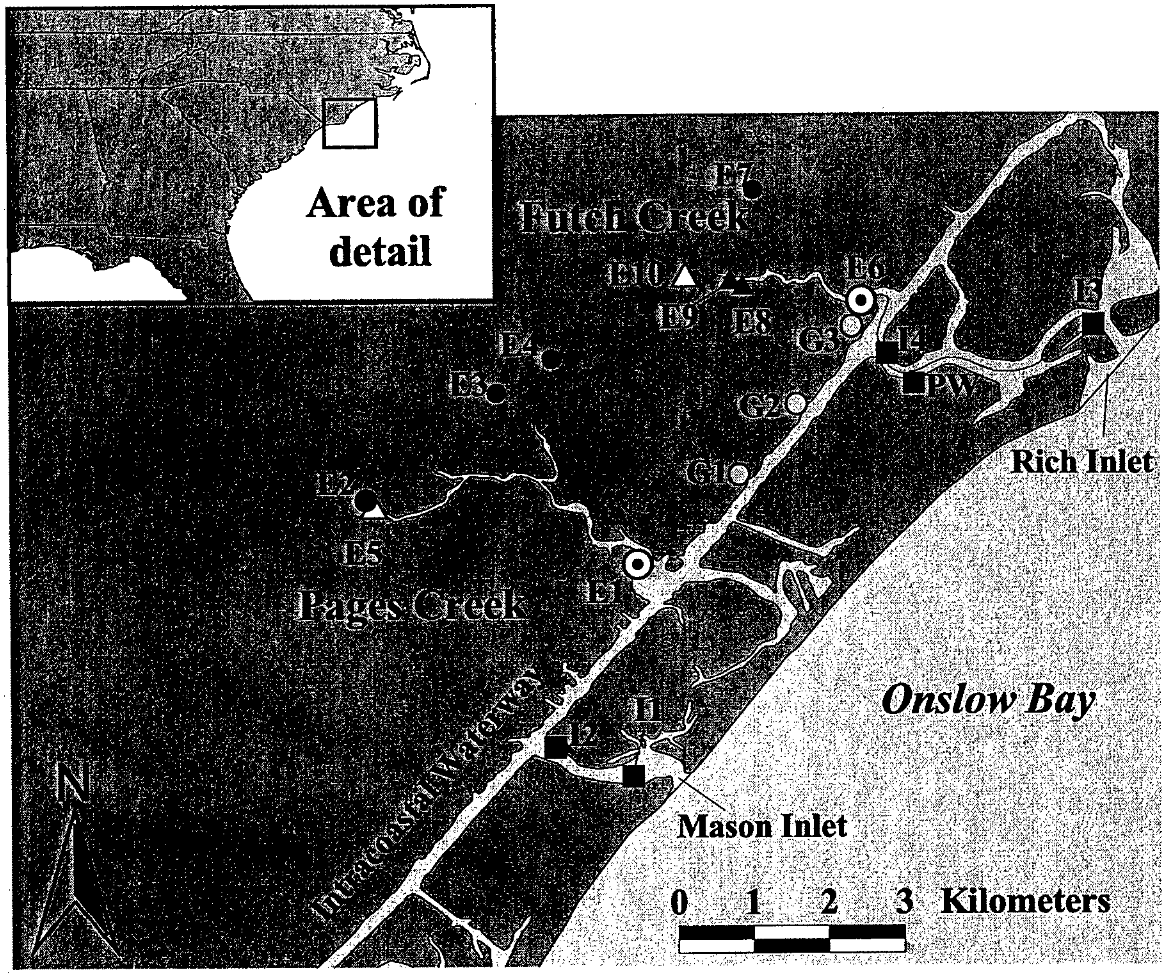


Uranium-238 decay series
Thorium-232 decay series
Uranium-235 decay series
^{238}U
4.5 x 10^9 yr
^{234}Th
24.1 d
^{234}Pa
1.18 min
^{234}U
2.5 x 10^5 yr
^{230}Th
7.5 x 10^4 yr
^{226}Ra
1620 yr
^{222}Rn
3.83 d
^{218}Po
3.11 min
^{232}Th
1.4 x 10^{10} yr
^{228}Ra
5.75 yr
^{228}Ac
6.13 hr
^{228}Th
1.91 yr
^{224}Ra
3.66 d
^{220}Rn
54.6 s
^{216}Po
0.15 s
^{235}U
7.0 x 10^8 yr
^{231}Th
1.06 d
^{231}Pa
3.3 x 10^4 yr
^{227}Ac
21.8 yr
^{227}Th
18.7 d
^{223}Ra
11.4 d
^{219}Rn
3.96 s
^{215}Po
1.78 ms
radionuclide half-life
alpha decay
beta decay

Figure IV-1

Figure IV-2

Map of Cape Fear region of North Carolina, with detail of Pages Creek, Futch Creek, Rich Inlet, and Mason Inlet sample locations.

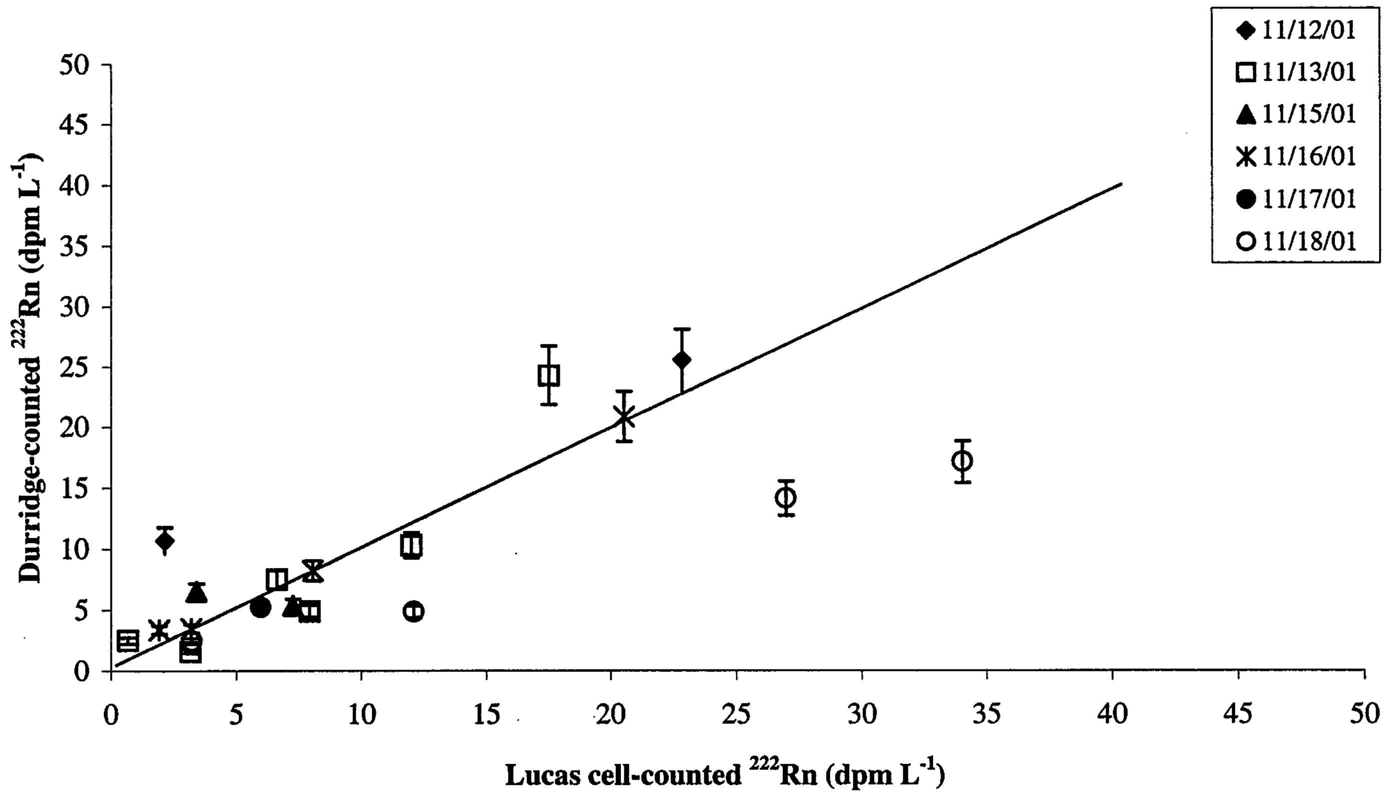


⊙ **Estuary stations (April 2001, November 2001, April 2002)**
● **Streams (November 1999, July 2000, April 2001, November 2001, April 2002)**
△ **Largest springs (November 1999, July 2000, April 2001, November 2001, April 2002)**
▲ **Other springs (April 2001)**
■ **Rich Inlet (November 2001)**
■ **Rich and Mason Inlets (April 2002)**
◎ **NENHC wells (July 2000, April 2002)**

Figure IV-2

Figure IV-3

Comparison of Durridge-counted and Lucas cell-counted ^{222}Rn (in dpm L^{-1}) from November 2001. Radon samples collected simultaneously and measured using both analysis techniques correlate well, and are generally within error.



11/12/01
11/13/01
11/15/01
11/16/01
11/17/01
11/18/01
50
45
40
35
30
25
20
15
10
5
0
Durridge-counted ^{222}Rn (dpm L^{-1})
0
5
10
15
20
25
30
35
40
45
50
Lucas cell-counted ^{222}Rn (dpm L^{-1})

Figure IV-3

Figure IV-4

Pages Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) ^{224}Ra. c) ^{223}Ra. The left circle in each box represents the high tide value (HT) and the right circle the low tide value (LT). Salinity decreased at Pages Creek from high to low tide on all sampling days, with the largest change in salinity in April 2001 and the smallest in November 2001. ^{224}Ra and ^{223}Ra both increased from high tide to low tide during most sampling days in April 2001 and April 2002, but showed no consistent high tide/low tide change during November 2001.

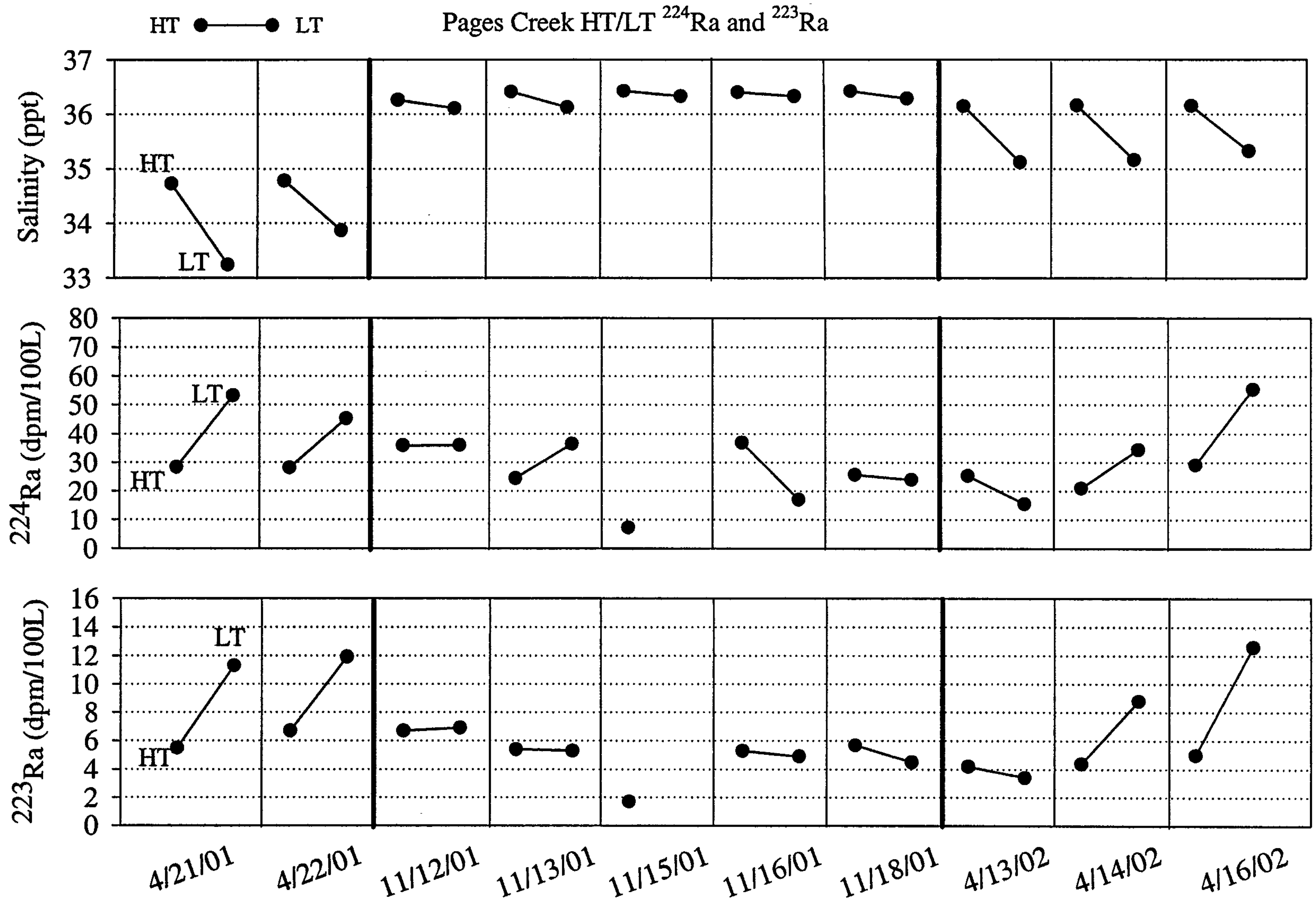

HT LT
Pages Creek HT/LT ^{224}Ra and ^{223}Ra
a.
Salinity (ppt)
37
36
35
34
33
HT
LT
b.
^{224}Ra (dpm/100L)
80
70
60
50
40
30
20
10
0
LT
HT
c.
^{223}Ra (dpm/100L)
16
14
12
10
8
6
4
2
0
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-4

Figure IV-5

Pages Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) ^{226}Ra. c) ^{228}Ra. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). ^{226}Ra and ^{228}Ra increased from high tide to low tide during most sampling days in April 2001 and April 2002, but showed no consistent high tide/low tide change in November 2001.

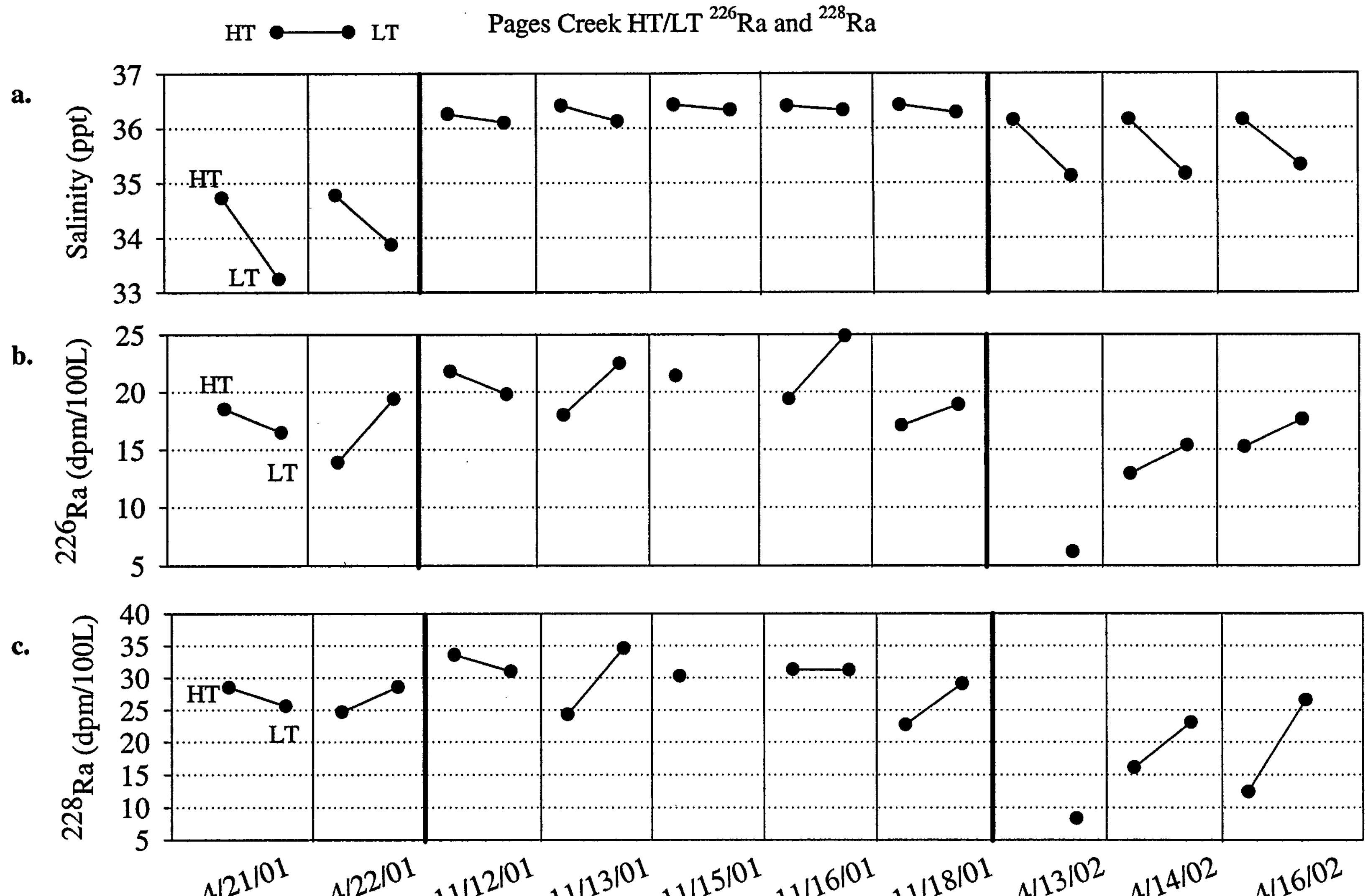

HT LT
Pages Creek HT/LT ^{226}Ra and ^{228}Ra
a.
Salinity (ppt)
37
36
35
34
33
b.
^{226}Ra (dpm/100L)
25
20
15
10
5
c.
^{228}Ra (dpm/100L)
40
35
30
25
20
15
10
5
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-5

Figure IV-6

Pages Creek estuary November 2001 and April 2002 high and low tide a) salinity. b) ^{222}Rn. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). ^{222}Rn increased during most sampling days in November 2001 and April 2002 (no ^{222}Rn samples were collected in April 2001).

Pages Creek

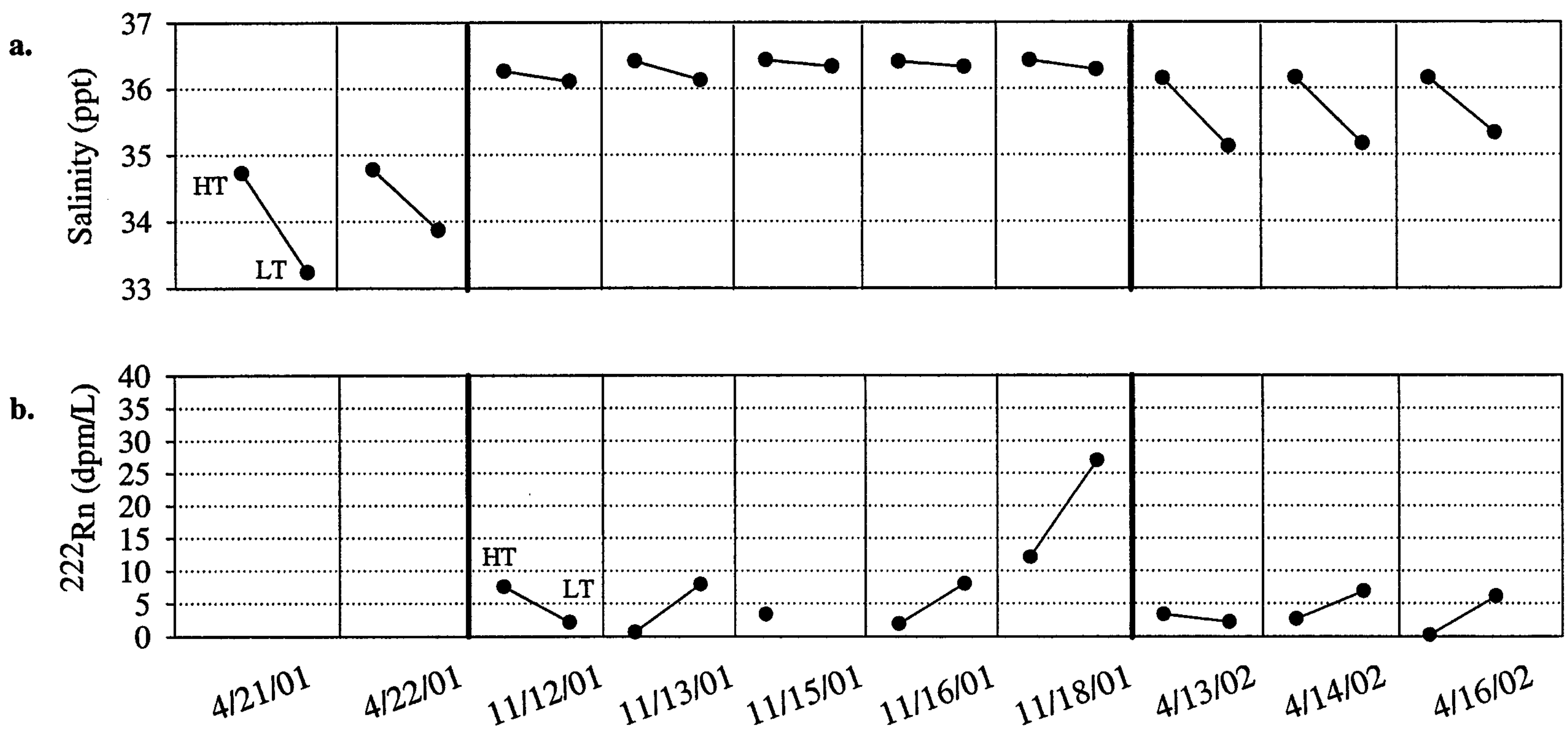
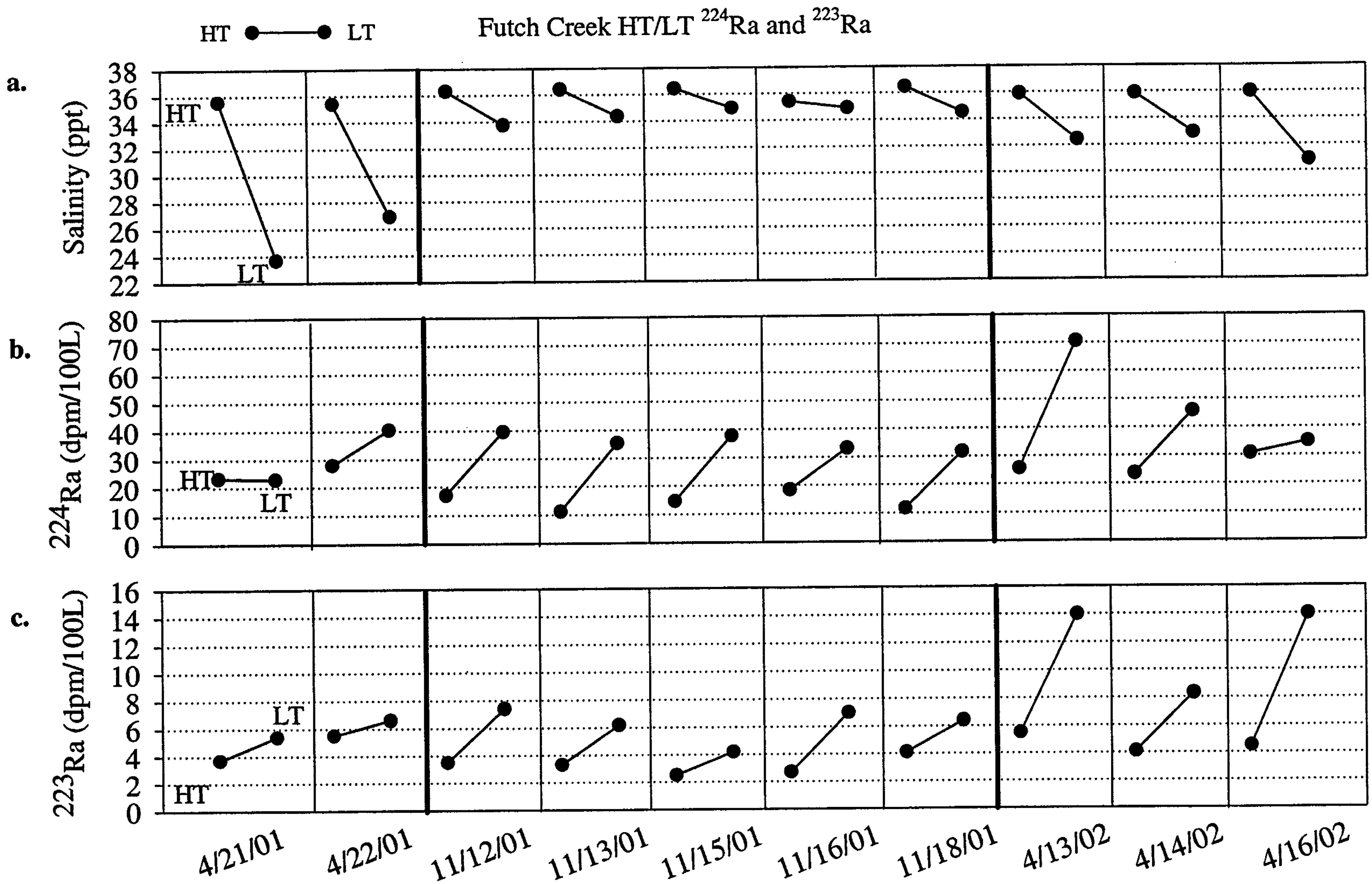


Figure IV-6

Figure IV-7

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) ^{224}Ra. c) ^{223}Ra. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). Salinity decreased from high to low tide during all sampling days, with the largest change in salinity occurring in April 2001, and the smallest in November 2001. ^{224}Ra and ^{223}Ra increased from high tide to low tide on all sampling days. Note that the scale for each isotope is identical to the scale in Figure IV-4 (Pages Creek ^{224}Ra and ^{223}Ra).

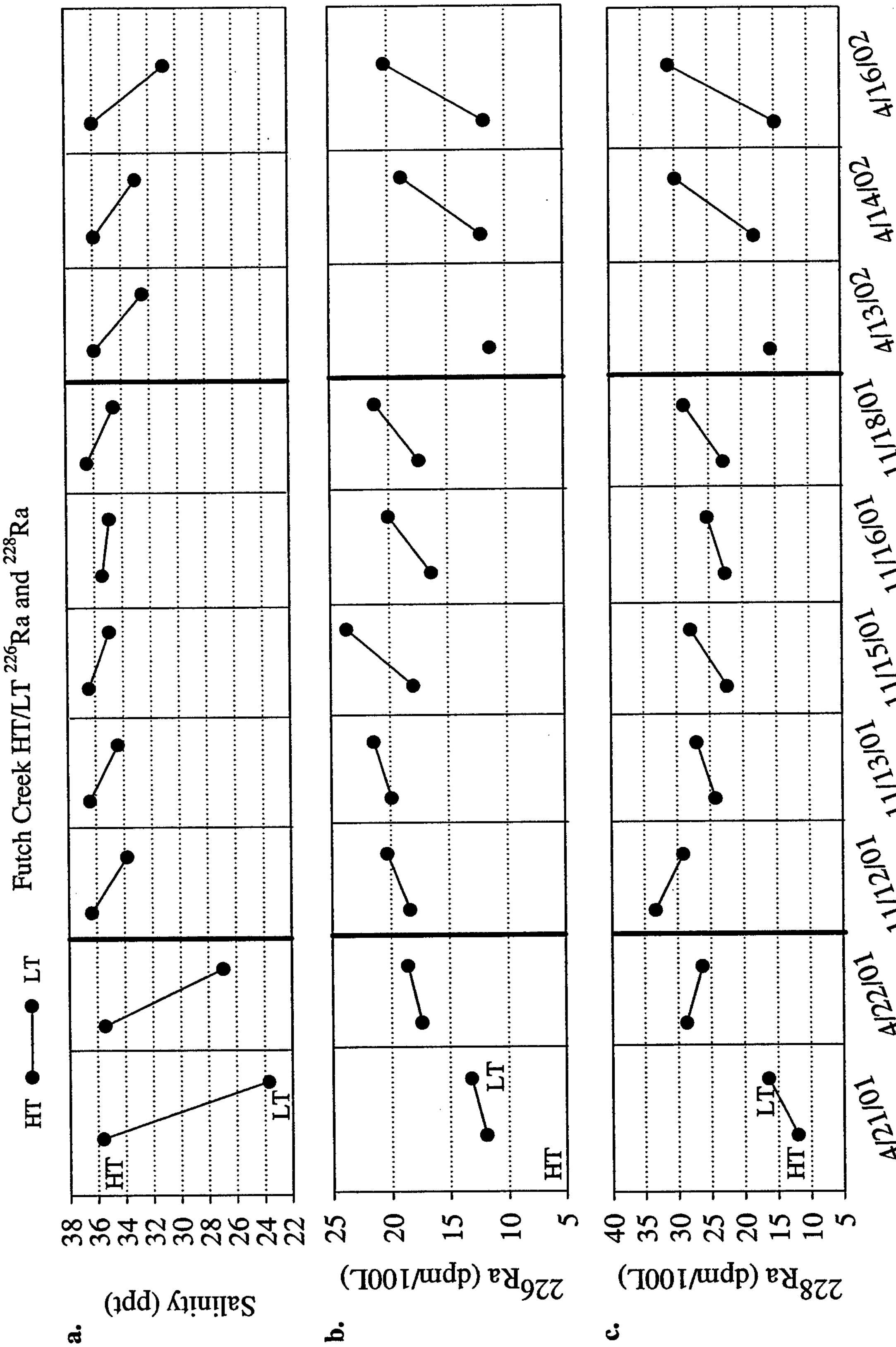


HT LT
Futch Creek HT/LT ^{224}Ra and ^{223}Ra
a.
Salinity (ppt)
38
36
34
32
30
28
26
24
22
HT
LT
b.
^{224}Ra (dpm/100L)
80
70
60
50
40
30
20
10
0
HT
LT
c.
^{223}Ra (dpm/100L)
16
14
12
10
8
6
4
2
0
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-7

Figure IV-8

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) ^{226}Ra. c) ^{228}Ra. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). ^{226}Ra increased from high tide to low tide on all sampling days, and ^{228}Ra on most sampling days. Note that the scale for each isotope is identical to the scale in Figure IV-5 (Pages Creek ^{226}Ra and ^{228}Ra).



Futch Creek HT/LT ^{226}Ra and ^{228}Ra
HT
LT
a.
Salinity (ppt)
38 36 34 32 30 28 26 24 22
b.
^{226}Ra (dpm/100L)
25 20 15 10 5
c.
^{228}Ra (dpm/100L)
40 35 30 25 20 15 10 5
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-8

Figure IV-9

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) ^{222}Rn. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). ^{222}Rn increased from high tide to low tide on all sampling days. Note that the scale for each isotope is identical to the scale in Figure IV-6 (Pages Creek ^{222}Rn); the high tide to low tide change in ^{222}Rn was much greater in the Futch Creek estuary than in the Pages Creek estuary during most sampling days.

Futch Creek

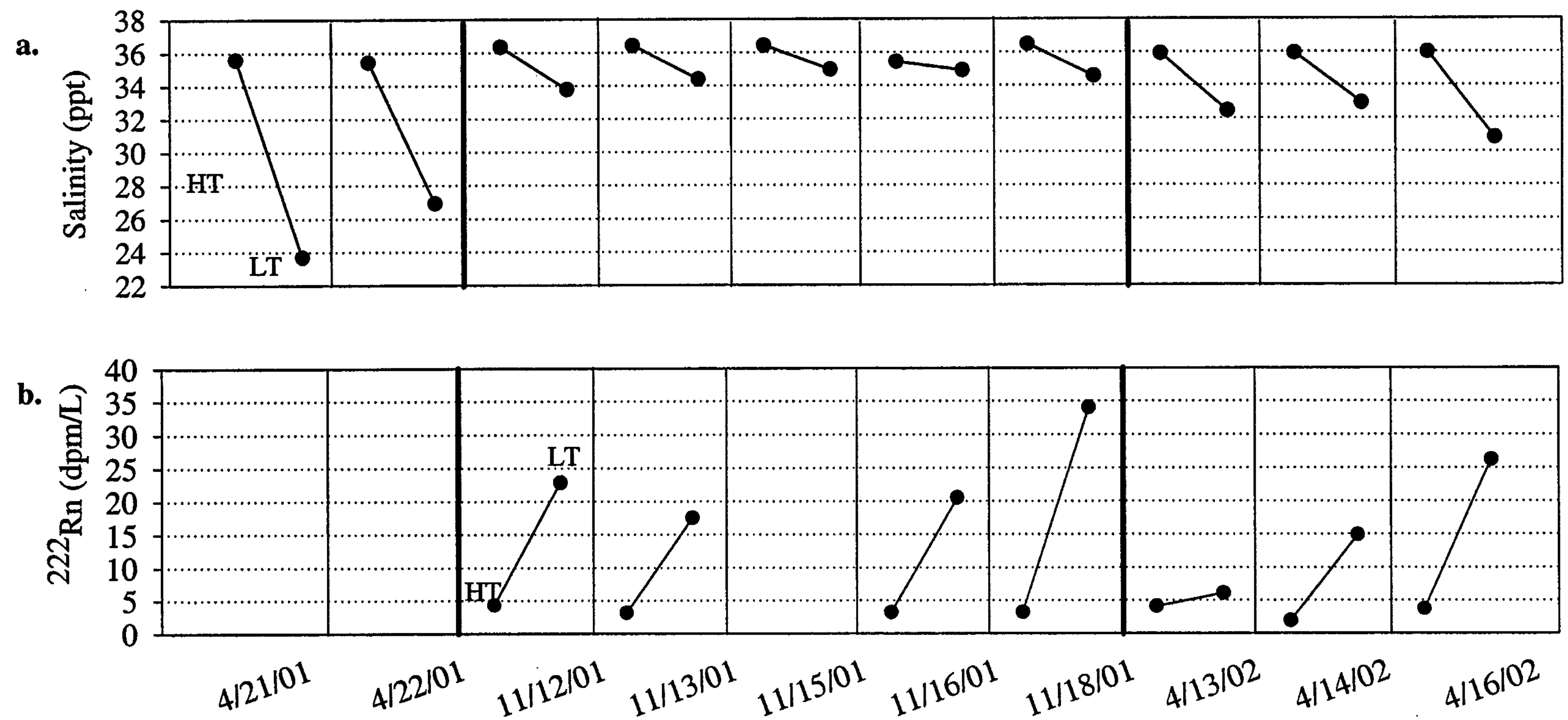


Figure IV-9

Figure IV-10

Time series ^{224}Ra and salinity data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Solid lines represent the salinity values throughout the tidal cycle. Error for each radium measurement is 10%. The Pages Creek November 2001 time series ^{224}Ra and the Futch Creek April 2002 time series ^{224}Ra activities are not closely related to the tidal cycle. However, the Pages Creek April 2002 time series ^{224}Ra activities show a minimum at high tide and a maximum at low tide.

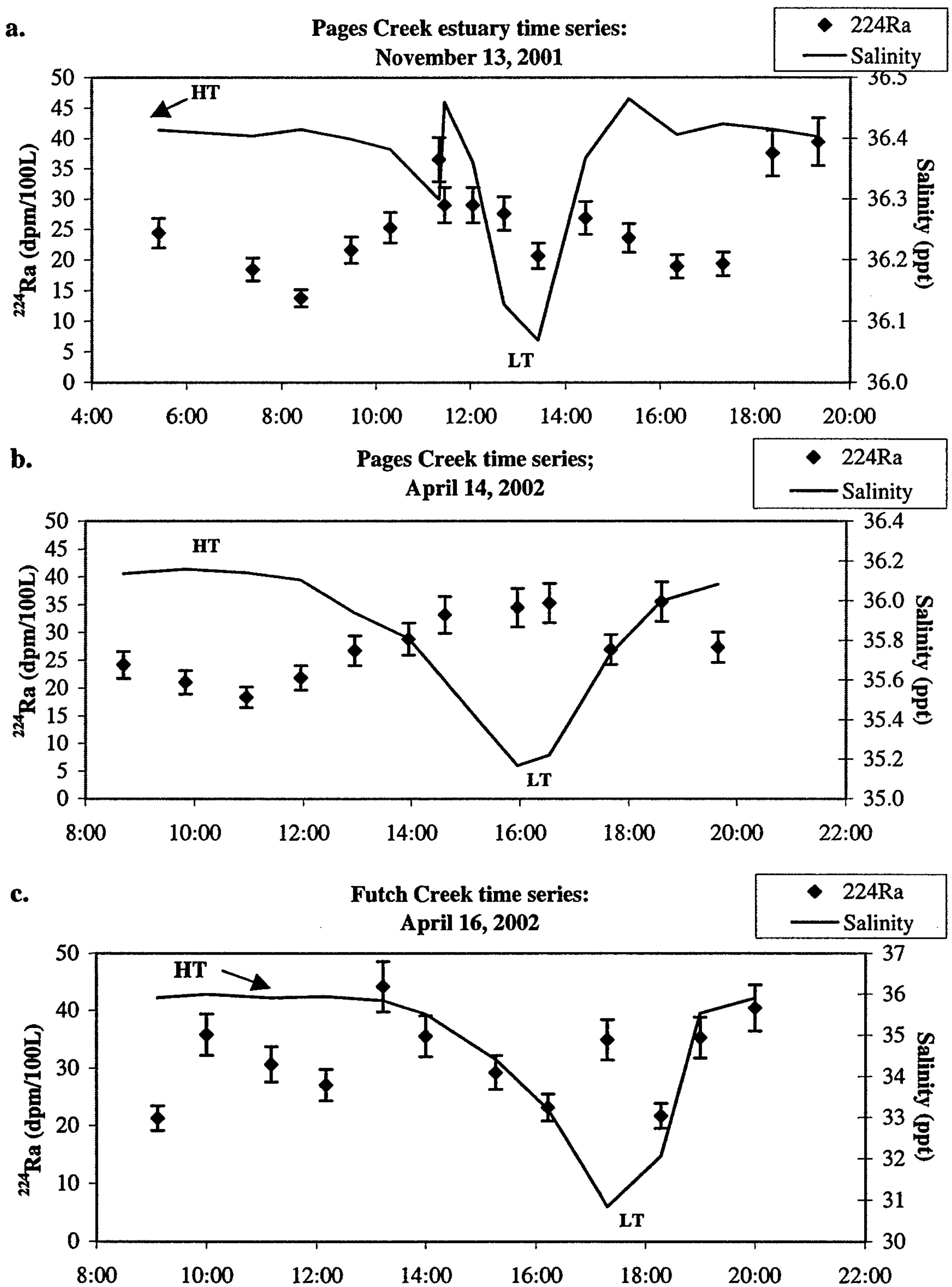

a.
Pages Creek estuary time series:
November 13, 2001
224Ra
Salinity
HT
LT
^{224}Ra (dpm/100L)
Salinity (ppt)
50
45
40
35
30
25
20
15
10
5
0
36.5
36.4
36.3
36.2
36.1
36.0
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
b.
Pages Creek time series;
April 14, 2002
224Ra
Salinity
HT
LT
^{224}Ra (dpm/100L)
Salinity (ppt)
50
45
40
35
30
25
20
15
10
5
0
36.4
36.2
36.0
35.8
35.6
35.4
35.2
35.0
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
c.
Futch Creek time series:
April 16, 2002
224Ra
Salinity
HT
LT
^{224}Ra (dpm/100L)
Salinity (ppt)
50
40
30
20
10
0
37
36
35
34
33
32
31
30
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00

Figure IV-10

Figure IV-11

Time series ^{223}Ra and salinity data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Solid lines represent the salinity values throughout the tidal cycle. Error for each radium measurement is 10%. The Pages Creek November 2001 time series ^{223}Ra shows a maximum at low tide, but little range throughout the rest of the tidal cycle. The Pages Creek April 2002 time series ^{223}Ra activities appear to be related to the tidal cycle, with a minimum at high tide and a maximum at low tide. The Futch Creek April 2002 time series ^{223}Ra activities show a maximum at low tide, but no pattern at other times in the tidal cycle.

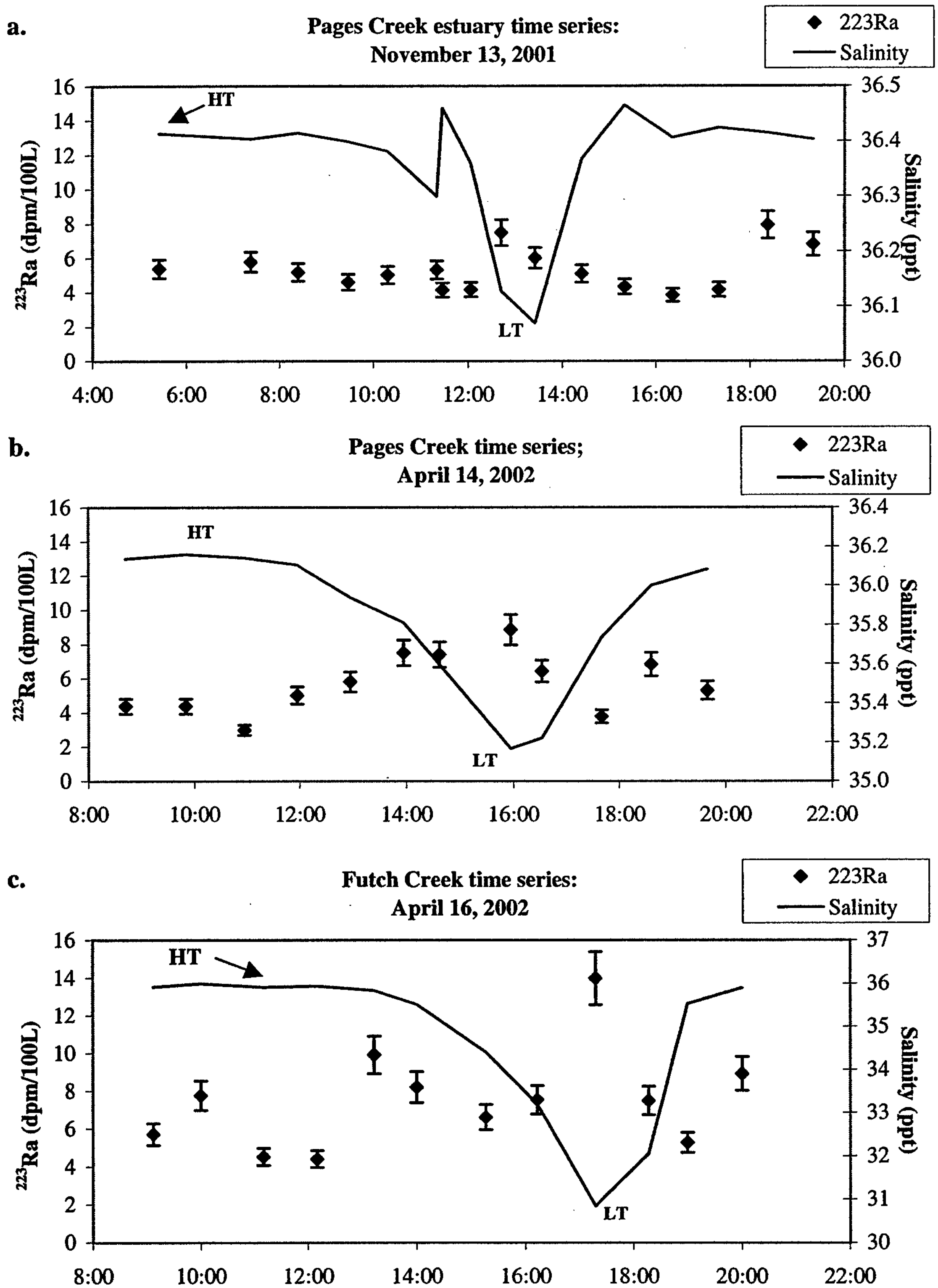
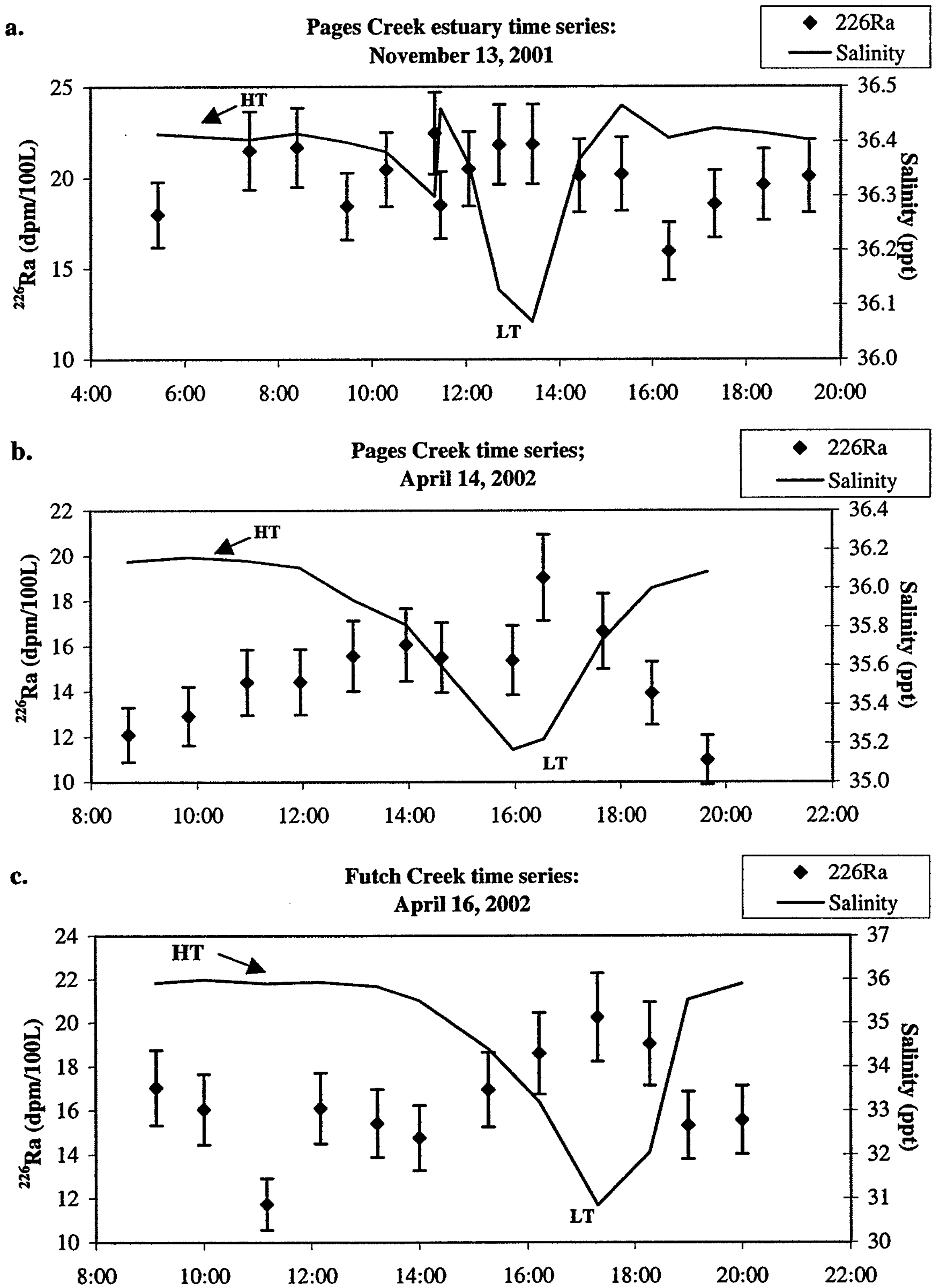

a.
Pages Creek estuary time series:
November 13, 2001
223Ra
Salinity
HT
LT
^{223}Ra (dpm/100L)
Salinity (ppt)
b.
Pages Creek time series;
April 14, 2002
223Ra
Salinity
HT
LT
^{223}Ra (dpm/100L)
Salinity (ppt)
c.
Futch Creek time series:
April 16, 2002
223Ra
Salinity
HT
LT
^{223}Ra (dpm/100L)
Salinity (ppt)

Figure IV-11

Figure IV-12

Time series ^{226}Ra and salinity data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Solid lines represent the salinity values throughout the tidal cycle. Error for each radium measurement is 10%. The Pages Creek November 2001 time series ^{226}Ra shows no clear pattern throughout the tidal cycle. However, both the Pages Creek and Futch Creek April 2002 time series ^{226}Ra activities have maxima at low tide and minima at high tide.



a.
Pages Creek estuary time series:
November 13, 2001
226Ra
Salinity
HT
LT
^{226}Ra (dpm/100L)
Salinity (ppt)
25
20
15
10
36.5
36.4
36.3
36.2
36.1
36.0
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
b.
Pages Creek time series;
April 14, 2002
226Ra
Salinity
HT
LT
^{226}Ra (dpm/100L)
Salinity (ppt)
22
20
18
16
14
12
10
36.4
36.2
36.0
35.8
35.6
35.4
35.2
35.0
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
c.
Futch Creek time series:
April 16, 2002
226Ra
Salinity
HT
LT
^{226}Ra (dpm/100L)
Salinity (ppt)
24
22
20
18
16
14
12
10
37
36
35
34
33
32
31
30
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00

Figure IV-12

Figure IV-13

Time series ^{228}Ra and salinity data for a) November 2001 in Pages Creek. b) April 2002 in Pages Creek. c) April 2002 in Futch Creek. Solid lines represent the salinity values throughout the tidal cycle. Error for each radium measurement is 10%. The Pages Creek November 2001 and April 2002 time series ^{228}Ra show no clear relationship to the tidal cycle. However, the Futch Creek April 2002 time series ^{228}Ra activities show a maximum at low tide, and a minimum at high tide.

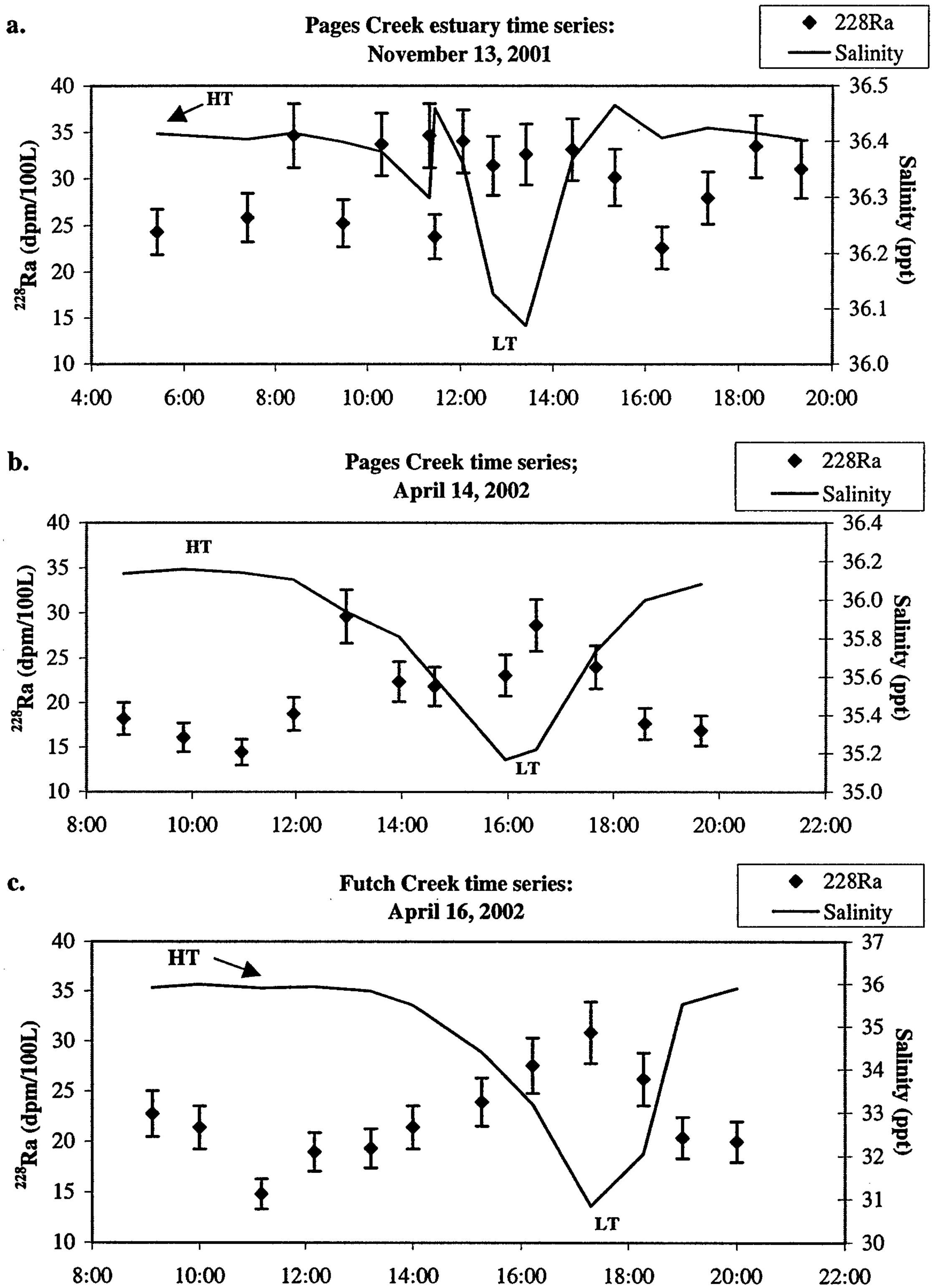
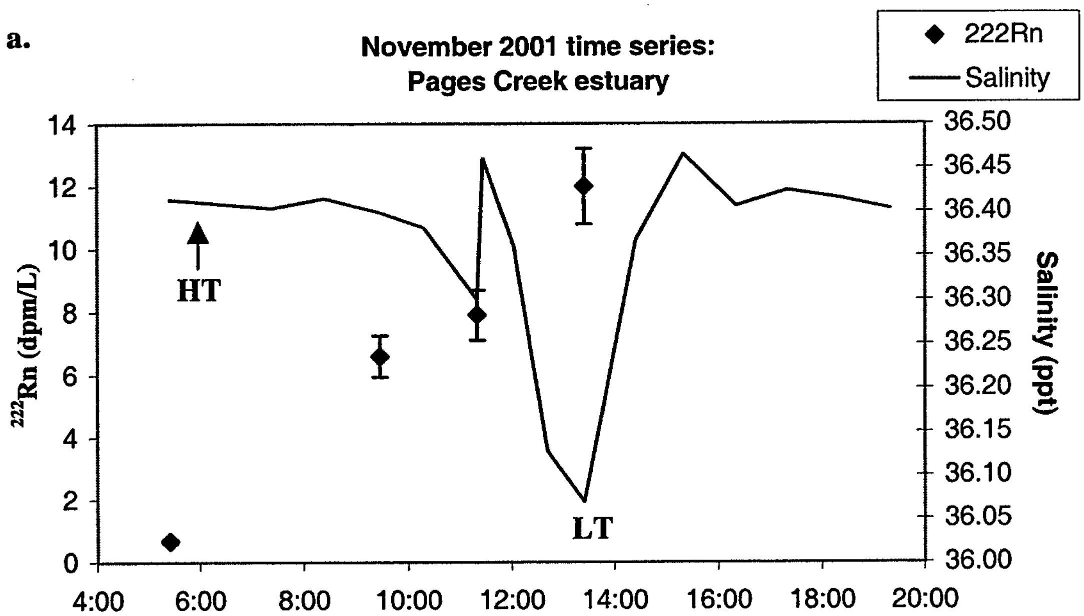

a.
Pages Creek estuary time series:
November 13, 2001
228Ra
Salinity
HT
LT
^{228}Ra (dpm/100L)
Salinity (ppt)
40
35
30
25
20
15
10
36.5
36.4
36.3
36.2
36.1
36.0
4:00
6:00
8:00
10:00
12:00
14:00
16:00
18:00
20:00
b.
Pages Creek time series;
April 14, 2002
228Ra
Salinity
HT
LT
^{228}Ra (dpm/100L)
Salinity (ppt)
36.4
36.2
36.0
35.8
35.6
35.4
35.2
35.0
8:00
10:00
12:00
14:00
16:00
18:00
20:00
22:00
c.
Futch Creek time series:
April 16, 2002
228Ra
Salinity
HT
LT
^{228}Ra (dpm/100L)
Salinity (ppt)
37
36
35
34
33
32
31
30

Figure IV-13

Figure IV-14

Time series ^{222}Rn and salinity data for a) November 2001 in Pages Creek. b) April 2002 in Futch Creek. The solid lines represent the salinity throughout the tidal cycle. Both time series show a strong inverse correlation between the tidal cycle (and salinity) and ^{222}Rn.

a.



b.

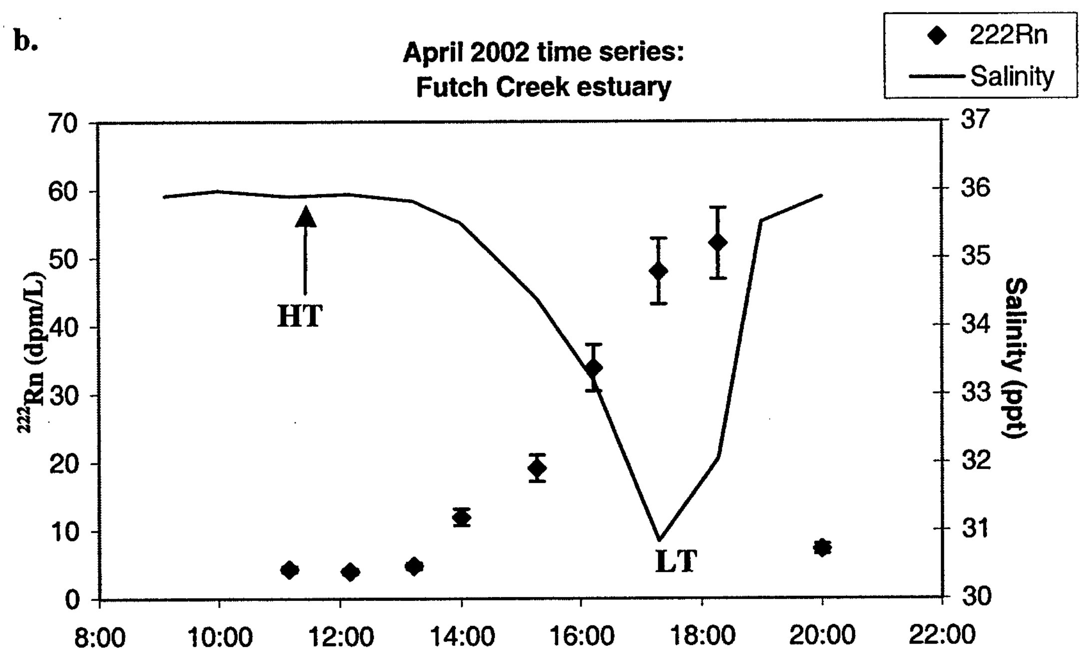


Figure IV-14

Figure IV-15

Rich and Mason Inlet November 2001 low tide and April 2002 high and low tide a) salinity values, b) ^{224}Ra activities, and c) ^{223}Ra activities. No high tide sample was collected from Rich Inlet in November 2001. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). ^{224}Ra and ^{223}Ra increased from high tide to low tide during all sampling days.

Rich and Mason Inlets ^{224}Ra and ^{223}Ra

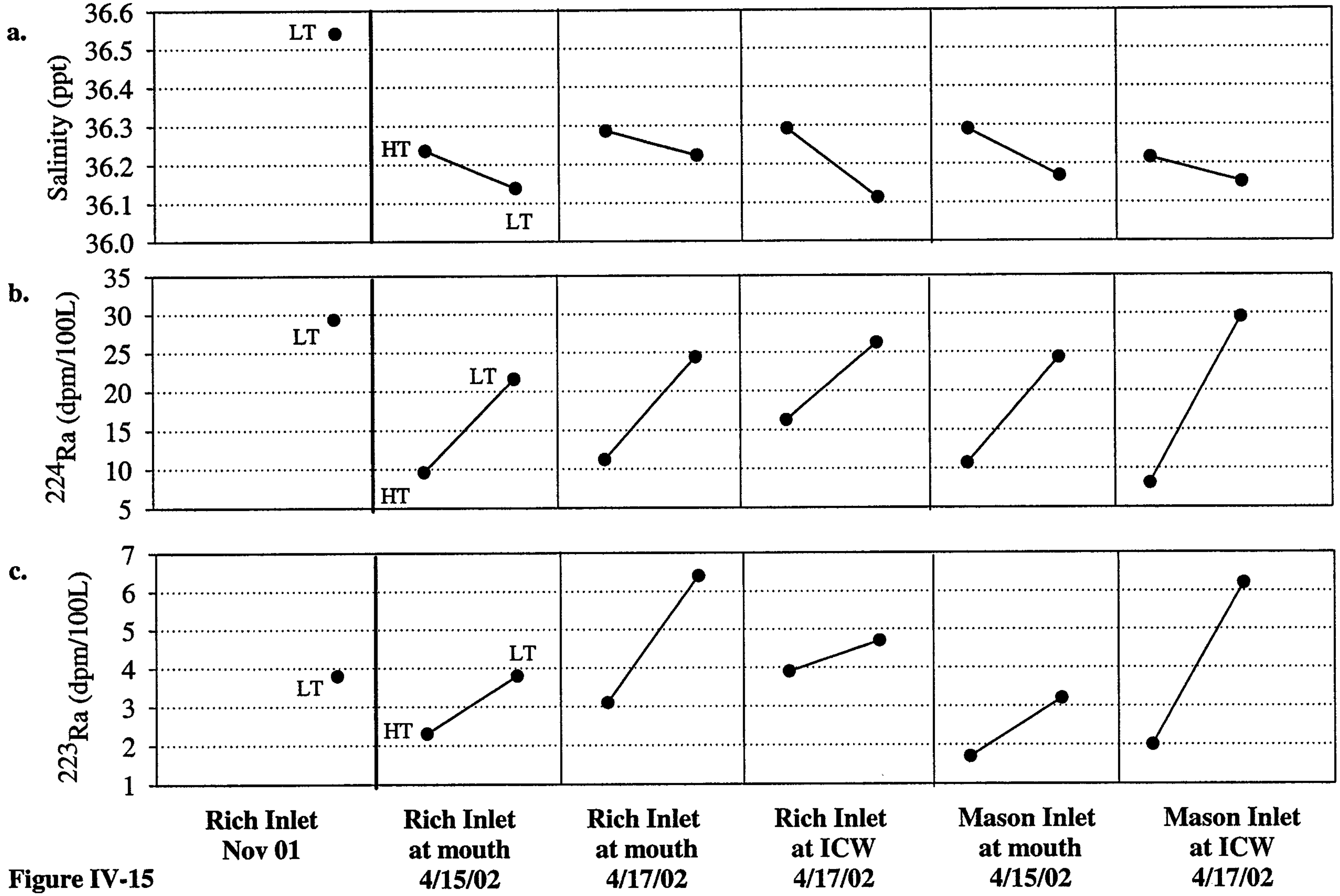


Figure IV-15

Figure IV-16

Rich and Mason Inlet November 2001 low tide and April 2002 high and low tide a) salinity values, b) ^{226}Ra activities, and c) ^{228}Ra activities. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). November 2001 LT ^{226}Ra and ^{228}Ra activities were 2-3 times as high as the April 2002 LT activities. ^{226}Ra and ^{228}Ra increased from high tide to low tide on 4/17/02, but decreased from high tide to low tide on 4/15/02. However, all high tide/low tide differences were small, within a 10% error for both ^{226}Ra and ^{228}Ra.

Rich and Mason Inlets ^{226}Ra and ^{228}Ra

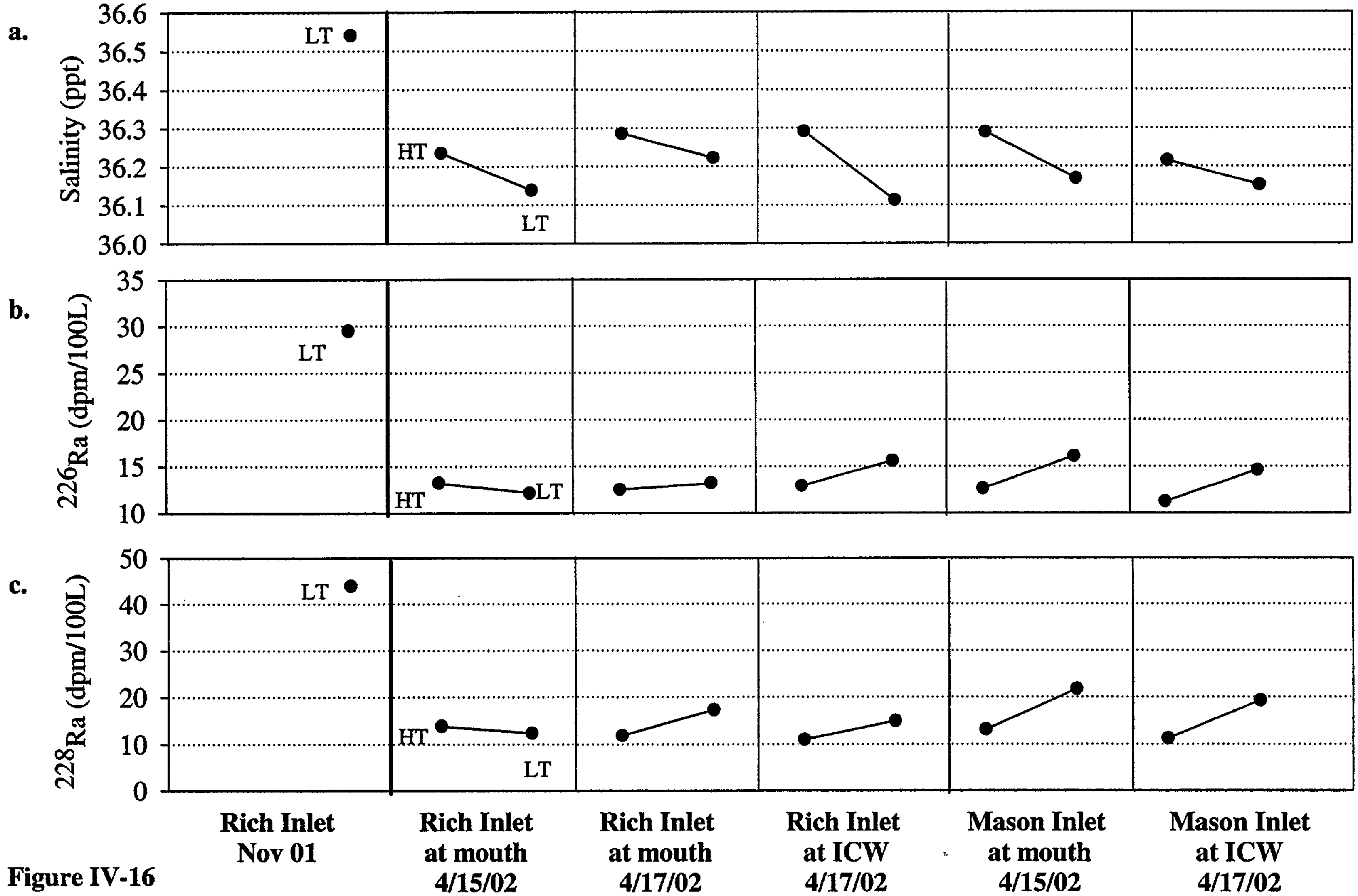
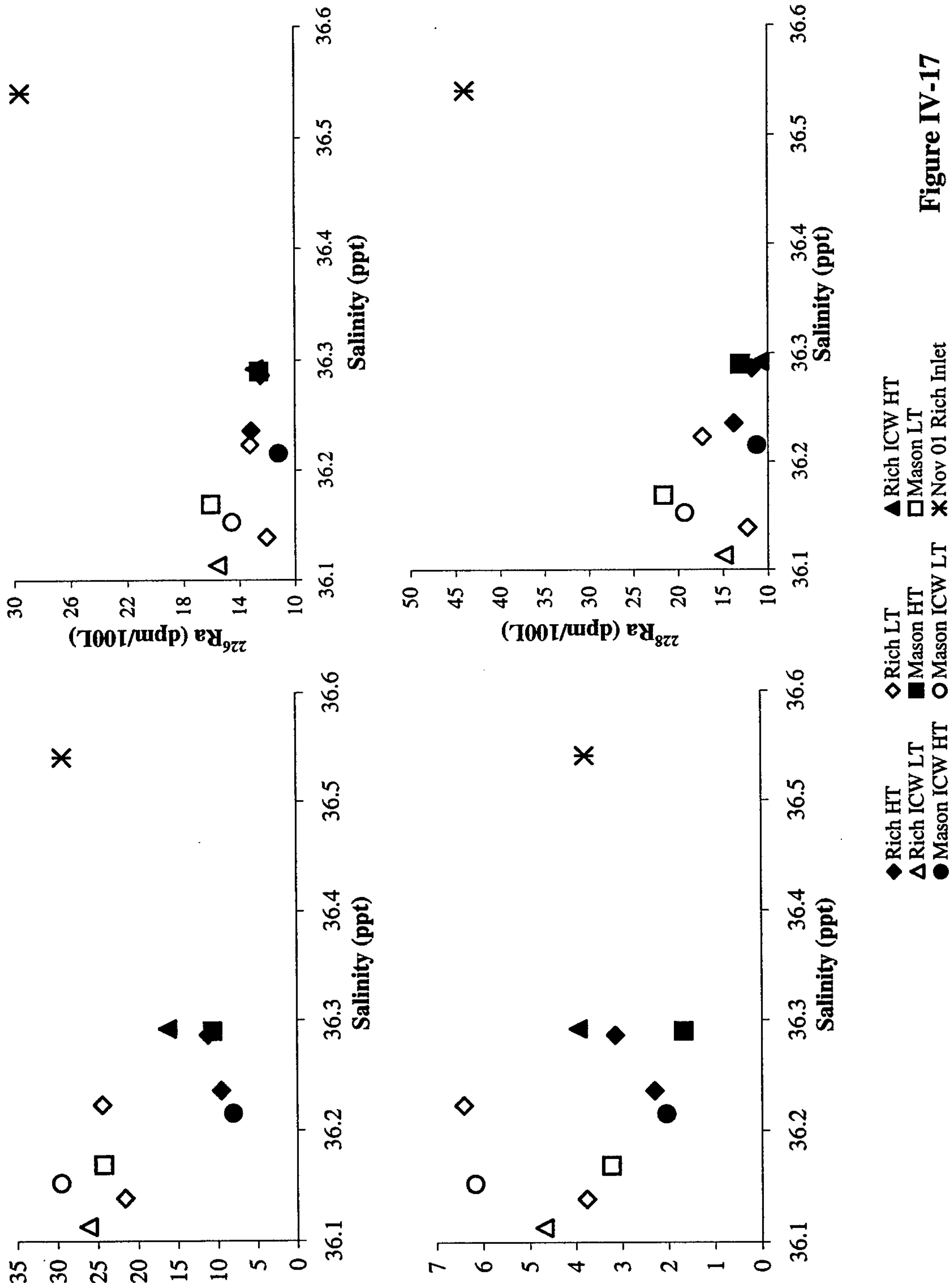


Figure IV-16

Figure IV-17

November 2001 and April 2002 Rich and Mason Inlet high tide (filled symbols) and low tide (open symbols) radium isotopes and salinity. The November 2001 low tide sample had the highest salinity of all inlet samples, and the highest ^{226}Ra and ^{228}Ra activities. The ^{223}Ra and ^{224}Ra activities were within the range of the April 2002 low tide activities.

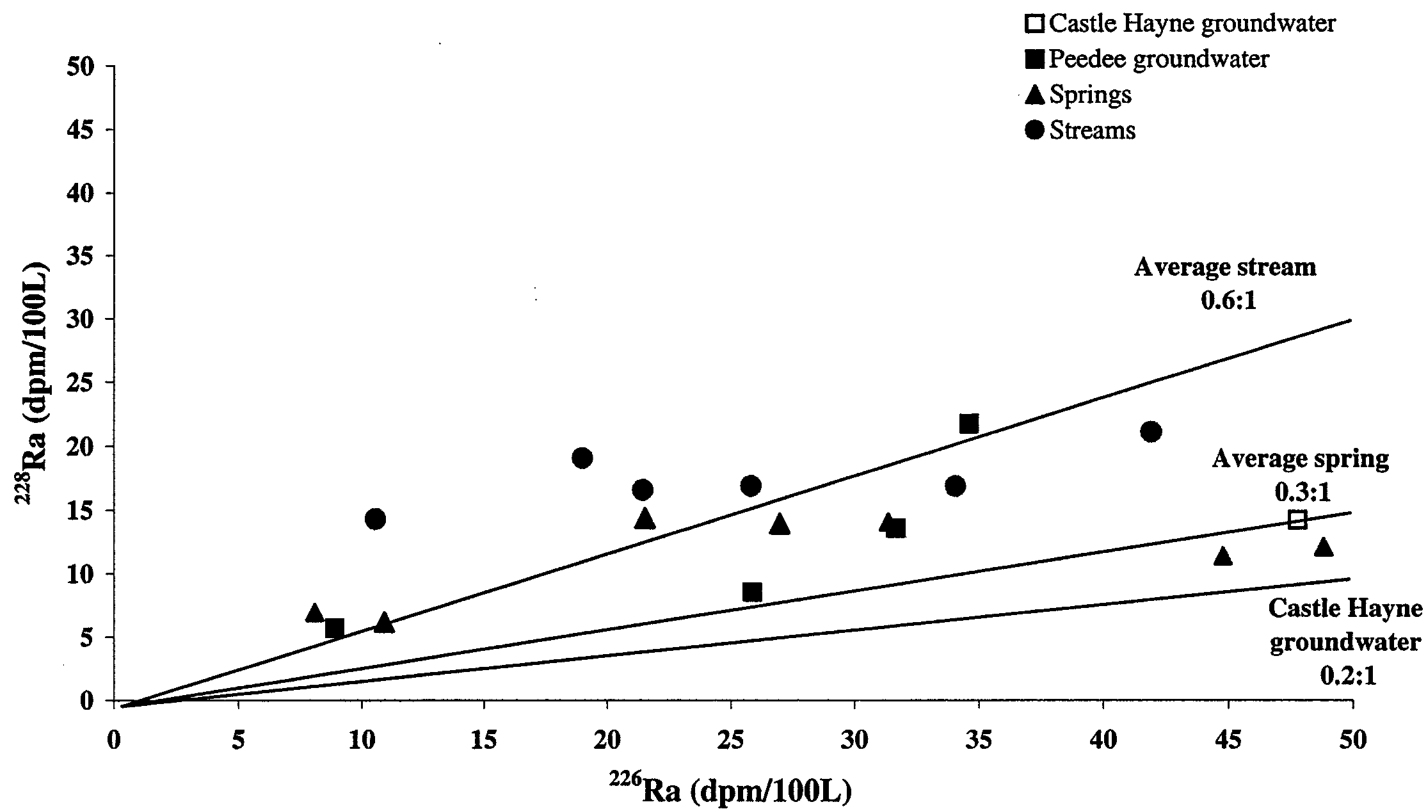


224Ra (dpm/100L)
Salinity (ppt)
226Ra (dpm/100L)
Salinity (ppt)
223Ra (dpm/100L)
Salinity (ppt)
228Ra (dpm/100L)
Salinity (ppt)
Rich HT
Rich ICW LT
Mason ICW HT
Rich LT
Mason HT
Mason ICW LT
Rich ICW HT
Mason LT
Nov 01 Rich Inlet

Figure IV-17

Figure IV-18

Spring, stream, and groundwater ^{228}Ra and ^{226}Ra activities. The average spring $^{228}Ra/^{226}Ra$ activity ratio (AR) is 0.3:1, while the average stream activity ratio is 0.6:1. The average Castle Hayne groundwater activity ratio is 0.2:1. The low $^{228}Ra/^{226}Ra$ activity ratio indicates interaction limestone; groundwater from a limestone aquifer can become enriched in the ^{238}U- and ^{235}U-series daughters ^{226}Ra and ^{223}Ra relative to the ^{232}Th-series daughters ^{228}Ra and ^{224}Ra.



Castle Hayne groundwater
Peedee groundwater
Springs
Streams
Average stream
0.6:1
Average spring
0.3:1
Castle Hayne
groundwater
0.2:1
^{228}Ra (dpm/100L)
^{226}Ra (dpm/100L)
0
5
10
15
20
25
30
35
40
45
50

Figure IV-18

Figure IV-19

Castle Hayne groundwater ^{228}Ra and ^{226}Ra activities (with spring and stream activities). Castle Hayne groundwater $^{228}Ra/^{226}Ra$ is low, with the average Castle Hayne groundwater activity ratio at 0.2:1.

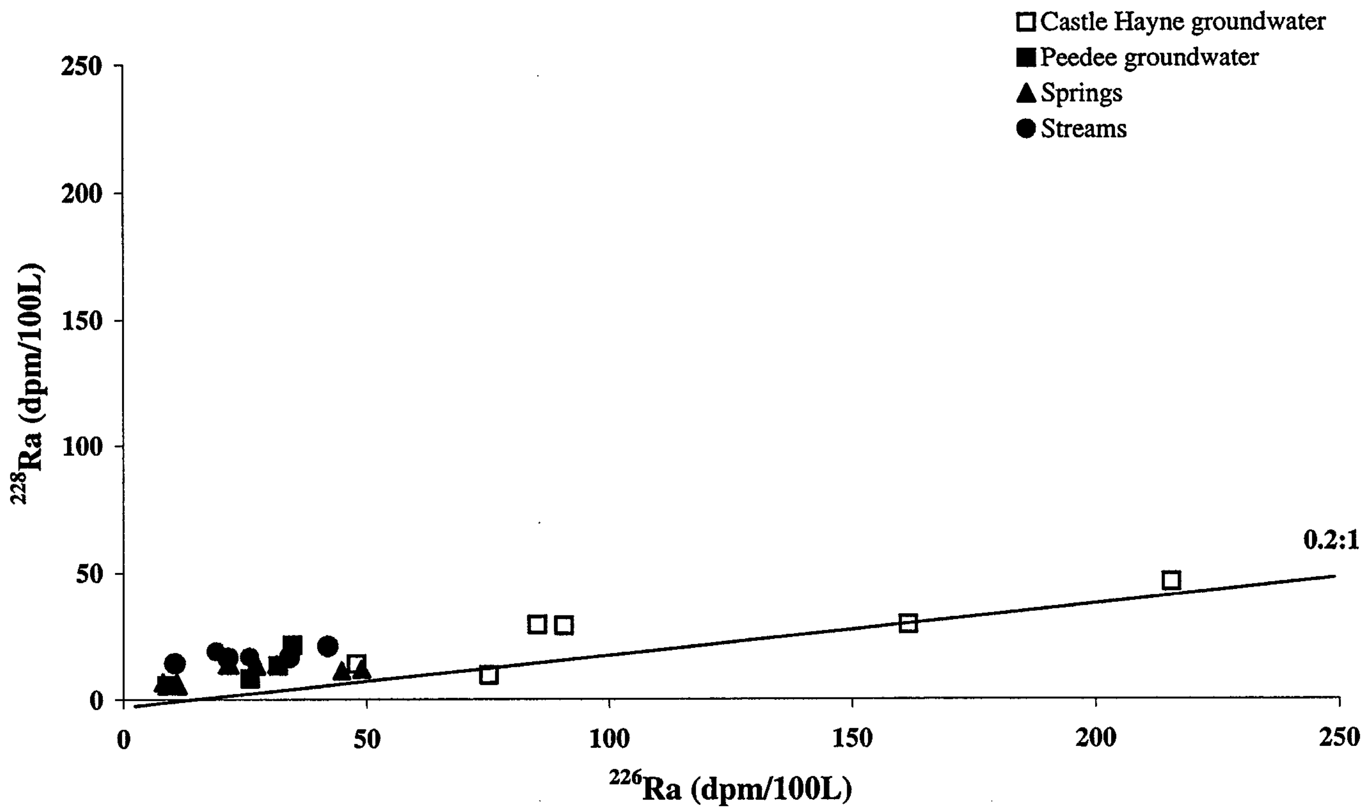
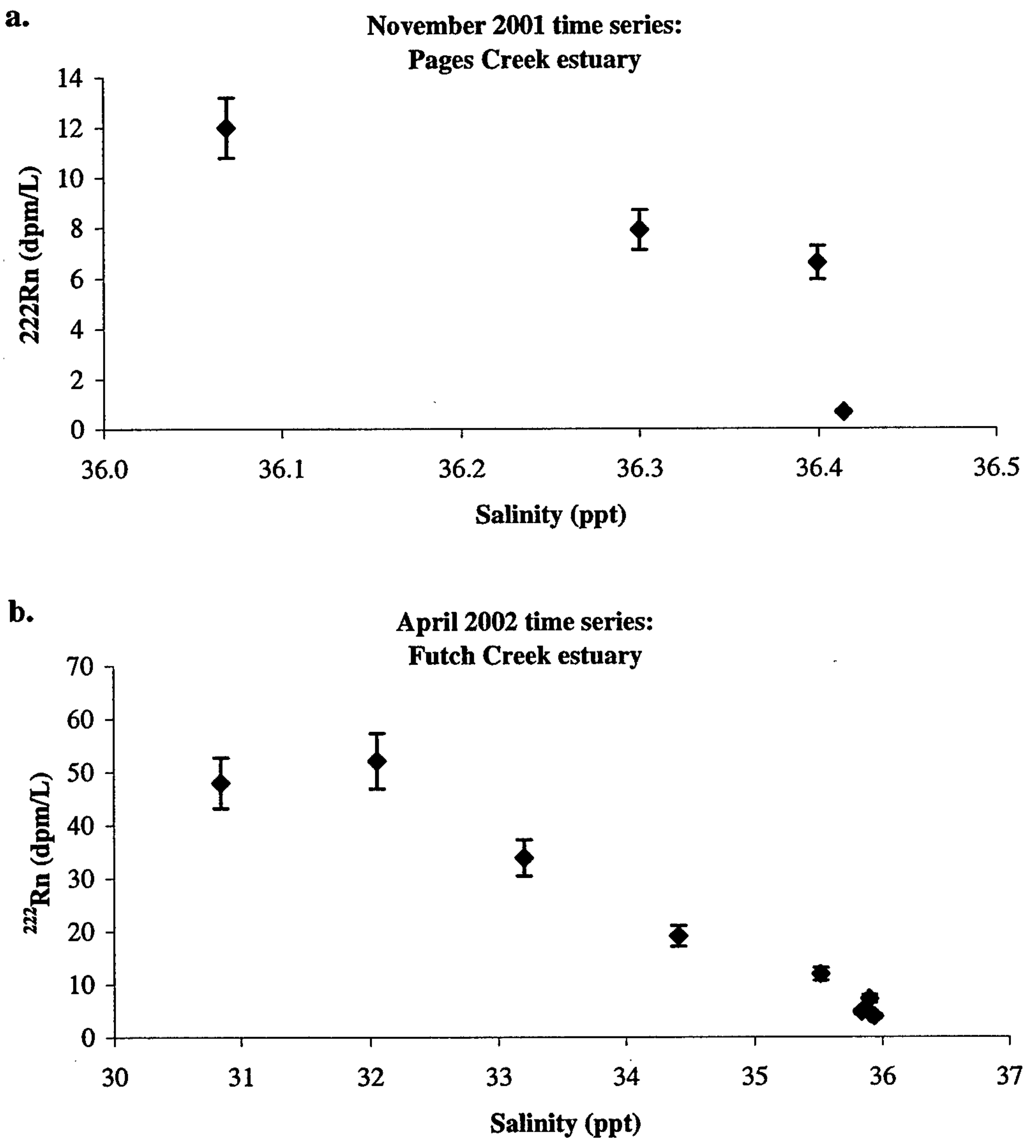

Castle Hayne groundwater
Peedee groundwater
Springs
Streams
250
200
150
100
50
0
228Ra (dpm/100L)
0
50
100
150
200
250
226Ra (dpm/100L)
0.2:1

Figure IV-19

Figure IV-20

^{222}Rn time series data from a) November 2001 Pages Creek. b) April 2002 Futch Creek. Both ^{222}Rn time series show a close inverse correlation with salinity.



a.
November 2001 time series:
Pages Creek estuary
222Rn (dpm/L)
0
2
4
6
8
10
12
14
36.0
36.1
36.2
36.3
36.4
36.5
Salinity (ppt)
b.
April 2002 time series:
Futch Creek estuary
222Rn (dpm/L)
0
10
20
30
40
50
60
70
30
31
32
33
34
35
36
37
Salinity (ppt)

Figure IV-20

Figure IV-21

^{222}Rn time series data plotted with a) spring ^{222}Rn activities and b) Castle Hayne groundwater ^{222}Rn activities. A regression through the time series data to the zero-salinity point plots within the range of Futch and Pages springs, suggesting that spring inputs can account for all of the observed excess ^{222}Rn in Futch Creek in April 2002. Castle Hayne groundwater ^{222}Rn is much higher than spring ^{222}Rn; much of the ^{222}Rn in the groundwater may be lost to the atmosphere during discharge.

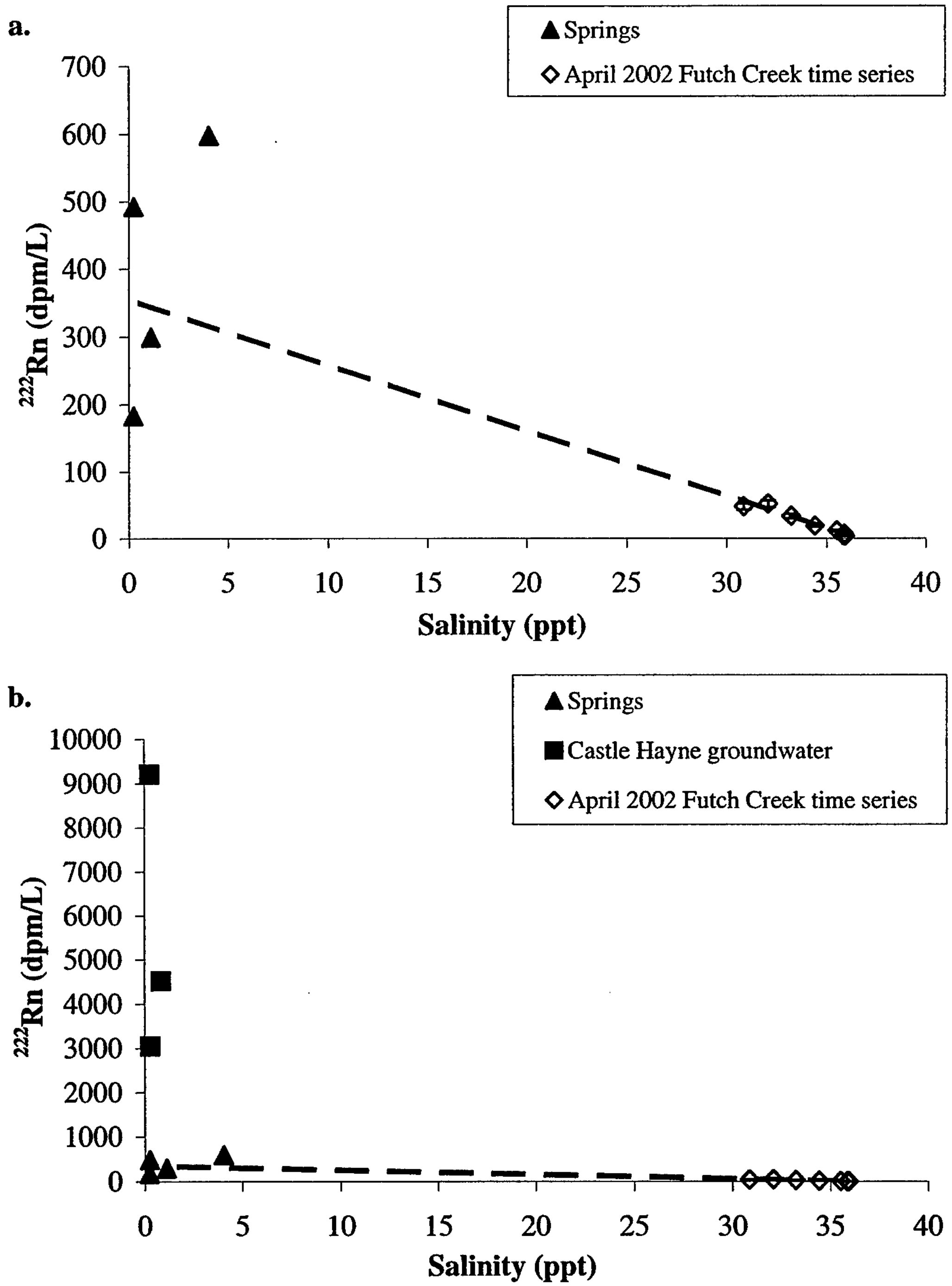
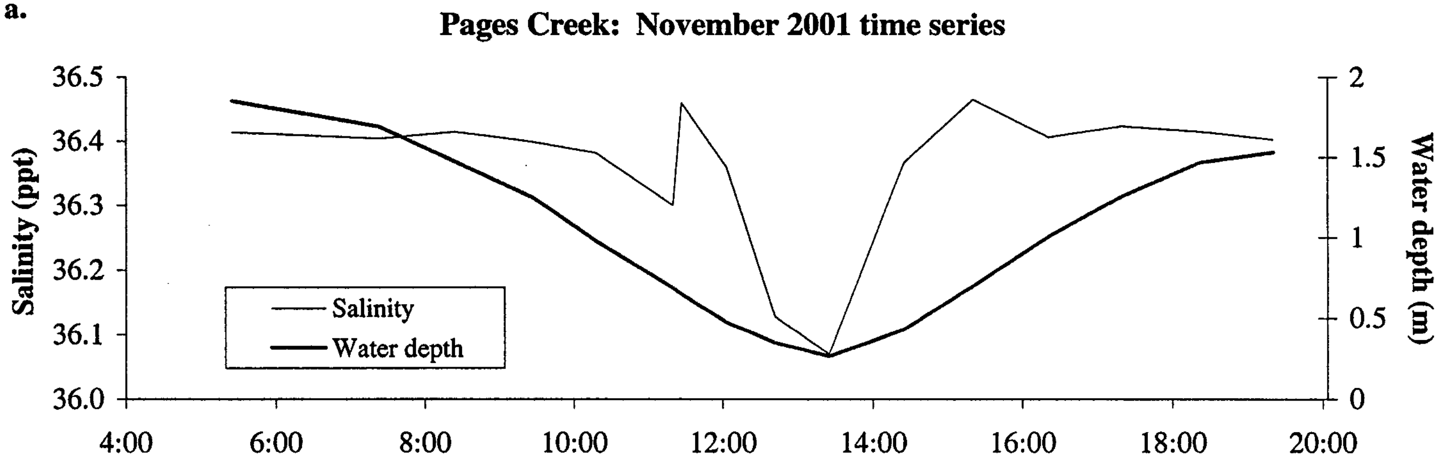

a.
Springs
April 2002 Futch Creek time series
700
600
500
400
300
200
100
0
^{222}Rn (dpm/L)
0
5
10
15
20
25
30
35
40
Salinity (ppt)
b.
Springs
Castle Hayne groundwater
April 2002 Futch Creek time series
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
^{222}Rn (dpm/L)
0
5
10
15
20
25
30
35
40
Salinity (ppt)

Figure IV-21

Figure IV-22

Pages Creek time series salinity and water depth data for a) one tidal cycle in November 2001. b) multiple tidal cycles in April 2002. Salinity data show a small peak ~ two hours prior to full low tide.

a.



b.

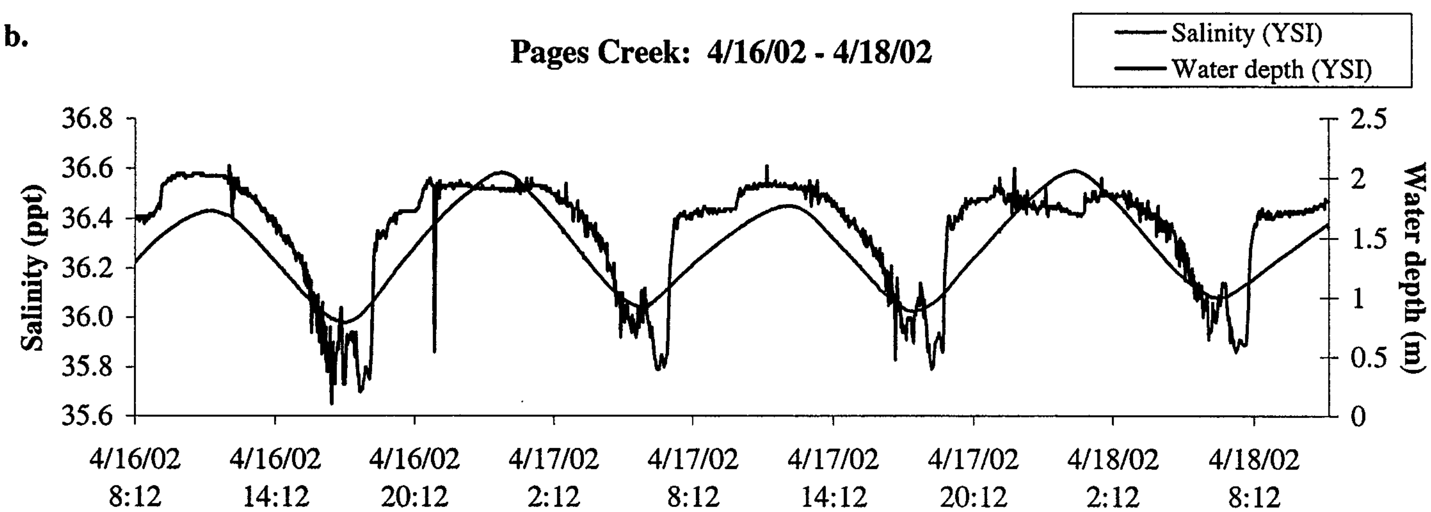


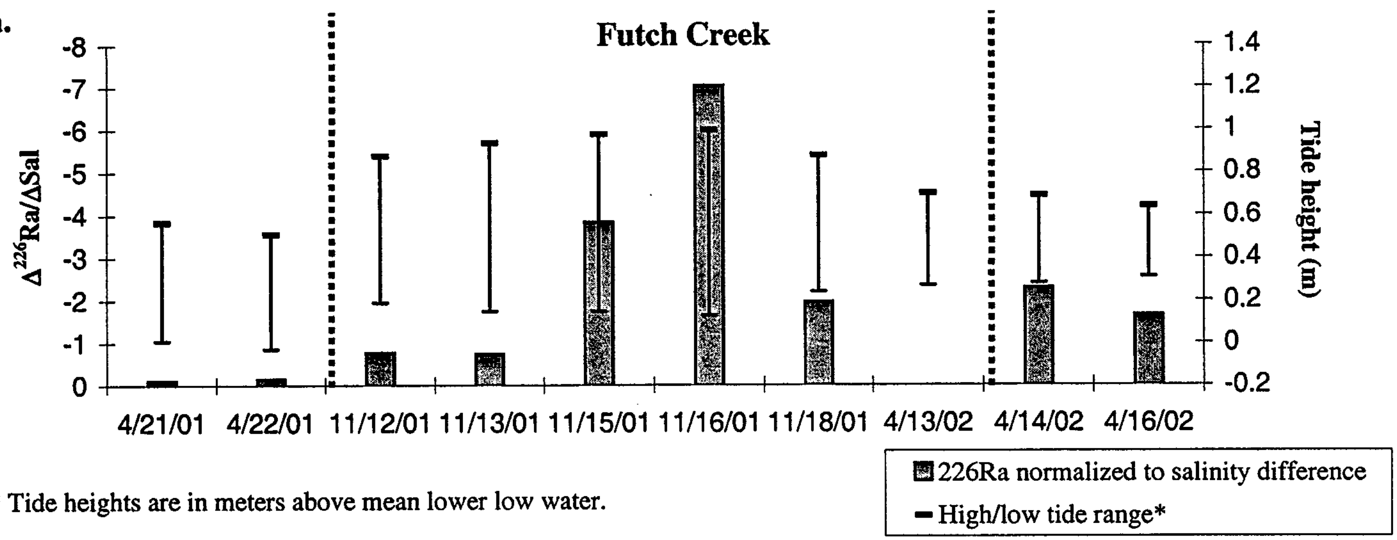
Figure IV-22

Figure IV-23

The high tide/low tide change in a) ^{226}Ra b) ^{228}Ra normalized to the high/low tide change in salinity (ΔSal) at Futch Creek. Bars represent Δ^{226}Ra /ΔSal and Δ^{228}Ra /ΔSal for each sampling day in April 2001, November 2001 and April 2002. Lines represent the tide range between high and low tide for Futch creek (secondary y-axis). In Futch Creek, the highest change in ^{226}Ra relative to salinity change occurred during the full spring tide on November 16, 2001.

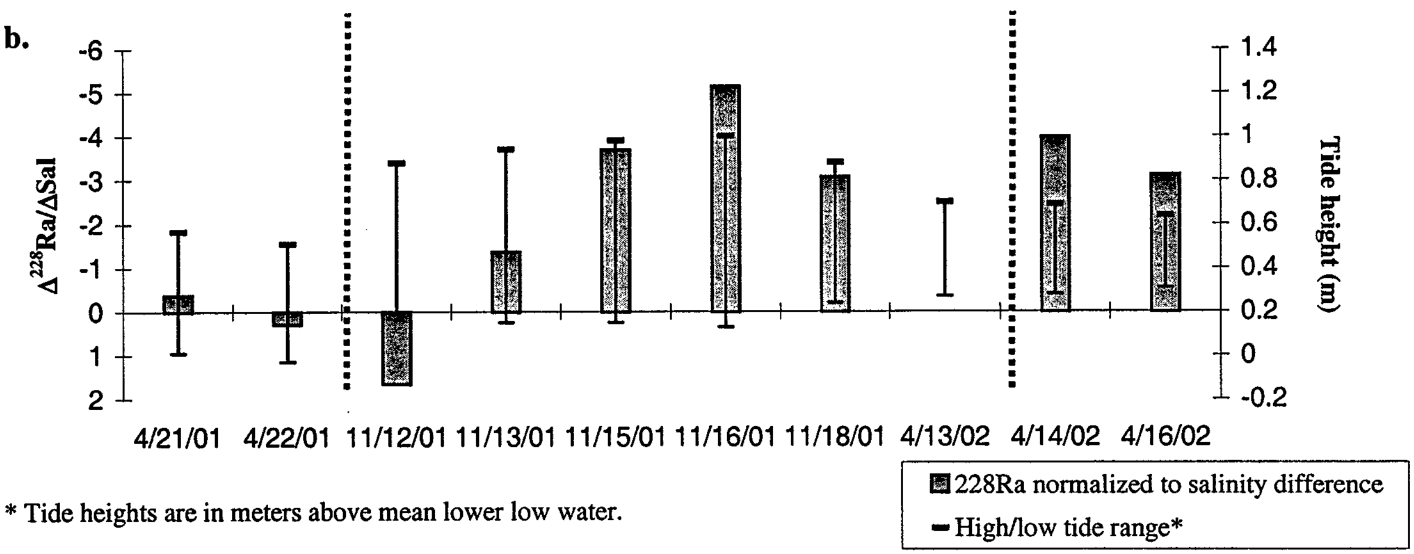
Figure IV-23

a.



* Tide heights are in meters above mean lower low water.

b.



* Tide heights are in meters above mean lower low water.

Figure IV-24

Surficial aquifer and Castle Hayne aquifer well head data for Topsail Beach well from January 2000 through November 2002. The well is located ~ 10 km north of Pages and Futch Creeks. Well head data is relative to meters above mean sea level. The lowest well heads in both the surficial and the Castle Hayne-screened wells occurred in November 2001, during a months-long drought.

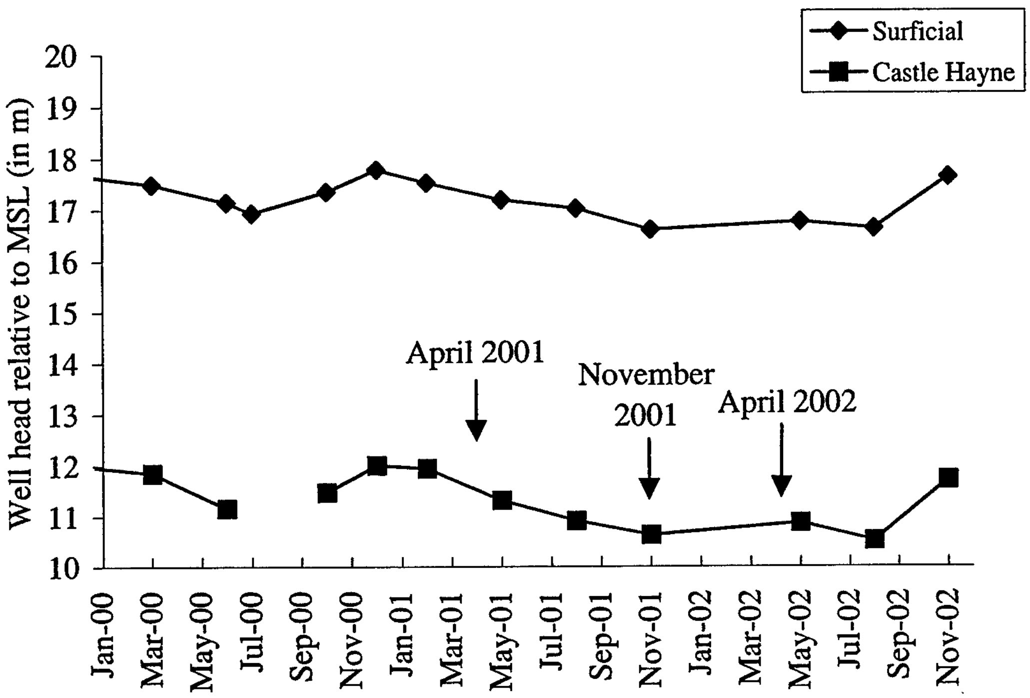

Surficial
Castle Hayne
Well head relative to MSL (in m)
20
19
18
17
16
15
14
13
12
11
10
April 2001
November 2001
April 2002
Jan-00
Mar-00
May-00
Jul-00
Sep-00
Nov-00
Jan-01
Mar-01
May-01
Jul-01
Sep-01
Nov-01
Jan-02
Mar-02
May-02
Jul-02
Sep-02
Nov-02

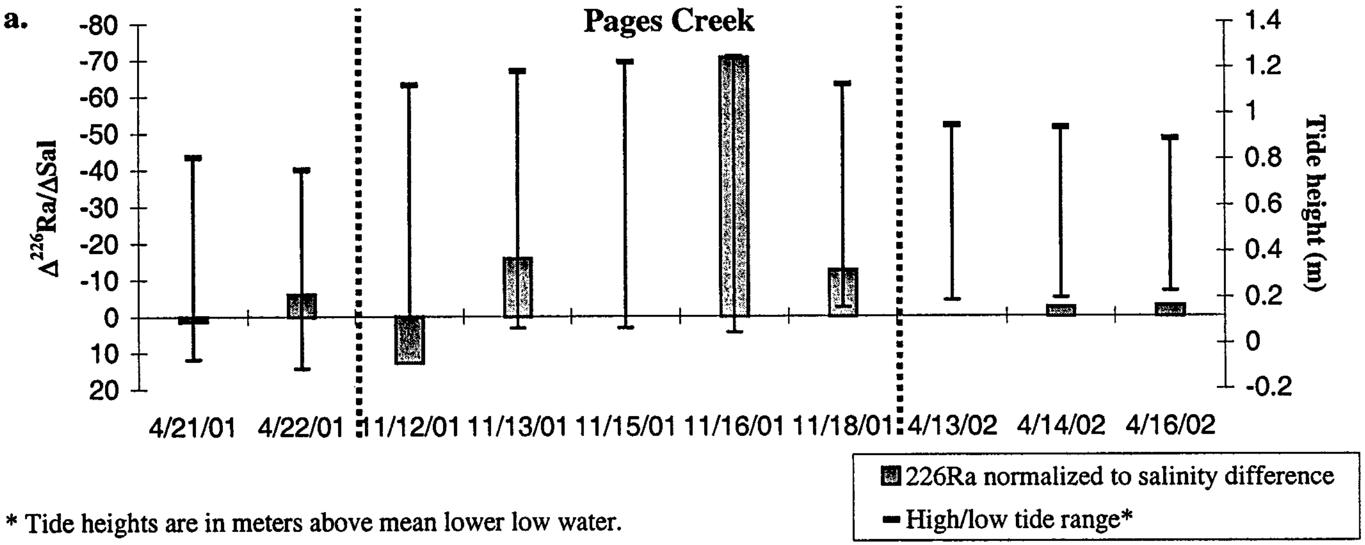
Figure IV-24

Figure IV-25

The high/low tide change in: a) ^{226}Ra, b) ^{228}Ra, normalized to the high tide/low tide change in salinity (ΔSal) at Pages Creek. Bars represent Δ^{226}Ra /ΔSal and Δ^{228}Ra /ΔSal for each sampling day in April 2001, November 2001 and April 2002. Lines represent the tide range between high and low tide for Pages creek (secondary y-axis). The largest change in ^{226}Ra relative to salinity occurred on the day of the full spring tide (Novmeber 16, 2001). However, the largest change in ^{228}Ra relative to salinity occurred on the next sampling day after the full spring tide, November 18, 2001.

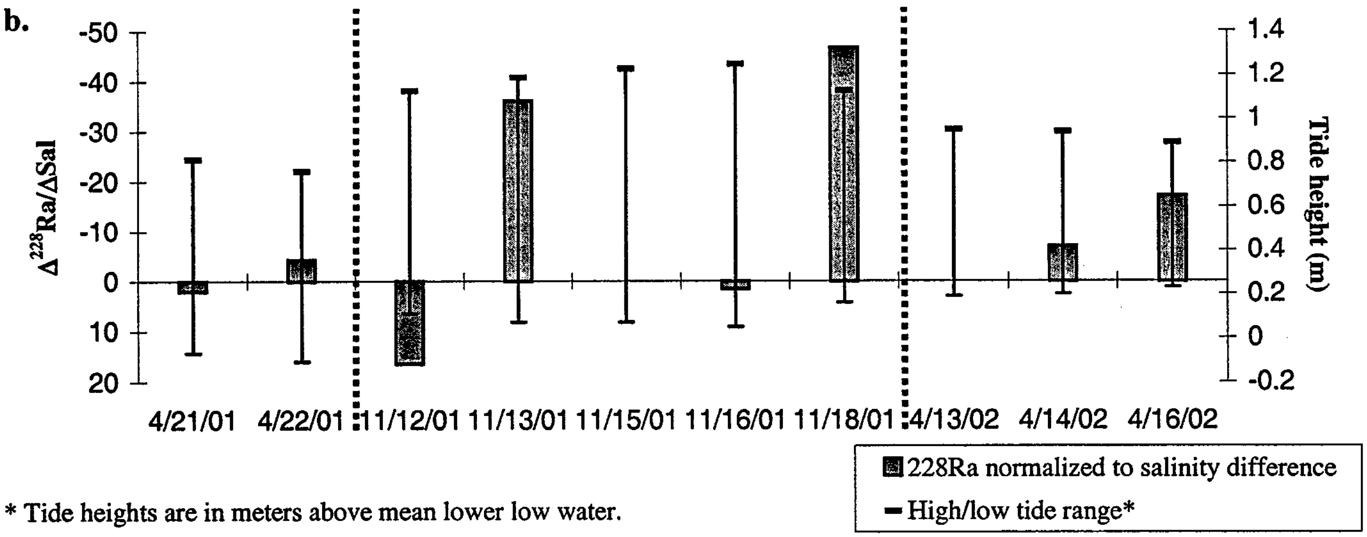
Figure IV-25

a.



* Tide heights are in meters above mean lower low water.

b.



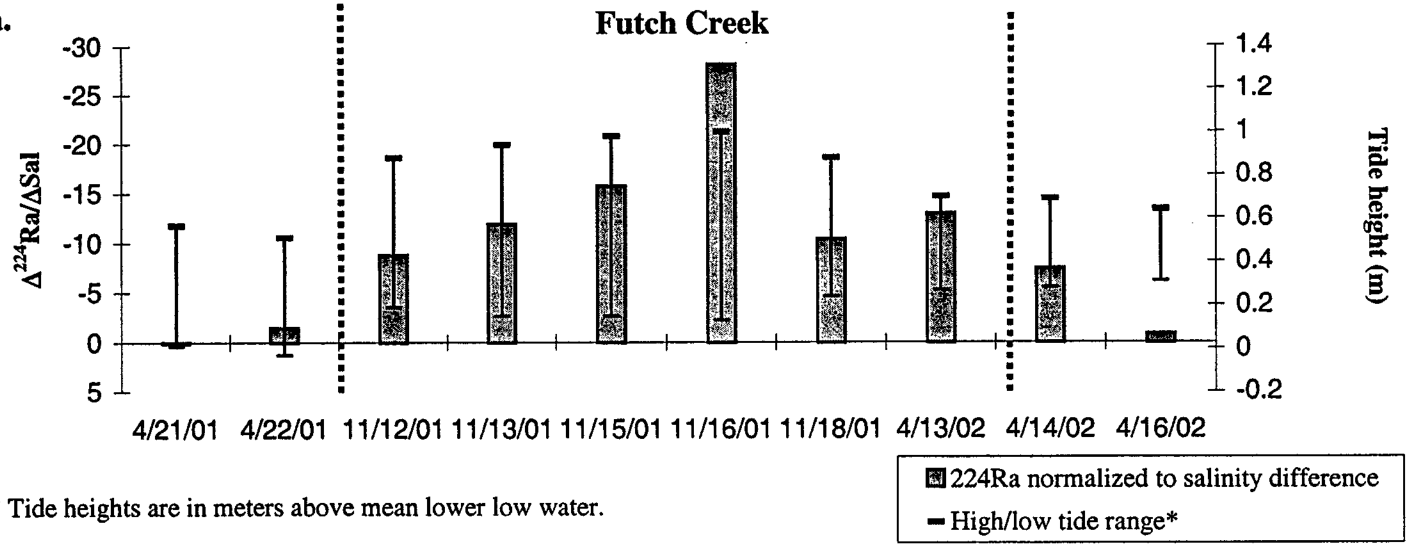
* Tide heights are in meters above mean lower low water.

Figure IV-26

The high/low tide change in a) ^{224}Ra b) ^{223}Ra normalized to the high/low tide change in salinity (ΔSal) at Futch Creek. Bars represent $\Delta^{224}Ra$ /ΔSal and $\Delta^{223}Ra$ /ΔSal for each sampling day in April 2001, November 2001 and April 2002. Lines represent the tide range between high and low tide for Futch creek (secondary y-axis). For both ^{223}Ra and ^{224}Ra, the largest change relative to salinity occurs on the day of the full spring tide (11/16/01).

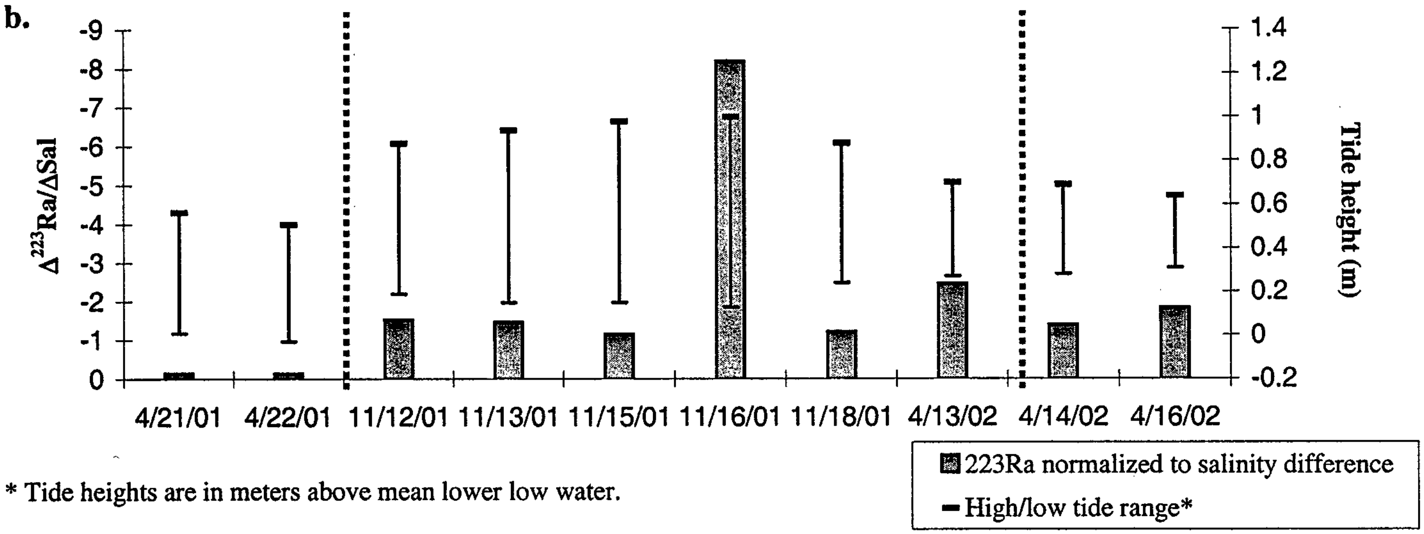
Figure IV-26

a.



* Tide heights are in meters above mean lower low water.

b.

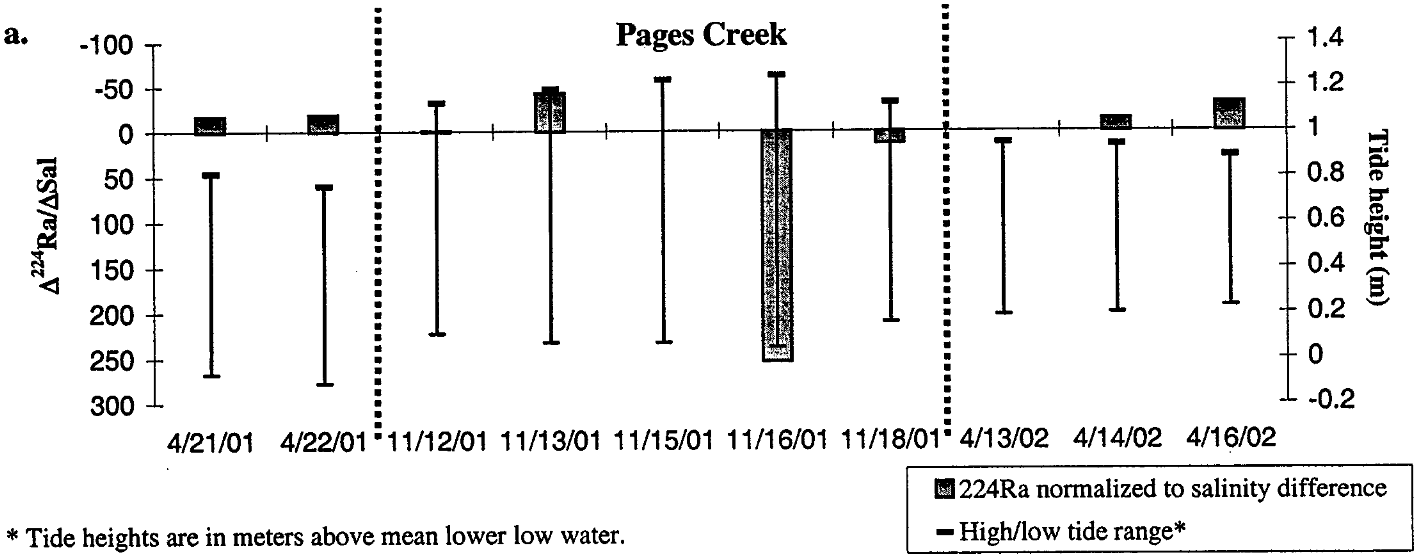


* Tide heights are in meters above mean lower low water.

Figure IV-27

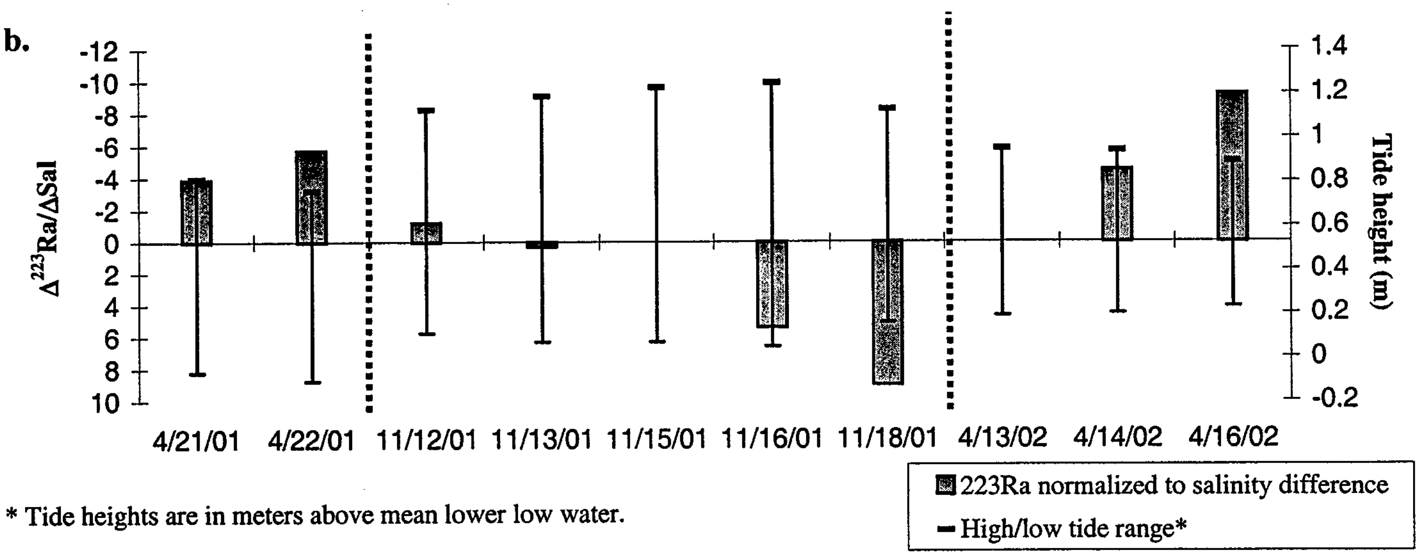
The high/low tide change in: a) ^{224}Ra, b) ^{223}Ra, normalized to the high tide/low tide change in salinity (ΔSal) at Pages Creek. Bars represent Δ^{224}Ra /ΔSal and Δ^{223}Ra /ΔSal for each sampling day in April 2001, November 2001 and April 2002. Lines represent the tide range between high and low tide for Pages creek (secondary y-axis). Both ^{224}Ra and ^{223}Ra decreased from high tide to low tide on the full spring tide (11/16/01), so that Δ^{224}Ra /ΔSal and Δ^{223}Ra /ΔSal are reversed.

Figure IV-27 a.



* Tide heights are in meters above mean lower low water.

b.

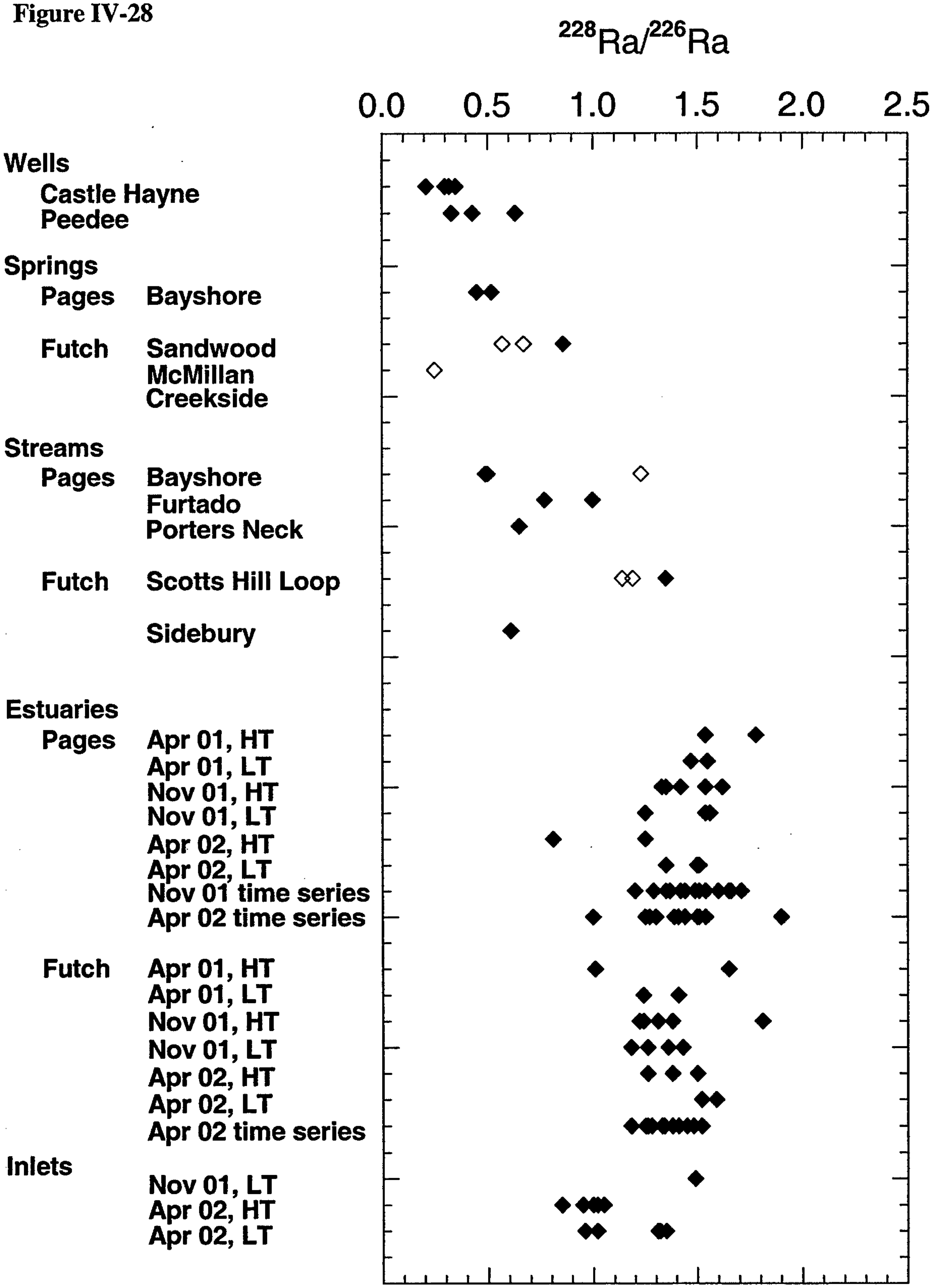


* Tide heights are in meters above mean lower low water.

Figure IV-28

$^{228}Ra/^{226}Ra$ activity ratios for wells, springs, streams, estuaries, and inlets. Groundwater and springs have the lowest $^{228}Ra/^{226}Ra$ activity ratios (0.2 – 0.8), while stream $^{228}Ra/^{226}Ra$ AR (0.5 – 1.4) are higher. Estuary and inlet $^{228}Ra/^{226}Ra$ ranges from 1-2, with low tide samples (averaging around 1.4) showing less variability than high tide samples.

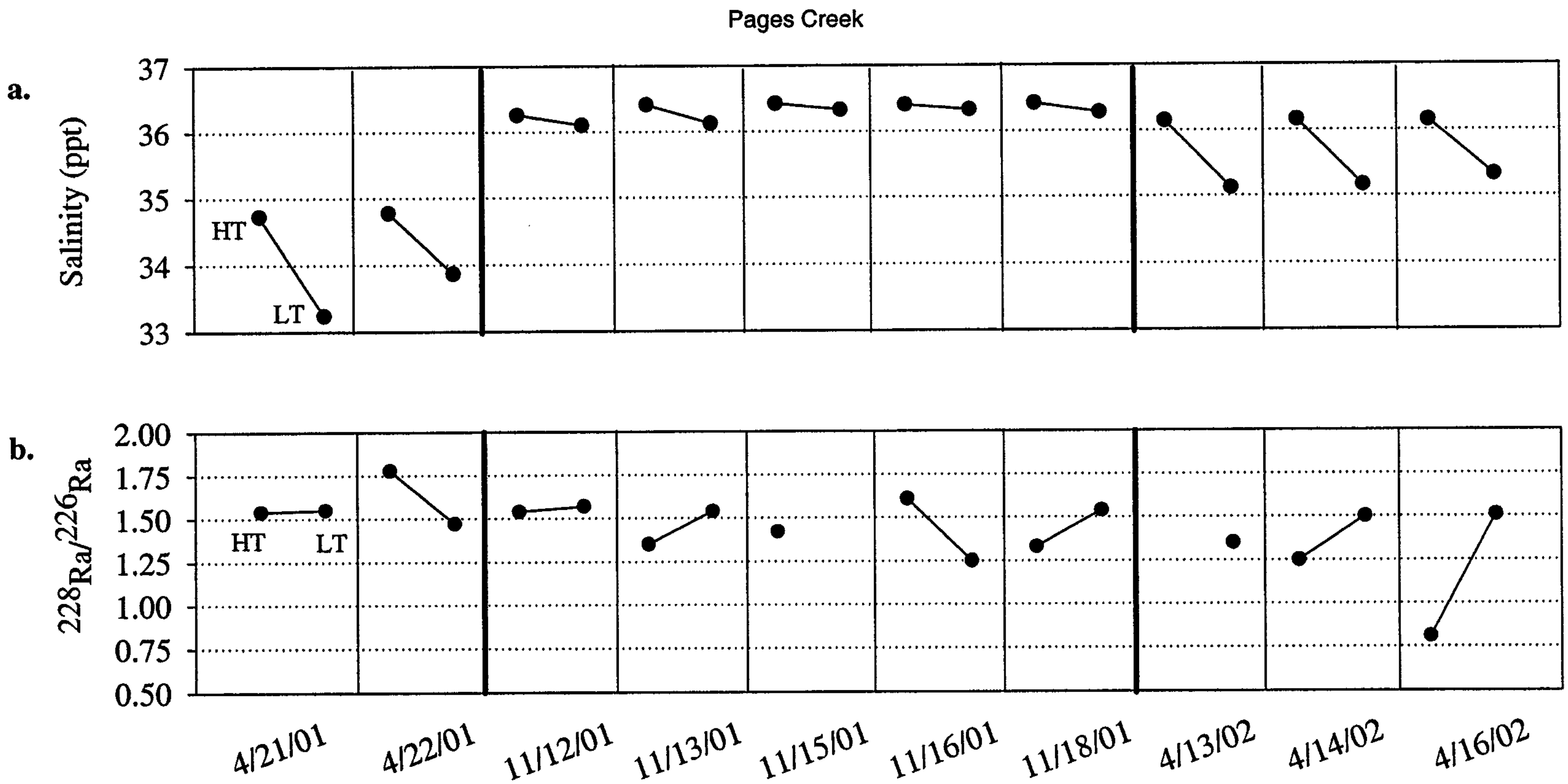
Figure IV-28



$^{228}Ra/^{226}Ra$
0.0
0.5
1.0
1.5
2.0
2.5
Wells
Castle Hayne
Peedee
Springs
Pages
Bayshore
Futch
Sandwood
McMillan
Creekside
Streams
Pages
Bayshore
Furtado
Porters Neck
Futch
Scotts Hill Loop
Sidebury
Estuaries
Pages
Apr 01, HT
Apr 01, LT
Nov 01, HT
Nov 01, LT
Apr 02, HT
Apr 02, LT
Nov 01 time series
Apr 02 time series
Futch
Apr 01, HT
Apr 01, LT
Nov 01, HT
Nov 01, LT
Apr 02, HT
Apr 02, LT
Apr 02 time series
Inlets
Nov 01, LT
Apr 02, HT
Apr 02, LT

Figure IV-29

Pages Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{228}Ra/^{226}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{228}Ra/^{226}Ra$ activity ratios showed no clear pattern from high tide to low tide in April 2001 or November 2001, but appeared to generally increase from high tide to low tide in April 2002.

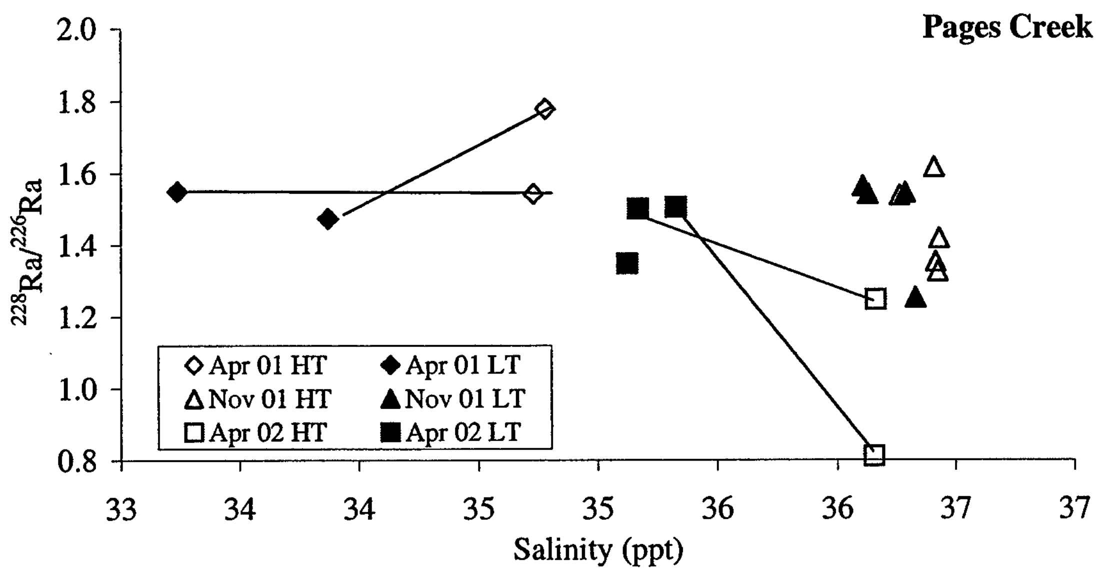


Pages Creek
a.
Salinity (ppt)
37
36
35
34
33
HT
LT
b.
$^{228}Ra/^{226}Ra$
2.00
1.75
1.50
1.25
1.00
0.75
0.50
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-29

Figure IV-30

Pages Creek $^{228}Ra/^{226}Ra$ high/low tide pair data, plotted against salinity. High tide $^{228}Ra/^{226}Ra$ AR were much more variable than low tide $^{228}Ra/^{226}Ra$ AR.

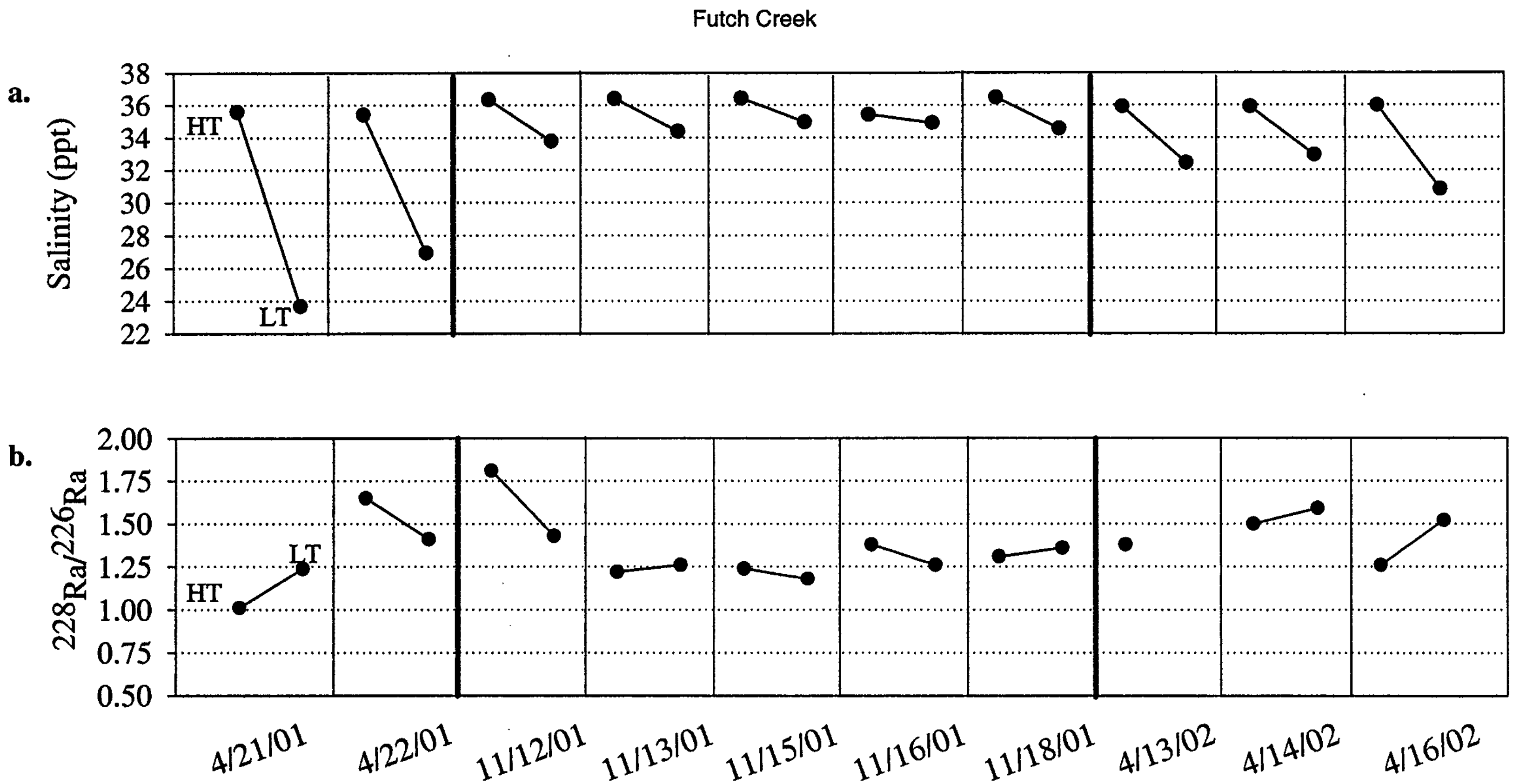


Pages Creek
2.0
1.8
1.6
1.4
1.2
1.0
0.8
$^{228}Ra/^{226}Ra$
Apr 01 HT
Apr 01 LT
Nov 01 HT
Nov 01 LT
Apr 02 HT
Apr 02 LT
33
34
34
35
35
36
36
37
37
Salinity (ppt)

Figure IV-30

Figure IV-31

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{228}Ra/^{226}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{228}Ra/^{226}Ra$ activity ratios showed no clear pattern from high tide to low tide during any sampling period, although they appear to generally increase from high tide to low tide in April 2002.



Futch Creek
a.
Salinity (ppt)
38
36
34
32
30
28
26
24
22
HT
LT
b.
228Ra/226Ra
2.00
1.75
1.50
1.25
1.00
0.75
0.50
HT
LT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-31

Figure IV-32

Futch Creek $^{228}Ra/^{226}Ra$ high/low tide pair data, plotted against salinity. As for Pages Creek, the low tide $^{228}Ra/^{226}Ra$ AR are less variable than the high tide $^{228}Ra/^{226}Ra$ AR.

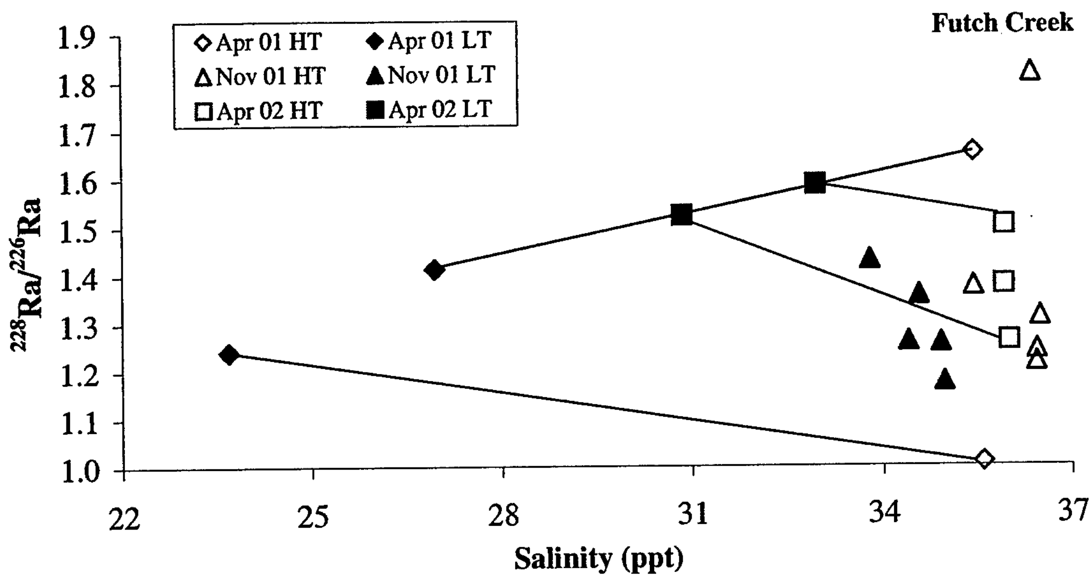

Futch Creek
Apr 01 HT
Apr 01 LT
Nov 01 HT
Nov 01 LT
Apr 02 HT
Apr 02 LT
$^{228}Ra/^{226}Ra$
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
22
25
28
31
34
37
Salinity (ppt)

Figure IV-32

Figure IV-33

Pages Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{224}Ra/^{228}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{224}Ra/^{228}Ra$ AR increased from high tide to low tide during April 2001, but in November 2001 and April 2002 showed no clear pattern from high tide to low tide.

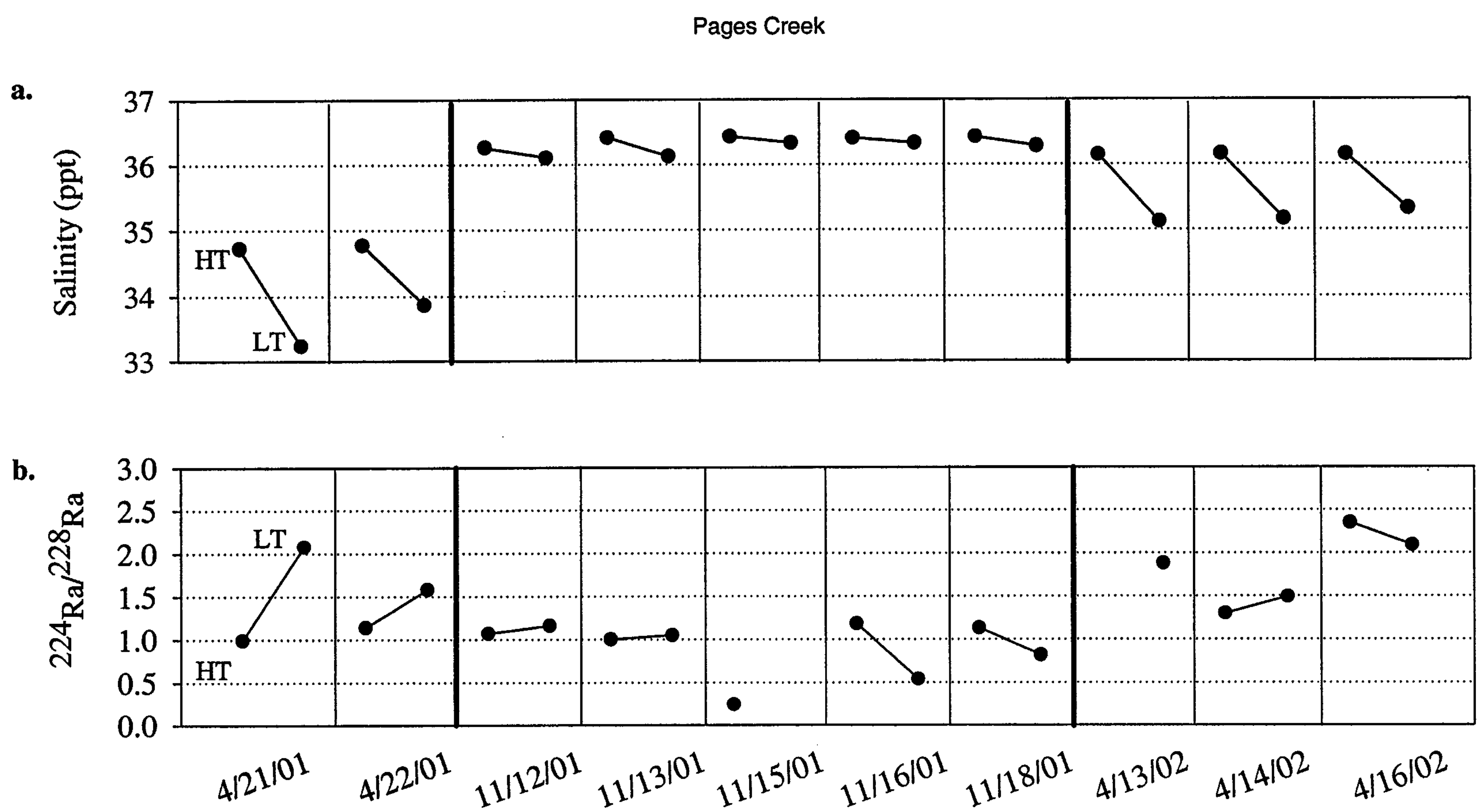

Pages Creek
a.
Salinity (ppt)
37
36
35
34
33
HT
LT
b.
$^{224}Ra/^{228}Ra$
3.0
2.5
2.0
1.5
1.0
0.5
0.0
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-33

Figure IV-34

Pages Creek $^{224}Ra/^{228}Ra$ high/low tide pair data, plotted against salinity. April 2001 and April 2002 low tide $^{224}Ra/^{228}Ra$ AR were less variable than high tide $^{224}Ra/^{228}Ra$.

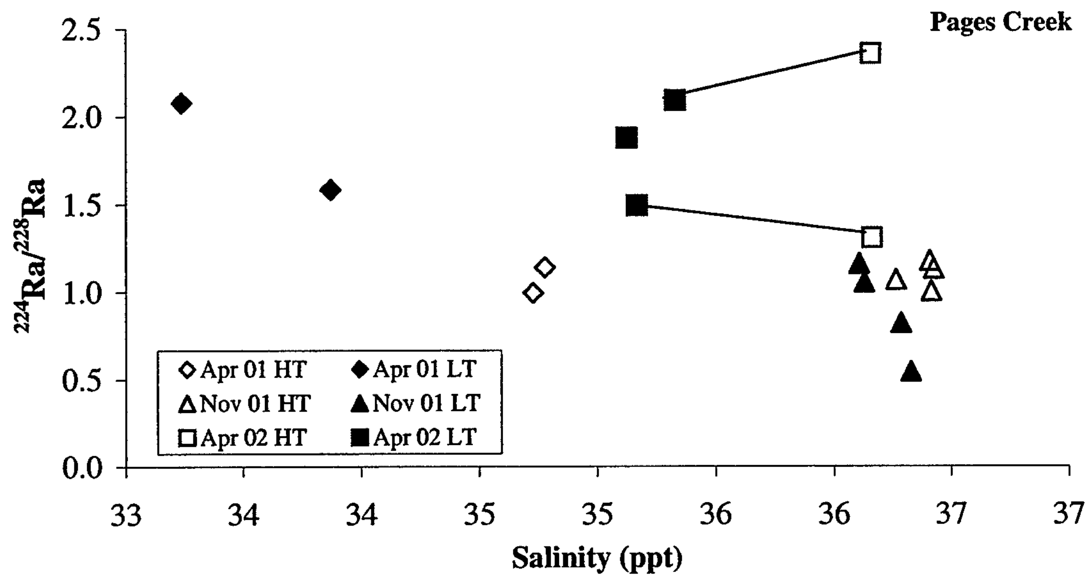

Pages Creek
2.5
2.0
1.5
1.0
0.5
0.0
$^{224}Ra/^{228}Ra$
Apr 01 HT
Apr 01 LT
Nov 01 HT
Nov 01 LT
Apr 02 HT
Apr 02 LT
33
34
34
35
35
36
36
37
37
Salinity (ppt)

Figure IV-34

Figure IV-35

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{224}Ra/^{228}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{224}Ra/^{228}Ra$ increased from high to low tide during all times in November 2001, but showed no clear pattern in April 2001 or April 2002.

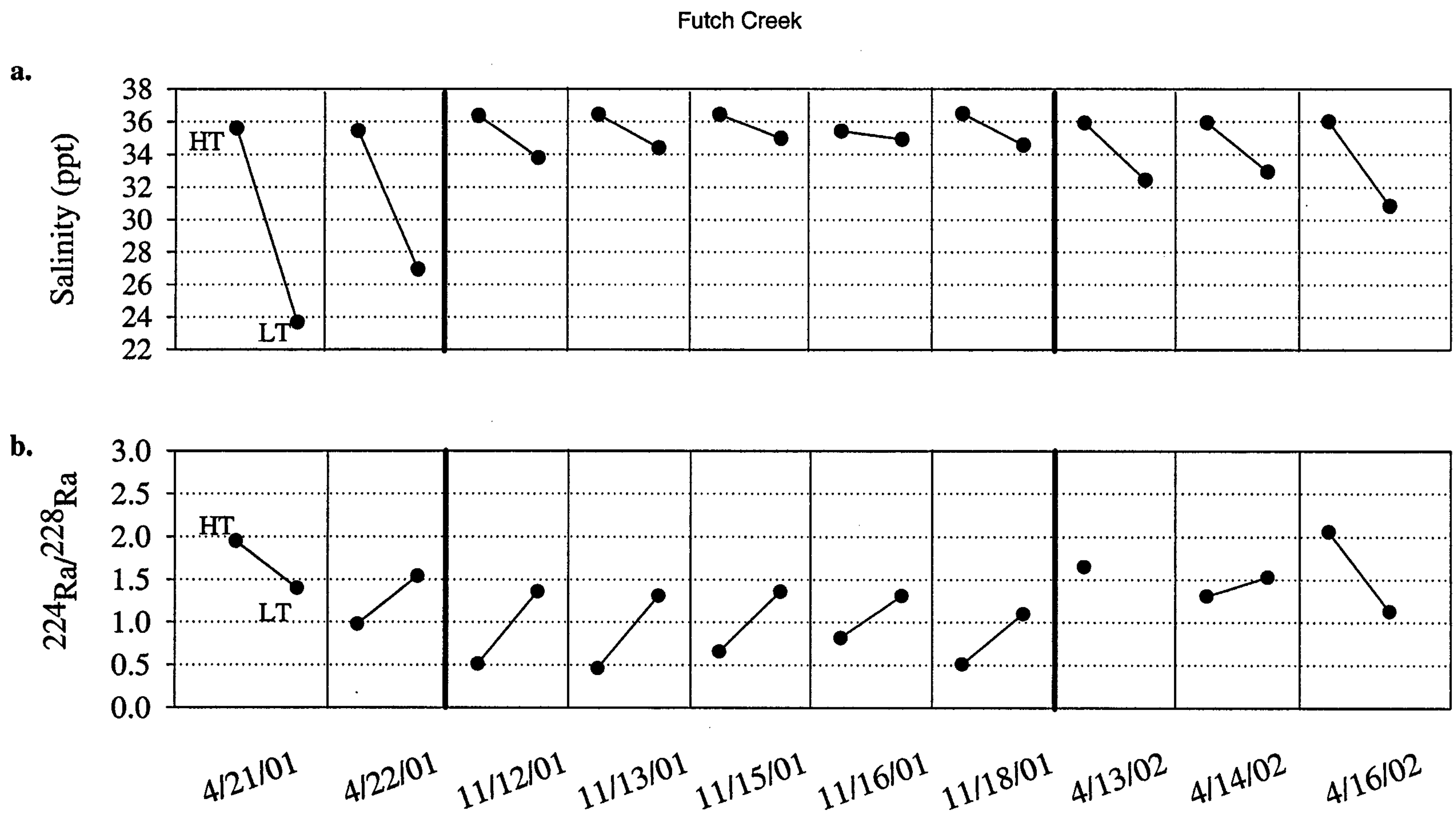

Futch Creek
a.
b.
Salinity (ppt)
38
36
34
32
30
28
26
24
22
HT
LT
$^{224}Ra/^{228}Ra$
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-35

Figure IV-36

Futch Creek $^{224}Ra/^{228}Ra$ high/low tide pair data, plotted against salinity. The low tide $^{224}Ra/^{228}Ra$ AR were much less variable than high tide $^{224}Ra/^{228}Ra$.

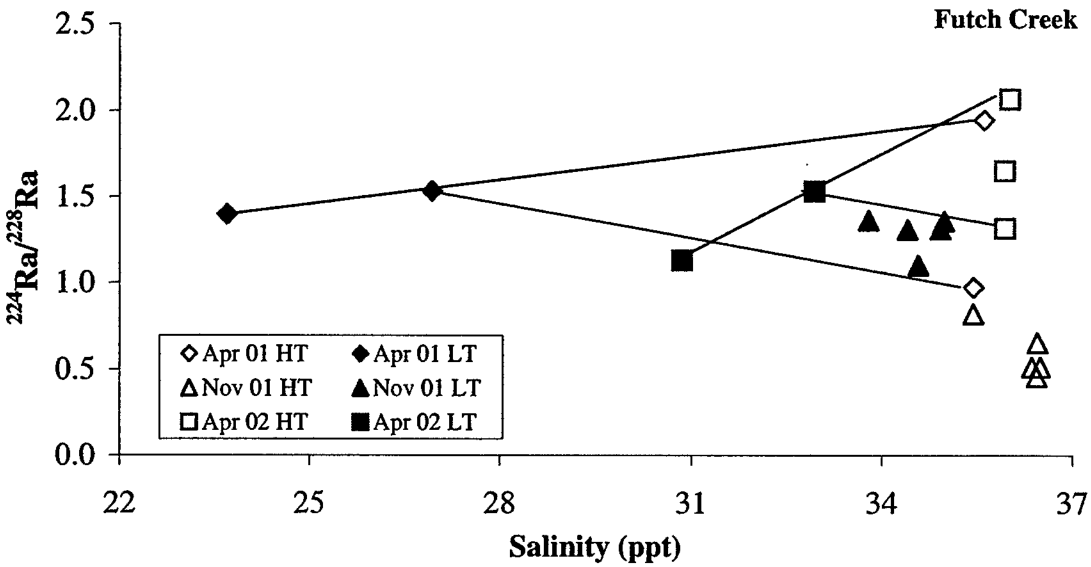

Futch Creek
2.5
2.0
1.5
1.0
0.5
0.0
$^{224}Ra/^{228}Ra$
Apr 01 HT
Apr 01 LT
Nov 01 HT
Nov 01 LT
Apr 02 HT
Apr 02 LT
22
25
28
31
34
37
Salinity (ppt)

Figure IV-36

Figure IV-37

Pages Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{223}Ra/^{226}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{223}Ra/^{226}Ra$ increased from high tide to low tide during April 2001 and April 2002, but generally decreased from high tide to low tide in November 2001.

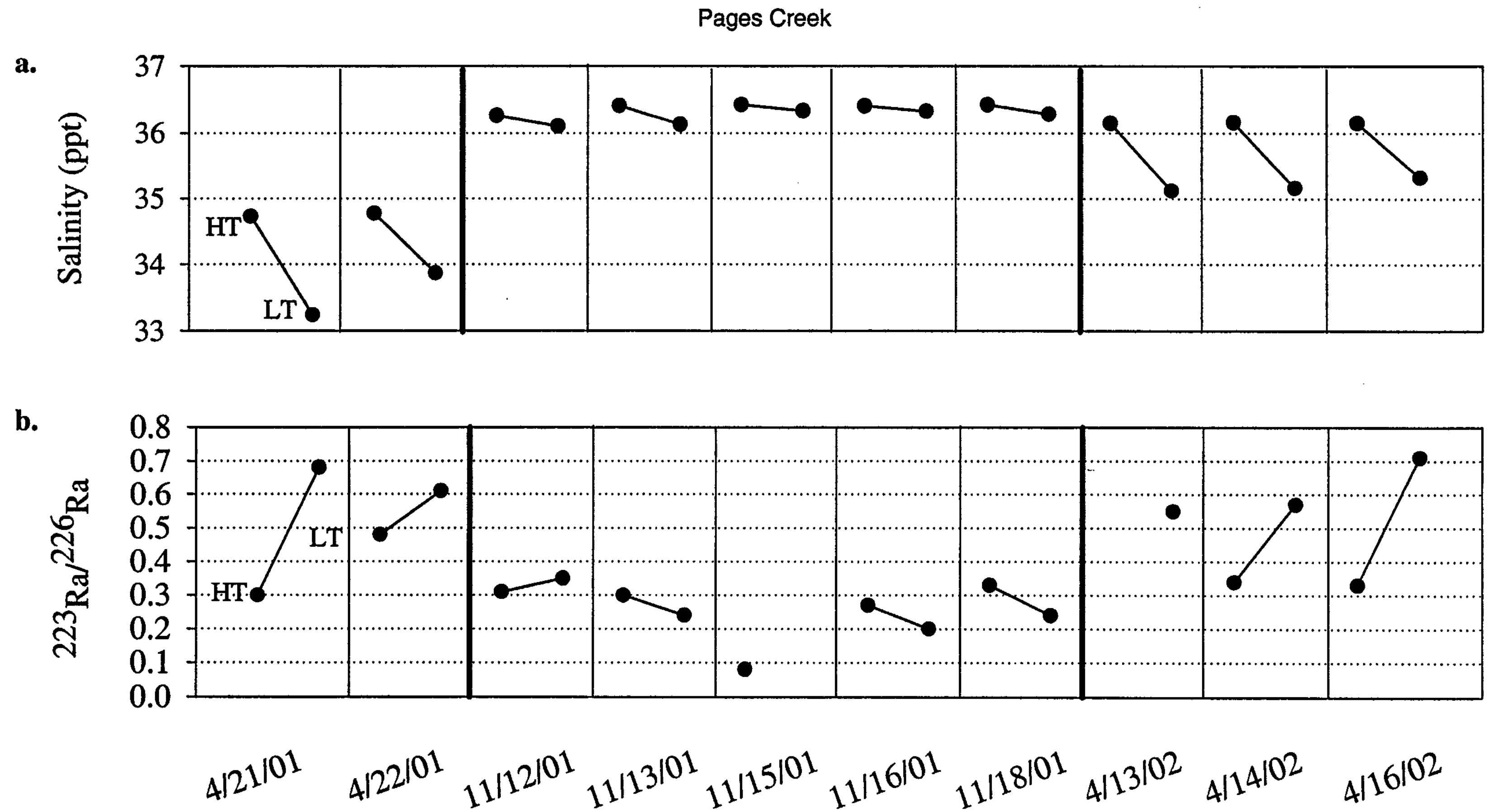

Pages Creek
a.
Salinity (ppt)
37
36
35
34
33
HT
LT
b.
$^{223}Ra/^{226}Ra$
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-37

Figure IV-38

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{223}Ra/^{226}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{223}Ra/^{226}Ra$ increased from high tide to low tide during all sampling days.

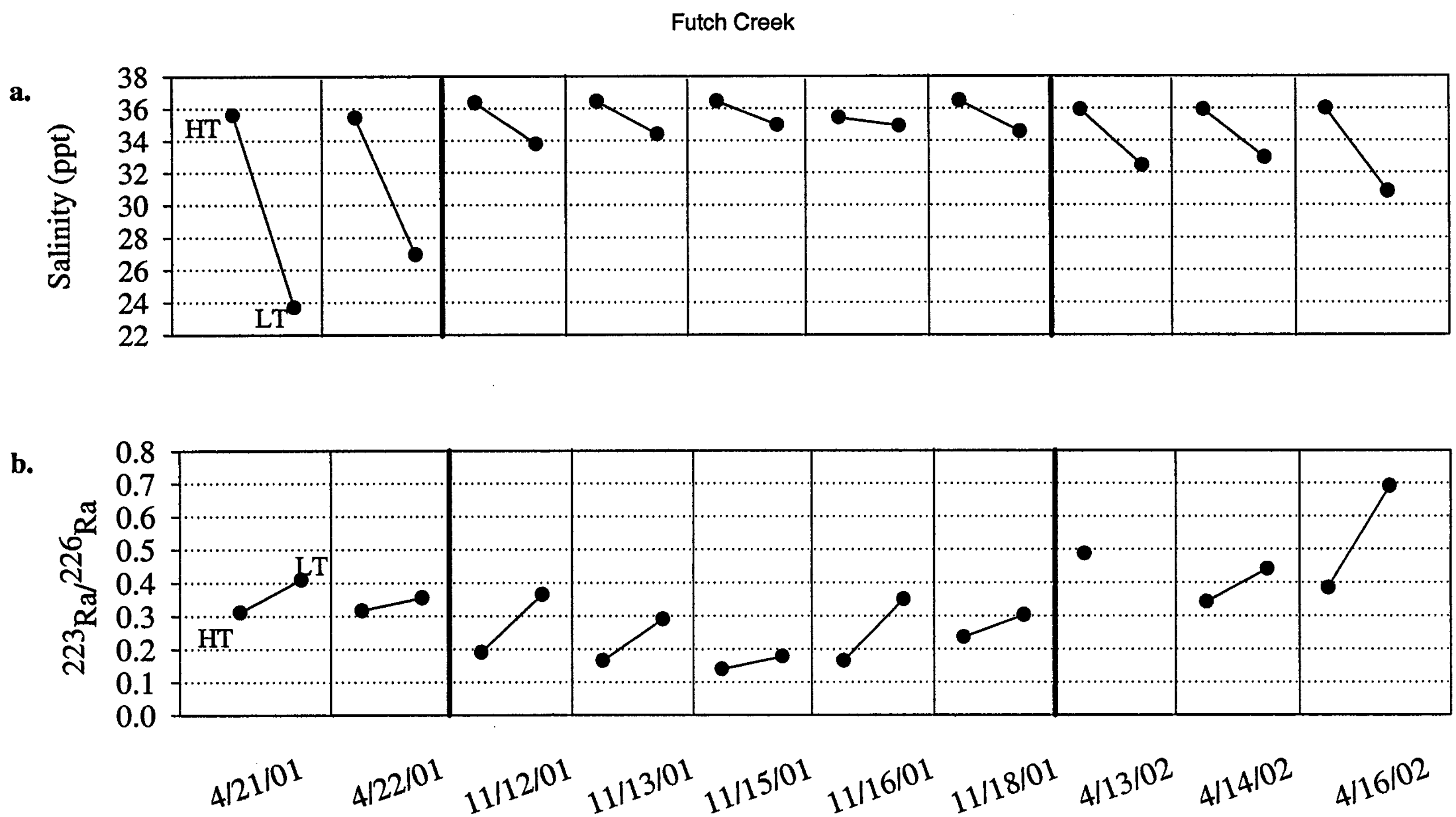
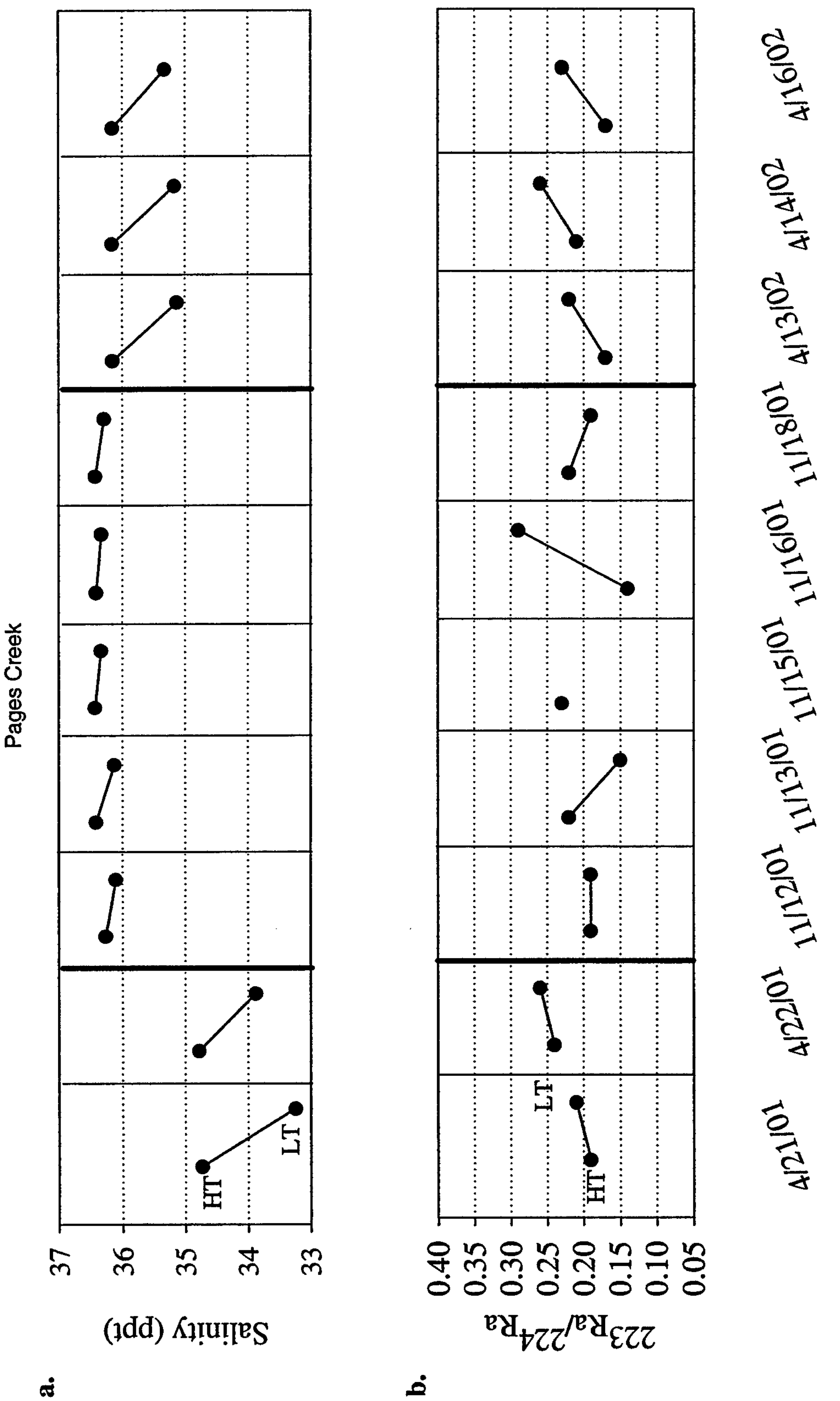

Futch Creek
a.
Salinity (ppt)
38
36
34
32
30
28
26
24
22
HT
LT
b.
$^{223}Ra/^{226}Ra$
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-38

Figure IV-39

Pages Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{223}Ra/^{224}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{223}Ra/^{224}Ra$ showed no pattern from high tide to low tide in November 2001, but increased in April 2001 and April 2002.



Pages Creek
a.
Salinity (ppt)
37
36
35
34
33
HT
LT
b.
$^{223}Ra/^{224}Ra$
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
LT
HT
4/21/01
4/22/01
11/12/01
11/13/01
11/15/01
11/16/01
11/18/01
4/13/02
4/14/02
4/16/02

Figure IV-39

Figure IV-40

Futch Creek estuary April 2001, November 2001, and April 2002 high and low tide a) salinity. b) $^{223}Ra/^{224}Ra$. Within each box, the left circle represents the high tide value (HT) and the right circle the low tide value (LT). $^{223}Ra/^{224}Ra$ showed no high tide/low tide pattern during any sampling period.

Futch Creek

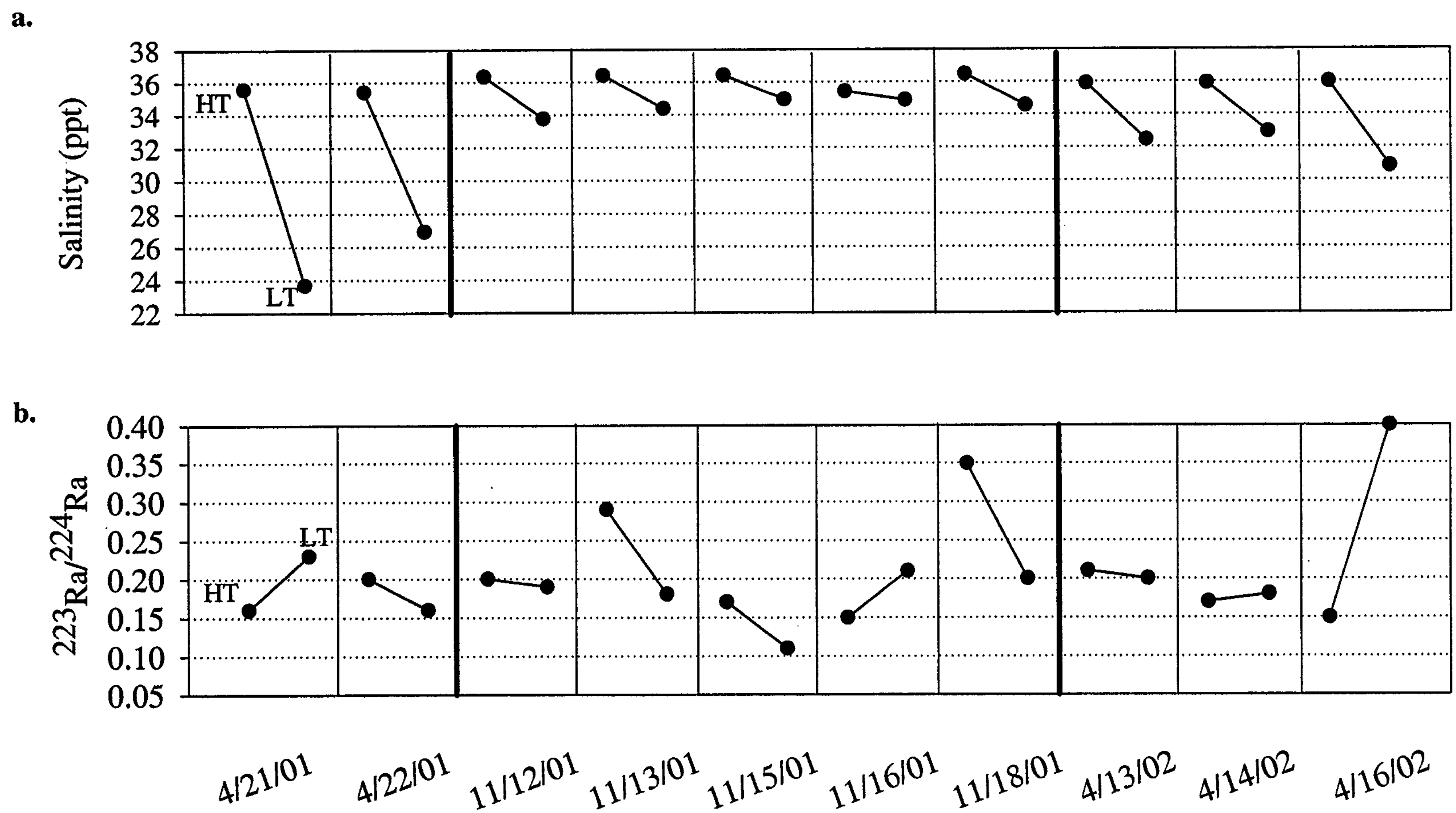


Figure IV-40

Chapter V. Multi-tracer measurements of groundwater discharge to coastal waters

Abstract

Concurrent estimates of submarine groundwater discharge (SGD) were derived from fluxes of the geochemical tracers radium, radon, and $\Delta^{14}C$ from two small estuaries in southeastern North Carolina. While $\Delta^{14}C$ is a tracer of the fresh, artesian component of the total SGD, fluxes of radium and radon are likely to include both terrestrially-driven and tidally-driven components of the total SGD.

Fluxes of each of these tracers to these estuaries were measured during April 2001, November 2001, and April 2002. For each tracer, a hypothetical, "inferred" spring flux was calculated, by assuming that all of the tracer flux was spring-derived (though in fact the springs are not expected to be a primary source of ^{224}Ra, ^{223}Ra, and ^{228}Ra, and may only partially support excess ^{222}Rn and ^{226}Ra).

In both estuaries, spring discharge estimates derived from fluxes of ^{228}Ra, ^{223}Ra, and ^{224}Ra were at least an order of magnitude higher than discharge estimates derived from $\Delta^{14}C$, ^{222}Rn, and ^{226}Ra, suggesting that springs were not a primary source for ^{228}Ra, ^{223}Ra, and ^{224}Ra to either estuary. In the Pages Creek estuary, spring discharge estimates derived from fluxes of ^{226}Ra were at least two times higher on all sampling days than spring fluxes derived from ^{222}Rn or $\Delta^{14}C$. In the Futch Creek estuary, flux estimates derived from ^{226}Ra were only ~10% of the $\Delta^{14}C$-estimated spring fluxes in April 2001 (no estimates were made with ^{222}Rn during this time), but during the other sampling times, ^{226}Ra-, ^{222}Rn-, and $\Delta^{14}C$-estimates of spring discharge compared well, and were generally within error. This suggests that additional sources contributed to the observed excess ^{222}Rn and ^{226}Ra during November 2001 in the Pages Creek estuary, and to the excess ^{226}Ra during April 2001 in the Pages Creek estuary. In the case of ^{226}Ra, an additional source may be advection from the surficial groundwater, while for ^{222}Rn it may be regeneration within estuarine sediments.

1. Introduction

"Submarine groundwater discharge" (SGD) can refer to subsurface water of any salinity or chemical composition that discharges into estuaries or the coastal ocean (Moore 1999; Burnett et al 2002). SGD is an important mechanism for the transport of nutrients and other dissolved chemical species to coastal waters, yet direct fluxes of groundwater are both temporally and spatially variable, and therefore difficult to quantify. Consequently, many different field methodologies have been used in recent years to determine SGD, including direct physical measurements made with seepage meters (Bokuniewicz 1992; Simmons 1992; Robinson et al 1998), modeling approaches (based on, for example, hydrologic water budgets, pore water concentrations of chloride, or numerical models) (Zektzer et al 1973; Choi and Harvey 2000) and approaches based on geochemical tracers such as ^{222}Rn (e.g. Cable et al 1996a, b; Corbett et al 1999, 2000), the four radium isotopes (^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra) (e.g. Bollinger and Moore 1993; Moore 1996; Rama and Moore 1996; Krest et al 2000), and Δ^{14}C (Gramling et al 2003).

Several recent studies of groundwater discharge at the land-sea interface have focused on the comparison and evaluation of different methodologies (Swarzenski et al 2001; Burnett et al 2002; Cable et al 2003). These studies have found that flux estimates based on radium and radon isotopes, as well as on seepage meters, were higher than fluxes calculated from a chloride pore water advection model or from hydrological models. One likely explanation for these differences is that such modeling estimates have considered only onshore-offshore hydraulic gradients, rather than tidal pumping or oscillatory wave motion, which drives seawater circulation through shallow sediments (Burnett et al 2002). The fluxes measured by seepage meters and by radium and radon, however, include both terrestrially-driven and tidally-driven components of the total groundwater discharge at the coast.

Radium and radon are useful geochemical tracers of SGD because they are enriched in groundwater, are relatively easy to measure, and behave conservatively with respect to biological processes (e.g. Bollinger and Moore 1993; Rama and Moore 1996; Cable et al 1996; Krest et al 2000; Corbett et al 1999, 2000). The range of half-lives of the four radium isotopes ^{226}Ra ($t_{1/2}$ = 1600 yr), ^{228}Ra ($t_{1/2}$ = 5.75 yr), ^{223}Ra ($t_{1/2}$ = 11.4 d), and ^{224}Ra ($t_{1/2}$ = 3.66 d) provides a means of quantifying fluxes and exchange rates between surface waters and sediment layers over different time scales. Radium desorption from aquifer or riverine particles is enhanced in waters of increasing ionic strength, and the groundwater radium flux is almost certainly elevated as radium is desorbed from aquifer sediments by salt water intrusion (e.g. Elsinger and Moore 1980; Burnett et al 1990; Moore 1996). Therefore, fluxes of radium are likely to provide an estimate of the total subsurface flux, including the recirculation of seawater through surface sediments, rather than of fresh, land-sea fluxes alone (e.g. Moore 1999; Burnett et al 2002; Cable et al 2003).

Radon (^{222}Rn ($t_{1/2} = 3.8$ days)) is not sensitive to salinity-linked desorption reactions, but it is quickly lost to the atmosphere once groundwater is exposed at the land surface. As a result, coastal ^{222}Rn activities may provide only a minimum estimate of the total groundwater flux (Corbett et al 1999; Swarzenski et al 2001).

$\Delta^{14}C$ can be used to trace SGD inputs from any source with a distinct radiocarbon content. In coastal North Carolina, fresh water artesian discharge is characterized by a low $\Delta^{14}C$ signature acquired from the carbonate aquifer rock, and thus can be used to estimate the artesian contribution to estuarine freshwater budgets (Gramling et al 2003). After determining the total fresh water input to an estuary by a salinity mass balance, the fresh water input can be partitioned between surface sources (including streams and the surficial aquifer) and artesian groundwater using a carbon isotope mass balance based on DIC concentrations and $\Delta^{14}C$ values.

In this study, concurrent groundwater flux estimates were derived from fluxes of the geochemical tracers radium, radon, and $\Delta^{14}C$ from two small estuaries in southeastern North Carolina. The objective of this work is to understand which of the components of the total SGD (including artesian discharge from confined aquifers, seepage from the estuarine bottom sediments, and tidal filling and draining of marsh sediments) is measured by each of these tracers, and to compare these estimates to better understand how the estuarine fluxes of water, salt, and the isotopic tracers are partitioned among these components.

Confined groundwater discharge to these estuaries is a source for all of the tracers – $\Delta^{14}C$, ^{222}Rn, and radium. However, the $\Delta^{14}C$-derived fluxes represent only the artesian component of the total SGD into each estuary, while the ^{222}Rn and radium fluxes include both artesian discharge and other components of the total flux (Figure 1). ^{226}Ra is supplied by both spring discharge and advection from the surficial aquifer. ^{223}Ra and

^{224}Ra (which are regenerated more rapidly than ^{226}Ra in sediments) are supplied to the estuaries by artesian discharge, but are primarily linked to regeneration and release within the bottom and tidal marsh sediments (Figure 1). ^{228}Ra can originate from all of these components. ^{222}Rn is supplied both by artesian discharge and by regeneration within sediments.

The artesian discharge to the two estuaries, Pages Creek and Futch Creek, was estimated by measuring fluxes of each of these tracers during three sampling periods in April 2001, November 2001, and April 2002. To directly compare these fluxes, a hypothetical, "inferred" spring flux was calculated for each tracer, by assuming that all of the tracer flux was spring-derived (though in fact the springs are not expected to be a primary source of ^{224}Ra, ^{223}Ra, and ^{228}Ra, and may only partially support excess ^{222}Rn and ^{226}Ra).

In both estuaries, spring discharge derived from fluxes of ^{228}Ra, ^{223}Ra, and ^{224}Ra were at least an order of magnitude higher than discharge estimates derived from $\Delta^{14}C$, ^{222}Rn, and ^{226}Ra, suggesting that springs were not a primary source for ^{228}Ra, ^{223}Ra, and ^{224}Ra to either estuary. In the Pages Creek estuary, spring discharge estimates derived from fluxes of ^{226}Ra were at least two times higher on all sampling days than spring fluxes derived from ^{222}Rn or $\Delta^{14}C$. In the Futch Creek estuary, flux estimates derived from ^{226}Ra were only ~10% of the $\Delta^{14}C$-estimated spring fluxes in April 2001, but during the other sampling times, ^{226}Ra-, ^{222}Rn-, and $\Delta^{14}C$-estimates of spring discharge compared well, and were generally within error.

2. Methods

2.1 Study site

Chapters III and IV of this dissertation provide detailed study site information for the Pages and Futch Creek estuaries (Figure 2). A description of the geologic and hydrogeologic characteristics of the Onslow Bay region of southeastern North Carolina is presented in Chapter II.

A conceptual cross-section of the interaction between a coastal groundwater system and an estuary in the Onslow Bay region is shown in Figure 3. Spring discharge can occur both within the estuary and in the upper marsh as a result of a leaky or locally absent confining unit over the Castle Hayne aquifer (1) (discussed in detail in Chapter II); advection of groundwater in the surficial aquifer leads to seepage into streams or directly into the estuary via bottom sediments (2); tidal filling of marsh sediment pore waters during rising tide stage and subsequent draining of the sediments during falling tide (3); and (4) mixing between the advected groundwater and tidal inundation of sediments.

2.2 Sample Collection and Analysis

^{226}Ra, ^{228}Ra, ^{223}Ra, ^{224}Ra, Δ^{14}C, and salinity samples were collected from the Pages Creek estuary and the Futch Creek estuary in April 2001, November 2001, and April 2002. ^{222}Rn was sampled in November 2001 and April 2002. Dissolved samples were collected at the mouth of each estuary just before high tide and just before low tide, as well as from fresh water spring and stream inputs into each estuary (Figure 2). DIC, DIC isotopic, and salinity collection and analysis is described in detail in Chapter III. Radium and radon sample collection and analysis is described in detail in Chapter IV.

2.3 Calculations and flux estimates

In this study, we compare groundwater discharge estimates derived from fluxes of the geochemical tracers ^{226}Ra, ^{228}Ra, ^{223}Ra, ^{224}Ra, ^{222}Rn, and Δ^{14}C from two estuaries. The total flux of groundwater to these estuaries is expected to include both fresh and brackish or saline components, and to derive from both artesian and surficial sources. As described in Chapter IV, fluxes of these tracers are linked to different estuarine processes, and it is expected that the various tracer-derived SGD estimates will be complementary, describing different portion(s) of the total SGD at the coast (Figure 1).

The potential sources of radium and radon to either estuary include inflowing water from the ICW, discharge from springs originating from the confined Castle Hayne aquifer, discharge from the surficial aquifer, regeneration and release from the estuarine bottom sediments, and regeneration and release from tidal marsh sediments. Aside from low tide outflow, the primary sink for ^{222}Rn is gas evasion (although decay within the water column is considered as a sink for ^{224}Ra, ^{223}Ra, and ^{222}Rn, it is not expected to significantly affect their budgets as the residence time of water within these estuaries is one tidal cycle, short relative to the half-lives of each of these isotopes). For Δ^{14}C, the sources and sinks include tidal exchange with the ICW, streams, and springs.

2.3.1 Radium isotopic mass balances and flux calculations

Excess radium (Ra_{ex}) is defined as the difference in radium activity between low tide outflow and high tide inflow. Daily total radium fluxes for each isotope of radium (in dpm m^{-2} d^{-1}) are calculated as

$$J_{Ra} = \frac{Ra_{ex} * \text{Tidal prism} * \text{Tides/day}}{\text{Estuary area}} \tag{1}$$

There are 1.9 tides per day, and the areas of both estuaries (in m^2), as well as the average tidal prisms (in m^3) for each sampling period, are given in Table 1.

The general, steady-state mass balance calculation for the flux of excess radium is:

$$J_{Ra} = J_{spring} + J_{stream} + J_{sediments} - \lambda A_{Ra} z \tag{2}$$

where J_{Ra} (dpm m^{-2} d^{-1}) is determined by Equation (1). J_{spring} (dpm m^{-2} d^{-1}) reflects discharge from artesian sources directly into the estuary or salt marshes, averaged over the entire area of the estuary. $J_{sediments}$ (dpm m^{-2} d^{-1}) includes seepage from the bottom estuarine sediments as both discharge from the surficial aquifer and release of radium produced within the sediments, likewise averaged over the area of the estuary. Fluxes of radium as either spring discharge or surficial aquifer seepage may include both dissolved and particulate radium fluxes. J_{marsh} (dpm m^{-2} d^{-1}) includes regeneration and release of radium from tidally inundated marsh sediments. λA_{Ra} (dpm m^{-3} d^{-1}) represents decay within the water column, and z (m) is the depth of the water column for each sampling location.

2.3.1.1 ^{226}Ra

The primary sources for ^{226}Ra are artesian discharge and seepage from the surficial aquifer (Figure 1). Due to the slow rate of ^{226}Ra regeneration from ^{230}Th, J_{marsh} is assumed to be equal to zero, as the sediments are expected to be deficient in desorbable ^{226}Ra (Rama and Moore 1996). Additionally, $\lambda A_{Ra} z$ is assumed to be equal to zero, as no decay is expected to occur within the water column due to the short residence time within the estuary relative to the half-life of ^{226}Ra. Taking J_{Ra} from Equation (1), the mass balance for ^{226}Ra then becomes:

$$J_{Ra} = J_{spring} + J_{stream} + J_{sediments} \tag{3}$$

where, for ^{226}Ra, $J_{sediments}$ represents fluxes from the surficial aquifer alone (rather than including sediment production).

2.3.1.2 ^{228}Ra

For ^{228}Ra, the mass balance is:

$$J_{Ra} = J_{spring} + J_{stream} + J_{sediments} \tag{4}$$

As discussed in Chapter IV, production of ^{228}Ra within sediments may occur on the time scales of this study (though this is likely to be small), and production is therefore included as a source term in the mass balance equation. As for ^{226}Ra, decay of ^{228}Ra within the water column is negligible due to the short residence time. For ^{228}Ra, $J_{sediments}$ includes both advection from the surficial aquifer and regeneration and release of ^{228}Ra within the sediments.

2.3.1.3 ^{223}Ra and ^{224}Ra

A similar equation is used for ^{223}Ra and ^{224}Ra:

$$J_{Ra} = J_{spring} + J_{stream} + J_{sediments} - \lambda A_{Ra} z \tag{5}$$

For both ^{223}Ra and ^{224}Ra, regeneration within estuarine bottom sediments and regeneration within tidal marsh sediments are likely to be significant source terms (Figure 1). Although water column residence time is still short relative to the half-lives of these isotopes, decay within the water column is included in these equations as a possible sink.

2.3.2 ^{222}Rn mass balance and flux calculations

Daily fluxes of ^{222}Rn from each estuary (in dpm m^{-2} d^{-1}) are calculated as the excess of low tide ^{222}Rn activities over high tide ^{222}Rn activities ($^{222}Rn_{ex}$) times the estuary tidal prism (in m^3), the number of tides per day, and divided by the area of each estuary (in m^2):

$$J_{222Rn} = \frac{^{222}Rn_{ex} * \text{Tidal prism} * \text{Tides/day}}{\text{Estuary area}} \tag{6}$$

Potential sources of excess ^{222}Rn to both estuaries include discharge from fresh water springs, input from fresh water streams, seepage from the surficial aquifer, regeneration and release from estuarine bottom sediments and from tidally inundated marsh sediments, and production within the water column from ^{226}Ra. Sinks for ^{222}Rn include gas evasion to the atmosphere and decay of ^{222}Rn within the water column. The mass balance can be expressed for each estuary as:

$$J_{222Rn} = J_{spring} + J_{stream} + J_{sediments} + \lambda A_{Ra} z - J_{atm} - \lambda A_{Rn} z \tag{7}$$

where J_{spring} (dpm m^{-2} d^{-1}) is discharge from artesian sources directly into the estuary and J_{stream} (dpm m^{-2} d^{-1}) is stream inputs. $J_{sediments}$ (dpm m^{-2} d^{-1}) includes both advective and diffusive fluxes of ^{222}Rn from sediments (as shown in Figure 1, this includes inputs from both the surficial aquifer and regenerated ^{222}Rn). J_{atm} (dpm m^{-2} d^{-1}) represents loss of ^{222}Rn from the water column to the atmosphere. λA_{Ra} and λA_{Rn} (dpm m^{-3} d^{-1}) represent production and decay within the water column, respectively, and z (m) is the depth of the water column for each sampling location.

Production and decay of ^{222}Rn within the water column are calculated by the activities of ^{226}Ra and ^{222}Rn and the height of the water column at outflow, respectively.

Atmospheric evasion of ^{222}Rn is a function of the relative concentrations of radon in air and water, of the rate of diffusion of the gas across the air-sea interface, and of hydrodynamic conditions (particularly wind speed). An empirical relationship between wind speed and the rate of transfer of a gas across the air-sea interface is given by:

$$J_{atm} = k\,(C_w - \alpha\, C_{atm}) \qquad (8)$$

where k is the gas transfer velocity (m d^{-1}), C_w is the concentration of the gas in water (dpm m^{-3}), α is the Ostwald solubility coefficient (dimensionless), and C_{atm} is the concentration of the gas in the atmosphere (dpm m^{-3}) (MacIntyre et al 1995). We use $\alpha = 0.22$ for all calculations, corresponding to an average temperature of 25 degrees Celsius, and an average atmospheric activity of ^{222}Rn of 560 dpm m^{-3} (Gesell 1983).

The gas transfer coefficient is a function of wind speed, temperature and salinity. Wanninkhof (1992) suggests the wind speed-gas transfer velocity relationship:

$$k = 1.92\, u^2 / Sc^{0.5} \qquad (9)$$

with k in units of m d^{-1}, where u is the wind speed (m s^{-1}) and Sc is the dimensionless Schmidt number, the ratio of the kinematic viscosity of water (at a given temperature and salinity) to the effective diffusion coefficient of a gas in water (for a given temperature and salinity). Field and laboratory studies support the assumption that the gas transfer velocity k is proportional to $Sc^{-0.5}$ in field conditions with occasional turbulence, rather than to $Sc^{-0.67}$, which is appropriate for smooth surfaces (MacIntyre et al 1995).

Wind speed data used to calculate the atmospheric evasion rate of ^{222}Rn in this study were obtained from a NOAA weather station located at the Wilmington International Airport in Wilmington, North Carolina. Daily wind speeds during sampling days in November 2001 and April 2002, as well as corresponding gas transfer coefficients and daily atmospheric evasion rates, are shown in Table 2. It is important to note that, as the estuaries are relatively sheltered relative to the NOAA weather station, the atmospheric fluxes in Table 2 may be overestimations of the true wind-driven evasion of ^{222}Rn from the Pages and Futch Creek estuaries.

2.3.3. $\Delta^{14}C$ flux calculations

Despite the fact that photosynthetic CO_2 uptake and CO_2 gas evasion can exert a strong influence on estuarine DIC (Cai and Wang 1998, Cai et al 1999), estuarine $\Delta^{14}C$ values will be determined by mixing between the DIC sources. This is due to the natural double label provided by paired ^{13}C and ^{14}C analyses (Spiker 1980), as well as the large difference between the input $\Delta^{14}C$ values to the Pages and Futch Creek estuaries (Gramling et al 2003).

$\Delta^{14}C$ (‰) is defined as:

$$\Delta^{14}C\ (‰) = 1000 \times \left[1 + \left(\frac{\delta^{14}C}{1000} \right) \times \left(\frac{0.975^2}{\left(1 + \frac{\delta^{13}C}{1000} \right)^2} \right) - 1 \right] \tag{10}$$

where $\delta^{13}C$ values are defined as:

$$\delta^{13}C\ (‰) = \left(\left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} \right) - 1 \right) \times 1000 \tag{11}$$

and $\delta^{14}C$ values are similarly defined as:

$$\delta^{14}C\ (‰) = \left(\left(\frac{(^{14}C/^{12}C)_{sample}}{(^{14}C/^{12}C)_{standard}} \right) - 1 \right) \times 1000 \tag{12}$$

In this equation for $\Delta^{14}C$, the $\delta^{14}C$ values are normalized to $\delta^{13}C$ = -25 ‰ to remove fractionation effects that can result from processes such as CO_2 gas evasion or photosynthesis (Stuiver and Robinson 1974). As a result of this normalization, $\Delta^{14}C$ values are unchanged by DIC removal processes that fractionate carbon isotopes. Consequently, groundwater flux estimates based on estuarine DIC $\Delta^{14}C$ values are largely unaffected by processes such as gas exchange, photosynthesis, and respiration of fresh organic matter.

In coastal North Carolina, fresh water artesian discharge is characterized by a low $\Delta^{14}C$ signature acquired from the carbonate aquifer rock, and thus can be used to estimate the artesian contribution to estuarine freshwater budgets (Gramling et al 2003). After determining the total fresh water input to an estuary by a salinity mass balance, the fresh water input can be partitioned between surface sources (including seawater and the surficial aquifer) and artesian groundwater using a carbon isotope mass balance based on DIC concentrations and $\Delta^{14}C$ values.

The total fresh water input is calculated by a mass balance between the high tide inflow salinity and the low tide outflow salinity for each sampling day in each estuary. The fresh water fraction of the outflow over a tidal cycle is calculated as:

$$\text{Freshwater fraction} = 1 - \left(\frac{\text{LT salinity}}{\text{HT salinity}} \right) \tag{13}$$

The flux J (in L m^{-2} d^{-1}) of fresh water added per day is given by

$$J_{FW} = \frac{\text{Freshwater fraction} * \text{ Tidal prism} * \text{ Tides/day}}{\text{Area of estuary}} \tag{14}$$

where the tides per day and estuary area values are the same as those used to calculate radium and radon fluxes (Table 1).

2.3.4 Tracer flux calculations: sources of error

There are two important caveats to these flux calculations. The flux of each tracer was determined by multiplying the low tide tracer excess (low tide activity/concentration minus high tide activity/concentration) by the total change in volume from high tide to low tide. This calculation results in a systematic overestimation of the total tracer flux per tidal cycle, as the maximum water outflow occurs in the middle of the falling tide, when tracer concentrations are not at their maximum values. However, each of the tracer fluxes was calculated using this same equation, so that the overestimation of tracer flux is the same from tracer to tracer, and the relative fluxes determined by each are valid (although the absolute magnitudes of these fluxes may be subject to error).

A second source of error in these flux calculations is linked to field sampling variability: although sampling was intended to occur at the same relative points in the tidal cycle on each sampling day, this was not always manageable. Consequently, the magnitudes of the fluxes of a given tracer are not necessarily directly comparable from sampling day to sampling day – however, because samples of each tracer were collected concurrently during each tidal cycle, this random error will also not affect their relative fluxes.

3. Results and Discussion

Radium, radon, $\Delta^{14}C$, and salinity values for the high tide inflow and low tide outflow at the Pages and Futch Creek estuaries are shown in Tables 3-4. The high/low tide values are shown for each sampling day within three different sampling periods, April 2001, November 2001, and April 2002. Spring and stream radium, radon, $\Delta^{14}C$, and salinity values are shown in Table 5.

In this section we present spring flux estimates derived from $\Delta^{14}C$, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra. For each tracer we calculate a hypothetical, "inferred" spring flux by assuming that all of the tracer flux is spring-derived (though in fact the springs are not expected to be a primary source of ^{224}Ra, ^{223}Ra, and ^{228}Ra, and may only partially support ^{222}Rn and ^{226}Ra excess). $\Delta^{14}C$ flux estimates are calculated by first determining the spring input as a percentage of the total fresh water input, and then by estimating the total fresh water input to each estuary during each sampling period. We compare the spring discharge estimates derived from ^{222}Rn and the four radium isotopes with discharge derived from $\Delta^{14}C$. To understand the differences among their inferred spring inputs, we consider possible additional sources for each of these tracers, including sediment production and advection of surficial groundwater.

3.1 $\Delta^{14}C$ estimates of spring flux

Fluxes calculated from $\Delta^{14}C$ represent the fresh, artesian component of the total SGD to these estuaries. In the Pages and Futch Creek estuaries, springs and streams are the only fresh water inputs (Table 5), with spring $\Delta^{14}C$ values considerably lower than $\Delta^{14}C$ values from the other DIC inputs (Gramling et al 2003). As shown in Table 5, stream inputs were variable with respect to both DIC concentration and $\Delta^{14}C$ value, and may represent a temporally and spatially variable mix of seepage from the surficial aquifer (which, as shown in Gramling et al (2003), has a high $\Delta^{14}C$ value) and low-$\Delta^{14}C$ artesian inputs. Once the total fresh water input is determined by a salinity mass balance (as a percentage of the outflow), the fresh input can then be parsed into spring input and stream input using $\Delta^{14}C$.

Three-component mixing models for each estuary, with spring, stream, and ICW inflow $\Delta^{14}C$ and DIC values, were used to calculate the relative inputs of spring and stream to the total fresh water budget of each estuary during each sampling period. Separate mixing models for each sampling day in April 2001, November 2001, and April 2002 are described in detail in Chapter III. The $\Delta^{14}C$ data shows that the spring flux was essentially 100% of the total fresh water budget to both estuaries in April 2001 and April 2002, and to the Futch Creek estuary in November 2001, while the November 2001 Pages Creek estuary fresh water inputs were 10-50% spring (Table 6). The range of these November 2001 spring input estimates is determined by the variability in stream $\Delta^{14}C$ and DIC values (as described in Chapter III).

Fresh water fluxes were calculated using Equations (13) and (14), and the estuary values from Table 1. To determine spring flux estimates, the total fresh water flux to the Pages Creek and Futch Creek estuaries is assumed to be 100% spring, with the exception of the Pages Creek November 2001 samples. For these samples, we calculate minimum (10%) and maximum (50%) estimates of spring flux as a percentage of the total fresh water flux. $\Delta^{14}C$-derived spring flux estimates to each estuary during each sampling period are shown in Table 7.

3.2 Spring flux estimates: ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra

We make the initial assumption that the excess ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra activities in both estuaries during all sampling periods are entirely supported by artesian inputs. With this assumption, we use the measured activities of each of these tracers in the springs to make an estimate of the spring discharge rate that would be necessary to support the observed excess of each tracer.

3.2.1 ^{222}Rn estimates of spring flux

Equation (7) (above) shows a mass balance of the sources and sinks for ^{222}Rn. In addition to inflow and outflow from the ICW, the possible sources of ^{222}Rn include springs, fluxes from the sediments, and production within the water column, while the possible sinks include atmospheric evasion and decay within the water column.

Because the surface water activities of the parent isotope of ^{222}Rn, ^{226}Ra, were small (~ 120 - 220 dpm m^{-3}) relative to ^{222}Rn surface water activities (~ 1400 - 24000 dpm m^{-3}), production of ^{222}Rn within the water column was not expected to be an important source term, compared with spring and sediment fluxes, and is assumed to be zero. Decay of ^{222}Rn within the water column was also found to be negligible compared to atmospheric evasion of ^{222}Rn, due to the short residence time of water within each estuary (~ 0.5 d).

To make the initial spring flux estimates, we assume that sediment fluxes of ^{222}Rn are negligible relative to spring inputs of ^{222}Rn. Equation (7) then becomes:

$$J_{222Rn} = J_{spring} - J_{atm} \tag{15}$$

where fluxes are in units of (dpm m^{-2} d^{-1}). J_{222Rn} represents the observed excess ^{222}Rn activities, and J_{atm}, as was described earlier, is dependent on wind speed and on the concentration of ^{222}Rn in the water column (Table 2). Using the atmospheric fluxes presented in Table 2 and the excess ^{222}Rn for each sampling day, Equation (15) is then solved for J_{spring}.

The ^{222}Rn-estimated rate of spring discharge (L m^{-2} d^{-1}) is calculated as:

$$\text{Spring discharge} = \frac{J_{spring}}{\left[{}^{222}Rn\right]_{spring}} \quad (16)$$

Spring ^{222}Rn activities ranged from 200 to 600 dpm L^{-1} (Table 5). To calculate a minimum rate of spring discharge, the highest ^{222}Rn activity observed in any of the springs (600 dpm L^{-1}) is used in Equation (16). It should be noted that, as observed in Chapter IV, ^{222}Rn activities measured in the springs are an order of magnitude lower than ^{222}Rn activities in the wells screened in the Castle Hayne aquifer. Therefore, gas evasion from the springs prior to discharge into the estuaries may be a considerable loss term for ^{222}Rn. Additionally, it is possible that ^{222}Rn activities in springs not measured in this study, but still discharging into these estuaries, could be much higher (which would then decrease the spring discharge rate required to support the observed excess ^{222}Rn).

^{222}Rn-derived spring discharge estimates calculated with this method for each estuary and sampling day are shown in Table 7.

3.2.2 ^{226}Ra, ^{228}Ra, ^{224}Ra, and ^{224}Ra estimates of spring flux

The primary sink terms for each radium isotope included decay within the water column. Because the residence time of the water in the estuaries is less than a day, decay is not expected to be a major source term, and even for the short lived isotopes ^{224}Ra and ^{223}Ra, decay was determined to be negligible. Therefore, Equation (2) becomes:

$$J_{Ra} = J_{spring} \quad (17)$$

As for ^{222}Rn, the spring discharge rate is calculated (in L m^{-2} d^{-1}) as:

$$\text{Spring discharge} = \frac{J_{spring}}{[Ra]_{spring}} \quad (18)$$

where $[Ra]_{spring}$ is the spring Ra activity in dpm $100L^{-1}$ for each of the four radium isotopes. We use the maximum ^{226}Ra (49 dpm $100L^{-1}$), ^{228}Ra (14 dpm $100L^{-1}$), ^{223}Ra (7 dpm $100L^{-1}$), and ^{224}Ra (21 dpm $100L^{-1}$) activities measured in the springs to determine a minimum spring discharge rate required to support the observed excess of each radium isotope on each sampling day (Table 5). We consider only the dissolved radium activities in the springs for this calculation, rather than the particulate radium activities; as discussed in Chapter IV, fluxes of particulate radium from the springs were negligible compared to the measured dissolved fluxes. The estimated spring discharge rates derived from each radium isotope are shown in Table 7.

3.2.3 "Inferred" spring flux comparison

Spring flux estimates derived from all six tracers fell into two groups (Figure 4). The average spring flux estimates derived with ^{228}Ra, ^{223}Ra, and ^{224}Ra ranged (with one exception) from 400 L m^{-2} d^{-1} to 2700 L m^{-2} d^{-1}, while flux estimates derived with Δ^{14}C, ^{222}Rn, and ^{226}Ra ranged from 1 L m^{-2} d^{-1} to 200 L m^{-2} d^{-1}. To support the observed excess of ^{228}Ra, ^{223}Ra, and ^{224}Ra, therefore, spring discharge estimates would need to be 1-2 orders of magnitude higher than the Δ^{14}C spring discharge estimates. Because Δ^{14}C tracks only spring discharge but ^{228}Ra, ^{223}Ra, and ^{224}Ra have other sources within the estuaries, this suggests that springs were not a primary source for ^{228}Ra, ^{223}Ra, and ^{224}Ra to either estuary.

In the Pages Creek estuary, spring discharge estimates derived from fluxes of ^{226}Ra were at least three times higher on all sampling days than spring fluxes derived from ^{222}Rn or Δ^{14}C (Figure 5). In the Futch Creek estuary, Δ^{14}C estimates were higher in April 2001, but during the other sampling times, ^{226}Ra-estimated spring discharge was two to five times higher than discharge estimated with Δ^{14}C. The April 2001 sampling showed the highest change in salinity between high and low tide for the Futch Creek estuary (averaging 10 ppt) (Table 4), and Δ^{14}C mixing models suggest that this fresh water input was entirely from the springs (Chapter III). However, in April 2001, the ^{226}Ra spring flux estimates were the smallest of all sampling periods, at only 20% of the Δ^{14}C-estimated spring fluxes (no estimates were made with ^{222}Rn during this time).

For both estuaries, the sampling days in November 2001 had the smallest change in salinity between high and low tide (ΔSal), with ΔSal always < 0.3 ppt at Pages Creek, and < 3 ppt at Futch Creek. As discussed in Chapter III, the ΔSal was linearly related to the high/low tide increase in Δ^{14}C value in both estuaries, although this was particularly evident at the Futch Creek estuary, where the change in both salinity and $\Delta^{14}C$ was generally larger. The November 2001 $\Delta^{14}C$-derived spring flux estimates were also the smallest of all sampling times. However, although the fresh water input was relatively small during this time, the ^{222}Rn and the ^{226}Ra flux estimates were high relative to other sampling days, and in November 2001, the $\Delta^{14}C$-derived spring fluxes represented only 1% (at Pages Creek) - 20% (at Futch Creek) of the fluxes derived from either ^{222}Rn or ^{226}Ra. Therefore, if the $\Delta^{14}C$-derived fluxes are assumed to represent spring discharge, the springs were not the primary source for either ^{222}Rn or ^{226}Ra in November 2001.

In April 2002, ^{226}Ra spring flux estimates were highest in both estuaries, but were only twice as high as $\Delta^{14}C$ and ^{222}Rn flux estimates. $\Delta^{14}C$ and ^{222}Rn estimates were similar in both estuaries, suggesting that during this sampling period, the springs dominated the budget of ^{222}Rn, and supplied ~ 50% of the excess ^{226}Ra in each estuary.

This suggests that additional sources contributed to the observed excess ^{222}Rn and ^{226}Ra during November 2001 in the Pages Creek estuary, and to the excess ^{226}Ra during April 2001 in the Pages Creek estuary. In the case of ^{226}Ra, this may be advection from the surficial groundwater, while for ^{222}Rn it may be regeneration within estuarine sediments as well as advection from the surficial aquifer. The non-spring-derived fluxes of ^{226}Ra and ^{222}Rn were variable from sampling period to sampling period (Figures 4 and 5).

3.3 Estimation of other contributions to excess ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra

As discussed above, additional inputs must have contributed to the ^{226}Ra budget in the Pages Creek estuary (and to the ^{222}Rn budget in Pages Creek during November 2001), as well as to the ^{228}Ra, ^{223}Ra, and ^{224}Ra budgets in both estuaries. Some of the possible input sources for each isotope are considered below.

3.3.1 Additional sources of ^{222}Rn

In addition to spring discharge, ^{222}Rn may be supplied to estuarine surface waters by fluxes from the sediments, including both advective and diffusive fluxes (Figure 1).

However, because pore water concentrations of ^{222}Rn were not measured in this study, we cannot distinguish between these fluxes to the Pages and Futch Creek estuaries. Previous studies have made measurements of diffusive fluxes of ^{222}Rn in Florida Bay and the Gulf of Mexico using several different methods (including sediment equilibration experiments and measurements of pore water gradients) (Cable et al 1996; Corbett et al 2000). However, the maximum diffusive fluxes estimated in these studies (~ 2600 dpm m^{-2} d^{-1}) would account for less than 20% of the observed excess ^{222}Rn from either estuary during November 2001 (Table 8). Therefore, diffusive fluxes were not likely to have been the primary source of the excess ^{222}Rn during November 2001.

3.3.2 Additional sources of ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra

3.3.2.1 Sediment production

The decay constants for ^{224}Ra and ^{223}Ra ($\lambda = 6.8 \times 10^{1}$ yr^{-1} and $\lambda = 2.3 \times 10^{1}$ yr^{-1}, respectively) are large enough that the sediments could provide a significant source of these isotopes to the estuaries. For ^{228}Ra, the decay constant is smaller ($\lambda = 1.2 \times 10^{-1}$ yr^{-1}), but could result in some regeneration within the sediments on the time scales in this study. The decay constant for ^{226}Ra is very small ($\lambda = 4.3 \times 10^{-4}$ yr^{-1}) and the resulting small rate of regeneration within the estuarine or tidal sediments was not likely to be a significant source of excess ^{226}Ra to the estuaries during the time scale of interest (Rama and Moore 1996).

3.3.2.2 Pore water advection

In both the Pages and Futch Creek estuaries, the ^{228}Ra/^{226}Ra of both the spring and stream inputs was low, at ^{228}Ra/^{226}Ra ~ 0.5:1 for the springs, and 0.6:1 for the streams (Figure 6a-b). However, the observed ^{228}Ra/^{226}Ra in the estuaries was about 1.5:1, with low tide ^{228}Ra and ^{226}Ra activities both increasing over high tide activities along the 1.5:1 gradient. This suggests that, with the springs as one source for ^{226}Ra to the estuaries (but not significantly for ^{228}Ra, thereby lowering the ^{228}Ra/^{226}Ra AR) an additional source is adding ^{228}Ra and ^{226}Ra at an activity ratio that is higher than 1.5:1.

Surficial groundwater seepage is a potential source of ^{228}Ra and ^{226}Ra to the estuaries. Pore water activities of ^{226}Ra and ^{228}Ra from the North Inlet marsh in South Carolina had very high ^{226}Ra and ^{228}Ra activities relative to surface waters, and had measured $^{228}Ra/^{226}Ra$ AR values ranging from 7:1 to 14:1 (Table 9) (Rama and Moore 1996; Krest et al 2000).

Three-component mixing diagrams between Pages and Futch Creek inflow and spring data, and the pore water $^{228}Ra/^{226}Ra$ AR from North Inlet, SC, show that average Pages Creek and Futch Creek estuarine outflow ^{228}Ra and ^{226}Ra activities fall within the mixing triangle, but close to the inflow-spring mixing line (Figures 7-8). The pore water contribution to the outflow can be estimated by constructing a three-endmember mixing calculation. For ^{226}Ra, this calculation is:

$$^{226}Ra_{outflow} = \left(X_{SW} \times {}^{226}Ra_{SW}\right) + \left(Y_{spring} \times {}^{226}Ra_{spring}\right) + \left(Z_{pore\ water} \times {}^{226}Ra_{porewater}\right) \tag{19}$$

where X,Y, and Z represent volume fractions of each component, and SW = the high tide inflow component. A similar calculation is used for ^{228}Ra. The inflow fraction is determined by a salinity mass balance, while the spring and pore water contributions to the outflow are determined by constructing mixing lines to match the outflow composition. If the pore water inputs to the Pages and Futch Creek estuaries have similar ^{226}Ra and ^{228}Ra activities to the North Inlet, SC average pore water, a contribution of only 1% by volume to the total outflow would be required (Figures 7-8) (Rama and Moore 1996). If the pore water input activities were similar to the Rama and Moore (1996) seep water, a contribution of 4% to the outflow would be required to match the observed outflow ^{226}Ra and ^{228}Ra activities. Since these salt marsh pore waters are likely to have salinity values similar to seawater, these small fractions (1 – 4%) would not be seen in the estuary salinity budgets.

4. Comparison of $\Delta^{14}C$-, ^{222}Rn-, and ^{226}Ra-derived flux estimates from Pages and Futch Creeks with SGD estimates from other studies

The estimates of SGD (in $m^3\ d^{-1}$) to the Pages and Futch Creek estuaries calculated in this study were one to three orders of magnitude smaller than geochemical tracer-based SGD estimates from other studies in the southeastern United States (Table 10). ^{226}Ra-derived SGD from the Futch Creek estuary was similar to SGD fluxes from Waquoit Bay, MA (calculated by both ^{226}Ra and by seepage meters), though ^{226}Ra-derived fluxes from the Pages Creek estuary were up to an order of magnitude higher.

^{226}Ra-derived estimates of total SGD from the Pages Creek estuary were an order of magnitude lower than ^{226}Ra-derived estimates of SGD from North Inlet, SC (Table 10). At the Futch Creek estuary, ^{226}Ra-derived estimates were about two orders of magnitude lower. The primary SGD source to the North Inlet site is the salty surficial aquifer, and there are no significant fresh water inputs to this site (including artesian inputs) (Krest et al 2000). However, artesian inputs dominated the excess ^{226}Ra in the Futch Creek estuary, so that if spring discharge (represented by $\Delta^{14}C$ flux) is subtracted from the total ^{226}Ra-derived SGD to this estuary, the remaining flux from non-spring sources is negligible. In the Pages Creek estuary, the majority (50-99%) of the excess ^{226}Ra is derived from non-spring sources; if spring discharge (represented by $\Delta^{14}C$ flux) is subtracted from the total ^{226}Ra-derived SGD, the remaining flux would be about two orders of magnitude lower than SGD from North Inlet.

^{222}Rn-derived estimates (and $\Delta^{14}C$-derived estimates) from Pages Creek and Futch Creek were three orders of magnitude lower than ^{222}Rn estimates of SGD flux to the northeast Gulf of Mexico (Cable et al 1996). In the NE Gulf of Mexico, though ^{222}Rn may be transported to surface waters both by discharge from the Floridan aquifer and by recirculated seawater, seepage and recirculated seawater may predominate over point-source discharge. However, the excess ^{222}Rn in both the Pages and Futch Creek estuaries is dominated by spring discharge. It is possible that the magnitude of point-source artesian fluxes to the NE Gulf of Mexico is similar to artesian flux to the Pages and Futch

Creek estuaries (Florida springs have been observed to discharge at rates from ~10^3 – 10^7 $m^3\ d^{-1}$), but that spring fluxes in that region are masked by much larger fluxes resulting from to seawater recirculation.

5. Conclusions

An intercomparison of total groundwater flux estimates using fluxes of the geochemical tracers $\Delta^{14}C$, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra was performed in two estuaries in southeastern North Carolina. While $\Delta^{14}C$ is a tracer of the fresh, artesian component of the total SGD, fluxes of radium and radon are likely to include both terrestrially-driven and tidally-driven components of the total SGD.

To compare tracer-derived fluxes, "inferred" spring discharge estimates were made by assuming that the low tide excess activity over the high tide activity of each tracer was supported entirely by spring inputs. In both estuaries, spring discharge derived from fluxes of ^{228}Ra, ^{223}Ra, and ^{224}Ra were at least an order of magnitude higher than discharge estimates derived from $\Delta^{14}C$, ^{222}Rn, and ^{226}Ra, suggesting that springs were not a primary source for ^{228}Ra, ^{223}Ra, and ^{224}Ra to either estuary.

In the Pages Creek estuary, spring discharge estimates derived from fluxes of ^{226}Ra were at least two times higher on all sampling days than spring fluxes derived from ^{222}Rn or $\Delta^{14}C$. In the Futch Creek estuary, flux estimates derived from ^{226}Ra were only ~10% of the $\Delta^{14}C$-estimated spring fluxes in April 2001 (no estimates were made with ^{222}Rn during this time), but during the other sampling times, ^{226}Ra-, ^{222}Rn-, and $\Delta^{14}C$-estimates of spring discharge compared well, and were generally within error. This suggests that additional sources contributed to the observed excess ^{222}Rn and ^{226}Ra during November 2001 in the Pages Creek estuary, and to the excess ^{226}Ra during April 2001 in the Pages Creek estuary. In the case of ^{226}Ra, an additional source may be advection from the surficial groundwater, while for ^{222}Rn it may be regeneration within estuarine sediments.

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Table V-1: Area, tide range, and tidal prism data from the Pages and Futch Creek estuaries

	Estuary area (m^2)	Date	Average tide range (m)		Average tidal prism during sampling period (m^3)	
Pages Creek estuary	6.74E+05	Apr-01	0.9		5.92E+05	
		Nov-01	1.1		7.37E+05	
		Apr-02	0.5		3.30E+05	
				0.8		**5.53E+05**
Futch Creek estuary	4.38E+05	Apr-01	0.5		2.40E+05	
		Nov-01	0.8		3.35E+05	
		Apr-02	0.4		1.71E+05	
				0.6		**2.48E+05**

Table V-2: November 2001 and April 2002 wind speed, gas transfer, and atmospheric evasion flux data for the Pages and Futch Creek estuaries.

Date	Average daily wind speed* ($m\ s^{-1}$)	Temperature (degrees Celsius)	Gas transfer coefficient ($m\ d^{-1}$)	Ostwald solubility coefficient (dimensionless)	C_{atm} $dpm\ m^{-3}$	Jatm ($dpm\ m^{-2}\ d^{-1}$)	$J^{222}Rn$ ($dpm\ m^{-2}\ d^{-1}$)
Pages Creek							
11/12/01							
11/13/01	4.40	17	1.06	0.22	560**	8.25E+03	2.52E+04
11/15/01							
11/16/01	4.40	22	1.23			9.72E+03	2.44E+04
11/18/01	3.58	23	0.81			2.18E+04	5.91E+04
Average	**4.13**	**21**	**1.03**			**1.33E+04**	**3.62E+04**
4/13/02							
4/14/02	2.10	23	0.28			1.90E+03	4.39E+04
4/16/02	3.76	29	1.17			6.93E+03	3.92E+04
Average	**2.93**	**26**	**0.72**			**4.42E+03**	**5.02E+04**
Futch Creek							
11/12/01	3.44	23	0.75			1.70E+04	7.22E+04
11/13/01	4.40	17	1.06			1.84E+04	5.14E+04
11/15/01							
11/16/01	4.40	22	1.23			2.50E+04	5.89E+03
11/18/01	3.58	23	0.81			2.75E+04	1.24E+04
Average	**3.96**	**22**	**0.96**			**2.20E+04**	**9.14E+03**
4/13/02	3.31	24	0.80			4.78E+03	6.24E+03
4/14/02	2.10	23	0.28			4.16E+03	1.38E+04
4/16/02	3.76	29	1.17			3.05E+04	4.72E+04
Average	**3.05**	**26**	**0.75**			**1.31E+04**	**3.05E+04**

* Wind speed data from the Wilmington International Airport NOAA weather station in Wilmington, North Carolina
** from Gesell 1983.

Table V-3: Pages Creek estuary high/low tide radium, radon, DIC, and salinity data

	Map Legend	Date	Salinity (ppt)	^{224}Ra	^{223}Ra dpm/100 L	^{226}Ra	^{228}Ra	^{222}Rn dpm/L	Δ^{14}C o/oo	DIC mmol/kg
Pages Creek-High Tide	E1	4/21/01	34.728	28.3	5.5	18.5	28.5		39.1	2.368
Pages Creek-High Tide	E1	4/22/01	34.778	28.2	6.7	13.9	24.7		40.0	2.363
Average 4/01 PC HT			**34.753**	**28.2**	**6.1**	**16.2**	**26.6**		**39.6**	**2.365**
Pages Creek-Low Tide	E1	4/21/01	33.238	53.3	11.3	16.5	25.6		-10.0	2.463
Pages Creek-Low Tide	E1	4/22/01	33.870	45.3	11.9	19.4	28.6		27.9	2.439
Average 4/01 PC LT			**33.554**	**49.3**	**11.6**	**18.0**	**27.1**		**9.0**	**2.451**
Pages Creek-High Tide	E1	11/12/01	36.262	35.9	6.7	21.8	33.6	7.5	46.3	2.339
Pages Creek-High Tide	E1	11/13/01	36.414	24.4	5.4	18.0	24.3	0.7	61.8	2.337
Pages Creek-High Tide	E1	11/15/01	36.428	7.3	1.7	21.4	30.3	3.4	65.9	2.301
Pages Creek-High Tide	E1	11/16/01	36.406	36.9	5.3	19.4	31.3	1.9	71.8	2.289
Pages Creek-High Tide	E1	11/18/01	36.424	25.7	5.7	17.1	22.7	12.1	63.4	2.289
Average 11/01 PC HT			**36.387**	**26.0**	**5.0**	**19.5**	**28.4**	**5.1**	**61.8**	**2.311**
Pages Creek-Low Tide	E1	11/12/01	36.106	36.0	6.9	19.8	31.0	2.1	46.0	2.343
Pages Creek-Low Tide	E1	11/13/01	36.128	36.5	5.3	22.5	34.6	7.9	52.8	2.355
Pages Creek-Low Tide	E1	11/15/01	36.333						34.2	2.301
Pages Creek-Low Tide	E1	11/16/01	36.328	17.0	4.9	24.9	31.2	8.0	53.0	2.279
Pages Creek-Low Tide	E1	11/18/01	36.285	24.0	4.5	18.9	29.1	27.0	54.9	2.188
Average 11/01 PC LT			**36.236**	**28.4**	**5.4**	**21.5**	**31.5**	**11.3**	**48.2**	**2.293**
Pages Creek-High Tide	E1	4/13/02	36.147	25.4	4.2	0.0	0.0	3.4		2.175
Pages Creek-High Tide	E1	4/14/02	36.160	21.0	4.4	12.9	16.1	2.7	55.3	2.171
Pages Creek-High Tide	E1	4/16/02	36.153	29.2	5.0	15.3	12.4	0.2	52.1	2.191
Average 4/02 PC HT			**36.153**	**25.1**	**4.7**	**14.1**	**14.2**	**1.4**	**53.7**	**2.181**
Pages Creek-Low Tide	E1	4/13/02	35.124	15.6	3.4	6.2	8.3	2.2		2.268
Pages Creek-Low Tide	E1	4/14/02	35.167	34.5	8.8	15.4	23.1	6.9	35.3	2.246
Pages Creek-Low Tide	E1	4/16/02	35.327	55.5	12.6	17.6	26.5	6.1	40.7	2.239
Average 4/02 PC LT			**35.206**	**35.2**	**8.3**	**13.1**	**19.3**	**5.1**	**38.0**	**2.251**

Table V-4: Futch Creek estuary high/low tide radium, radon, DIC, and salinity data

	Map Legend	Date	Salinity (ppt)	^{224}Ra	^{223}Ra dpm/100 L	^{226}Ra	^{228}Ra	^{222}Rn dpm/L	$\Delta^{14}C$ o/oo	DIC mmol/kg
Futch Creek-High Tide	E6	4/21/01	35.587	23.4	3.7	11.9	12.0		59.9	2.288
Futch Creek-High Tide	E6	4/22/01	35.429	28.0	5.5	17.4	28.7		43.7	2.328
Average 4/01 FC HT			**35.508**	**25.7**	**4.6**	**14.7**	**20.4**		**51.8**	**2.308**
Futch Creek-Low Tide	E6	4/21/01	23.693	23.0	5.4	13.2	16.4		-139.5	2.700
Futch Creek-Low Tide	E6	4/22/01	26.936	40.4	6.6	18.6	26.3		-100.4	2.591
Average 4/01 FC LT			**25.314**	**31.7**	**6.0**	**15.9**	**21.4**		**-120.0**	**2.645**
Futch Creek-High Tide	E6	11/12/01	36.348	17.1	3.5	18.4	33.3	4.3	67.8	2.207
Futch Creek-High Tide	E6	11/13/01	36.427	11.2	3.3	19.9	24.2	3.2	69.5	2.182
Futch Creek-High Tide	E6	11/15/01	36.434	14.7	2.5	18.0	22.4		75.8	2.204
Futch Creek-High Tide	E6	11/16/01	35.427	18.5	2.7	16.4	22.6	3.2	76.6	2.225
Futch Creek-High Tide	E6	11/18/01	36.481	11.7	4.1	17.4	22.8	3.2	62.4	2.207
Average 11/01 FC HT			**36.223**	**14.7**	**3.2**	**18.0**	**25.1**	**3.5**	**70.4**	**2.205**
Futch Creek-Low Tide	E6	11/12/01	33.783	39.6	7.4	20.3	29.1	22.8	6.1	2.358
Futch Creek-Low Tide	E6	11/13/01	34.392	35.4	6.2	21.4	27.0	17.5	12.5	2.311
Futch Creek-Low Tide	E6	11/15/01	34.964	37.8	4.2	23.7	27.8		36.0	2.214
Futch Creek-Low Tide	E6	11/16/01	34.908	33.1	7.0	20.1	25.2	20.5	29.8	2.248
Futch Creek-Low Tide	E6	11/18/01	34.560	31.7	6.4	21.2	28.7	34.0	20.9	2.264
Average 11/01 FC LT			**34.521**	**35.5**	**6.3**	**21.3**	**27.6**	**23.7**	**21.1**	**2.279**
Futch Creek-High Tide	E6	4/13/02	35.911	25.7	5.5	11.3	15.6	4.1		2.175
Futch Creek-High Tide	E6	4/14/02	35.917	23.7	4.1	12.0	18.0	1.9	55.8	2.176
Futch Creek-High Tide	E6	4/16/02	35.991	30.6	4.5	11.7	14.8	3.7	41.9	2.214
Average 4/02 FC HT			**35.939**	**26.7**	**4.7**	**11.7**	**16.1**	**3.2**	**48.9**	**2.188**
Futch Creek-Low Tide	E6	4/13/02	32.446	70.6	14.0	0.0	0.0	6.1		2.268
Futch Creek-Low Tide	E6	4/14/02	32.934	45.8	8.3	18.8	29.9	14.9	-3.2	2.315
Futch Creek-Low Tide	E6	4/16/02	30.843	34.9	14.0	20.3	30.9	26.2	-44.7	2.392
Average 4/02 FC LT			**32.074**	**40.4**	**11.1**	**19.5**	**30.4**	**20.6**	**-24.0**	**2.354**

Table V-5: Spring and stream radium, radon, DIC, and salinity data

	Map Legend	Date	Salinity (ppt)	^{224}Ra	^{223}Ra	^{226}Ra	^{228}Ra	^{222}Rn	Δ^{14}C	DIC
					dpm/100 L			dpm/L	o/oo	mmol/kg
Streams										
Pages Creek										
Stream at Bayshore	E2	11/7/99	0.000						-79.4	0.866
Stream at Bayshore	E2	7/28/00	0.189						-162.3	1.645
Stream at Bayshore	E2	4/23/01	0.164	11.9	2.4	41.9	21.0		-126.6	1.311
Stream at Bayshore	E2	4/11/02	0.261	11.0	2.5	34.0	16.8	54.7	-199.7	2.092
Stream at Furtado Road	E3	4/19/01	0.177	12.4	1.4	19.0	19.0		-176.5	2.530
Stream at Porters Neck Road	E4	4/19/01	0.142	10.4	1.0	25.8	16.8		-191.8	1.218
Stream at Furtado Road	E3	11/15/01	3.662						86.4	3.806
Stream at Furtado Road	E3	4/13/02	0.201	9.9	0.8	21.4	16.5	31.6		2.859
Futch Creek										
Stream at Scotts Hill Loop Road	E7	4/23/01	0.080	4.8	0.4	10.6	14.3		86.5	0.677
Stream at Scotts Hill Loop Road	E8	11/15/01	9.919	49.4	4.5	43.0	49.2		-160.5	3.188
Stream at Scotts Hill Loop Road	E9	4/15/02	3.057	20.2	4.3	30.8	36.6	37.6	-186.0	3.248
Springs										
Pages Creek										
Bayshore spring	E5	11/7/99	0.000						-406.4	4.485
Bayshore spring	E6	7/20/00	0.526						-403.2	4.432
Bayshore spring	E7	11/15/01	0.239	15.7	1.8	27.0	13.9	492.9	-404.8	4.118
Bayshore spring	E8	4/11/02	0.232	20.5	2.8	31.3	14.0	183.6	-410.3	4.157
Futch Creek										
Spring upstream of 1021 Creekside	E8	4/20/01	0.404	5.7	1.0	10.4			-445.0	4.863
Spring at 1021 Creekside	E9	4/20/01	0.483						-440.4	4.287
Saltwood Lane spring	E10	4/23/01	0.283	3.3	0.2	8.1	6.9		-453.8	2.805
Saltwood Lane spring	E11	11/16/01	4.032	14.6	1.6	21.5	14.4	597.8	-418.1	2.837
Saltwood Lane spring	E12	4/18/02	1.115	8.0	0.5	10.9	6.2	299.7	-449.3	2.850

Table V-6: Fresh water inputs as percent of outflow, and spring inputs as percent of fresh inputs.

		% fresh in outflow	% of fresh input = spring	HT-LT salinity (ΔSal)
Pages Creek	11/7/99	11	100	3.3
	7/26/00	35	0	11.687
	4/21/01	6.7	100	1.490
	4/22/01	2.6	100	0.908
	11/12/01	0.43	100	0.157
	11/13/01	0.79	100	0.286
	11/15/01	0.26	10-44*	0.095
	11/16/01	0.21	16-48*	0.079
	11/18/01	0.38	18-50*	0.138
	4/13/02	2.8	@	1.023
	4/14/02	2.7	100	0.993
	4/16/02	2.3	100	0.826
Futch Creek**	4/21/01	33	100	11.894
	4/22/01	24	100	8.493
	11/12/01	7.1	100	2.565
	11/13/01	5.6	100	2.035
	11/15/01	4.0	100	1.470
	11/16/01	1.5	100	0.519
	11/18/01	5.3	100	1.921
	4/13/02	9.6	@	3.465
	4/14/02	8.3	100	2.983
	4/16/02	14	100	5.148

* Varies with stream endmember

** Stream input may be negligible

@ $\Delta^{14}C$ not analyzed.

Table V-7: Estimates of spring flux (in L m^{-2} d^{-1}) derived from $\Delta^{14}C$, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra

Date	$\Delta^{14}C$ Max	Std Dev	$\Delta^{14}C$ Min	Std Dev	^{222}Rn Flux	Std Dev	^{226}Ra Flux	Std Dev	^{228}Ra Flux	Std Dev	^{223}Ra Flux	Std Dev	^{224}Ra Flux	Std Dev
Pages Creek estuary														
4/21/01	72										2663		3268	
4/22/01	44						189		540		2371		2246	
Average	**58**	**20**					**189**		**540**		**2517**	**206**	**2757**	**723**
11/12/01	8.9										108		20	
11/13/01	8.7				39		191		1775				1981	
11/15/01	2.4		0.5											
11/16/01	2.1		0.7		38		236							
11/18/01	4.0		1.4		88		74		1108					
Average	**5.2**	**3.3**	**0.9**	**0.5**	**55**	**29**	**167**	**84**	**1441**	**472**	**108**		**1000**	**1387**
4/13/02	23													
4/14/02	26				10		47		537		1137		982	
4/16/02	21				21		45		1089		1939		1921	
Average	**23**	**3.5**			**15**	**7.7**	**46**	**1.3**	**813**	**390**	**1538**	**567**	**1451**	**664**
Futch Creek estuary														
4/21/01	343						28		379		470			
4/22/01	246						26				323		1015	
Average	**295**	**69**					**27**		**379**		**397**	**104**	**1015**	
11/12/01	102				73		59				1559		2565	
11/13/01	54				66		45		333		1186		2759	
11/15/01	59						168		650		673		2634	
11/16/01	21				84		108		320		1688		1661	
11/18/01	76				121		112		707		929		2271	
Average	**62**	**30**			**86**	**24**	**98**	**49**	**502**	**204**	**1207**	**423**	**2378**	**439**
4/13/02	85				10						1728		2613	
4/14/02	62				23		103		725		844		1285	
4/16/02	106				79		129		982		1919		246	
Average	**84**	**22**			**38**	**36**	**116**	**18**	**854**	**182**	**1497**	**573**	**1382**	**1186**

Table V-8: Literature diffusive fluxes of 222Rn as percent of total 222Rn excess

	J_{222Rn} dpm m^{-2} d^{-1}	J_{diff} = % of J_{222Rn}
J_{diff} (dpm m^{-2} d^{-1})	2600*	
Pages Creek estuary		
11/12/01		
11/13/01	15057	17
11/15/01		
11/16/01	12745	20
11/18/01	30894	8
Futch Creek estuary		
11/12/01	26879	10
11/13/01	20832	12
11/15/01		
11/16/01	25147	10
11/18/01	44702	6

* from Corbett et al 2000

Table V-9: Pore water values of ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra from the North Inlet salt marsh, SC.

	Salinity ppt	^{226}Ra dpm $100L^{-1}$	^{228}Ra dpm $100L^{-1}$	$^{228}Ra/^{226}Ra$	^{223}Ra dpm $100L^{-1}$	^{224}Ra dpm $100L^{-1}$	$^{224}Ra/^{223}Ra$
Rama and Moore 1996							
Average pore water (0-85 cm)		85	561	6.6	100	927	1.7
Average of refill after pore squeezing		43	588	14	85	725	1.2
Seep		15	176	12	44	410	2.3
Krest et al 2000	30	88	658	7.9			

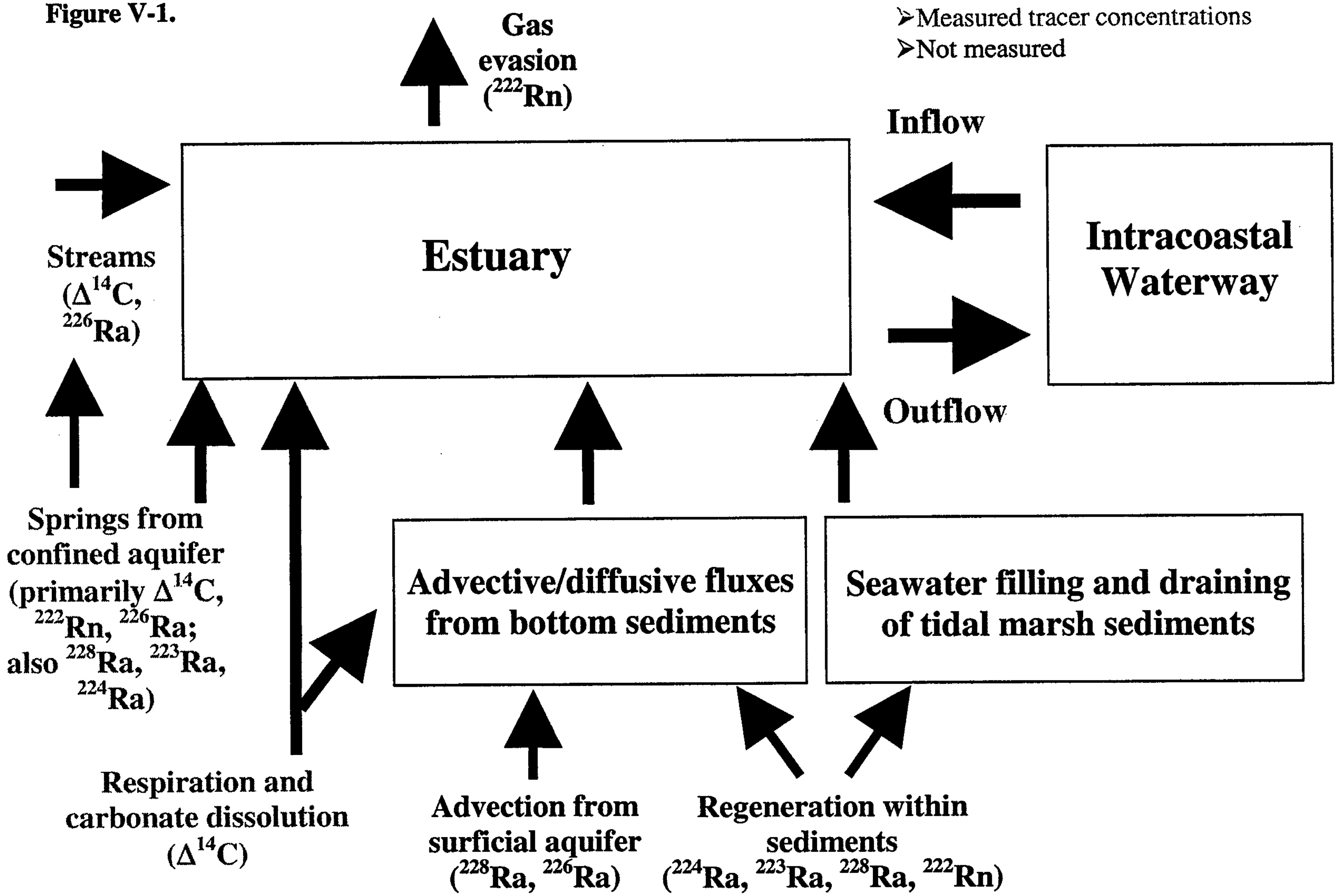
Table V-10: Comparison of flux estimates with estimates of SGD from other sites

	Study site	Method	L $m^{-2}d^{-1}$	m^3 d^{-1}
This study	Pages Creek, NC	$\Delta^{14}C$	2.1 - 72	$0.1 - 4.9 \times 10^4$
	Futch Creek, NC	$\Delta^{14}C$	21 - 343	$0.1 - 1.5 \times 10^5$
Charette et al 2001	Waquoit Bay, MA	^{226}Ra	9.5	3.7×10^4
Krest et al 2000	North Inlet, SC	^{226}Ra	40	1.5×10^6
	North Inlet, SC	^{228}Ra	20	6.8×10^5
Moore 1996	South Carolina coast	^{226}Ra		3.0×10^7
This study	Pages Creek, NC	^{226}Ra	46 - 189	$0.3 - 1.3 \times 10^5$
	Pages Creek, NC	^{228}Ra	540 - 1440	$3.6 - 9.7 \times 10^5$
	Futch Creek, NC	^{226}Ra	27 - 116	$1.2 - 5.1 \times 10^4$
	Futch Creek, NC	^{228}Ra	380 - 850	$1.7 - 3.7 \times 10^5$
Cable et al 1996	NE Gulf of Mexico	^{222}Rn	26 - 98	$1.6 - 6.1 \times 10^7$
This study	Pages Creek, NC	^{222}Rn	15 - 55	$1.0 - 3.7 \times 10^4$
	Futch Creek, NC	^{222}Rn	37 - 86	$1.6 - 3.8 \times 10^4$
Cambareri and Eichner 1998	Waquoit Bay, MA	Seepage meters		$2.4 - 2.8 \times 10^4$
Whiting and Childers 1989	North Inlet, SC	Seepage meters	7.8 - 28	$2.7 - 9.5 \times 10^5$
Morris 1995	North Inlet, SC	Salt diffusion/E-T rates	10	3.4×10^5
Spring discharge rates				
Cable et al 1996	Florida springs: Lanark			3.5×10^3
Rosenau et al 1977	Florida springs: Wakulla			9.5×10^6

Figure V-1

Conceptual model of estuarine sources and sinks of the geochemical tracers of groundwater discharge: $\Delta^{14}C$, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra. Springs supply low-^{14}C DIC, ^{222}Rn, and ^{226}Ra, and to a lesser extent ^{228}Ra, ^{223}Ra, and ^{224}Ra. ^{226}Ra and ^{228}Ra are also supplied by advection from the surficial aquifer, which can enter the estuary via seepage through the bottom sediments. ^{228}Ra, ^{223}Ra, and ^{224}Ra are regenerated within both bottom sediments and tidally inundated marsh sediments, and can be released to estuarine surface waters via diffusion or advection from the bottom sediments, or during draining of the marsh sediments on the falling tide. ^{222}Rn is also regenerated within the sediments, and can enter estuarine surface waters via diffusion. The primary sink term for $\Delta^{14}C$ and all four radium isotopes is low tide outflow from the estuaries; for ^{222}Rn, the primary sink terms are outflow and evasion to the atmosphere.

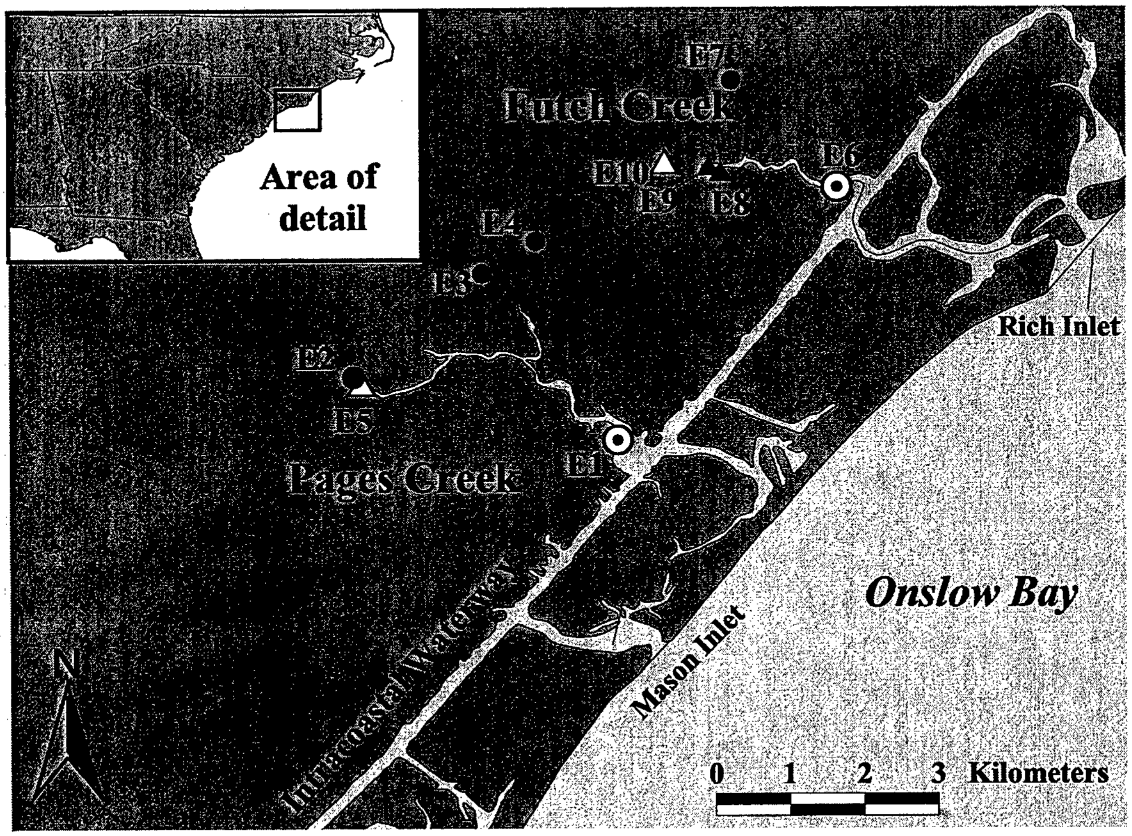
Figure V-1.



Gas evasion (^{222}Rn)
➢Measured tracer concentrations
➢Not measured
Inflow
Estuary
Intracoastal Waterway
Outflow
Streams ($\Delta^{14}C$, ^{226}Ra)
Springs from confined aquifer (primarily $\Delta^{14}C$, ^{222}Rn, ^{226}Ra; also ^{228}Ra, ^{223}Ra, ^{224}Ra)
Advective/diffusive fluxes from bottom sediments
Seawater filling and draining of tidal marsh sediments
Respiration and carbonate dissolution ($\Delta^{14}C$)
Advection from surficial aquifer (^{228}Ra, ^{226}Ra)
Regeneration within sediments (^{224}Ra, ^{223}Ra, ^{228}Ra, ^{222}Rn)

Figure V-2

Pages and Futch Creek estuaries in southeastern North Carolina, with sample locations.



⊙ **Estuary stations (April 2001, November 2001, April 2002)**

● **Streams (November 1999, July 2000, April 2001, November 2001, April 2002)**

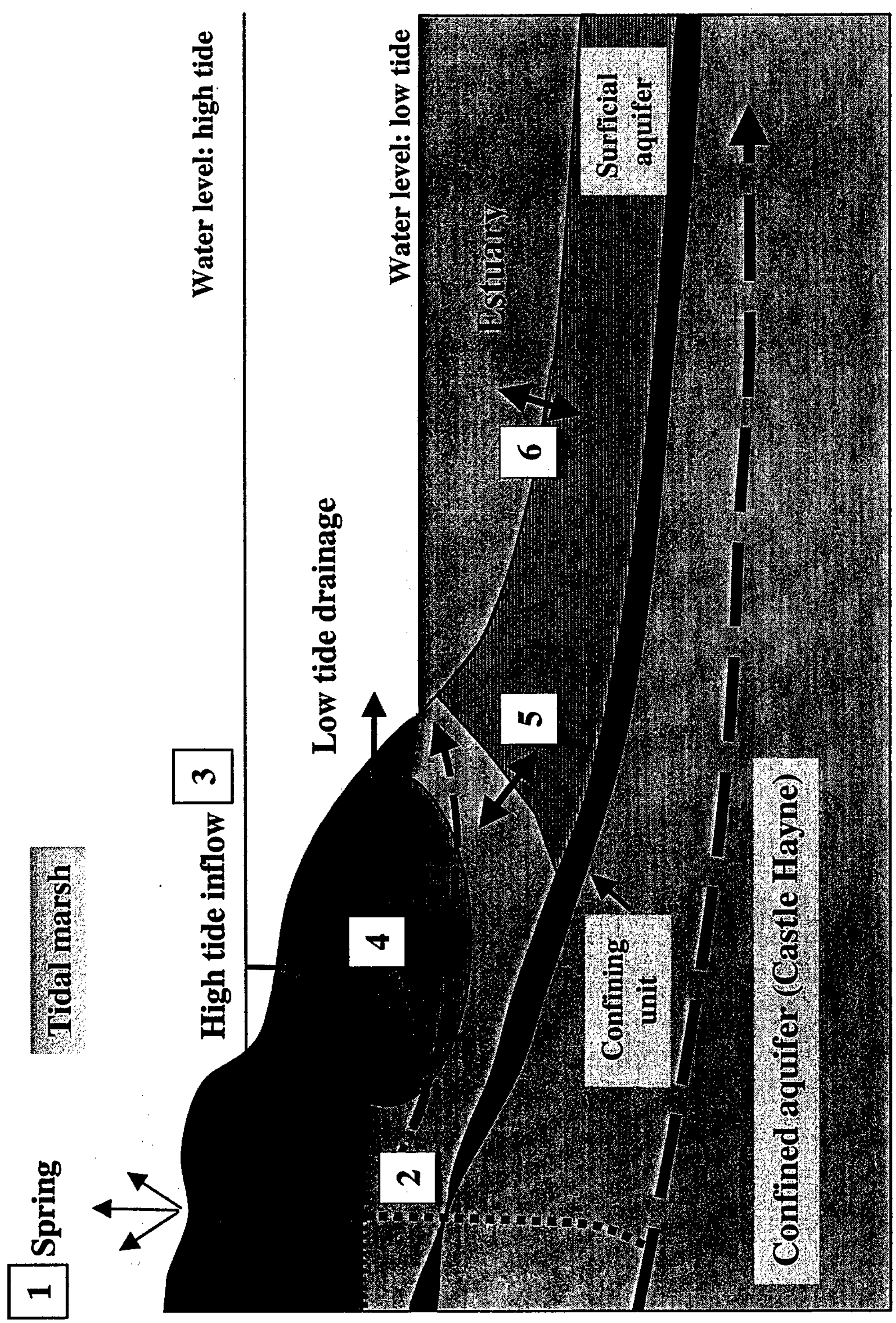
△ **Largest springs (November 1999, July 2000, April 2001, November 2001, April 2002)**

▲ **Other springs (April 2001)**

Figure V-2

Figure V-3

A conceptual cross-section of the interaction between a coastal groundwater system and estuarine processes in the Onslow Bay region. (1) Spring discharge can occur both within the estuary and in the upper marsh as a result of a leaky or locally absent confining unit over the Castle Hayne aquifer; (2) advection of groundwater in the surficial aquifer leads to seepage into streams or directly into the estuary via bottom sediments; (3) tidal filling of marsh sediment pore waters during rising tide stage and subsequent draining of the sediments during falling tide; (4) mixing between the advected groundwater and tidal inundation of sediments; (5) tidal oscillation of brackish water zone through surface aquifer sediments; and (6) tidal pumping of seawater into surface sediments. Arrows indicate fluid movement.

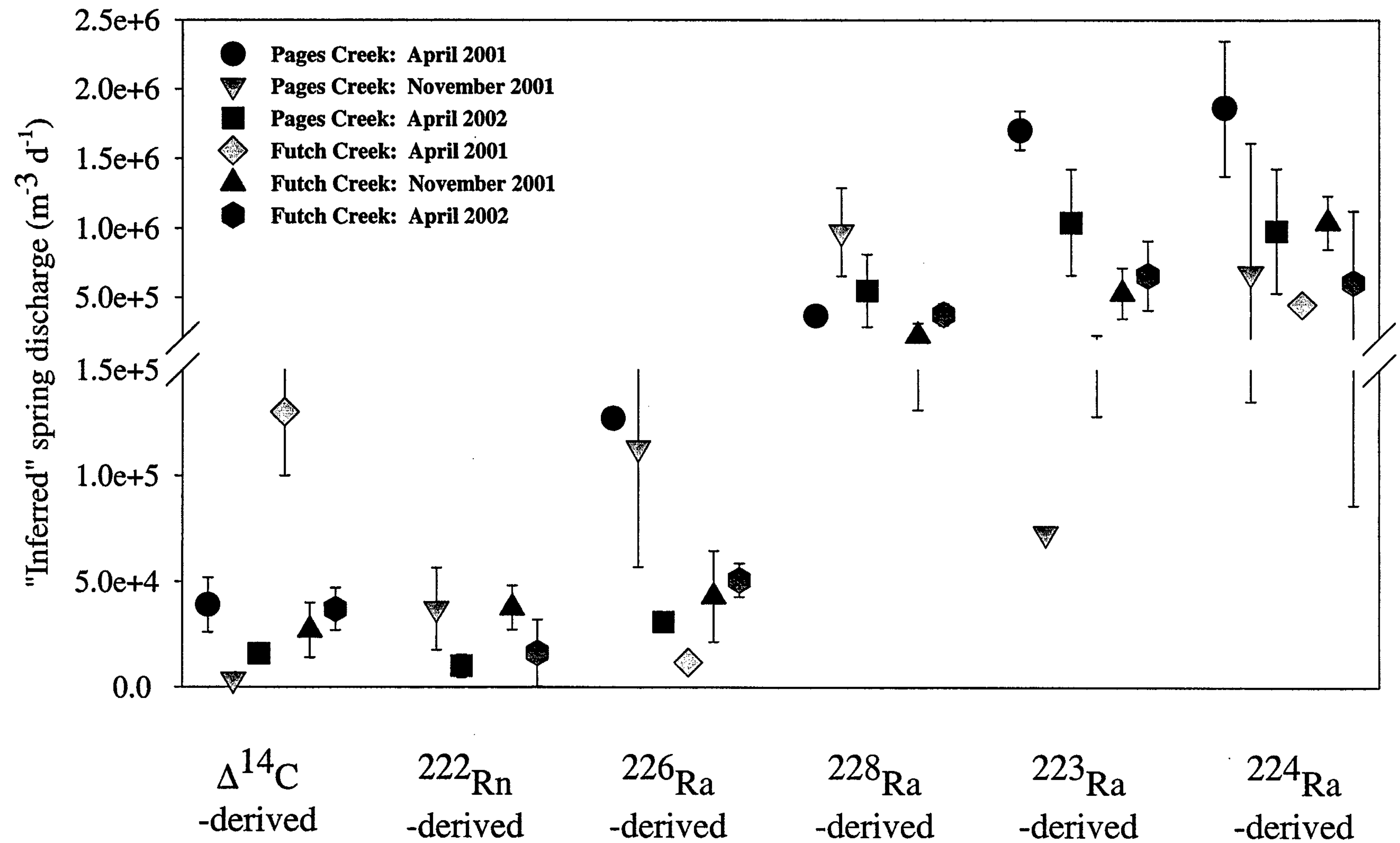


1 Spring
Tidal marsh
High tide inflow 3
Water level: high tide
Low tide drainage
Water level: low tide
2
4
5
6
Estuary
Surficial aquifer
Confining unit
Confined aquifer (Castle Hayne)

Figure V-3

Figure V-4

April 2001, November 2001, and April 2002 "inferred" spring discharge estimates (in m^{-3} d^{-1}) based on $\Delta^{14}C$, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra fluxes from the Pages and Futch Creek estuaries. Estimates are made by assuming that springs are the only source of each tracer to these estuaries. Error bars represent variability in flux estimates for all sampling days within each collection period, and in each estuary. As discussed in the text, in both estuaries, spring discharge derived from fluxes of ^{228}Ra, ^{223}Ra, and ^{224}Ra were at least an order of magnitude higher than discharge estimates derived from $\Delta^{14}C$, ^{222}Rn, and ^{226}Ra, suggesting that springs were not a primary source for ^{228}Ra, ^{223}Ra, and ^{224}Ra to either estuary.



"Inferred" spring discharge (m-3 d-1)
2.5e+6
2.0e+6
1.5e+6
1.0e+6
5.0e+5
1.5e+5
1.0e+5
5.0e+4
0.0
Pages Creek: April 2001
Pages Creek: November 2001
Pages Creek: April 2002
Futch Creek: April 2001
Futch Creek: November 2001
Futch Creek: April 2002
Δ14C -derived
222Rn -derived
226Ra -derived
228Ra -derived
223Ra -derived
224Ra -derived

Figure V-4

Figure V-5

Smaller-scale graph of $\Delta^{14}C$-, ^{222}Rn-, and ^{226}Ra-derived "inferred" spring flux estimates (in $m^{-3}\ d^{-1}$) from the Pages and Futch Creek estuaries, grouped by sampling period. Dark blue bars represent $\Delta^{14}C$-derived spring flux estimates, pink bars represent ^{222}Rn estimates, and light blue bars ^{226}Ra estimates. Error bars represent variability in flux estimates for all days within each collected period and estuary. Note that no ^{222}Rn data was collected from either estuary in April 2001. These data show that while the springs were a significant source of ^{226}Ra and could support all of the observed excess ^{222}Rn to both estuaries during April 2002, spring fluxes were too small in November 2001 to support either ^{222}Rn or ^{226}Ra excess. One or more additional sources therefore contributed to the observed excess ^{222}Rn and ^{226}Ra during November 2001, and to the excess ^{226}Ra during April 2001 and April 2002. In the case of ^{226}Ra, this may be advection from the surficial groundwater, while for ^{222}Rn it may be regeneration within estuarine sediments.

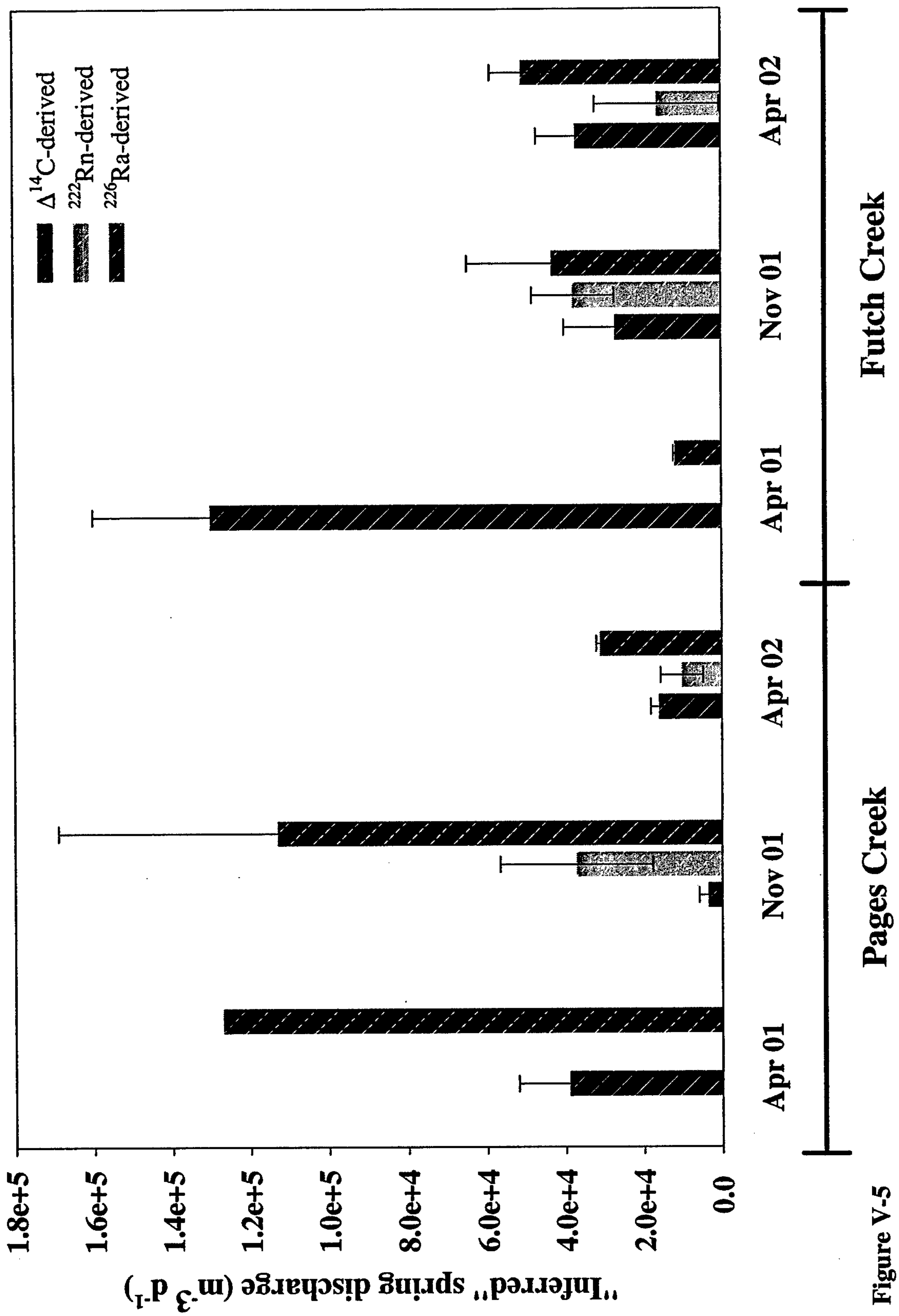

"Inferred" spring discharge (m-3 d-1)
1.8e+5
1.6e+5
1.4e+5
1.2e+5
1.0e+5
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
Δ14C-derived
222Rn-derived
226Ra-derived
Apr 01
Nov 01
Apr 02
Apr 01
Nov 01
Apr 02
Pages Creek
Futch Creek

Figure V-5

Figure V-6

^{228}Ra and ^{226}Ra activities in springs, streams and estuaries. a) Pages Creek estuary. b) Futch Creek estuary. Estuary $^{228}Ra/^{226}Ra$ activity ratios averaged ~1.4:1, while the $^{228}Ra/^{226}Ra$ activity ratios in the springs and streams tended to be less than 0.6:1. Outflow estuary ^{228}Ra and ^{226}Ra activities (filled symbols) were higher than inflow activities, suggesting that the additional source of ^{226}Ra and ^{228}Ra to both estuaries has a high $^{228}Ra/^{226}Ra$ AR (> 1.5:1).

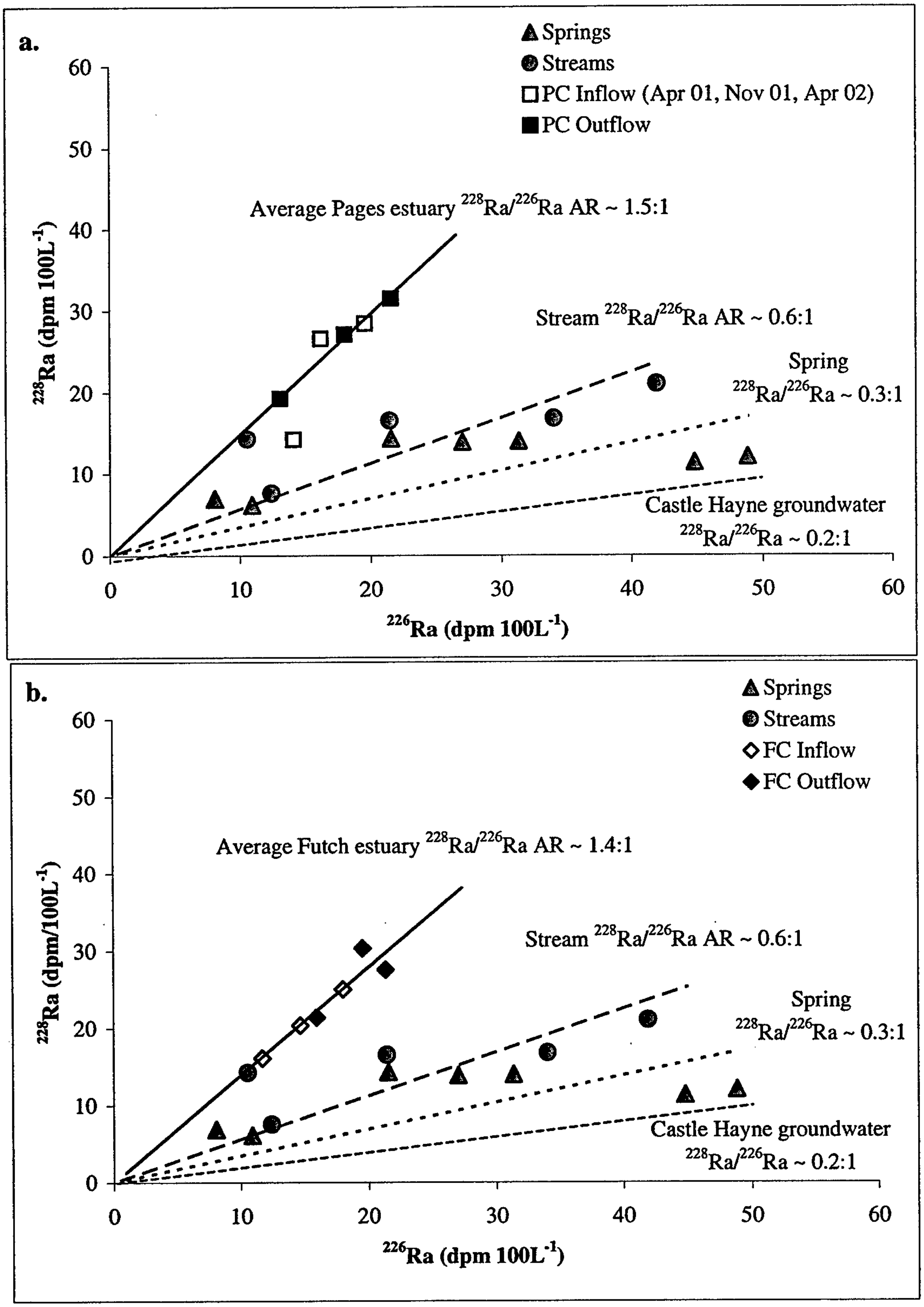

a.
Springs
Streams
PC Inflow (Apr 01, Nov 01, Apr 02)
PC Outflow
Average Pages estuary $^{228}Ra/^{226}Ra$ AR ~ 1.5:1
Stream $^{228}Ra/^{226}Ra$ AR ~ 0.6:1
Spring
$^{228}Ra/^{226}Ra$ ~ 0.3:1
Castle Hayne groundwater
$^{228}Ra/^{226}Ra$ ~ 0.2:1
^{228}Ra (dpm 100L^{-1})
^{226}Ra (dpm 100L^{-1})
0
10
20
30
40
50
60
b.
Springs
Streams
FC Inflow
FC Outflow
Average Futch estuary $^{228}Ra/^{226}Ra$ AR ~ 1.4:1
Stream $^{228}Ra/^{226}Ra$ AR ~ 0.6:1
Spring
$^{228}Ra/^{226}Ra$ ~ 0.3:1
Castle Hayne groundwater
$^{228}Ra/^{226}Ra$ ~ 0.2:1
^{228}Ra (dpm/100L^{-1})
^{226}Ra (dpm 100L^{-1})

Figure V-6

Figure V-7

^{228}Ra and ^{226}Ra three-component mixing curves between average Pages Creek estuary inflow, average spring, and North Inlet, SC pore water activities. Other pore water and spring ^{228}Ra and ^{226}Ra activities are also shown. The low tide outflow ^{228}Ra and ^{226}Ra activities are also shown (grey square). a) Mixing with high-activity, high $^{228}Ra/^{226}Ra$ AR (11:1) pore water (radium activities from Rama and Moore 1996). b) Mixing with low-activity, low $^{228}Ra/^{226}Ra$ (7:1) pore water (Rama and Moore 1996). The pore water percent contribution to the Pages Creek outflow composition varies from 1 to 3% by volume.

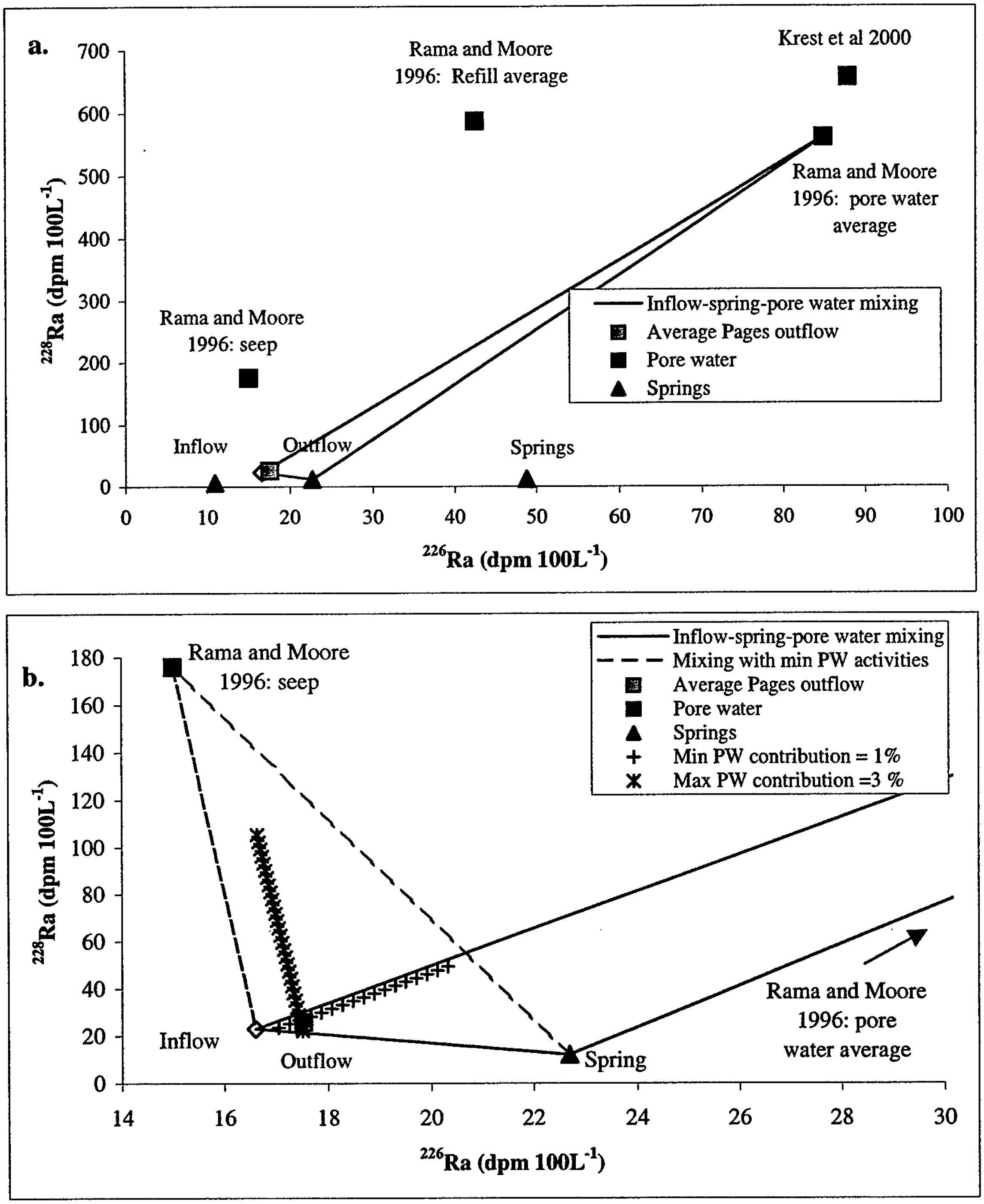
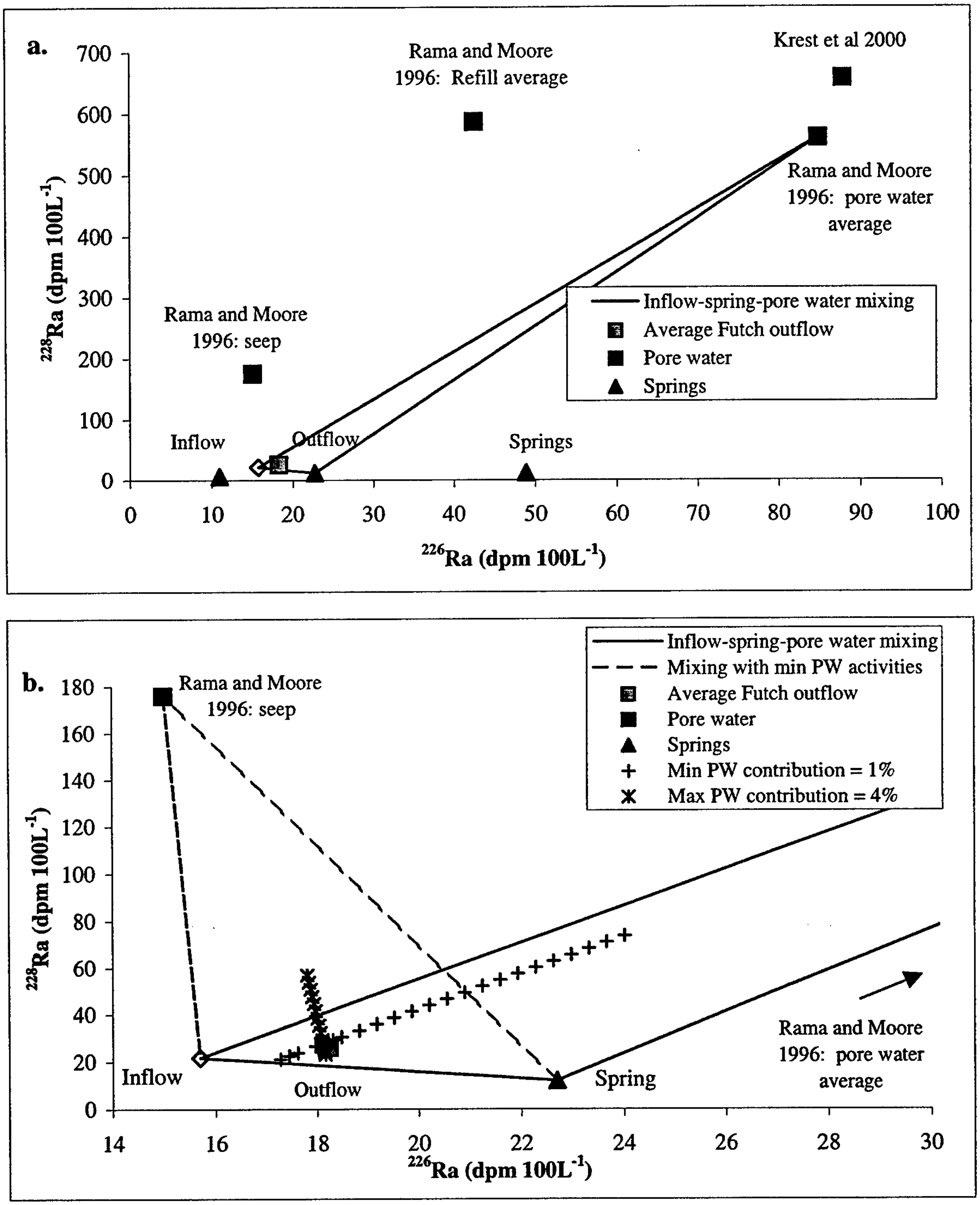

a.
Rama and Moore 1996: Refill average
Krest et al 2000
Rama and Moore 1996: pore water average
Rama and Moore 1996: seep
Inflow
Outflow
Springs
Inflow-spring-pore water mixing
Average Pages outflow
Pore water
Springs
^{228}Ra (dpm 100L^{-1})
^{226}Ra (dpm 100L^{-1})
b.
Rama and Moore 1996: seep
Inflow-spring-pore water mixing
Mixing with min PW activities
Average Pages outflow
Pore water
Springs
Min PW contribution = 1%
Max PW contribution =3 %
Rama and Moore 1996: pore water average
Inflow
Outflow
Spring
^{228}Ra (dpm 100L^{-1})
^{226}Ra (dpm 100L^{-1})

Figure V-7

Figure V-8

^{228}Ra and ^{226}Ra three-component mixing curves between average Futch Creek estuary inflow, average spring, and North Inlet, SC pore water activities. Other pore water and spring ^{228}Ra and ^{226}Ra activities are also shown. The low tide outflow ^{228}Ra and ^{226}Ra activities are also shown (grey square). a) Mixing with high-activity, high $^{228}Ra/^{226}Ra$ AR (11:1) pore water (radium activities from Rama and Moore 1996).
b) Mixing with low-activity, low $^{228}Ra/^{226}Ra$ (7:1) pore water (Rama and Moore 1996). The pore water percent contribution to the Futch Creek outflow composition varies from 1 to 4% by volume.



a.
Rama and Moore 1996: Refill average
Krest et al 2000
Rama and Moore 1996: pore water average
Rama and Moore 1996: seep
Inflow
Outflow
Springs
Inflow-spring-pore water mixing
Average Futch outflow
Pore water
Springs
^{228}Ra (dpm 100L^{-1})
^{226}Ra (dpm 100L^{-1})
b.
Rama and Moore 1996: seep
Inflow-spring-pore water mixing
Mixing with min PW activities
Average Futch outflow
Pore water
Springs
Min PW contribution = 1%
Max PW contribution = 4%
Inflow
Outflow
Spring
Rama and Moore 1996: pore water average
^{228}Ra (dpm 100L^{-1})
^{226}Ra (dpm 100L^{-1})

Figure V-8

Chapter VI: Synthesis and Conclusions

Introduction: The multi-tracer approach to estimates of SGD

In recent years, the term SGD has been increasingly used to include not only the net discharge of fresh groundwater to the ocean (as supplied by aquifer recharge), but also to include the recirculation of seawater through coastal aquifers, driven by both "wave-setup" (a temporary rise in sea level due to wave action) and by tidal oscillations (e.g. Li et al 1999; Moore 1999; Burnett et al 2002). This more general definition is used in this thesis as well, and forms the basis for the intercomparison of tracer fluxes presented here (and in, for example, Burnett et al 2002 and Cable et al 2003). Because each tracer is controlled by a different set of input processes, the flux of each tracer reflects these three SGD components differently, so that an intercomparison of these different methods provides a more comprehensive picture of the total flux.

Earliest global estimates of SGD into oceans, defined as fresh, terrestrially-driven discharge, estimated it to be from 0.2 – 10% of river flow (Garrels and Mackenzie 1971). However, Moore (1996) used coastal ^{226}Ra activities to suggest that SGD fluxes to the South Carolina coast were as much as 40% of the total river flux. A study by Li et al (1999) showed that the terrestrial fluxes, driven by aquifer recharge, were only 4% of the total SGD measured in the Moore (1996) study, while the remaining 96% of the flow was driven by tidal and wave oscillations. These local circulation and oscillating flows can contribute significantly to the rate of SGD to the coast, and therefore these local effects can be responsible for much of the transfer of chemical species, including land-based pollutants and nutrients, to the ocean (Li et al 1999).

Although it is important to specify how SGD is defined when making flux estimates, both terrestrially-driven and circulation fluxes can have a significant impact on coastal geochemistry. The budgets of nutrient species may be influenced by either direct discharge of fresh groundwater into coastal waters, or by chemical reactions occurring during seawater recirculation through shallow coastal aquifers (Taniguchi et al 2002). The relative importance of these terrestrially-driven fluxes and of seawater recirculation to the transfer of nutrients and pollutants to coastal waters is likely to vary by location. The simultaneous study of multiple tracers provides a mechanism by which to identify the relative magnitudes of these components of SGD, and by which to evaluate the inputs of chemical species from each component.

Conclusions/contributions of this thesis

This thesis describes a new, radiocarbon-based method for quantifying one component of the total groundwater flux into coastal waters: the fresh flux from confined aquifers. Using this method, the fresh water inputs to the Pages Creek estuary were shown in Chapters II and III to be dominated by direct discharge from a confined aquifer via springs during November 1999, April 2001, and April 2002. Stream flow accounted for all the fresh water inputs in July 2000, while in November 2001, springs were responsible for 10-50% of the fresh water input to this estuary. In Chapter III, spring inputs were shown to dominate the fresh water inputs to the Futch Creek estuary during all sampling times (April 2001, November 2001, and April 2002).

Although the results from the Pages Creek estuary suggest that spring and stream inputs alternate in their dominance of fresh water inputs to this estuary, the relative magnitude of these inputs is to some extent dependent on the choice and variability of endmembers used in the mixing models. The two primary spring sites, sampled five times over four years, were highly consistent with respect to $\Delta^{14}C$. The substantial variability observed in the stream $\Delta^{14}C$ values is likely to reflect, at least in part, variable contributions of artesian groundwater to the streams.

In both estuaries, spring discharge derived from fluxes of ^{228}Ra, ^{223}Ra, and ^{224}Ra was at least an order of magnitude higher than discharge estimates derived from $\Delta^{14}C$, ^{222}Rn, and ^{226}Ra, suggesting that springs were not a primary source for ^{228}Ra, ^{223}Ra, and ^{224}Ra to either estuary. While the springs were a significant source of ^{226}Ra and could support all of the observed excess ^{222}Rn during April 2002, spring fluxes were too small in November 2001 to support either ^{222}Rn or ^{226}Ra excess. This suggests that additional sources contributed to the observed excess ^{222}Rn and ^{226}Ra during this sampling period, as well as to the excess ^{226}Ra during April 2001 and April 2002. In the case of ^{226}Ra, the additional source is hypothesized to be advection from the surficial groundwater, while for ^{222}Rn it may be regeneration within the sediments, possibly transported by diffusion or by advection through the surficial aquifer. These non-spring-derived fluxes of ^{226}Ra and ^{222}Rn were highly variable among the sampling periods in this study.

In contrast, previous studies comparing ^{226}Ra, ^{228}Ra (e.g. Rama and Moore 1996; Krest et al 2000; Kelly and Moran 2002) and ^{222}Rn (e.g. Hussein et al 1999; Swarzenski et al 2001; Burnett et al 2002; Cable et al 2003) have determined similar estimates of SGD from each tracer. As an example, at the North Inlet, SC, salt marsh, measurements of the long-lived radium isotopes ^{226}Ra and ^{228}Ra appeared to be coupled and provided similar estimates of SGD (Rama and Moore, 1996; Krest et al 2000). However, at North Inlet, the source of the measured SGD is assumed to be the surficial aquifer alone (with very high ^{228}Ra and ^{226}Ra activities); there are no significant fresh water inputs to this site (including artesian inputs). ^{226}Ra- and ^{228}Ra-based estimates of SGD from the Pettaquamscutt estuary, RI, were also found to be similar; in this estuary, excess radium is also attributed to a single source: weathered bedrock with a constant $^{228}Ra/^{226}Ra$ activity ratio (Kelly and Moran 2002).

Burnett et al (2002) conducted an intercomparison study (using ^{222}Rn, ^{226}Ra, ^{228}Ra, seepage meters, and hydrogeologic modeling) to estimate SGD to the northeast Gulf of Mexico, a region that may receive inputs both from nearshore seepage from a (sandy) surficial aquifer and from the shallowest confined aquifer (limestone) in the region. In that study, ^{222}Rn-based estimates of SGD compared well with both ^{226}Ra and ^{228}Ra estimates and with seepage meter estimates, while hydrogeologic models calculated terrestrial fluxes that were an order of magnitude lower. Cable et al (1996), in an earlier study in the northeast Gulf of Mexico, noted that while submarine springs exist in this area, disseminated seepage and recirculated seawater are likely to be much more volumetrically important to the budgets of dissolved species in this coastal area than springs.

In the North Carolina estuaries, spring inputs (originating from a limestone aquifer with elevated ^{222}Rn and ^{226}Ra but not ^{228}Ra activities) were a significant portion of the total SGD (particularly at Futch Creek), so that fluxes of these tracers were decoupled from the ^{228}Ra fluxes. ^{222}Rn in the Pages and Futch Creek estuaries was largely controlled by spring inputs. ^{226}Ra fluxes were at least partially controlled by spring inputs, while ^{228}Ra fluxes showed very little spring influence. Although pore water radium measurements would provide additional constraints on estimates of SGD from these estuaries, it is still apparent that ^{226}Ra-based SGD estimates and ^{228}Ra-based SGD estimates differed by an order of magnitude.

This suggests that in a region with groundwater inputs from two different sources, each with different relative ^{226}Ra and ^{228}Ra activities, these two tracers may provide very different estimates of SGD. However, in a site where recirculation-driven seepage dominates the total SGD (over fluxes from a confined limestone aquifer), ^{222}Rn and ^{226}Ra fluxes are likely to reflect these recirculation fluxes, and to provide similar flux estimates to estimates derived from ^{228}Ra. Consequently, whether these tracers will provide similar estimates is likely to be a site-specific question. This further supports the idea that a multi-tracer approach to quantifying discharge at the coast provides the most comprehensive information about the various components contributing to the total SGD.

Suggestions for future research

There are many ways to build on the work presented in this thesis. One important direction would be to apply this multi-tracer study to additional sites that may be similar geologically to southeastern North Carolina but where the presence of confined groundwater inputs is less certain.

Additionally, while organic matter decomposition in salt marshes did not appear to be a source of low $\Delta^{14}C$ DIC to the Pages and Futch Creek estuaries, respiration DIC-$\Delta^{14}C$ additions can be further constrained by a more comprehensive assessment of pore waters at other sites.

Within the Pages and Futch Creek estuaries, field observations of the relative magnitude of the spring and stream inputs appeared to agree with the results derived from the $\Delta^{14}C$ mixing models: that spring fluxes generally dominated fresh water inputs. Ground-truthing of the $\Delta^{14}C$-based estimates would be provided by actual flow gauging of these spring and stream inputs. Additionally, sediment pore water radium activities were not measured in these estuaries; such measurements would provide a more concrete estimation of the relative contribution of pore waters to the excess radium budgets.

Spring-neap tides may have a dramatic effect on the rate of SGD, and therefore on chemical transfer to coastal waters (Taniguchi 2002; Kim and Hwang 2002). Monthly measurements of SGD using automated seepage meters have found that SGD can increase sharply from neap to spring tide, suggesting that fluxes of recirculating seawater into surface waters via estuarine bottom sediments, as controlled by tidal pumping oscillation, may be an important control on the total SGD rate (Taniguchi 2002). Although sampling in the Pages and Futch Creek estuaries attempted to observe some of the spring tide (November 2001) and neap tide (April 2002) variability, these sampling efforts lasted only for 2-5 days per sampling period, and were insufficient to capture the full range in fluxes resulting from monthly tidal variation. A true assessment of the degree of possible enhancement of recirculation fluxes during spring tide would require at least a full month of daily sampling.

Finally, because SGD is an important pathway for nutrients to coastal waters, an important direction of future research would be the determination of nutrient fluxes from the Pages and Futch Creek estuaries. Though nutrient samples ($NO_2^- + NO_3^-$, and NH_4^+) were collected concurrently with all radium samples in this thesis (data presented in Appendix A), fluxes of these nutrients from the estuaries were not calculated, nor were they partitioned into relative fluxes of nutrients from the different groundwater sources: the springs (in which nutrients were measured) and sediment seepage, driven by tidal and wave forces (in which nutrients were not measured). An estimation of these nutrient fluxes would provide an important window into the relative importance of these sources to the nutrient budgets of this coastal region.

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Appendix A: Nutrient concentrations in Pages and Futch Creek estuaries

Introduction

Submarine groundwater discharge has been shown to be an important pathway for the transport of nutrients, including dissolved inorganic nitrogen (DIN) to estuaries and coastal areas (e.g. Giblin and Gaines 1990; Valiela et al 1990; Krest et al 2000). DIN (as NO_3^- + NO_2^- and as NH_4^+) was measured in the Pages and Futch Creek estuaries (in high tide/low tide pairs, time series, inlets, springs, and streams) in November 2001 and April 2002, concurrently with radium, radon, and $\Delta^{14}C$ sampling.

Nutrient Sampling and Analysis

All nutrient samples were collected by hand at each site, syringe-filtered through a 0.2 μm filter into a 100-ml acid-cleaned polyethylene bottle and frozen prior to analysis. Nutrients (NO_3^- + NO_2^- and NH_4^+) were quantified with an autoanalyzer.

Results and Discussion

Nitrate levels in November 2001 were higher in both the estuaries and in the inlets relative to April 2002 (Tables A1-A3, Figures A1-A2). While Futch Creek exports nitrogen as $NO3^-$ + NO_2 and as NH_4^+ in both November 2001 and April 2002, nitrogen is not always exported in Pages Creek. In November 2001, NO_3^- + NO_2^- and NH_4^+ are exported on the days immediately surrounding the spring tide, but are imported on other days. Pages Creek NH_4^+ fluxes were generally greater than Futch Creek fluxes, with the exception of the day when NH_4^+ was imported.

April 2002 time series data for NO_3^- + NO_2^- in both creeks show an increase leading up to low tide, followed by a rapid decrease when the tide turns (Table A-2). During the Futch Creek estuary time series, NH_4^+ in the water column increased initially, followed by a sudden drop and then a rise to a maximum value at low tide, which then dropped off sharply as the tide turned. The Pages Creek estuary time series also showed a slight drop during the falling tide, though of a smaller magnitude.

In general, more nitrogen was exported from the system in April 2002 than in November 2001, with the exception of a few events during the spring tide. Inflow nitrogen concentrations, in the form of both $NO_3^- + NO_2^-$ and NH_4^+, were five to ten times higher in the fall than in the spring, possibly reflecting nitrogen inputs from the inlet marshes, which then re-entered the estuaries on the rising tide. Outflow concentrations of NH_4^+ from the inlets in November 2001 were two to five times higher than inlet outflow concentrations in April 2002, and $NO_3^- + NO_2^-$ in the outflow from the inlets was about ten times higher in November 2001 than in April 2002.

Roberts (2002) observed a sudden, large spike in NO_3^- (from <1 in August 2001 to ~10 mg/L in September 2001) in the farthest inland Futch Creek spring (map legend E10 in Chapter III figure III-1), though not in other springs. In that study, NO_3^- concentrations in this spring remained above the North Carolina state nitrate standard, 10 mg/L, through most of the autumn, rising to a maximum of 16 mg/L in December 2001 before dropping back to the winter/spring average of <1 mg/L by January 2002. However, $NO_3^- + NO_2^-$ concentrations measured in the same spring for this study were only 1.3 mg/L (21.5 μM) in November 2001 and 0.9 mg/L (15.2 μM) in April 2002.

NO_3^- in the Futch and Pages Creek estuaries, as noted, was considerably elevated in November 2001 relative to April 2002. High NO_3^- levels were also observed in the outflow from marsh in Rich Inlet. This fall increase in NO_3^- may be a seasonal feature, with nutrient levels in the estuaries strongly affected by summer fertilization of the Porters Neck Golf Course, up-dip of the site. Mallin et al (2000) describes the fertilization schedule of the golf course, as of 1982, as consisting of three major events, in July, September, and November. This is highly consistent with observed elevated levels of NO_3^- in the system during the November 2001 sampling time, as described in Roberts (2002). However, as is noted in Roberts (2002), and as is apparent from our own spring NO_3 data, these nutrient levels are highly spatially (and perhaps temporally) variable, from well to well and from spring to spring.

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Table A-1: Pages and Futch Creek estuary nutrients

	Sampling Date	Nitrate (uM)	Ammonia (uM)
Pages Creek			
HT/LT pairs			
Pages High Tide	11/12/01	1.14	0.50
Pages High Tide	11/13/01	0.47	-0.01
Pages High Tide	11/15/01	1.24	0.28
Pages High Tide	11/16/01	1.14	1.60
Pages High Tide	11/18/01	1.89	1.00
Pages Low Tide	11/12/01	1.03	0.28
Pages Low Tide	11/13/01	1.07	0.70
Pages Low Tide	11/16/01	1.58	1.75
Pages Low Tide	11/18/01	1.14	0.38
Pages High Tide	4/13/02	0.10	1.01
Pages High Tide	4/14/02	0.11	1.68
Pages High Tide	4/16/02	0.12	1.33
Pages Low Tide	4/13/02	0.35	3.78
Pages Low Tide	4/14/02	0.31	1.92
Pages Low Tide	4/16/02	0.23	1.25
Futch Creek			
HT/LT pairs			
Futch High Tide	11/12/01	0.96	0.28
Futch High Tide	11/13/01	1.07	0.10
Futch High Tide	11/15/01	1.15	0.43
Futch High Tide	11/16/01	1.17	0.27
Futch High Tide	11/18/01	1.16	0.45
Futch Low Tide	11/12/01	1.74	0.67
Futch Low Tide	11/13/01	1.46	0.46
Futch Low Tide	11/15/01	1.41	6.38
Futch Low Tide	11/16/01	1.82	1.22
Futch Low Tide	11/18/01	1.53	0.61
Futch High Tide	4/13/02	0.16	1.04
Futch High Tide	4/14/02	0.10	1.01
Futch High Tide	4/16/02	0.09	0.69
Futch Low Tide	4/13/02	0.34	1.67
Futch Low Tide	4/14/02	0.47	2.17
Futch Low Tide	4/16/02	0.68	2.75

Table A-2: Time series nutrients

Sampling Date/Time	Nitrate (uM)	Ammonia (uM)
Pages Creek Nov 01 time series		
11/13/01 7:23	0.88	-0.04
11/13/01 8:24	1.01	0.08
11/13/01 9:28	1.33	0.23
11/13/01 10:18	1.01	0.10
11/13/01 11:27	0.86	0.49
11/13/01 12:03	0.66	0.17
11/13/01 12:42	0.70	0.36
11/13/01 13:25	1.34	0.36
11/13/01 14:25	0.97	0.03
11/13/01 15:20	1.10	-0.05
11/13/01 16:21	0.98	-0.18
11/13/01 17:20	1.07	-0.09
11/13/01 18:22	0.98	-0.11
11/13/01 19:20	1.00	-0.09
Pages Creek April 02 time series		
4/14/02 8:37	0.104	1.030
4/14/02 9:45	0.113	1.682
4/14/02 10:50	0.108	0.904
4/14/02 11:50	0.136	1.373
4/14/02 12:50	0.183	1.560
4/14/02 13:48	0.188	1.862
4/14/02 14:30	0.213	1.707
4/14/02 15:50	0.309	1.921
4/14/02 16:25	0.321	3.022
4/14/02 17:32	0.301	1.391
4/14/02 18:27	0.175	0.772
4/14/02 19:29	0.143	0.559
Futch Creek April 02 time series		
4/16/02 9:00	0.094	1.859
4/16/02 10:00	0.061	0.733
4/16/02 11:00	0.093	0.688
4/16/02 12:00	0.127	0.820
4/16/02 13:00	0.201	2.499
4/16/02 14:00	0.201	1.537
4/16/02 15:03	0.349	2.535
4/16/02 16:01	0.456	2.917
4/16/02 17:02	0.675	2.752
4/16/02 18:00	0.532	2.203
4/16/02 19:00	0.148	1.748
4/16/02 20:00	0.143	0.818

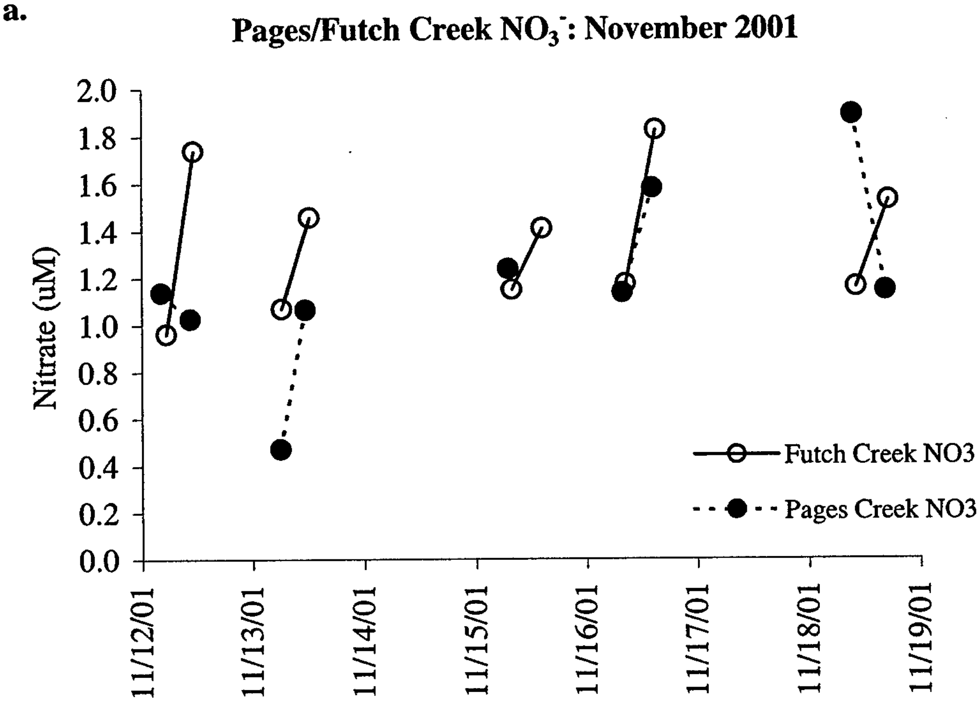
Table A-3: Inlet and fresh water nutrients

Location	Sampling Date	Nitrate (uM)	Ammonia (uM)
Inlets			
Rich Inlet - Low Tide	11/17/01	0.98	0.95
Rich Inlet Mouth-HT	4/15/02	0.02	0.41
Rich Inlet Mouth-HT	4/17/02	0.03	0.12
Rich Inlet @ ICW-HT	4/17/02	0.03	0.14
Rich Inlet Mouth-LT	4/15/02	0.08	0.23
Rich Inlet Mouth-LT	4/17/02	0.10	0.38
Rich Inlet @ ICW-LT	4/17/02	0.08	0.19
Mason Inlet Mouth HT	4/15/02	0.03	0.28
Mason Inlet @ ICW-HT	4/17/02	0.06	0.12
Mason Inlet Mouth LT	4/15/02	0.11	0.45
Mason Inlet @ ICW-LT	4/17/02	0.10	0.26
Fresh water samples			
Springs			
Pages			
Bayshore spring	11/15/01	1.49	1.04
Bayshore spring	4/11/02	0.11	16.37
Futch			
Saltwood spring	11/16/01	21.48	0.92
Saltwood spring	4/18/02	15.20	0.86
Streams			
Pages			
Bayshore stream	11/15/01	1.25	3.52
Bayshore stream	4/11/02	0.69	3.09
Furtado Road stream	4/13/02	2.03	2.05
Futch			
Scotts Hill Loop stream	11/15/01	28.71	1.45
Scotts Hill Loop stream	4/15/02	8.36	16.85

Figure A-1

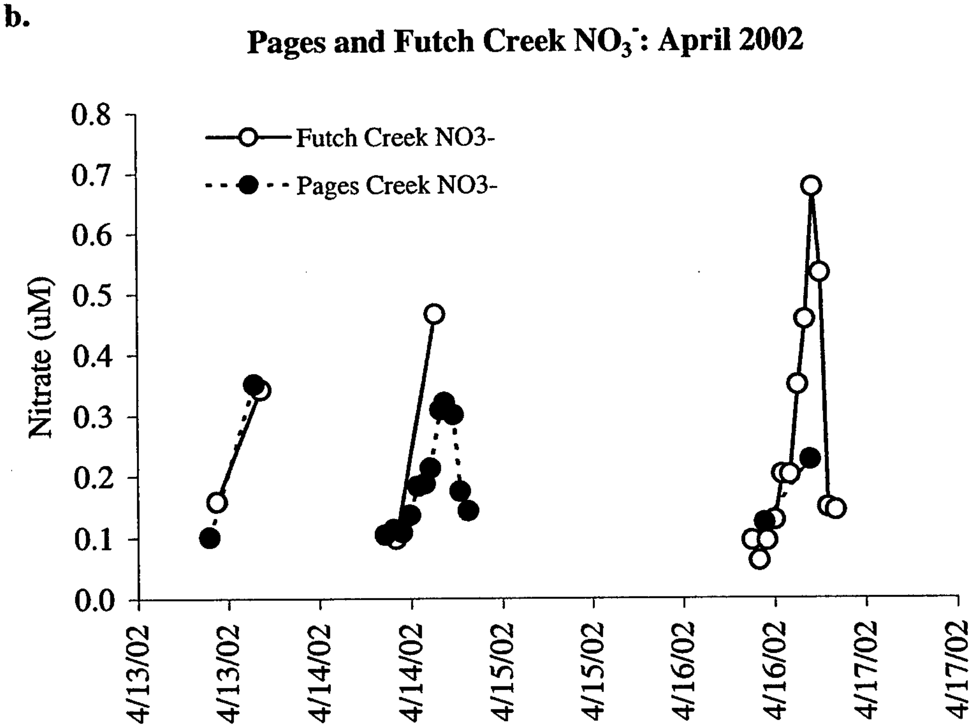
Nitrate data from the Pages and Futch Creek estuaries in: a. November 2001. b. April 2002. Open circles represent data from the Futch Creek estuary; filled circles represent data from the Pages Creek estuary. The 4/14/02 Pages Creek hourly time series and the 4/16/02 Futch Creek hourly time series are also shown. NO_3^- always increased in the Futch Creek estuary from high tide to low tide. NO_3^- increased from high to low tide in the Pages Creek estuary on all sampling days during April 2002, but not on all sampling days in November 2001.

a.



Pages/Futch Creek NO_3^-: November 2001
Nitrate (uM)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Futch Creek NO3
Pages Creek NO3
11/12/01
11/13/01
11/14/01
11/15/01
11/16/01
11/17/01
11/18/01
11/19/01

b.



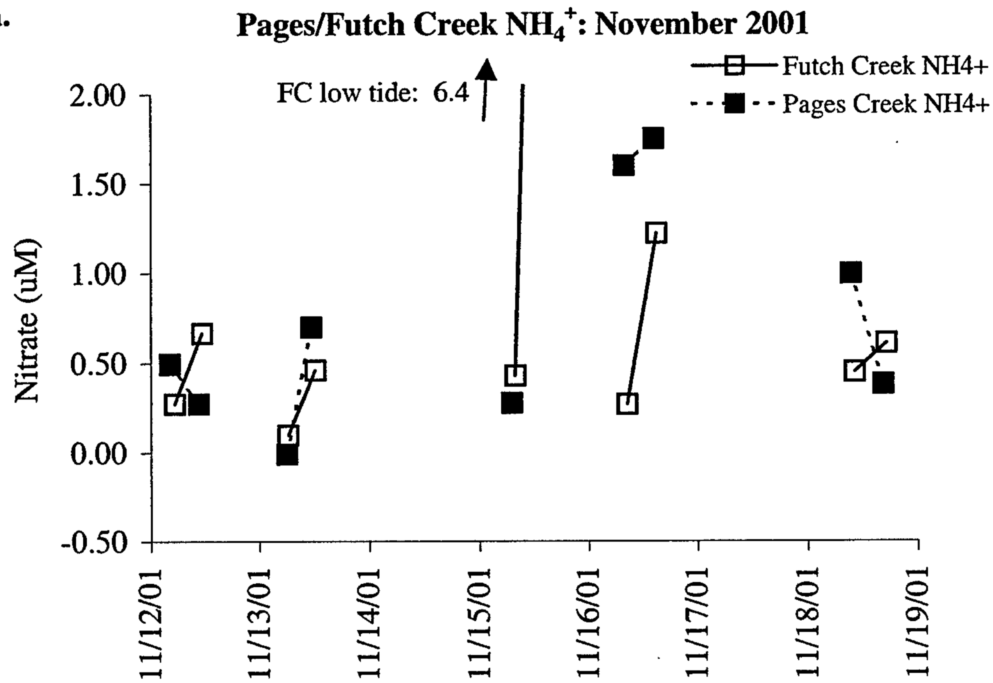
Pages and Futch Creek NO_3^-: April 2002
Nitrate (uM)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Futch Creek NO3-
Pages Creek NO3-
4/13/02
4/13/02
4/14/02
4/14/02
4/15/02
4/15/02
4/16/02
4/16/02
4/17/02
4/17/02

Figure A-1

Figure A-2

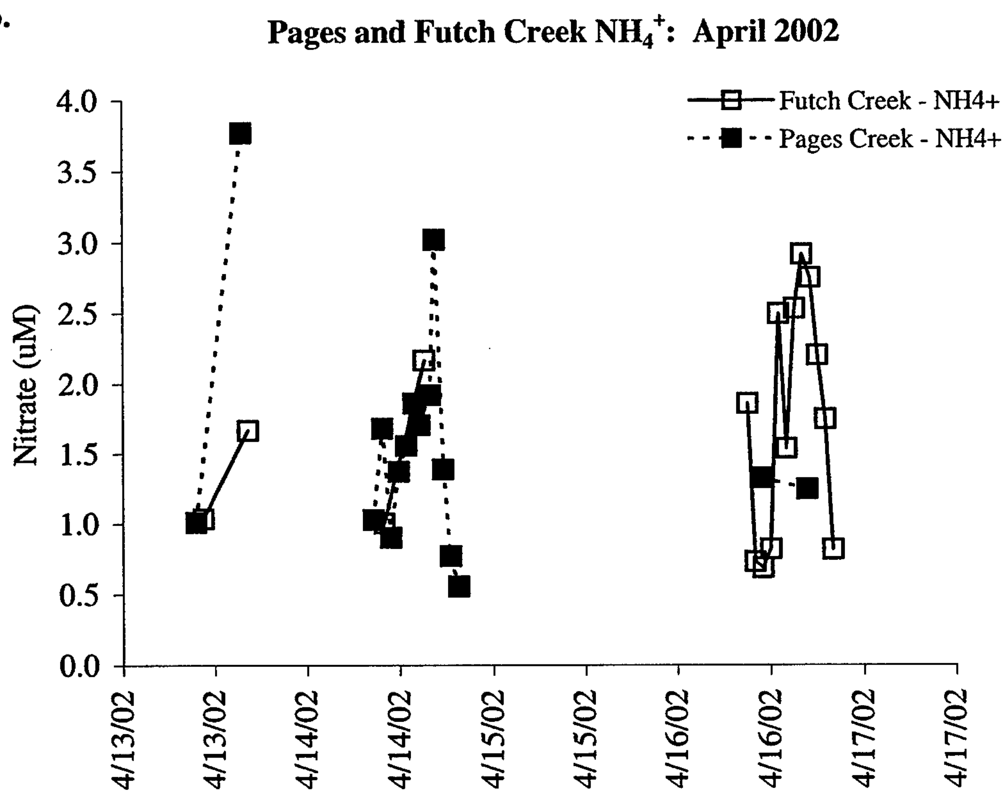
Ammonium data from the Pages and Futch Creek estuaries in: a. November 2001. b. April 2002. Open squares represent data from the Futch Creek estuary; filled squares represent data from the Pages Creek estuary. The 4/14/02 Pages Creek hourly time series and the 4/16/02 Futch Creek hourly time series are also shown. NH_4^+ always increased in the Futch Creek estuary from high tide to low tide, although the time series data in April 2002 showed more scatter than the nitrate time series data. NH_4^+ increased from high to low tide in the Pages Creek estuary on all sampling days during April 2002, but not on all sampling days in November 2001 (showing similar trends to the NO_3^- data).

a.



Pages/Futch Creek NH$_4^+$: November 2001
Futch Creek NH4+
Pages Creek NH4+
FC low tide: 6.4
Nitrate (uM)
2.00
1.50
1.00
0.50
0.00
-0.50
11/12/01
11/13/01
11/14/01
11/15/01
11/16/01
11/17/01
11/18/01
11/19/01

b.



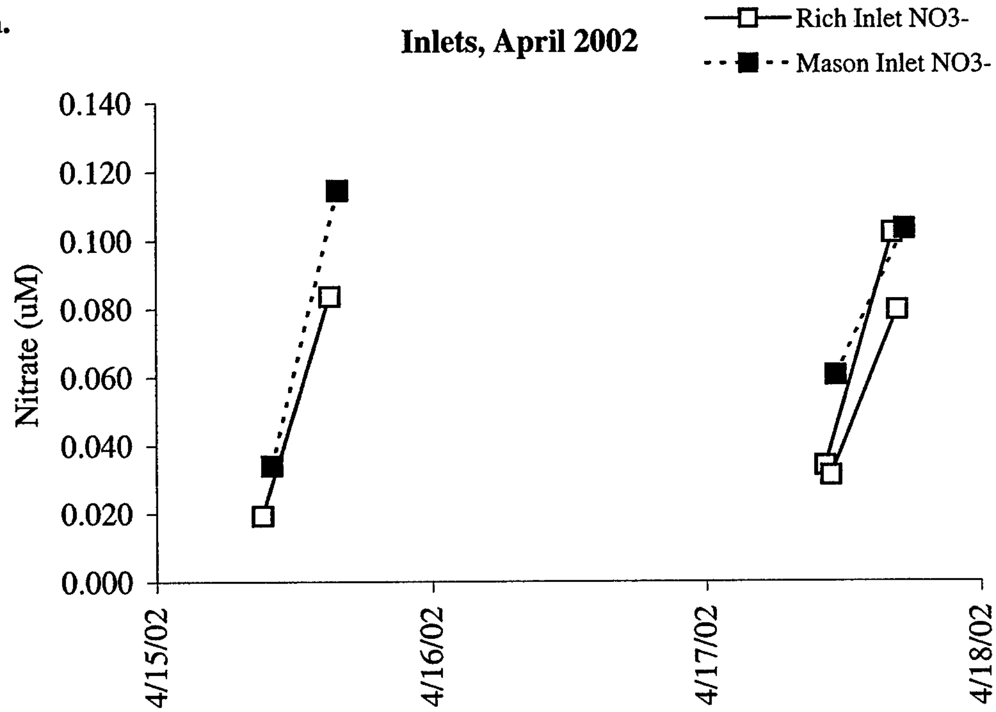
Pages and Futch Creek NH$_4^+$: April 2002
Futch Creek - NH4+
Pages Creek - NH4+
Nitrate (uM)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
4/13/02
4/13/02
4/14/02
4/14/02
4/15/02
4/15/02
4/16/02
4/16/02
4/17/02
4/17/02

Figure A-2

Figure A-3

April 2002 nutrient data from Rich and Mason Inlets. a. NO_3^-. b. NH_4^+. Open squares represent data from Rich Inlet; filled squares represent data from the Mason Inlet. Nutrients tended to increase from high to low tide in both inlets, with the exception of Rich Inlet on 4/15/02, when NO_3^- increased but NH_4^+ decreased at low tide.

a.


Inlets, April 2002
Rich Inlet NO3-
Mason Inlet NO3-
Nitrate (uM)
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
4/15/02
4/16/02
4/17/02
4/18/02

b.

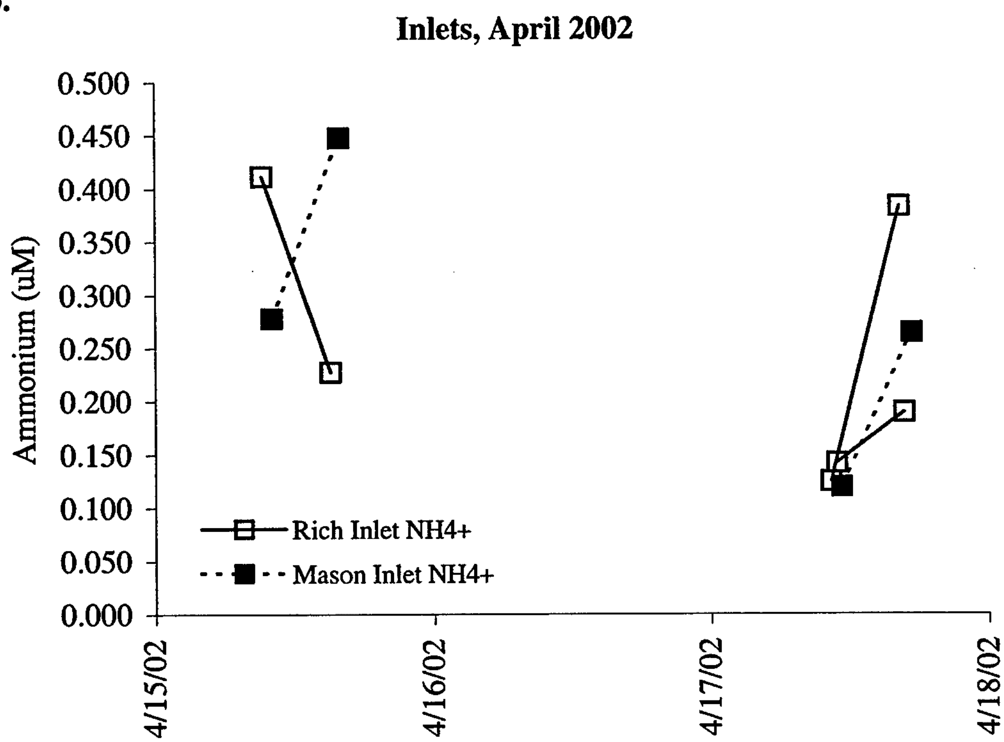

Inlets, April 2002
Ammonium (uM)
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
Rich Inlet NH4+
Mason Inlet NH4+
4/15/02
4/16/02
4/17/02
4/18/02

Figure A-3

Appendix B: $\Delta^{14}C$ measurements from mid-continental shelf wells

DIC and DIC isotopic analyses were performed on samples collected from a high-permeability zone (HPZ) 2 m below the seabed offshore of southeastern North Carolina. The HPZ, consisting of a meter of sand and shell between an overlying clay layer and an underlying carbonate layer, is located in Long Bay, 20 km south of Holden Beach, NC, in water 15 m deep. Moore et al (2002) measured a temperature cycle within the HPZ that was in phase with the tide, suggesting that tidal pumping drives water exchange between the HPZ and the ocean. This HPZ may be a source for nutrients to coastal waters (Moore et al 2002).

DIC and DIC isotopic values from two wells (Well 1 and Well A) installed within the HPZ and from the overlying bottom water are shown in Table 1. Figure 1 shows DIC-$\delta^{13}C$ and DIC-$\Delta^{14}C$ trends for mixing between the bottom water and dissolved carbonate aquifer rock ($\delta^{13}C \sim +1‰$, $\Delta^{14}C \sim -1000‰$), marine organic matter ($\delta^{13}C \sim -20‰$) and a 50:50 mix of DIC added from both carbonate and marine organic matter ($\delta^{13}C \sim -10‰$). These preliminary $\delta^{13}C$-DIC and $\Delta^{14}C$-DIC mixing models suggest that water in the HPZ wells may be the result of mixing between bottom water and an input with very low $\delta^{13}C$ and $\Delta^{14}C$ values (Figure 1). For $\delta^{13}C$-DIC mixing, the input DIC $\delta^{13}C$ values were between –10‰ and –20‰. For $\Delta^{14}C$-DIC mixing, input DIC $\Delta^{14}C$ values were between –500‰ and –1000‰. These data are preliminary, but suggest that $\Delta^{14}C$ has potential as a tracer of salty groundwater discharge from confined aquifers, as well as of fresh discharge.

References

Moore, W.S., J. Krest, G. Taylor, E. Roggenstein, S. Joye, and R. Lee. (2002) Thermal evidence of water exchange through a coastal aquifer: implications for nutrient fluxes. Geophysical Research Letters 29(14), 49-1 – 49-4.

Table B-1: DIC and DIC isotopic values of Well 1, Well A, and bottom water

			DIC mmol/kg	$\Delta^{14}C$ o/oo	$\delta^{13}C$ o/oo
Well 1	Top of HPZ:	+ 2.0 m	3.609	-5.21	-379.1
	Bottom of HPZ:	+ 0 m	2.410	-2.52	-185.6
Well A	Top of HPZ:		3.091	-3.63	-213.2
	Bottom of HPZ:		3.286	-4.29	-250.4
Bottom water	outside Well 1		2.049	0.80	84.1
	outside Well A		2.057	0.73	73.2

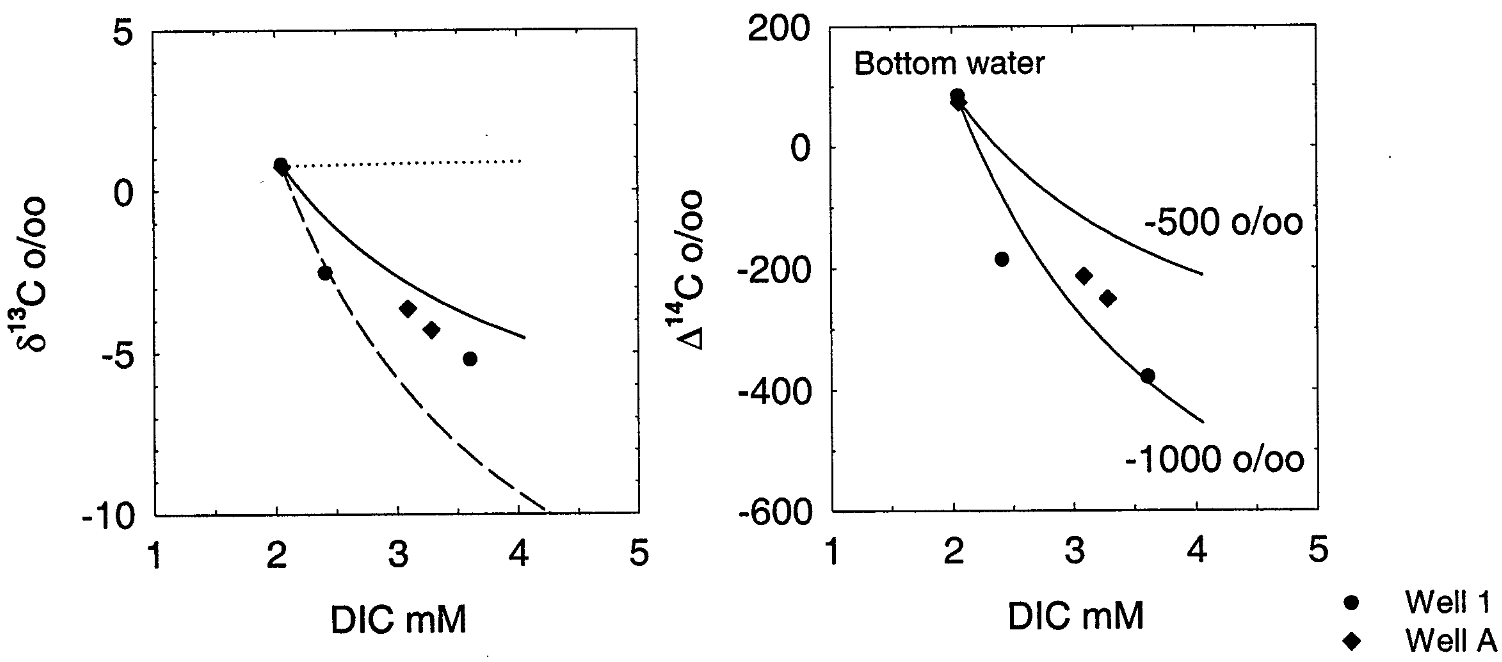


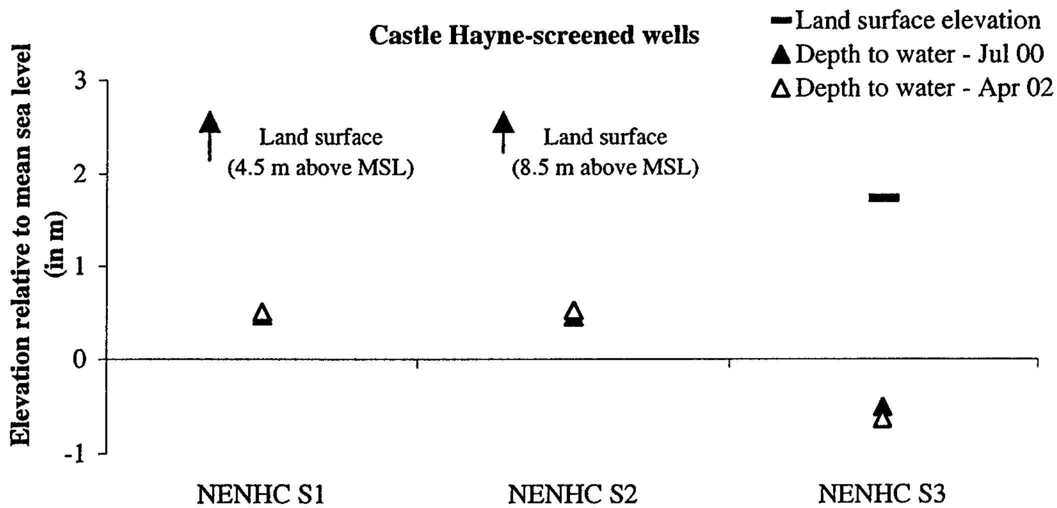
Figure B-1. Cape Fear mid-shelf bottom water and well data reflect an input of low $\delta^{13}C$, low $\Delta^{14}C$ DIC. (Model curves show DIC additions with given isotopic compositions.)

Appendix C:
Well head data from Topsail Beach and NENHC wells

Table C-1: Well data from the six NENHC wells in July 2000 and April 2002

	Well depth from land surface (LS) (m)	Depth to water (m) (from LS) (July 2000)	Depth to water (m) (from LS) (April 2002)	Land surf elevation (m)	Aquifer	Salinity (ppt) (July 2000)	Salinity (ppt) (April 2002)
NENHC* S1	-7.28	0.47	0.50	4.61	CH	0.294	0.2569
NENHC S2	-8.07	0.45	0.52	8.39	CH	0.249	0.2813
NENHC S3	-9.24	-0.51	-0.63	1.73	CH	0.895	0.8177
NENHC D1	-50.32	-1.23	0.40	4.54	PD	0.410	0.3791
NENHC D2	-49.45	-2.57	0.05	8.46	PD	1.461	0.6674
NENHC D3	-50.00	-3.48	-1.14	1.81	PD	0.777	0.5121

*NENHC = Northeast New Hanover Conservancy monitoring wells on Porters Neck Rd



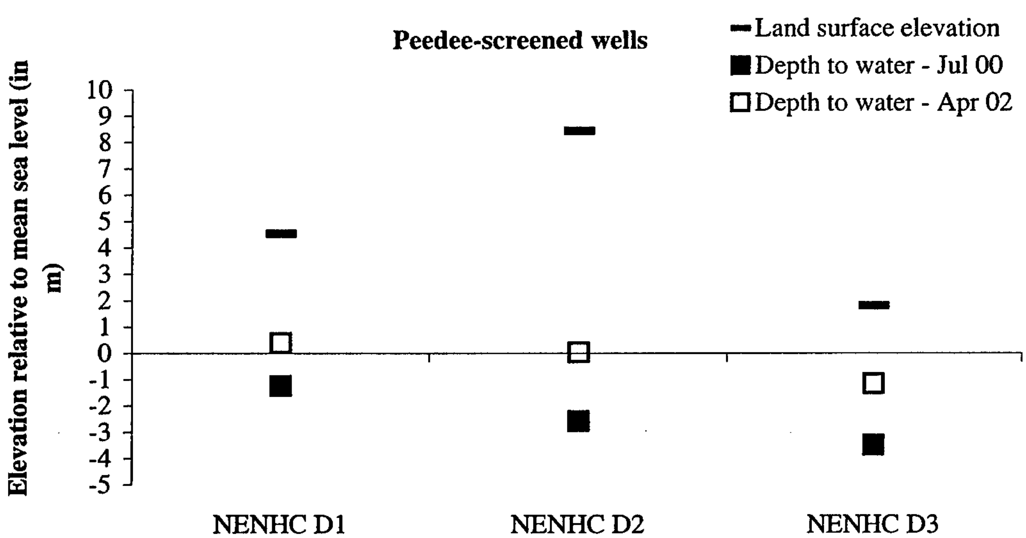


Figure C-1. July 2000 and April 2002 well head data for the NENHC S (Castle Hayne) and D (Peedee) wells (between Pages and Futch Creeks).

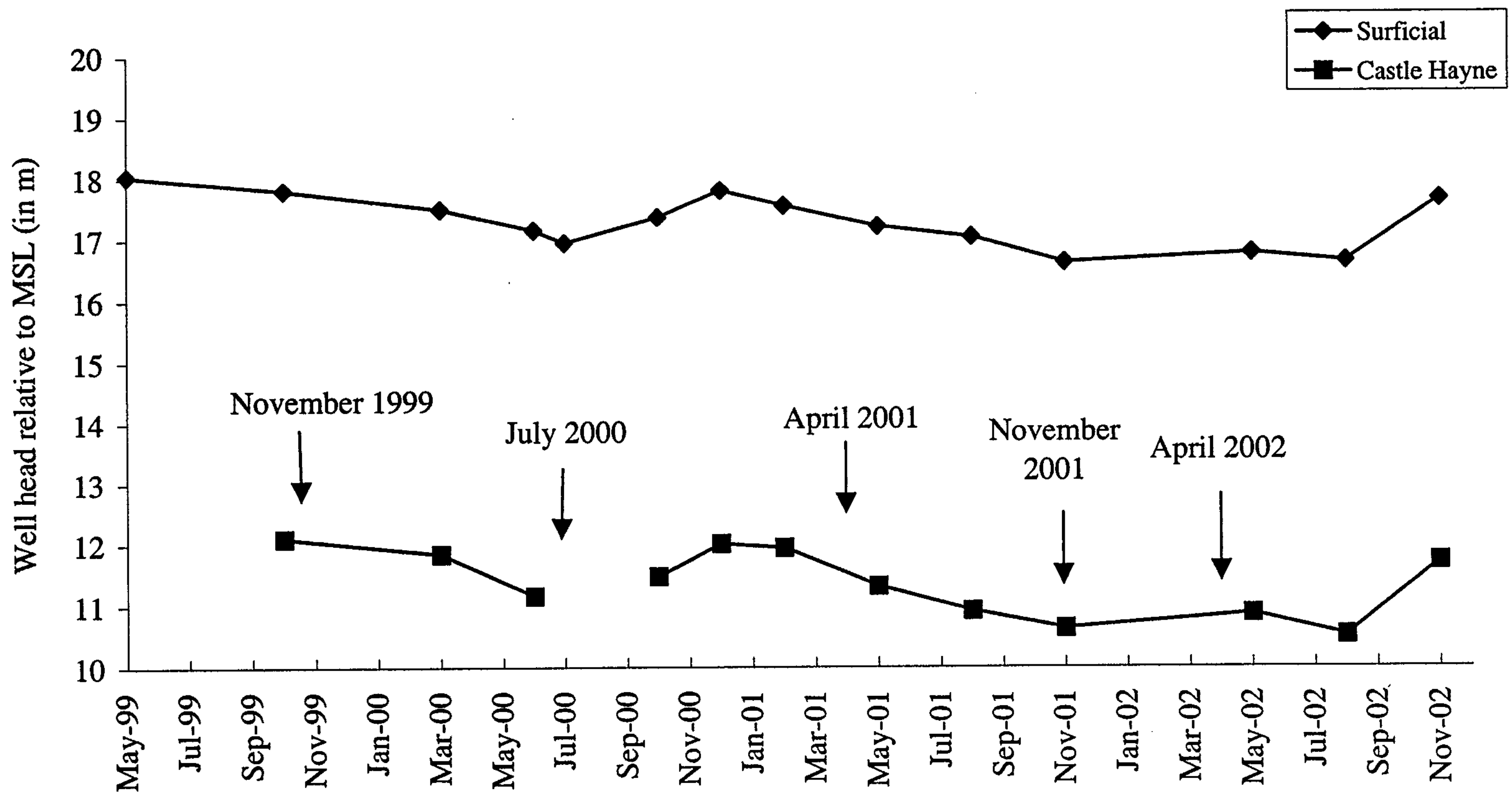


Figure C-2. Well head data at NC-DENR Topsail Beach station (well location is shown in Chapter II). Diamonds indicate surficial aquifer head levels; squares indicate Castle Hayne aquifer head levels. Arrows indicate the five sampling periods discussed in this dissertation.

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Supplementary Notes

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Abstract (Limit: 200 words)

Groundwater discharge is important to the transport of dissolved chemical species to coastal waters. $\Delta^{14}C$ was developed as a tracer of one component of total discharge: fresh fluxes from confined aquifers during sampling from November 1999 to April 2002 in two small estuaries in North Carolina. In this region, fresh artesian discharge has a carbonate-derived low-$\Delta^{14}C$ signature. Mixing models were used to evaluate the inputs from potential sources of DIC-$\Delta^{14}C$ to each estuary, including seawater, springs, streams, and respiration DIC. These calculations showed that artesian discharge generally dominated the total fresh water input to these estuaries.

A comparison of these $\Delta^{14}C$-based SGD estimates with estimates derived from radium isotopes and ^{222}Rn showed how these tracers describe different components of the total SGD. The fluxes of low-$\Delta^{14}C$ and of ^{222}Rn were dominated by artesian discharge. Estuarine ^{226}Ra showed artesian influence, but also reflected the salty SGD processes that controlled the other three radium isotopes. ^{228}Ra fluxes seemed to reflect seepage from the surficial aquifer as well as seawater recirculation through estuarine sediments. ^{224}Ra and ^{223}Ra fluxes were dominated by seawater recirculation through salt marsh sediments. This multi-tracer approach provides a comprehensive assessment of the various components contributing to the total SGD.

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