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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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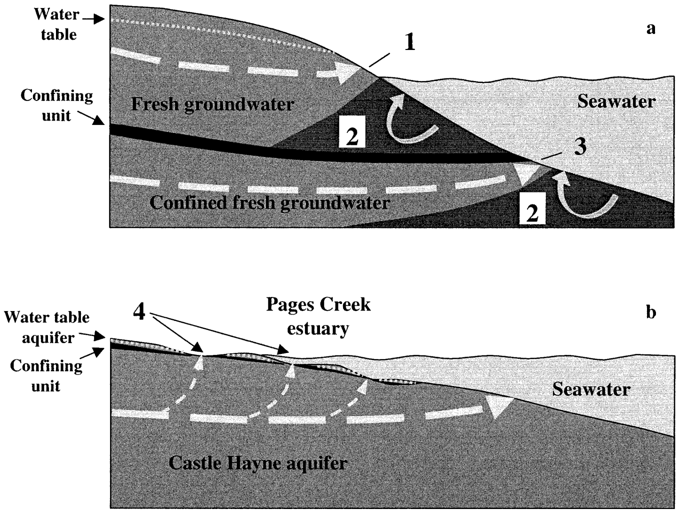

Fig. 1. (a) Simplified cross-section of a coastal groundwater system, with principal transport features: (1) surficial groundwater discharge at seepage face (dashed arrows represent schematic regional flow lines); (2) seawater recirculation/intrusion; and (3) freshwater discharge from confined aquifer. (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 (Δ^{14}C and δ^{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 Δ^{14}C values. Artesian groundwater and springs are expected to have lower Δ^{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.

Δ^{14}C systematics—Although the DIC and δ^{13}C-DIC values can be significantly modified by estuarine carbon cycle processes, the very large difference between input end-member Δ^{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 Δ^{14}C values will be largely unaffected by processes such as gas exchange, photosynthesis, and respiration of fresh organic matter.

δ^{13}C values are defined as

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

δ^{14}C is similarly defined as

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

The δ^{14}C values are typically normalized to $\delta^{13}\mathrm{C} = -25‰$ 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 ~1.2 × 10^7 m^2. The Pages Creek estuary, including its salt marshes, has an area of ~6.7 × 10^5 m^2. 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 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.

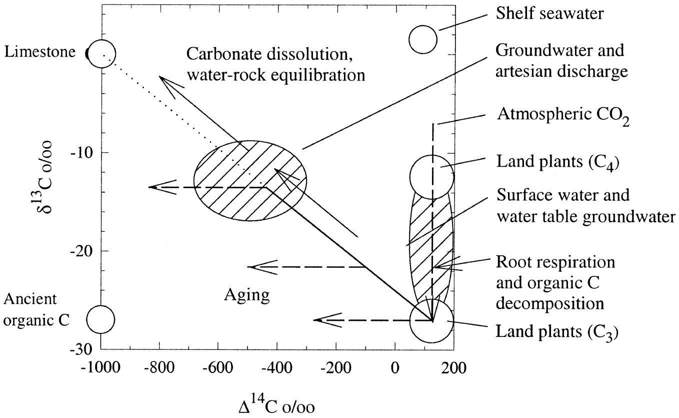

Fig. 2. Reservoir compositions and process trends. Today, atmospheric $\Delta^{14}C$ and $\delta^{13}C$ values are about +125‰ and −7.5‰, respectively. Surface seawater $\Delta^{14}C$ is about +90‰–100‰; seawater $\delta^{13}C$ is 0‰–1‰. Living vegetation incorporates the high atmospheric $\Delta^{14}C$ 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‰).

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-

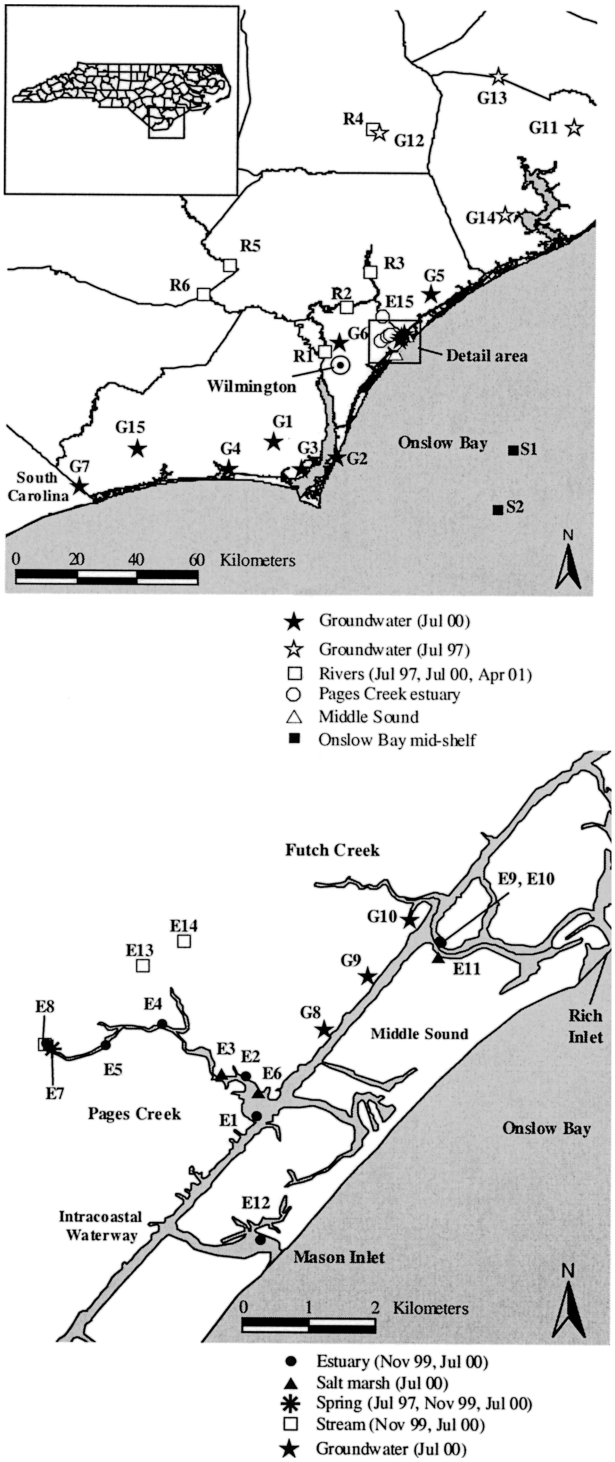

Fig. 3. Wilmington/Cape Fear region with sample locations, with detail of Pages Creek and Middle Sound sample locations.

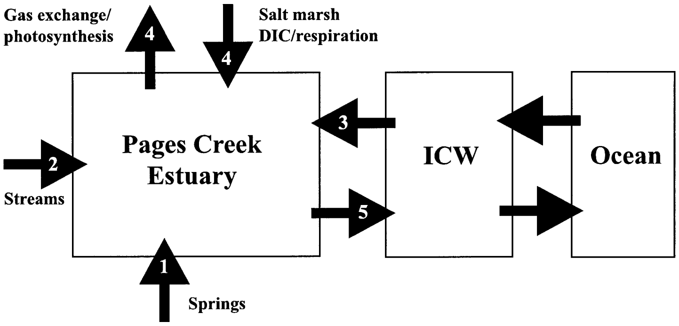

Fig. 4. Conceptual model of DIC inputs and outputs to the Pages Creek estuary. As discussed in the text, DIC inputs to Pages Creek are springs (1), streams (2), inflowing ICW water (3), and net exchange with salt marsh (4). The primary DIC output is water flowing out of the estuary at low tide (5). Gas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

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. 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 $\pm$5‰; for $\delta^{13}C$, $\pm$0.1‰, and for DIC, $\pm$3%.

April 2001 alkalinity samples were titrated using a poten-

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

Pages Creek estuary samples	Map legend	Date	Salinity	DIC (mmol kg^{-1})	Δ ^{14}C (‰)	δ^{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 Δ^{14}C values than the Castle Hayne and Peedee groundwater samples (Table 2; Fig. 5). The δ^{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 Δ^{14}C values are generally higher than deeper groundwater Δ^{14}C, ranging from about +18‰ to about +88‰ (Table 2; Fig. 5). The range in δ^{13}C values (−15‰ to −27‰) for surficial groundwater is large, and these values tend to be lower than the δ^{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), Δ^{14}C, δ^{13}C, and titration alkalinity (TA) values.

Well sample*	Date	Map legend	Aquifer†	Screened interval (m below surface)	Salinity	DIC (mmol kg^{-1})	Δ^{14}C (‰)	δ^{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 Δ^{14}C values (−396.9‰ and −407.9‰, respectively) than the other surficial wells. However, the relatively high δ^{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 Δ^{14}C, but the values are spatially variable (−473‰ to −748‰) (Table 2; Fig. 5). The range in δ^{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 Δ^{14}C and lower δ^{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 Δ^{14}C values—generally lower than Castle Hayne wells but with some overlap (−548‰ to −998‰) (Table 2; Fig. 5). The δ^{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 Δ^{14}C and δ^{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

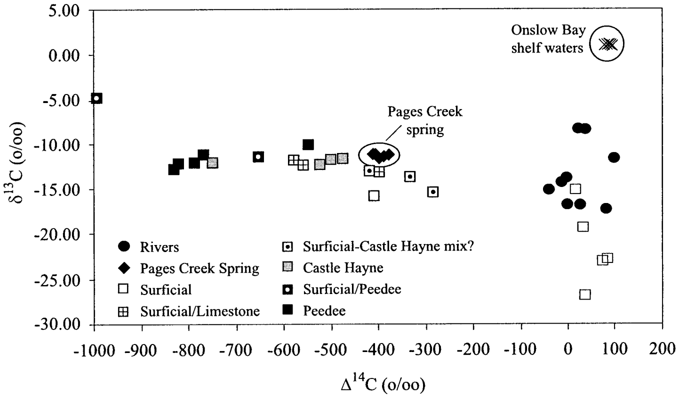

Fig. 5. $\Delta^{14}C$ and $\delta^{13}C$ values of groundwater, artesian spring, and river samples from the Cape Fear region of North Carolina. Peedee and Castle Hayne groundwaters have much lower $\Delta^{14}C$ than surficial groundwaters, rivers, and Onslow Bay shelf waters. Wells with carbon isotopic 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.

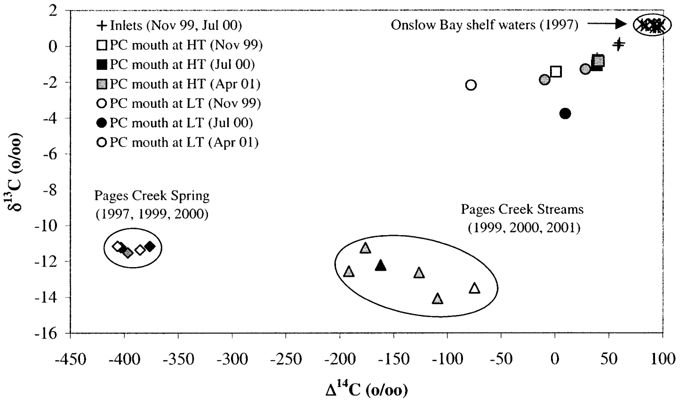

Fig. 6. $\Delta^{14}C$ and $\delta^{13}C$ values of Pages Creek estuary samples at low and high tide. Onslow Bay shelf waters, Mason Inlet (high and low tide), and Rich Inlet (high and low tide) have high $\Delta^{14}C$ and $\delta^{13}C$ values. Samples collected at the mouth of Pages Creek at low tide 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.

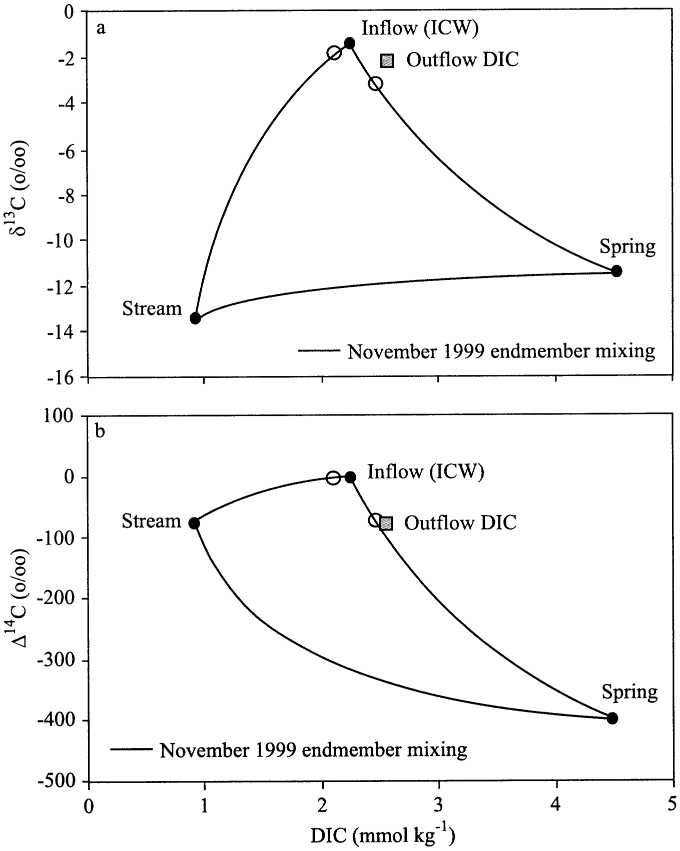

Fig. 7. November 1999 DIC concentration-isotope mixing curves among three Pages Creek estuary input sources: inflow from the ICW at high tide, freshwater stream input, and artesian groundwater/spring input. (a) DIC-$\delta^{13}C$ end-member mixing. (b) DIC-$\Delta^{14}C$ end-member mixing. Analytical 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.

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):

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

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

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

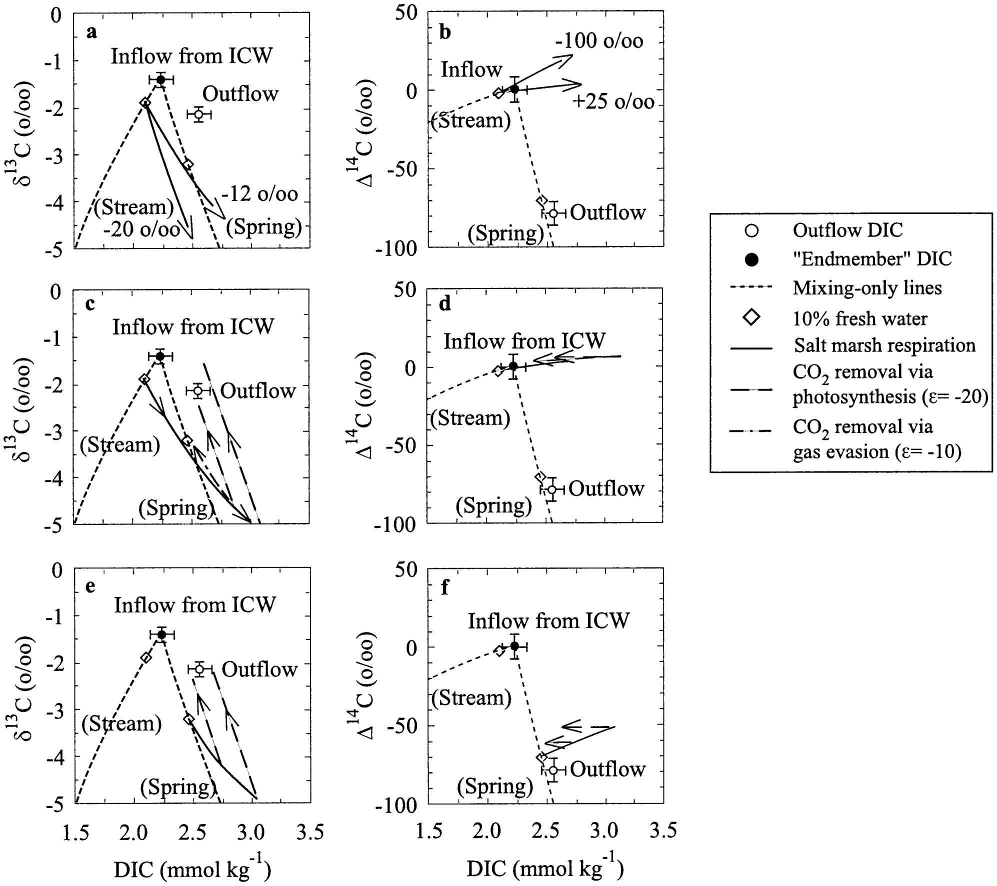

Fig. 8. (a,b) Salt marsh DIC additions (δ^{13}C = −12‰ to −20‰; Δ^{14}C = +25‰ to +100‰) to an inflow-stream mixture cannot match the outflow composition. (c,d) Salt marsh DIC input to an inflow-stream mixture plus DIC loss via photosynthesis (ε = 20‰) and gas evasion (ε = 10‰) still cannot match Outflow Δ^{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 Δ^{14}C.

artesian and surficial groundwater even if there were no δ^{13}C fractionation effects due to photosynthesis, respiration, or CO$_2$ gas evasion. The Δ^{14}C value of the spring is, however, distinct from both the ICW inflow Δ^{14}C and the stream Δ^{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 Δ^{14}C and DIC values of the calculated result plot very close to the Δ^{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 Δ^{14}C-DIC mixing model and give support to the premise that biological carbon cycling is not a major controlling factor in the Δ^{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 δ^{13}C values of −12‰ and −20‰ and respiration Δ^{14}C values of +25‰ and +100‰. The range of respiration δ^{13}C values is chosen to represent the types of vegetation in the estuary, from *Spartina* marsh grass (δ^{13}C = −12‰) to marine organic matter (δ^{13}C = −20‰). As discussed above, we believe that relatively high Δ^{14}C values are appropriate for salt marsh–derived DIC, because the Δ^{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 δ^{13}C value can be obtained if salt marsh respiration CO$_2$ (δ^{13}C = −12‰ and Δ^{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 Δ^{14}C value essentially unchanged at +5‰; it does not improve the match to the low outflow Δ^{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 δ^{13}C values without an artesian contribution to the freshwater budget. However, no combination of inputs and removal of modern (high Δ^{14}C) DIC alone can match the observed outflow Δ^{14}C values. Only if the 10% freshwater is derived entirely from the spring is it possible to approach the observed outflow Δ^{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 Δ^{14}C values discharge into the Pages Creek estuary or if the high tide inflow composition had higher DIC or Δ^{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 Δ^{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 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.

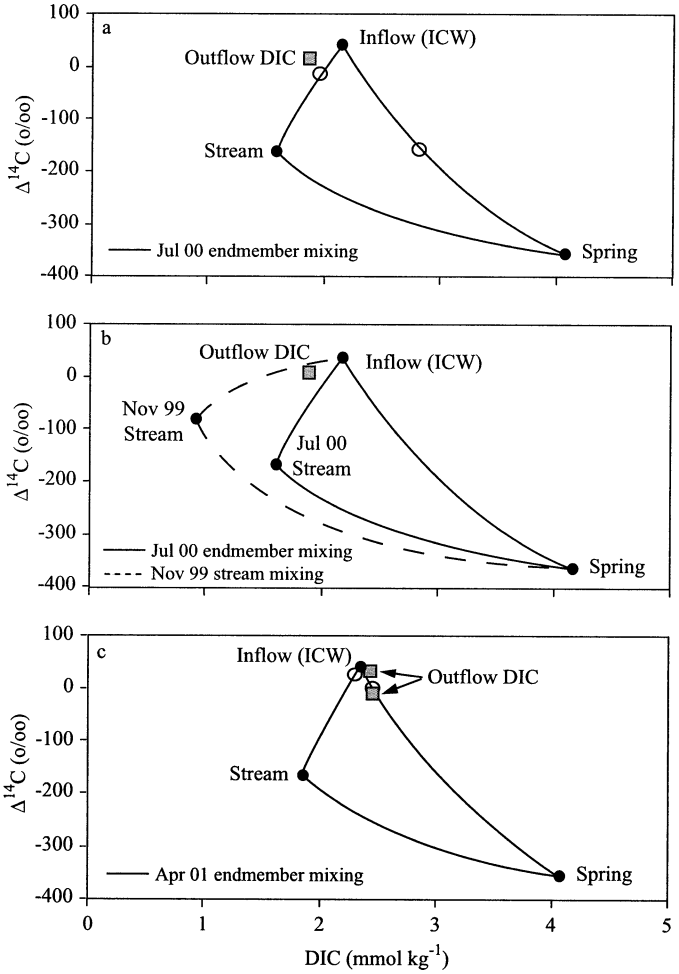

Fig. 9. DIC-DIC isotope mixing curves: (a) July 2000 DIC-Δ^{14}C mixing, suggesting that stream inputs were the dominant source of freshwater to Pages Creek at low tide in July 2000. (b) July 2000 end-member mixing triangle with November 1999 stream composition (higher Δ^{14}C and lower δ^{13}C values 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-Δ^{14}C mixing, suggesting that artesian spring inputs were the dominant source of freshwater to Pages Creek at low tide in April 2001.

Sensitivity analysis—Even if respiration-derived CO$_2$ does not add low-Δ^{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 Δ^{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 Δ^{14}C value of +100‰, representing the respiration of young organic matter, and a δ^{13}C = -12‰, the δ^{13}C value of the dominant vegetation in the marsh, *Spartina alterniflora.* Additions of high-Δ^{14}C DIC produce an upward slope in the DIC addition lines. This slope, combined with the ana-

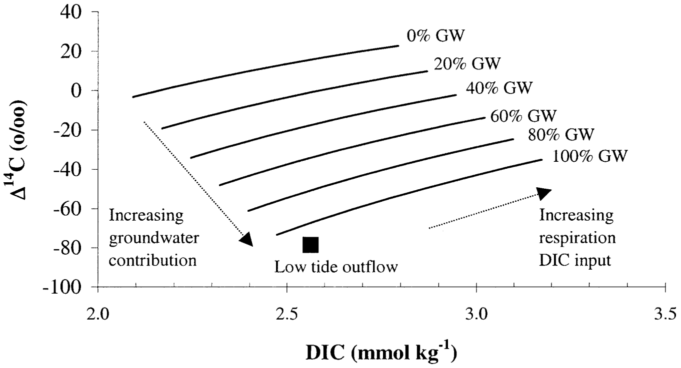

Fig. 10. Sensitivity calculations of the impact of salt marsh DIC additions to the DIC isotopic composition of Pages Creek at low tide in November 1999, for varying percentage contributions of artesian groundwater to the total freshwater input. Total freshwater input is 10%, based on a salt balance at 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%.

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.

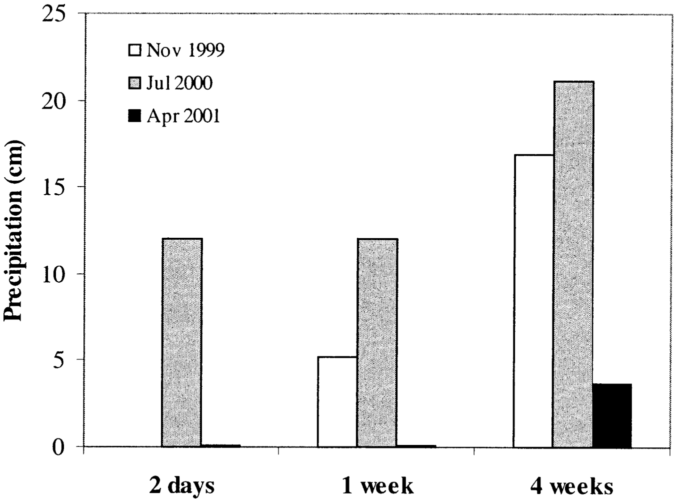

Fig. 11. Precipitation measured at the Wilmington airport (20 km northwest of Pages Creek; precipitation data provided by the State Climate Office of North Carolina at NC State University) for several time periods prior to sampling in November 1999, July 2000, and April 2001. Changes in the relative 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.

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 Δ^{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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