

## **<sup>14</sup>C GROUNDWATER AGE AND THE IMPORTANCE OF CHEMICAL FLUXES ACROSS AQUIFER BOUNDARIES IN CONFINED CRETACEOUS AQUIFERS OF NORTH CAROLINA, USA**

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**ABSTRACT.** Radiocarbon activity, He concentrations, and other geochemical parameters were measured in groundwater from the confined Black Creek (BC) and Upper Cape Fear (UCF) aquifers in the Coastal Plain of North Carolina. <sup>14</sup>C ages adjusted for geochemical and diffusion effects ranged from 400 to 21,900 BP in the BC, and 13,400 to 26,000 BP in the underlying UCF; ages increased coastward in both aquifers. Long-term average linear groundwater velocity is about 2.5 m/yr for the BC, and somewhat larger for the UCF. Aquifer-aquitard exchange is an important influence on the DIC concentration, <sup>14</sup>C activity, and estimated age of aquifer groundwater. Accounting for this exchange in <sup>14</sup>C age calculations places the groundwater samples with the lowest estimated recharge temperatures nearest in time to the last glacial maximum. Traditional geochemical correction models that do not account for aquifer-aquitard exchange significantly overestimate groundwater age. He concentration in groundwater varies with both age and stratigraphic position. Dissolved He data provide strong evidence of upward vertical He transport through the study aquifers; data from the UCF are broadly consistent with the pattern expected for a confined aquifer receiving a concentrated, localized He flux from below (based on a previously published model for this situation), in this case most likely from crystalline bedrock. He has potential as an indicator of groundwater age in the study aquifers, if interpreted within an appropriate analytical framework that includes the observed strong vertical transport.  $\delta^{18}\text{O}$  in the oldest groundwater is enriched (relative to modern groundwater) by 1 to 1.2‰, the opposite of the  $\delta^{18}\text{O}$  depletion found in many old groundwaters but consistent with the enrichment found in groundwater in this age range in Georgia and Florida.

### **INTRODUCTION**

Radiocarbon and helium have been widely applied to study the flow rate and subsurface residence time of groundwater in deep confined aquifers (Castro et al. 2000; Geyh 2000; Aeschbach-Hertig et al. 2002; McMahon et al. 2004). He may be a useful age-dating tracer in groundwater too old to be dated with <sup>14</sup>C (Mazor and Bosch 1992). The traditional piston-flow approach to <sup>14</sup>C age dating does not explicitly account for the potential influence on age by vertical chemical and isotopic fluxes to or from the aquitards or basement rocks above and/or below the aquifer (Sanford 1997; Bethke and Johnson 2002). Input from below is generally included in studies of dissolved He in deep aquifers (Solomon 2000), while He flux through the tops of these aquifers has been considered negligible in some cases (Torgersen and Ivey 1985; Castro et al. 2000). There is growing recognition that chemical and isotopic exchanges between aquitards and aquifers may be a strong influence on aquifer groundwater age, and accounting for this may be essential to correct interpretation of geochemical signals of groundwater age (Sudicky and Frind 1981; Maloszewski and Zuber 1991; Sanford 1997; Bethke and Johnson 2002), especially in aquifers bounded by thick aquitards (confining layers) and in which groundwater ages are large (many thousands of years).

This study addresses this topic for <sup>14</sup>C and He in the Black Creek and Upper Cape Fear aquifers in North Carolina, USA, deep confined aquifers that are critical water supplies for the Coastal Plain of eastern North Carolina (Lautier 2001). These aquifers have been the subject of a number of geochemical and modeling studies (e.g. Reid et al. 1986; Aucott 1988; Lee and Strickland 1988; Zack and Roberts 1988; Eimers et al. 1990; Chapelle and McMahon 1991; McMahon and Chapelle 1991a,b; Winner and Coble 1996; Giese et al. 1997; Knobel et al. 1998; Lautier 2001), but groundwater ages have not previously been estimated. There is a pressing need for information on groundwater age that could be used to calibrate groundwater flow models and improve management practices for these aquifers. Also, conducting this work in North Carolina addresses a significant spatial

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gap in knowledge of confined aquifers of the US Atlantic Coastal Plain, given prior work to the north in Maryland (Purdy et al. 1992; Aeschbach-Hertig et al. 2002) and to the south in South Carolina, Georgia, and Florida (Marine 1979; Burt 1993; Plummer 1993; Landmeyer and Stone 1995; Plummer and Sprinkle 2001).

Previous work (Chapelle and McMahon 1991; McMahon and Chapelle 1991a,b) documents the importance of aquifer:aquitard exchange to dissolved inorganic carbon (DIC) in the Black Creek aquifer in South Carolina, about 200 km south of our study site. In the work reported here, we: 1) used  $^{14}\text{C}$  to estimate the age of groundwater samples from the Black Creek and Upper Cape Fear aquifers in North Carolina; 2) evaluated the potential for He as an age-dating tracer in these same aquifers; and 3) tested the hypothesis that aquifer:aquitard exchange is a significant influence on DIC,  $^{14}\text{C}$ , and He in the groundwater of these aquifers. We also evaluated whether the  $^{14}\text{C}$  ages,  $\delta^{18}\text{O}$  data, and estimates of recharge temperature (based on dissolved Ar and  $\text{N}_2$ ), taken together, were consistent with the known timing of the last glacial maximum (LGM) in North America and with other such data from the Atlantic Coastal Plain of the southeastern US.

## STUDY AREA

The Coastal Plain of North Carolina is roughly 140 to 240 km wide and includes 10 sedimentary aquifers deposited mostly under nonmarine and marginal-marine conditions (Winner and Coble 1996). The Cretaceous Black Creek and Upper Cape Fear aquifers are composed mainly of sandy siliclastic sediments separated by silty to clayey layers acting as aquitards (Figures 1 and 2; Winner and Coble 1996; Giese et al. 1997). Black Creek aquifer mineralogy consists of quartz, carbonate shell material, kaolinite, glauconite (Reid et al. 1986), and about 0.2% organic matter (mainly degraded plant remains) (McMahon et al. 1990). Upper Cape Fear aquifer mineralogy consists of quartz, kaolinite, and probably glauconite (Sohl and Owens 1991), with small amounts of organic matter and carbonate shell material that would be expected from a near-shore marine depositional environment (Winner and Coble 1996). Aquifer thicknesses vary considerably but generally increase toward the coast. Prior to development, groundwater flow was generally toward the coast (Figure 1). Groundwater flow is still generally coastward with local deviations in the vicinity of cones of depression in the piezometric surfaces (e.g. Giese et al. 1997); the extent to which draw-down in hydraulic head may have altered recharge patterns and rates is not well known.

Groundwater chemistry in the study aquifers evolves downgradient toward higher dissolved solids and sodium-bicarbonate dominance (Knobel et al. 1998; Lee and Strickland 1988), mainly through weathering of silicate minerals, calcite dissolution, organic matter oxidation, and cation exchange ( $\text{Na}^+$  sorbed to clay exchanges with dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) (Lee and Strickland 1988; Zack and Roberts 1988; McMahon and Chapelle 1991a; Winner and Coble 1996; Knobel et al. 1998).

Seven monitoring wells located at 3 North Carolina Department of Environment and Natural Resources (NCDENR) well sites were used to collect groundwater samples (Table 1; Figures 1, 2). The wells are used by NCDENR to monitor groundwater levels and were chosen because they are screened in the Black Creek and Upper Cape Fear aquifers and lie along a trend roughly parallel to groundwater flow (Figure 1).

## METHODS

Groundwater samples were collected in late July 2003 (Table 1) for chemical (dissolved solids, gases) and isotopic ( $^3\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^{14}\text{C}$ ) analyses. Prior to sampling, the wells were purged of 1.2 to 2.7 well volumes (Kennedy 2004); stability in water temperature, specific conductance, and pH were the principal criteria used to determine when wells had been sufficiently purged for sampling.

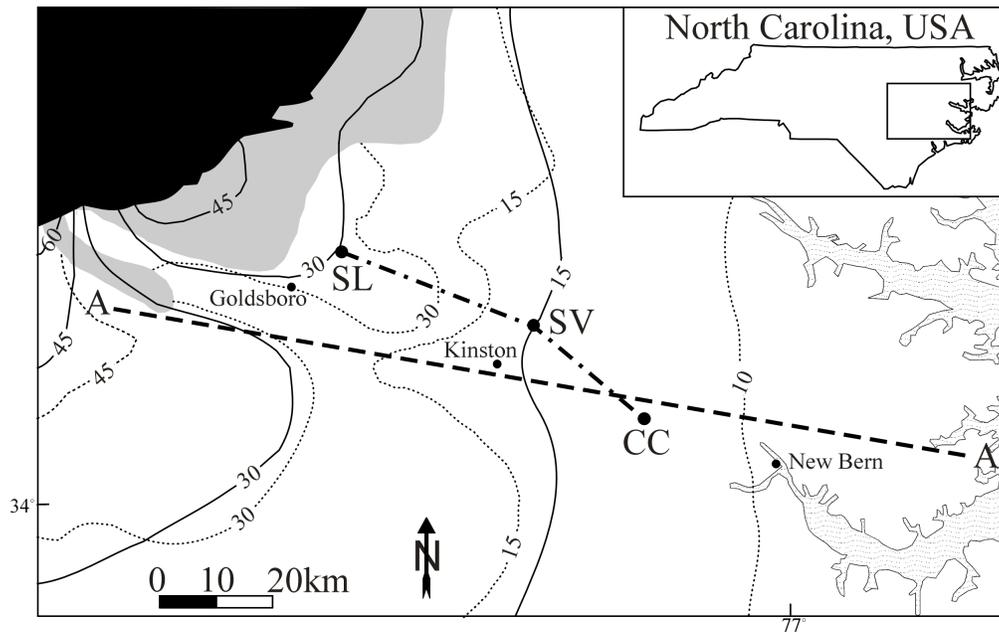


Figure 1 Map of the study area, based on Figures 77 and 78 in Geise et al. (1997), with major cities. The black and gray areas correspond to areas where the Upper Cape Fear and Black Creek aquifers, respectively, are absent (i.e. the eastern margin of the gray area represents the western margin of the Black Creek aquifer and the eastern margin of the black area represents the western margin of the Upper Cape Fear aquifer). The sampling transect (dash-dotted line) extends from the NCDENR Saulston well site (SL) to the Savannah well site (SV) to the Cove City well site (CC). Estimated contours of predevelopment (before ~1900) hydraulic heads in the Black Creek (dotted line) and Upper Cape Fear (solid line) aquifers (Geise et al. 1997) are given in intervals of 15 m and are referenced to sea level (Geise et al. 1997). The dashed line A-A' corresponds to the geological cross-section shown in Figure 2.

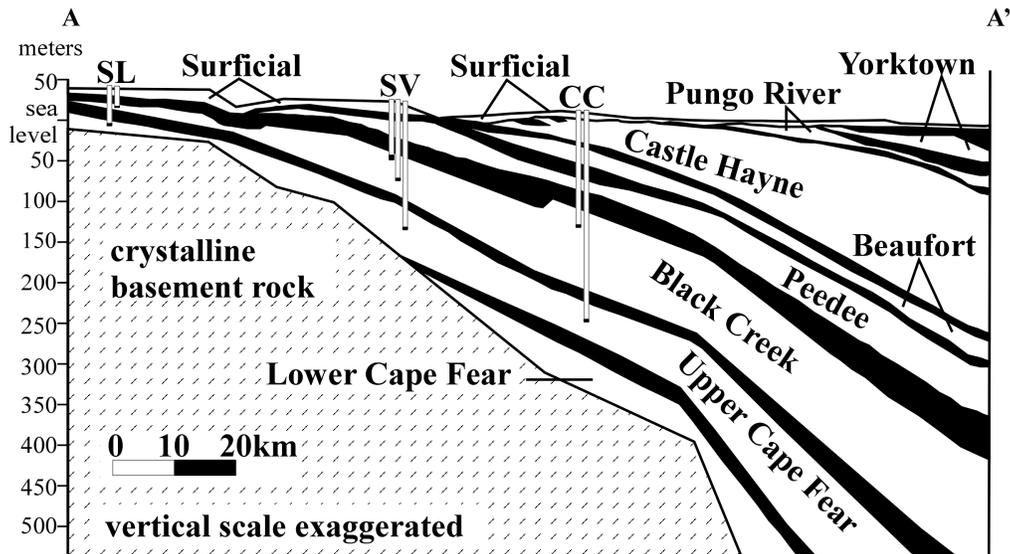


Figure 2 East-west hydrogeologic cross-section through the Coastal Plain of North Carolina along the line A-A' shown in Figure 1 (Geise et al. 1997). Aquifers are shown in white and aquitards in black. The sampling transect does not correspond exactly to the line of the hydrogeologic transect (see Figure 1), but the sampling wells are shown here to illustrate their approximate relationship to the geology and to one another. From left to right, the 3 well sites are Saulston (SL; wells O30J3 and O30J1), Savannah (SV; wells P26U8, P26U7, and P26U5), and Cove City (CC; wells R23X8 and R23X9) (Table 1).

Table 1 Data for wells sampled. BC = Black Creek; UCF = Upper Cape Fear; SL = Saulston; SV = Savannah; CC = Cove City.

Well ID	Date constructed <sup>a</sup>	Date sampled	Aquifer <sup>b</sup> , well site	Aquifer thickness <sup>b</sup> (m)	Overlying aquitard thickness <sup>b</sup> (m)	Distance from recharge area (km)	Top of screen <sup>a</sup> (m)	Bottom of screen <sup>a</sup> (m)	Water depth <sup>c</sup> (m)	Well diameter <sup>d</sup> (cm)
O30J1	8/17/82	7/24/03	BC, SL	21	1.5	0.5	12.2	13.7	3.1	10.2 [0-13.7]
P26U8	10/18/99	7/28/03	BC, SV	52	14	29	74.4	80.5	44.4	10.8 [0-74.4] 10.2 [74.4-80.5]
P26U7	10/27/99	7/28/03	BC, SV	52	14	39	109.1	112.2	55.8	10.8 [0-109.1] 10.2 [109.1-112.2]
R23X8	10/13/00	7/30/03	BC, CC	86	20	65	150.0	153.0	53.4	10.8 [0-153.0]
O30J3	9/14/82	7/24/03	UCF, SL	28	5.8	39	50.3	53.4	38.2	10.2 [0-38.4] 6.4 [38.4-53.4]
P26U5	7/9/84	7/28/03	UCF, SV	75	6.4	72	164.0	167.0	56.0	10.2 [0-63.7] 6.4 [63.7-167.0]
R23X9	9/29/00	7/30/03	UCF, CC	34	4.9	93	260.0	263.4	53.4	10.8 [0-263.4]

<sup>a</sup>Well construction logs (Nat Wilson, NCDENR, personal communication, January 2003).

<sup>b</sup>NCDENR Web site ([http://www.ncwater.org/Data\\_and\\_Modeling/Ground\\_Water\\_Databases/frameaccess.php](http://www.ncwater.org/Data_and_Modeling/Ground_Water_Databases/frameaccess.php)); well sites are shown in Figures 1 and 2.

<sup>c</sup>Water depth below ground surface before start of purging.

<sup>d</sup>Brackets indicate depth range to which the corresponding diameter applies (e.g. the inner diameter of well P26U8 is 10.8 cm over the upper 74.4 m and 10.2 cm from 74.4 m to 80.5 m). Top diameter was measured in the field by authors; other diameters were obtained from well construction logs and NCDENR Web site.

These parameters (and dissolved oxygen) were monitored continuously during well purging and sampling. Well R23X9, the deepest well (Table 1), had the smallest purge volume relative to well volume (1.2 well volumes), due to the slow rate of groundwater inflow to the well and the large well volume. Even at this well, stable temperature, pH, and specific conductance were achieved prior to sampling. Also, the sampling pump was placed 30.3 m below the water level during sampling, to reach downward past an additional 0.15 well volumes (the 30.3 m of water above the pump in the well casing) for sample collection (the purge pump had been placed within 2 m of the water level in the well).

Purging at the Savannah and Cove City well sites was carried out with a Grundfos JS submersible electric pump powered by a gasoline-powered electrical generator. Sampling at all wells was done with a stainless steel Model 140 Bennett pump, a submersible positive displacement pump (3.6 cm diameter) driven by high-purity compressed nitrogen gas (<http://www.bennettsamplepump.com/>). The Bennett pump was used for both sampling and purging at the Saulston well site.

Samples for the determination of <sup>3</sup>H were collected in 1-L polyethylene bottles and sent to the University of Utah for analysis. <sup>3</sup>H analysis was carried out by the <sup>3</sup>He ingrowth method (Clarke et al. 1976); measurement precision (1 standard deviation) was about 0.1 TU.

Samples for analysis of dissolved gases (Ar, CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, He, Ne) were collected in 150-mL glass bottles and sent to the US Geological Survey's Reston Chlorofluorocarbon Laboratory (<http://water.usgs.gov/lab/cfc/>) for analysis by gas chromatography (Busenberg et al. 1998, 2000). Uncertainties were 2–4% for Ar, CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>; and 10–20% for He and Ne. (Because of overlap between the He and Ne peaks in the presence of high He concentrations, Ne analysis was limited to samples with relatively low He concentration.)

Samples for determination of major ions (Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>) and trace elements (Al, Fe, Mn, Si) were filtered to 0.45 μm during collection in 20-mL and 125-mL polyethylene bottles, respectively. Major cation samples and trace element samples were acidified in the field with about 50 μL and 1.25 mL of 70% HNO<sub>3</sub><sup>-</sup>, respectively. Samples were analyzed for major ions by ion chromatography (USEPA 1993) at North Carolina State University and for trace elements by inductively coupled plasma mass spectrometry (ICPMS) (USEPA 1994) at the US Geological Survey's Reston Chlorofluorocarbon Laboratory. Uncertainties of major ion and trace element analyses were about 5% and 5–10%, respectively.

Samples for analysis of δ<sup>13</sup>C and <sup>14</sup>C of dissolved inorganic carbon (DIC) were filtered to 0.45 μm during collection in 500-mL glass bottles and poisoned upon collection with 300 to 500 μL of 7% (saturated) HgCl<sub>2</sub> solution. The samples were then sent to the NOSAMS facility at Woods Hole Oceanographic Institute for analysis by accelerator mass spectrometry (AMS) (McNichol and Jones 1991). δ<sup>13</sup>C was reported on the Vienna Pee Dee belemnite scale, and <sup>14</sup>C was reported relative to NBS oxalic acid I (Olsson 1970) normalized for isotope fractionation effects to a δ<sup>13</sup>C value of -25‰ (Stuiver and Polach 1977). The <sup>14</sup>C activities, from which groundwater ages were calculated, are presented non-normalized for isotope fractionation (Mook and van der Plicht 1999; Kalin 2000; Plummer et al. 2004). Measurement error ranged from 1 to 17% for <sup>14</sup>C analyses, and between 0.3 and 0.5‰ for δ<sup>13</sup>C analyses.

Samples for analysis of total S, NO<sub>3</sub><sup>-</sup>, dissolved organic carbon (DOC), and DIC were collected in 20-mL glass bottles and were filtered to 0.45 μm. About 100 μL of 6N HCl were added in the field to the S, NO<sub>3</sub><sup>-</sup>, and DOC samples to preclude microbial degradation. Analyses were conducted in the Analytical Service Laboratory at North Carolina State University, where total S was analyzed by inductively coupled atomic emission spectroscopy (Eaton et al. 1995a; Method 3120 B), NO<sub>3</sub><sup>-</sup> by

ion chromatography (USEPA 1993), and DIC and DOC by high-temperature combustion (Eaton et al. 1995b; Method 5310 B), with uncertainties of about 5%.

$\delta^{18}\text{O}$  analyses were carried out by the Environmental Isotope Lab at the University of Waterloo (<http://www.science.uwaterloo.ca/research/eilab/>). Mass spectrometric analyses were conducted on  $\text{CO}_2$  that had been equilibrated with water samples at constant temperature (Epstein and Mayeda 1953; Fritz et al. 1986). Results are expressed as  $\delta^{18}\text{O}$  relative to standard mean ocean water (SMOW); measurement precision was about 0.1‰.

$^{14}\text{C}$  dating of groundwater requires 1) estimating the initial  $^{14}\text{C}$  activity in water at the time of recharge and 2) estimating the extent of geochemical effects on dissolved  $^{14}\text{C}$  activity so that the groundwater age calculation is based only on the decrease in  $^{14}\text{C}$  activity by radioactive decay. Several geochemical models (e.g. Ingerson and Pearson 1964; Tamers 1975; Fontes and Garnier 1979; Eichinger 1983) approach this using measured DIC, pH, and  $^{14}\text{C}$  activity in groundwater, and information on  $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  gas and carbonate minerals. These models generally account for effects on groundwater  $^{14}\text{C}$  activity from exchange with soil-zone  $\text{CO}_2$ , carbonate-mineral dissolution and precipitation, and cation exchange. The models cited above have been widely applied and discussed in the literature (e.g. Aravena et al. 1995; Geyh 2000; Kalin 2000; Plummer and Sprinkle 2001) and are therefore not discussed in detail here; Fontes and Garnier (1979) is perhaps the most widely used. We used all 4 models separately to estimate  $^{14}\text{C}$  ages for our groundwater samples. NETPATH, an inverse mass-balance model that determines mass transfers along a groundwater flowpath (Plummer et al. 1994), was also used to correct for geochemical effects on  $^{14}\text{C}$  activity and estimate groundwater age. Although the geochemical models listed above may be well-suited for limestone aquifers where carbonate dissolution is the principal geochemical reaction affecting  $^{14}\text{C}$  activity in groundwater, NETPATH also accounts for processes such as organic matter oxidation, incongruent dissolution, and carbonate mineral recrystallization (Plummer et al. 1994).

As a means of computing approximate groundwater velocities from the  $^{14}\text{C}$  dates, estimates were made of the distance between each well and its recharge area (Table 1), using stratigraphic geological information in Winner and Coble (1996: Plate 6) and from North Carolina Geological Survey (1985). These estimates are based on the assumption that most recharge occurred in the unconfined western portions of the 2 study aquifers, an assumption consistent with the known coastward (eastward) movement of groundwater and with numerical simulations of groundwater flow suggesting little or no vertical head differences across the confining layers of the study aquifers under natural pre-pumping conditions (Giese et al. 1997).

#### **$^{14}\text{C}$ MODEL AGES AND GROUNDWATER VELOCITIES**

The dominant dissolved constituents in groundwater of the Black Creek and Upper Cape Fear aquifers are DIC and  $\text{Na}^+$  (Table 2). The increase in concentration of DIC and  $\text{Na}^+$  with distance from recharge area (Figure 3) is consistent with past work (Lee and Strickland 1988; Chapelle and McMahon 1991; McMahon and Chapelle 1991b). It suggests that calcite dissolution followed by  $\text{Ca}^{2+}/\text{Na}^+$  ion exchange is an important process affecting groundwater chemistry of the aquifers and that groundwater age increases coastward. In all but the shallowest well (O30J1), concentrations of  $^3\text{H}$  are within a 95% confidence interval ( $2\sigma$ ) of zero, indicating the absence of young water in the deep portions of the aquifers studied here (Table 2). Calcite saturation indices ( $\text{SI}_{\text{calcite}}$ ) calculated using WATEQF (Plummer et al. 1976), a chemical equilibrium model contained within NETPATH, indicate that groundwater is undersaturated with respect to calcite at all wells except P26U8.

Table 2 Chemical and isotopic data for groundwater in the Black Creek and Upper Cape Fear aquifers. Calcite saturation index (SI<sub>calcite</sub>) for each sample was calculated in WATEQF as log(IAP/K<sub>sp</sub>), where IAP is the ion activity product for calcite (product of the aqueous Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> activities) and K<sub>sp</sub> is the solubility product constant for calcite. SI<sub>calcite</sub>>0 indicates oversaturation, SI<sub>calcite</sub><0 undersaturation. All concentrations are in mM, except as noted (n.d. = not determined). CBE is the charge balance error (sum of positive charges minus sum of negative charges, divided by the average of the 2 sums). The <sup>14</sup>C activity values shown here are normalized for isotope fractionation, as reported by WHOI (non-normalized values were used for calculation of groundwater ages; see Table 3 and text for explanation).

	O30J1	P26U8	P26U7	R23X8	O30J3	P26U5	R23X9
t (° C)	18.8	22.2	19.3	22.2	21.1	20.8	22.9
pH	6.23	7.79	8.49	7.76	7.5 <sup>a</sup>	7.76	7.72
Na <sup>+</sup>	0.175	2.04	2.77	9.43	3.16	3.43	16.2
K <sup>+</sup>	0.063	0.226	0.174	0.487	0.398	0.140	0.656
Mg <sup>2+</sup>	0.052	0.214	0.021	0.117	0.505	0.013	0.082
Ca <sup>2+</sup>	0.128	0.531	0.051	0.097	0.764	0.060	0.096
Cl <sup>-</sup>	0.167	0.125	0.182	0.480	4.31	0.553	15.7
SO <sub>4</sub> <sup>-</sup>	0.063	<0.001	0.005	0.019	0.055	0.029	0.088
NO <sub>3</sub> <sup>-</sup> (μM)	<7	<7	<7	<7	<7	<7	<7
S (μM)	204	7	13	64	186	92	274
Fe (μM)	134.30	0.79	<0.18	1.43	<0.18	<0.18	0.20
Mn (μM)	2.17	0.20	0.03	0.05	0.11	0.05	0.12
Al (μM)	0.445	0.074	0.741	0.148	0.815	0.228	0.139
Si	0.301	0.218	0.156	0.154	0.167	0.170	0.169
DOC	0.15	0.09	0.10	0.16	0.13	0.15	0.13
DIC	0.75	4.25	3.25	10.8	1.75	3.29	7.04
δ <sup>13</sup> C (‰)	-21.4	-12.9	-15.0	-9.5	-17.4	-16.1	-9.8
<sup>14</sup> C (pMC)	87.6 ± 0.5	8.30 ± 0.08	1.37 ± 0.04	0.11 ± 0.05	7.72 ± 0.08	0.80 ± 0.03	0.19 ± 0.03
CH <sub>4</sub> (μM)	2.9	1.4	0.8	1.6	6.6	0.9	0.9
CO <sub>2</sub> (μM)	548.7	80.8	11.3	63.8	0.3	5.4	47.2
O <sub>2</sub> (μM)	2.4	3.4	8.2	2.0	1.6	4.6	1.7
N <sub>2</sub> (μM)	830	765	814	727	736	776	760
Ar (μM)	17.2	18.4	19.7	18.0	17.9	18.9	18.1
Ne (nM)	19.9	19.6	22.3	23.2	n.d.	n.d.	n.d.
He (nM)	8.4	11.1	27.9	23.4	545.0	56.5	100.7
<sup>3</sup> H (TU)	5.7	0.1	0.2	0.1	n.d.	0.0	0.0
δ <sup>18</sup> O (‰)	-5.2	-4.4	-4.7	-4.0	-4.5	-4.4	-4.2
SI <sub>calcite</sub>	-3.185	0.057	-0.399	-0.398	-0.513	-1.030	-0.668
CBE (%)	8.6	-6.3	-6.0	-3.0	0.2	2.0	-13.8

<sup>a</sup>The measured pH at well O30J3 was unrealistically high (pH = 10.07) due to a tear in the semi-permeable membrane attached to the pH probe. We calculated an alkalinity of 1.7 meq/L for this sample from concentrations of strong base cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) and strong acid anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>). This value of alkalinity and the measured DIC of the sample were used to estimate the pH of the sample (Stumm and Morgan 1996:177).

<sup>14</sup>C groundwater ages were calculated using 4 widely used geochemical models: Ingerson and Pearson (1964), Tamers (1975), Fontes and Garnier (1979), and Eichinger (1983). In applying these models, we used standard assumptions: <sup>14</sup>C activity of 0 pMC for calcite (e.g. Fontes and Garnier 1979; Aeschbach-Hertig et al. 2002) and 100 pMC for CO<sub>2</sub> gas (e.g. Fontes and Garnier 1979; Aravena et al. 1995; Aeschbach-Hertig et al. 2002); δ<sup>13</sup>C of 0‰ for calcite (e.g. Craig 1953; Pearson and White 1967; Fontes and Garnier 1979; McMahon and Chapelle 1991b; Aravena et al. 1995;

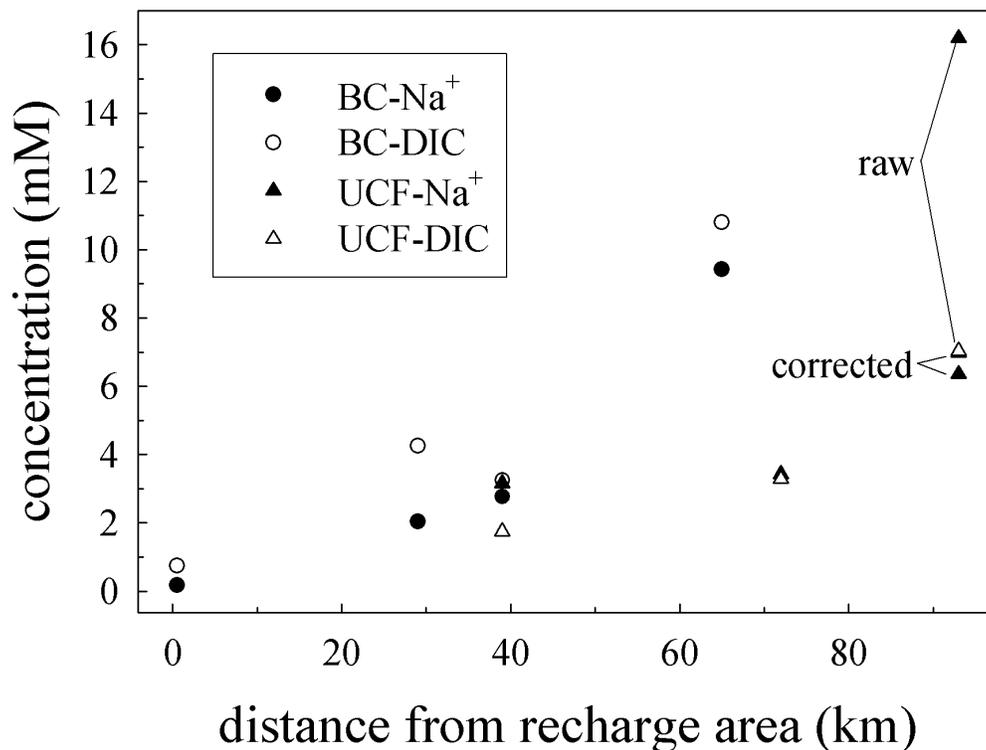


Figure 3 Concentration of Na<sup>+</sup> and DIC versus distance from recharge area. Two sets of values are shown for well R23X9: raw (measured) data, and the raw data corrected for mixing-in of 2.00% seawater (see text). UCF = Upper Cape Fear aquifer; BC = Black Creek aquifer.

Aeschbach-Hertig et al. 2002); and <sup>14</sup>C isotopic enrichment factor between gaseous CO<sub>2</sub> and solid carbonate equal to 0.2 times that of <sup>13</sup>C (Craig 1953; Fontes and Garnier 1979).  $\delta^{13}\text{C}$  of soil gas was calculated assuming a completely open system in which  $\delta^{13}\text{C}$  of soil gas is defined by the  $\delta^{13}\text{C}$  of the initial water and CO<sub>2</sub> gas-solution equilibrium fractionation (e.g. Plummer and Sprinkle 2001).

Groundwater ages from the 4 models are similar, and as expected all are younger than the “unadjusted ages” presented only for purposes of comparison (Table 3). Unadjusted ages do not account for changes in the <sup>14</sup>C activity of groundwater by geochemical processes, such as the reduction caused by calcite dissolution, and are generally greater than ages that account for geochemical processes. Within each aquifer, groundwater age increases toward the coast, consistent with coastward groundwater flow.

For each aquifer, NETPATH modeling was performed to estimate groundwater age accounting for net geochemical mass transfers into and out of groundwater, between the “initial water” (the up-gradient groundwater sample, from the Saulston well site) and “final waters” (groundwater samples at the Savannah and Cove City well sites, from the same aquifer as the initial water). In the Black Creek simulations, groundwater from well O30J1 was the initial water and the final waters were from wells P26U8, P26U7, and R23X8; in the Upper Cape Fear simulations, groundwater from well O30J3 was the initial water and the final waters were from wells P26U5 and R23X9. NETPATH simulations were constrained by measured dissolved groundwater concentrations of C, S (as SO<sub>4</sub><sup>-2</sup>), Ca, Na, Fe, Al, K, Mg, and Si (and Cl, for well R23X9 only), and changes in redox state. In our first

Table 3 Summary of unadjusted and adjusted <sup>14</sup>C groundwater ages (yr BP). BC = Black Creek aquifer; UCF = Upper Cape Fear aquifer; n.d. = not determined (sample served as “initial water” in NETPATH simulations).

Well	Aquifer	pMC	Groundwater ages based on different models									
			Unadjusted					NETPATH				
			Age <sup>a</sup>	Tamers (1975)	Ingerson and Pearson (1964)	Eichinger (1983)	Fontes and Garnier (1979)	NDC <sup>b</sup>	WDC <sup>b</sup>	NDC <sup>b</sup>	WDC <sup>b</sup>	
O30J1	BC	87.6	1100	-800	300	200	800	400	n.d.	n.d.	n.d.	
P26U8	BC	8.3	20,600	15,100	16,700	16,400	17,700	10,400	5500	3200	3200	
P26U7	BC	1.37	35,500	29,800	31,900	31,600	32,900	19,400	23,100	13,600	13,600	
R23X8	BC	0.11	56,400	50,900	51,400	50,900	51,900	33,400	34,000	21,900	21,900	
O30J3	UCF	7.72	21,200	16,000	18,300	18,200	19,400	13,400	n.d.	n.d.	n.d.	
P26U5	UCF	0.8	40,000	34,500	36,800	36,500	37,800	26,500	29,900	20,900	20,900	
R23X9	UCF	0.19	51,900	46,400	47,100	46,600	47,700	33,500	37,000	26,000	26,000	

<sup>a</sup>Unadjusted age calculated assuming A<sub>0</sub> of 100 pMC and a decay constant of 3.83 × 10<sup>-12</sup> s<sup>-1</sup> (no geochemical corrections, for comparison purposes only).

<sup>b</sup>NDC = no diffusion correction; WDC = with diffusion correction based on Sanford (1997).

simulations, the processes responsible for observed chemical differences between initial and final waters were 1) mass exchanges of calcite, lignite, pyrite, glauconite, illite, kaolinite, quartz, and/or CO<sub>2</sub> gas; 2) Ca<sup>2+</sup>/Na<sup>+</sup> and Mg<sup>2+</sup>/Na<sup>+</sup> exchange between aquifer and groundwater; and 3) mixing with seawater (for well R23X9 only, the deepest well at the site closest to the coast). The solid phases used were included in the NETPATH simulations based on the known mineralogy of the study aquifers (Reid et al. 1986; McMahon et al. 1990; Sohl and Owens 1991; Winner and Coble 1996; Knobel et al. 1998). A redox state of -0.4 was used for DOC and lignite (Plummer et al. 1994). The seawater used for mixing at well R23X9 had the average chemical composition of Nordstrom et al. (1979), and DIC with δ<sup>13</sup>C of -2‰ (e.g. Ingerson and Pearson 1964) and <sup>14</sup>C activity of 2 pMC (e.g. Plummer and Sprinkle 2001).

These initial NETPATH simulations showed net transfers of CO<sub>2</sub> gas (averaging 3.3 mM) into groundwater, somewhat larger than the net CO<sub>2</sub> transfers reported by Plummer and Sprinkle (2001) for simulations of the Floridan aquifer. These transfers were required to close the carbon budget in the NETPATH simulations (i.e. carbon concentration in final water = carbon concentration in initial water + carbon mass transfers). The simulated net CO<sub>2</sub> transfers suggest a source of dissolved inorganic carbon (DIC) to the aquifers was missing from the first simulations. Three possible sources for this DIC were considered, and the first 2 seem much less likely than the third: 1) higher DIC in the actual recharge water than in the initial water used in the NETPATH simulations; 2) “proton exchange” as discussed by Appelo (1994); 3) aquitard-to-aquifer transport of DIC in the study aquifers (McMahon and Chapelle 1991b).

Higher DIC in the paleo-recharge-water to the study aquifers would imply that the partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>) in the soil of the recharge area was significantly higher during the last glacial period (see groundwater ages in Table 3) than at present, a conclusion at odds with the general association of lower P<sub>CO2</sub> with lower temperature (e.g. Drake 1980; Brook et al. 1983; Kiefer and Amey 1992). Also, the largest simulated CO<sub>2</sub> mass transfers (5.4 mM for R23X8 and 5.2 mM for R23X9) occurred in the groundwaters farthest downgradient, consistent with a transport mechanism by which carbon is continually added to the groundwater over time rather than all at once as higher DIC in the recharge area. The “proton exchange” described by Appelo (1994) involves calcite dissolution with subsequent cation exchange of dissolved Ca<sup>2+</sup> for sorbed Na<sup>+</sup>, Mg<sup>2+</sup>, and H<sup>+</sup> (instead of just Na<sup>+</sup> and Mg<sup>2+</sup>, as in our first simulations). The net result for groundwater chemistry is that DIC addition with this process is essentially from a combination of calcite and CO<sub>2</sub> (not just from calcite). In simulations with proton exchange, more calcite dissolved to eliminate the CO<sub>2</sub> transfer found in the first simulations, with the result that the simulated δ<sup>13</sup>C values of DIC were too high (on average, 7‰ larger than those measured in the final waters). For these reasons, higher DIC values in initial water and proton exchange in the study aquifers seem unlikely to explain the simulated net CO<sub>2</sub> transfers in the first NETPATH simulations. For reasons discussed below, aquitard-to-aquifer transport of DIC is a more likely explanation for these CO<sub>2</sub> transfers.

McMahon and Chapelle (1991b) found that aquitards (confining layers) of the Black Creek aquifer in South Carolina act as sources of DIC to the aquifer, both by direct transport of DIC from aquitard to aquifer and by transport of dissolved organic acids and sulfate, which ultimately react to produce additional DIC in the aquifer. It is plausible that these same processes occur in the Black Creek aquifer in North Carolina (and possibly the Upper Cape Fear aquifer). McMahon and Chapelle (1991b) modeled this aquitard-to-aquifer transport by including 2 “phases” to represent Black Creek aquitard groundwater in NETPATH simulations of the Black Creek aquifer groundwater; mass transfers of the aquitard groundwater “phases” into the aquifer groundwater were calculated as part of their simulations, along with the mass transfers of actual mineral phases in the aquifer. This approach

Table 4 NETPATH-calculated mass transfers between initial and final waters (in units of mM), as well as computed and observed  $\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{com}}$  and  $\delta^{13}\text{C}_{\text{obs}}$ , respectively) and <sup>14</sup>C age of groundwater. Positive mass transfer values represent solute additions to the aquifer groundwater (e.g. dissolution), negative values are losses (e.g. precipitation). Aquitard-to-aquifer transport of solutes is represented by mass transfers of the 2 “Aquitard GW” phases (based on McMahon and Chapelle [1991b], as discussed in the text). “Seawater” represents the percentage of seawater present in the final water. Large precipitation of calcite suggests the simulations (and ages shown here) for P26U5 and R23X9 may not be realistic; ages based on simulations without aquitard-to-aquifer transport are given in Table 3 for these 2 wells (see discussion in text).

Phase	P26U8	P26U7	R23X8	P26U5	R23X9
Calcite	-0.12	0.11	0.34	-2.76	-5.13
CaX/Na <sub>2</sub> X <sup>a</sup>	-0.34	0.30	0.88	-1.83	-3.76
MgX/Na <sub>2</sub> X <sup>b</sup>	-0.16	0.05	-0.14	0.24	1.14
Illite <sup>c</sup>	-0.21	-0.06	-0.93	-1.27	-2.16
Glauconite <sup>d</sup>	0.01	-0.01	0.13	0.09	0.32
SiO <sub>2</sub>	0.04	-0.02	0.01	0.74	0.25
Pyrite <sup>e</sup>	-0.16	-0.11	-0.39	-0.18	-0.64
Aquitard GW1 <sup>f</sup>	0.69	0.49	1.70	0.71	2.53
Aquitard GW2 <sup>g</sup>	1.09	0.70	3.04	1.37	2.99
Kaolinite <sup>h</sup>	0.22	0.10	0.77	1.32	1.75
Seawater (%)	0.00	0.00	0.00	0.00	2.00
<sup>13</sup> C <sub>com</sub> (‰)	-13.2	-13.6	-11.6	-13.1	-12.1
<sup>13</sup> C <sub>obs</sub> (‰)	-13.2	-15.3	-9.7	-16.5	-10.1
Age (yr BP)	5500	23,100	34,000	24,100	27,700

<sup>a</sup>Ca-for-Na cation exchange.

<sup>b</sup>Mg-for-Na cation exchange.

<sup>c</sup>K<sub>0.6</sub>Mg<sub>0.25</sub>Al<sub>2.5</sub>Si<sub>3.5</sub>O<sub>10</sub>(OH)<sub>2</sub> (Henderson 1985).

<sup>d</sup>K<sub>2</sub>Fe<sub>2</sub>Al<sub>6</sub>(Si<sub>4</sub>O<sub>10</sub>)<sub>3</sub>(OH)<sub>12</sub> (Chapelle and Knobel 1983; McMahon and Chapelle 1991b).

<sup>e</sup>FeS<sub>2</sub>.

<sup>f</sup>HCO<sub>1.5</sub>Na, dissolved organic acids from aquitard porewater (McMahon and Chapelle 1991b).

<sup>g</sup>Na<sub>2.0</sub>K<sub>0.238</sub>Ca<sub>0.167</sub>Mg<sub>0.050</sub>C<sub>2.637</sub>(SO<sub>4</sub>)<sub>0.241</sub> (Na content modified from McMahon and Chapelle 1991b).

<sup>h</sup>Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>.

focuses on geochemical mass balance in the aquifer and does not discriminate between advection and diffusion as possible aquitard-to-aquifer transport mechanisms (making it a good approach for a case in which the relative contributions of advection and diffusion are not known and the focus is on the net effects on aquifer groundwater).

We ran a second group of NETPATH simulations for our groundwater samples using the approach of McMahon and Chapelle (1991b), outlined above, to represent aquitard-to-aquifer chemical transport (Table 4). The goal was to see if our data from North Carolina were consistent with the aquitard-to-aquifer transport previously described for the Black Creek aquifer in South Carolina. We made 2 small changes in the aquitard groundwater phases from McMahon and Chapelle (1991b): 1) we lowered the stoichiometric coefficient of Na in “Aquitard Groundwater2” (Table 4) by 18% to avoid calcite precipitation in the simulations for wells other than P26U8, in accord with the negative calcite saturation indices measured at these wells; and 2) we lowered the  $\delta^{13}\text{C}$  of the carbon in the aquitard groundwater phases from -12 to -11‰ to make a slightly better fit between simulated and observed  $\delta^{13}\text{C}$  (the value from McMahon and Chapelle was approximate, based on their estimate that the dissolved carbon in the aquitard groundwater was derived from roughly equal contributions from calcite and biogenic CO<sub>2</sub>). We view these as small reasonable adjustments, limited by data

(calcite saturation indices and  $\delta^{13}\text{C}$  in the aquifer groundwater), to the model aquitard groundwater chemistry. McMahon and Chapelle (1991b) also lowered the stoichiometric coefficient of Na in the "porewater 2" they used in their simulations (relative to its measured value) to achieve simulated calcite mass transfers that were consistent with their observed saturation indices, i.e. dissolution rather than precipitation (PB McMahon, personal communication, July 2006; McMahon and Chapelle 1991b, their Tables 1 and 4).

For the Black Creek aquifer, the NETPATH simulations including aquitard-to-aquifer solute transport gave nearly identical groundwater ages to the simulations without this process, largely because the  $^{14}\text{C}$  activity of the carbon added to the aquifer in each type of simulation was taken as zero. In the absence of specific data on the  $^{14}\text{C}$  activity of aquitard groundwater, the limiting assumption of zero concentration is reasonable based on the much greater age expected for aquitard (as compared to aquifer) groundwater (e.g. Sanford 1997; Bethke and Johnson 2002). With few exceptions (e.g. Wassenaar and Hendry 2000; Hendry and Wassenaar 2005), data are lacking on  $^{14}\text{C}$  in aquitard groundwater, in this case and in general, in part because well screens are generally purposefully set in aquifers and not in aquitards due to the low yields of aquitards (Wassenaar and Hendry 1999). When deep monitoring wells are installed at significant expense, the focus is generally on measuring and monitoring conditions in the aquifer (especially when the aquifer is an important water supply, as in our case), not in the adjacent low-permeability aquitards. Based on the results of this study and previous work (e.g. McMahon 2001 and references therein), we believe collection of geochemical and isotopic data for groundwater in aquitards should generally be a higher priority as part of  $^{14}\text{C}$  dating and other studies in deep confined aquifers; aquitard data may be important to the interpretation of aquifer geochemistry, groundwater age, and flow rate.

For the Upper Cape Fear aquifer, the ages estimated with aquitard-to-aquifer chemical transport were 20–25% lower than those without. The Upper Cape Fear simulations also had significant calcite precipitation, which seems unrealistic given the negative calcite saturation indices observed in the Upper Cape Fear (Table 2). As a result, comparing between simulations with aquitard-to-aquifer transport, the age estimated for Upper Cape Fear groundwater at the Cove City site (well R23X9) was about 6000 yr less than that estimated for the shallower Black Creek groundwater at the same site (well R23X8); it seems unlikely this could be correct. These unrealistic outcomes for the Upper Cape Fear may be related to the use of aquitard groundwater chemistry from the Black Creek aquitard in the simulations for the Upper Cape Fear; no chemical data are available for groundwater in the Upper Cape Fear aquitard. Given that ages estimated with and without aquitard-to-aquifer transport agree for the Black Creek aquifer (the aquifer for which this transport is better understood and better modeled; McMahon and Chappelle 1991b), and that the Upper Cape Fear simulations with this transport included led to the unrealistic results described above, the best estimates of age for the Upper Cape Fear groundwaters are probably those from the simulations without aquitard-to-aquifer transport (Table 3). Precise uncertainty is difficult to estimate, but we consider the ages estimated for the Upper Cape Fear more uncertain than those for the Black Creek.

To summarize, the carbon concentration and isotope data from the Black Creek aquifer (and possibly the Upper Cape Fear aquifer) in North Carolina seem consistent with the aquitard-to-aquifer carbon transport observed in the Black Creek aquifer in South Carolina (Chappelle and McMahon 1991; McMahon and Chapelle 1991b):

1. Initial NETPATH simulations without this transport showed positive net  $\text{CO}_2$  mass transfers into aquifer groundwater, indicating the simulations were missing a source of DIC.
2. The largest  $\text{CO}_2$  mass transfers calculated in the NETPATH simulations without aquitard-to-aquifer transport occurred in the groundwaters farthest downgradient, consistent with a trans-

port mechanism by which carbon is added to the aquifers over time (as with the McMahon and Chapelle [1991b] aquitard-to-aquifer mechanism) rather than all at once (e.g. higher DIC in the initial water in the recharge area).

3. NETPATH simulations with aquitard-to-aquifer transport (Table 4) give plausible results (e.g. calcite mass transfers consistent with observed calcite saturation indices, mass transfers of similar magnitude to those reported by McMahon and Chapelle [1991b], and no physically impossible results such as negative mass transfers of the aquitard groundwater phases, which would imply loss of aquitard groundwater from aquifer groundwater), with the exception of calcite saturation indices for the Upper Cape Fear, the aquifer for which no aquitard groundwater geochemical data are available.
4. The resulting estimates of groundwater age, after further correction for diffusive loss of <sup>14</sup>C to aquitards (see below), give a reasonable estimate of long-term average groundwater velocity in the Black Creek aquifer (discussed below) and cause the groundwater samples with the lowest recharge temperatures to fall nearest in age to the time of the last glacial maximum (see below).

Together, this gives reasonable confidence that aquitard-to-aquifer chemical transport does affect the carbon geochemistry in at least the Black Creek aquifer (perhaps the Upper Cape Fear as well) in both North and South Carolina, and that the age interpretations from our NETPATH simulations are reasonable but could probably be improved with additional geochemical data from the adjacent aquitards. The NETPATH simulations with aquitard-to-aquifer transport give younger ages than any of the traditional geochemical correction models for <sup>14</sup>C groundwater dating (Table 3), suggesting that these models overestimate age (and therefore underestimate groundwater velocity) when applied to aquifers that experience geochemical exchange with adjacent aquitards.

Diffusive loss of <sup>14</sup>C from active aquifer flow zones into “stagnant zones” or aquitards with very low <sup>14</sup>C may cause significant overestimation of groundwater age in some aquifers (e.g. Neretnieks 1981; Sudicky and Frind 1981; Maloszewski and Zuber 1991; Sanford 1997; Wassenaar and Hendry 2000; Bethke and Johnson 2002; McMahon et al. 2004). In these cases, correction for diffusive loss of <sup>14</sup>C leads to younger and more realistic groundwater ages. We used the model of Sanford (1997) to make this correction (Table 3). DePaolo (2006) used a modified form of the Sanford (1997) model in his analysis of fluid-rock isotopic exchange in fractured rock systems. McMahon et al. (2004) found that corrections based on Sanford (1997) lowered their estimated <sup>14</sup>C groundwater ages by 20%. The Sanford (1997) model assumes a steady-state diffusive loss of <sup>14</sup>C from aquifers into adjacent aquitards, which is justified if groundwater age is much greater than the diffusion relaxation time  $L^2/D$  (Carslaw and Jaeger 1959:24; Bethke and Johnson 2002), where  $L$  is half the aquitard thickness and  $D$  is the effective diffusion coefficient. Relaxation times (Table 5) estimated using  $D = 10^{-10}$  m<sup>2</sup>/s, a value within the range characteristic of clayey deposits (Freeze and Cherry 1979:393), and aquitard thicknesses measured from cross-section F-F’ of Winner and Coble (1996), were much less than groundwater ages (Table 3), satisfying the condition on which the Sanford (1997) model is based. The Sanford (1997) model was applied to the Fontes and Garnier (1979) and NETPATH ages (Table 3), to generate a diffusion-corrected version of each age. We used a porosity value of 0.25 for the aquifers (Chapelle and Lovley 1990).

A bicarbonate concentration gradient may drive a net DIC flux into an aquifer from adjacent aquitards (as apparently occurs in the Black Creek and Upper Cape Fear), but this net DIC flux does not preclude diffusion of relatively higher-<sup>14</sup>C bicarbonate into the aquitard from the aquifer (given the underlying random nature of the diffusion process at the molecular scale, there must be some diffusion of higher-<sup>14</sup>C bicarbonate from an aquifer into adjacent aquitards containing lower-<sup>14</sup>C bicarbonate). The aquitard groundwater phases in the NETPATH simulations (Table 4) account for

Table 5 Average aquifer and aquitard thicknesses between each well and its estimated recharge area, and corresponding relaxation times (see text).

Well	Average thickness (m)		Relaxation time (yr)
	Aquifer	Aquitard	
O30J1	19.6	4.6	1680
P26U8	43.2	9.7	7460
P26U7	41.4	9.0	6420
R23X8	59.8	11.6	10,700
O30J3	22.1	2.5	500
P26U5	28.9	3.2	810
R23X9	36.0	4.0	1330

the net flux of DIC into the study aquifers from the adjacent aquitards; the correction of Sanford (1997) accounts for the diffusive loss of  $^{14}\text{C}$  in the opposite direction (from aquifers to the adjacent aquitards).

The mean difference between unadjusted age and NETPATH age (i.e. the mean magnitude of the geochemical correction to age) is 15,000 yr ( $n = 5$ ), while the mean difference between NETPATH ages with and without diffusion correction (i.e. the mean magnitude of the diffusion correction to age) is 8800 yr (Table 3). The diffusion correction is smaller but still large, suggesting that diffusive loss of  $^{14}\text{C}$  to aquitards may be a significant aquifer-to-aquitard transport mechanism affecting  $^{14}\text{C}$  activity in the Black Creek and Upper Cape Fear aquifers and further arguing for greater emphasis on collection of aquitard groundwater data in attempts to interpret geochemical results from, and groundwater flow in, these and other confined aquifers.

We estimated long-term average linear groundwater velocity ( $v$ ) in the Black Creek aquifer by plotting distance from recharge area versus  $^{14}\text{C}$  groundwater ages from the last column of Table 3. The slope of the best-fit line gave  $v = 2.5$  m/yr ( $r^2 = 0.88$ ). Chapelle and Lovley (1990) calculated average linear groundwater velocities to 5 wells in the Black Creek aquifer in South Carolina that ranged from 1.5 to 2.7 m/yr with a mean of 2.1 m/yr and a coefficient of variation of 25%. Using the approach described above for the Black Creek, we estimated an average linear velocity of 4.3 m/yr for the Upper Cape Fear aquifer. There are no literature values against which to compare this value, and we view it as less certain than that from the Black Creek aquifer (because the groundwater ages are likely more uncertain in the Upper Cape Fear due to greater uncertainty in aquifer:aquitard exchange for this aquifer).

## He CONCENTRATIONS

The dissolved helium (He) budget of the groundwater in an aquifer can be expressed:

$$He_{tot} = He_{sol} + He_{ea} + He_{terr} \quad (1)$$

where  $He_{tot}$  is the total (measured) dissolved He concentration in the groundwater;  $He_{sol}$  is the concentration of He from pressure-temperature-dependent equilibrium partitioning of He between the atmosphere and recharge water;  $He_{ea}$  is the concentration of He from “excess air” (e.g. air bubbles trapped in groundwater and later dissolved; Heaton and Vogel 1981; Stute and Schlosser 2000);  $He_{terr}$  represents the “terrigenic” He acquired in the groundwater system (as distinct from He acquired prior to recharge), through radiogenic production of  $^4\text{He}$  and diffusion of He into the aquifer (usually from below) (Heaton 1981; Torgersen and Ivey 1985). Equation 1 is based on a similar equation in Castro et al. (2000).

The rate of growth of He<sub>terr</sub> over time can in principle be an indicator of relative or even absolute groundwater age (e.g. Castro et al. 2000), and in principle He<sub>terr</sub> can be used to date groundwater too old to be dated with <sup>14</sup>C (Mazor and Bosch 1992). We set out to evaluate the relationship between groundwater He<sub>terr</sub> concentration and groundwater age (estimated from <sup>14</sup>C), to determine whether He<sub>terr</sub> offers a signal that is potentially relevant to groundwater age dating in the Black Creek and Upper Cape Fear aquifers. As with the carbon data, the He data also provide a compelling example of significant vertical chemical transport in the study aquifers.

He<sub>sol</sub> was estimated from He solubility data (Weiss 1971) using calculated salinity values (1.05‰ for well R23X9 and less than or equal to 0.39‰ for the other wells) and estimates of recharge temperature (Figure 4) determined from groundwater concentrations of N<sub>2</sub> and Ar using solubility data from Weiss (1970) at sea-level pressure (1 atm). While exact recharge elevations are unknown, ground surface elevation over the western, unconfined area of the study aquifers is at most 183 m, corresponding to a mean atmospheric pressure of about 0.98 atm (Stute and Schlosser 2000:353); recharge elevation was at least 14 m (land surface elevation at the lowest and easternmost site, Cove City). This uncertainty in recharge elevation (i.e. in recharge pressure) translates to about 1 °C uncertainty in recharge temperature.

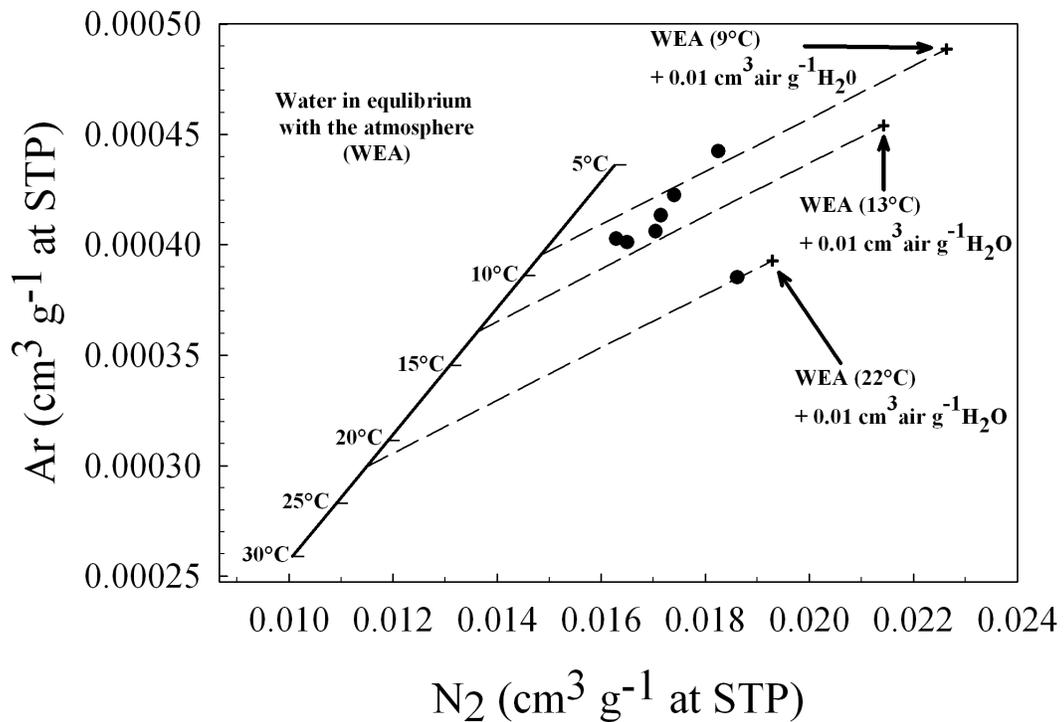


Figure 4 N<sub>2</sub> and Ar concentrations from groundwater samples in the Black Creek and Upper Cape Fear aquifers. The solid line shows concentrations expected for water in equilibrium with the atmosphere (WEA). The dashed lines show the effect of adding 0.01 cm<sup>3</sup> of excess air to WEA at 9, 13, and 22 °C. The majority of recharge temperatures are between 7.8 and 12.1 °C and seem reasonable. Well O30J1 falls almost directly on the 22 °C line; this seems unrealistically high for recharge temperature, and may be due to excess N<sub>2</sub> from denitrification.

This approach assumes that the atmosphere is the only significant source of dissolved N<sub>2</sub> and Ar in the groundwater. With regard to Ar, using the approach of Pearson et al. (1991) with the oldest

groundwater age estimated in this study and the maximum potassium content given by Raymond (1995:375) for an arkosic sandstone suggests that radioactive decay of  $^{40}\text{K}$  could produce less than 0.001% of the dissolved Ar measured in our groundwater samples. Thus, radiogenic Ar does not pose a problem for estimation of groundwater recharge temperature with groundwater  $\text{N}_2$  and Ar data.

Also, with respect to  $\text{N}_2$ , the old groundwater samples obviously predate the local agricultural contamination that might lead to significant dissolved nitrogen (and therefore, under some conditions, dissolved  $\text{N}_2$ ) concentrations from a source other than atmospheric  $\text{N}_2$ . Denitrification of natural background levels of  $\text{NO}_3^-$  in this area (0.2 mg/L nitrate-nitrogen; Madison and Brunett 1984) would produce a quantity of dissolved  $\text{N}_2$  (0.2  $\text{cm}^3 \text{N}_2$  at STP per kg of  $\text{H}_2\text{O}$ ) sufficient to elevate the  $\text{N}_2$ -Ar estimate of recharge temperature by 0.4 °C; this is less than the  $\pm 0.5$  °C accuracy of the method (Plummer et al. 2003), suggesting the denitrification of naturally occurring  $\text{NO}_3^-$  would not introduce significant uncertainty into estimates of recharge temperature based on  $\text{N}_2$  and Ar data. One possible exception to this is the youngest sample, from well O30J1, which may have some excess  $\text{N}_2$  from non-atmospheric sources. This relatively shallow well is located on a farm, and the  $\text{N}_2$ -Ar method gave an unrealistically high recharge temperature of 21.9 °C. Therefore, the 1903 to 2002 average of mean annual air temperature at nearby Goldsboro, North Carolina, 16.4  $\pm$  1.3 °C (North Carolina State Climate Office, Raleigh, North Carolina, USA: <http://www.nc-climate.ncsu.edu/>), was used as the recharge temperature for purposes of estimating  $\text{He}_{\text{sol}}$  for groundwater from well O30J1.

“Excess air” is derived from air bubbles that are trapped in water during recharge and then are dissolved as a result of increased groundwater pressure (Heaton and Vogel 1981; Stute and Schlosser 2000). Because Ar has no significant subsurface source in these aquifers (see above),  $\text{He}_{\text{ea}}$  was determined from the difference between the measured Ar concentration and the Ar concentration expected from equilibrium between recharge water and the atmosphere (e.g. Pearson et al. 1991):

$$\text{He}_{\text{ea}} = (\text{Ar}_{\text{tot}} - \text{Ar}_{\text{sol}})R_{\text{He/Ar}} \quad (2)$$

where  $\text{Ar}_{\text{tot}}$  is the measured Ar concentration in the groundwater sample;  $\text{Ar}_{\text{sol}}$  is the Ar concentration expected from equilibrium between recharge water and the atmosphere (at the recharge temperature estimated in Figure 4); and  $R_{\text{He/Ar}}$  is the molar He/Ar ratio (0.000561) in the atmosphere (Kazemi et al. 2006:302).

Groundwater age, stratigraphic proximity to crystalline basement rock, and vertical transport of He appear to be important factors influencing  $\text{He}_{\text{terr}}$  concentration (Table 6; Figure 5). There are 4 critical observations in this regard:

1. At each well site (Saulston, Savannah, and Cove City),  $\text{He}_{\text{tot}}$  and  $\text{He}_{\text{terr}}$  are higher in the Upper Cape Fear aquifer than in the overlying Black Creek aquifer.
2. Results from well P26U8 and deeper well P26U7 show a significant increase in  $\text{He}_{\text{tot}}$  and  $\text{He}_{\text{terr}}$  with depth in the Black Creek aquifer at the Savannah well site.
3. Well O30J3 in the Upper Cape Fear aquifer is the only well that directly overlies crystalline basement rocks, and groundwater at this well has by far the highest  $\text{He}_{\text{tot}}$  and  $\text{He}_{\text{terr}}$ .
4.  $\text{He}_{\text{terr}}$  is much lower at the next well downgradient from O30J3 (well P26U5) in the Upper Cape Fear.

Table 6 He<sub>terr</sub> and data from which it was calculated. The second column gives recharge temperatures estimated from Ar/N<sub>2</sub> data (Figure 4).

Well ID	T, °C	Ar <sub>meas</sub>	Ar <sub>sol</sub>	He <sub>tot</sub>	He <sub>sol</sub>	He <sub>ea</sub>	He <sub>terr</sub>
		(10 <sup>-4</sup> cm <sup>3</sup> at STP g <sup>-1</sup> )		(10 <sup>-8</sup> cm <sup>3</sup> at STP g <sup>-1</sup> )			
O30J1	16.4 <sup>a</sup>	3.85	3.35	18.8	4.52	2.89	11.49
P26U8	10.8	4.13	3.79	24.8	4.62	1.95	18.25
P26U7	7.8	4.42	4.06	62.6	4.69	2.01	55.90
R23X8	10.9	4.03	3.77	52.5	4.62	1.43	46.47
O30J3	11.7	4.01	3.71	1222	4.60	1.72	1216
P26U5	9.7	4.23	3.88	126.6	4.65	1.91	120.0
R23X9	12.1	4.06	3.66	225.6	4.58	2.27	218.7

<sup>a</sup>1903 to 2002 average of the mean annual air temperature from Goldsboro, North Carolina (see text).

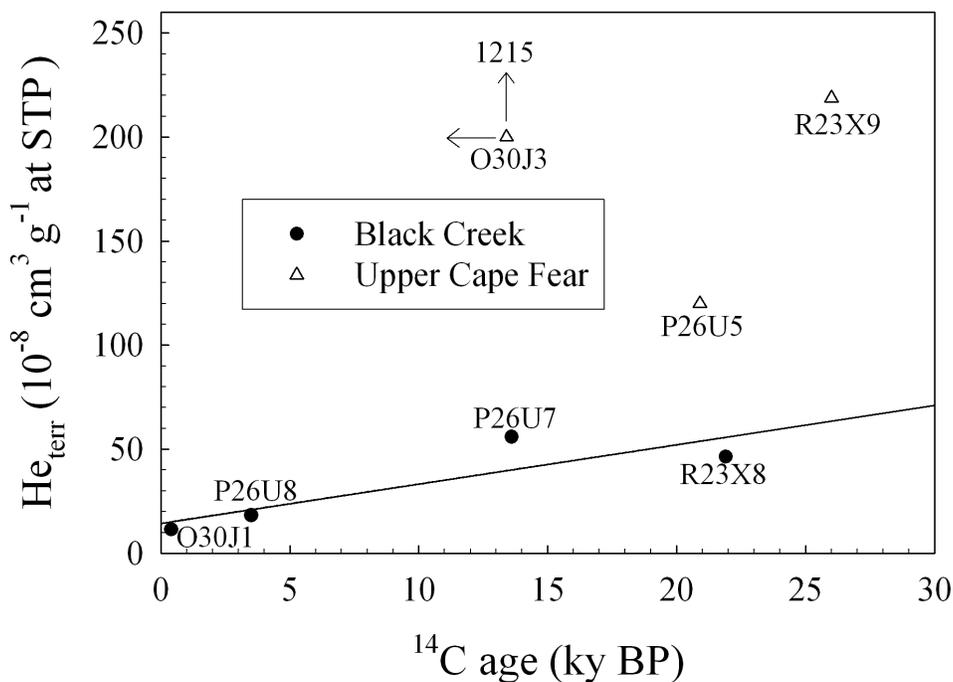


Figure 5 Relationship between He<sub>terr</sub> and <sup>14</sup>C groundwater age (from the last column of Table 3) in the Black Creek and Upper Cape Fear aquifers. The net He<sub>terr</sub> accumulation rate is about 19 × 10<sup>-12</sup> cm<sup>3</sup> g<sup>-1</sup> yr<sup>-1</sup> (r<sup>2</sup> = 0.74) for the Black Creek aquifer. The age estimate for well O30J3 (based on the Fontes and Garnier method) is likely an overestimate (see Table 3).

Taken together, these observations are consistent with upward vertical He transport through the study aquifers, in through the bottom of the Upper Cape Fear and upward toward the top of the Black Creek. Observations 1, 2, and 4 in particular suggest the vertical transport of He from the Upper Cape Fear to the Black Creek. Dispersive/diffusive transport of He into sedimentary strata from below has been observed or at least postulated in prior work, though transport out of strata across their upper surfaces has been considered insignificant in some previous work (Torgersen and Ivey 1985; Castro et al. 2000). Existing models that do not consider He flux from the top of a study

aquifer would not be expected to accurately describe  $\text{He}_{\text{tot}}$  and  $\text{He}_{\text{terr}}$  dynamics in the Upper Cape Fear aquifer. The recognition that dissolved He is lost from aquifers such as the Upper Cape Fear (observation 4 above) requires that  $\text{He}_{\text{terr}}$  be viewed as a net gain that reflects inputs (transport from below and production within the aquifer) minus outputs (across the top of the aquifer), not just a simple continuous accumulation.

In addition, the He observations above are consistent with (and observations 3 and 4 especially suggest) the He distribution expected in a confined aquifer that receives an upward He flux concentrated in a small area rather than evenly distributed over its lower surface. Simulation results from Zhao et al. (1998: Figure 4) show groundwater He concentrations decreasing downgradient in a hypothetical confined aquifer with a concentrated, localized “basal” He flux from below; hydrodynamic dispersion causes the decrease downgradient of the area of high basal flux. This simulated decrease is suggestive of the actual decrease we measured in He concentration in the Upper Cape Fear between wells O30J3 and P26U5. The opposite (He concentration increasing downgradient) is expected in an aquifer receiving a spatially uniform He input from below (Zhao et al. 1998). Also, the geology at well O30J3 (a thin portion of the Upper Cape Fear resting directly on crystalline basement rock; see Figure 2) is consistent with the high He concentration there being due to high He input from below. Thus, these He data from the Upper Cape Fear aquifer likely represent a real-world field example of the hypothetical situation simulated by Zhao et al. (1998) of a confined aquifer with He input from below concentrated in small area. Overall, the He data suggest that  $\text{He}_{\text{terr}}$  has potential as an indicator of groundwater age in the Black Creek and Upper Cape Fear aquifers, if interpreted within an appropriate analytical framework that includes the clear vertical transport of He.

In situ production rates of  $^4\text{He}$  in some previous studies of sandstone aquifers (Torgersen and Ivey 1985; Castro et al. 2000) average about  $4 \times 10^{-12} \text{ cm}^3$  of gas at STP (standard temperature and pressure) per gram of water per year ( $\text{cm}^3 \text{ g}^{-1} \text{ yr}^{-1}$  at STP). The net He accumulation rate (including in situ production and vertical diffusion) giving rise to  $\text{He}_{\text{terr}}$  in the Black Creek aquifer is about  $19 \times 10^{-12} \text{ cm}^3 \text{ g}^{-1} \text{ yr}^{-1}$  at STP (Figure 5). If the rate of radiogenic production of  $^4\text{He}$  in the Black Creek is similar to previously published rates for sandstones, He diffusion into the Black Creek from below would appear to be more important than in situ radiogenic production in producing the observed He concentrations (again emphasizing the importance of vertical He transport in any framework for extracting groundwater age information from groundwater He data in these aquifers).

### **RECHARGE TEMPERATURE, $\delta^{18}\text{O}$ , AND PALEOCLIMATE**

Diffusion-corrected NETPATH model ages for groundwater samples from wells P26U7 (13.6 kyr) and P26U5 (20.9 kyr) bracket the time of the last glacial maximum (LGM) in North America, and estimated recharge temperatures for these 2 samples (7.8 and 9.7 °C, respectively) are the lowest in the study (Table 6). These data suggest a cooling of about 7.7 °C at our study site near the time of the LGM (16.4 °C minus the average of 7.8 °C and 9.7 °C, the estimated recharge temperatures bracketing the LGM; Table 6). This temperature difference is slightly smaller than values based on groundwater dissolved gas data from Maryland (9.0 °C; Aeschbach-Hertig et al. 2002) and Hungary (8.6 °C; Stute and Sonntag 1992), and larger than the cooling of about 5 °C in New Mexico (Stute et al. 1995), Colorado (Clark et al. 1998), Texas (Stute et al. 1992), and 4 °C in Georgia (Plummer 1993; Clark et al. 1997). Aeschbach-Hertig et al. (2002) suggest that the relatively large Holocene–LGM temperature difference in Maryland could be due to the fact that Maryland was closer to the continental ice sheet.

Worldwide, groundwater recharged during the LGM has been recognized by depletion in  $\delta^{18}\text{O}$  in comparison to Holocene groundwater (Bath et al. 1979; Blavoux and Olive 1981; Dutton and Simpkins 1989; Clark et al. 1997; Aeschbach-Hertig et al. 2002). Data from this study indicate the opposite: enrichments in groundwater  $\delta^{18}\text{O}$  that were as high as 1.0 to 1.2‰, comparing the relatively young groundwater at well O30J1 to the oldest groundwater collected at the Cove City site (wells R23X8 and R23X9). Enrichment in  $\delta^{18}\text{O}$  of old groundwaters (to an even larger degree, up to 2.3‰) has been observed in the Floridan aquifer in Florida and southeast Georgia, USA (Plummer 1993; Plummer and Sprinkle 2001). Plummer (1993) suggests this enrichment may be due to the older groundwater having had a different recharge season (a shift toward summer from the modern recharge maximum in late winter and spring), with associated additional inputs of  $\delta^{18}\text{O}$ -enriched precipitation from tropical cyclones. Results presented here provide a second example of  $\delta^{18}\text{O}$  enrichment in old groundwaters of the southeastern US and provide further motivation to investigate the effects of region-specific climatic variables (e.g. moisture transport mechanisms, storm trajectories, recharge season) on stable isotopes in modern and old groundwaters.

Also, the data presented here place the deep Coastal Plain aquifers of North Carolina ( $\delta^{18}\text{O}$  enrichment of about 1‰, LGM cooling of about 7.7 °C) as intermediate between those of Maryland to the north (no  $\delta^{18}\text{O}$  enrichment, cooling of 9 °C) and Florida to the south ( $\delta^{18}\text{O}$  enrichment up to 2.3‰, cooling of 4 °C), an outcome in accord with the intermediate geographic location of North Carolina and therefore suggesting: 1) the reasonableness of the data interpretation (including recharge temperatures and groundwater ages); and 2) the potential utility of these and further groundwater data from North Carolina in interpreting paleoclimatic gradients across the southeastern US.

## CONCLUSIONS

Geochemical data presented here for the Black Creek and Upper Cape Fear aquifers in the North Carolina Coastal Plain show an expected coastward increase in <sup>14</sup>C groundwater age and suggest that vertical chemical fluxes across the upper and lower boundaries of the aquifers (aquifer: aquifer exchange and, in the case of He in the Upper Cape Fear, crystalline basement rock to aquifer exchange) are important controls on the observed DIC and He concentrations, and <sup>14</sup>C activity, in aquifer groundwater. As noted in a recent review (McMahon 2001), other studies have shown the importance of aquifer: aquitard chemical exchange in general, and the specific importance for DIC in the Black Creek aquifer in South Carolina.

The aquitard-to-aquifer flux of DIC for the Black Creek aquifer in South Carolina has been previously quantified and modeled using geochemical mass-balance software (McMahon and Chapelle 1991b); incorporating this approach into our NETPATH simulations of the Black Creek aquifer in North Carolina led to <sup>14</sup>C groundwater ages that were smaller than those from any of the well-known geochemical correction models for <sup>14</sup>C age dating of groundwater (Table 3). Further correction for diffusive loss of <sup>14</sup>C from aquifer groundwater to aquitard groundwater based on Sanford (1997) lowered <sup>14</sup>C groundwater age estimates even further (Table 3). The resultant groundwater ages, recharge temperatures, and  $\delta^{18}\text{O}$  values form a data set that seems consistent both internally and with other data from the Atlantic Coastal Plain of the US (Plummer 1993; Aeschbach-Hertig 2002), providing confidence in the overall interpretation (including the importance of aquifer: aquitard exchange in <sup>14</sup>C dating of aquifer groundwater). Other characteristics of our data (e.g. the increase in Na<sup>+</sup> and DIC concentrations with distance from recharge area and the near 1:1 relation of Na<sup>+</sup>: DIC) are consistent with results from the Black Creek aquifer in South Carolina (Chapelle and McMahon 1991; McMahon and Chapelle 1991b), further supporting the use in our study of an approach to aquifer: aquitard DIC exchange pioneered in the South Carolina work. Groundwater in

the Black Creek and Upper Cape Fear aquifers shows a  $\delta^{18}\text{O}$  enrichment near the LGM (relative to modern groundwater), a feature present in confined aquifers of the US Atlantic Coastal Plain in Florida and southeastern Georgia but absent in Maryland; data from North Carolina could be useful in better defining and understanding the origin of this regional gradient in the  $\delta^{18}\text{O}$  of old groundwaters.

In combination with estimates of distance from recharge area, the  $^{14}\text{C}$  groundwater ages suggest an average linear groundwater velocity of 2.5 m/yr for the Black Creek aquifer in North Carolina, similar to the estimate of 2.1 m/yr for this aquifer in South Carolina (Chapelle and Lovley 1990). We suggest that traditional geochemical models (Table 3) used in  $^{14}\text{C}$  groundwater dating will lead to overestimation of age and underestimation of groundwater velocity if applied to aquifers in which groundwater has significant chemical/isotopic exchange with the groundwater of adjacent aquitards. Also, collection of geochemical and isotopic data for groundwater in aquitards should generally become a higher priority as part of  $^{14}\text{C}$  groundwater dating and other studies in deep confined aquifers; as other authors have suggested on the basis of groundwater data and/or theoretical considerations (e.g. Sanford 1997; Wassenaar and Hendry 1999, 2000; Bethke and Johnson 2002; Hendry and Wassenaar 2005), aquitard data may be important to the interpretation of aquifer geochemistry, groundwater age, and flow rate.

He concentration in groundwater varies as a function of both age and stratigraphic location (especially proximity to basement rocks), and may be useful as a quantitative age-dating tracer in the Black Creek and Upper Cape Fear aquifers if an analytical framework (i.e. model) that accounts for vertical He transport and the influence of geology/stratigraphy on He concentration is employed. The importance of vertical He transport in these aquifers is particularly evident in the Black Creek wells at the Savannah well site, where the deeper of the 2 wells has a  $\text{He}_{\text{terr}}$  concentration that is more than 3 times larger than the shallower one. In the Upper Cape Fear, He concentrations and stratigraphic proximity to basement rocks are broadly consistent with the pattern in the Zhao et al. (1998) simulation for a confined aquifer with a localized basal He flux (as opposed to an evenly distributed basal He flux) into the bottom of the aquifer. The Upper Cape Fear aquifer in North Carolina seems to represent an actual field example of the phenomenon modeled by Zhao et al. (1998).

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