Unexpected Sources of Strontium to the Neuse and Cape Fear River Basins, North Carolina: Implications for the Global Strontium Isotope Budget in Seawater

Elena M. Watts[1] (iD), **Drew S. Coleman[1]** (iD), **Angel M. Colon-Ramirez[1]**, and **Aleah R. Walsh[1]**

[1]Department of Geological Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC, USA

Abstract Water, bedrock, and saprolite samples from the Neuse and Cape Fear River basins, North Carolina, were analyzed for $^{87}Sr/^{86}Sr$ and [Sr] to evaluate the control of exposed bedrock on fluvial Sr isotopic compositions and the influence of geology on Sr delivered to the ocean. The $^{87}Sr/^{86}Sr$ and [Sr] of the two rivers start low and rise downstream, eventually approximating recent ocean isotopic compositions before entering their estuaries. Groundwater samples from the headwaters have $^{87}Sr/^{86}Sr$ ratios that are lower than expected from the dominant exposed bedrock. The isotopic compositions of bedrock and saprolite samples vary predictably with rock type and age and show no correlation with degree of weathering. The data indicate that dominant surficial bedrock is not the primary source of Sr to the headwaters of the rivers. Rather, mafic dikes that focus groundwater flow and are more easily weathered than their silicic hosts impact the $^{87}Sr/^{86}Sr$ of the waters more than their limited exposure might suggest. Furthermore, the Sr isotopic composition of the water delivered to the marine environment is buffered by groundwater from coastal plain sedimentary rocks, leaving no evidence of upstream geology. The data suggest that rock type and structure exert significant control on the Sr isotope geochemistry of groundwater that enters into streams. Considering the global fluvial Sr budget, these results emphasize that, in some settings, (1) rock exposure area can be a poor indication of the geologic influence on Sr isotopic compositions of surface waters, and (2) downstream Sr isotopic compositions may not reflect upstream geology.

Plain Language Summary In this study we characterize how the chemical signatures (Sr isotopic ratios) of underlying rock influence the chemical signatures of river water. Rivers contribute a significant amount water to the ocean, and thus, the chemical signatures of rivers help determine the overall chemical signature of the ocean throughout geologic time. This is important for understanding how the composition of the oceans reflects geologic processes such as mountain building, volcanism, and weathering. By studying the relationships between bedrock and rivers, we can better understand how continental geology influences the geochemistry of the ocean. We found that, in some cases, bedrock types that are not abundant on the surface can impact groundwater chemical signatures disproportionately, and that rivers which run through large, young coastal geologic provinces can ultimately deliver water with an isotopic signature similar to that of the ocean.

1. Introduction

The evolution of the Sr isotope composition of seawater throughout geological history can be reconstructed from well-preserved carbonate rocks. Understanding the controls on the Sr isotopic composition of the oceans is important for using this record to unravel the history of global tectonics (e.g., seafloor spreading rates, mountain building, and magmatism), erosion, and chemical weathering (Burke et al., 1982). In order to interpret the global implications of these data, the modern budget of oceanic Sr must be characterized (Veizer & Compston, 1974). Throughout the Cenozoic, the Sr isotopic composition of the ocean has steadily risen (Veizer, 1989). Rivers and mid-ocean ridge hydrothermal circulation are considered the primary sources of radiogenic and nonradiogenic Sr (respectively) to the oceans, and the rise in radiogenic Sr in oceans has been attributed to the uplift and erosion of the Himalayas (Palmer & Edmond, 1989, 1992). Quantitative estimates of the fluxes of Sr into the oceans suggest the Sr isotopic composition should be significantly more radiogenic than it is (Palmer & Edmond, 1989). There are many proposed explanations for this discrepancy including the following: (1) Modern weathering rates are relatively high and not

representative of average rates over the last several million years (Crocket et al., 2012), (2) suspended volcanic sediment may be highly reactive and release significantly more Sr in the oceans than is delivered by the dissolved load (Jones et al., 2014), and (3) variations in the nature of young silicic arc magmas has a rapid and direct impact on the isotopic composition of the oceans, and that composition is a reflection of the proportion of evolved:unevolved rocks in the continental crust (Bataille et al., 2017). Basu et al. (2001) also suggested that groundwater may contribute significantly to the Sr budget of the oceans. All of these possibilities suggest that important factors controlling the isotopic composition of the oceans have been overlooked (Allegre et al., 2010; Bataille et al., 2014).

Palmer and Edmond (1992) conducted one of the most comprehensive analyses of global fluvial Sr input to oceans and analyzed 47% of the total global runoff from the world's largest rivers. However, their study assumed that the $^{87}Sr/^{86}Sr$ output of smaller river basins would be essentially the same as the nearest large river (Palmer & Edmond, 1989, 1992). A study that modeled the fluvial input of Alaskan rivers found that the Sr isotopic composition of Alaska's small river basins likely differ from that of the Yukon, Alaska's largest river (Bataille et al., 2014). This indicates a need for direct analyses of small river basins and their contributions to oceanic Sr.

Though sources of Sr to the ocean are well studied, the sources of Sr to river basins, and especially small river basins, are not as well known. Recently, characterization of isotope variability (spatially and temporally) has been described in terms of isoscapes (West et al., 2008), which recognize that many factors contribute to the variation in Sr isotopic composition in river water. These include rock type, weatherability, topography, precipitation, groundwater, and the complexity of interconnected stream networks (Bataille et al., 2014; Bataille & Bowen, 2012; Brennan et al., 2016; Christian et al., 2011; Land et al., 2000; Palmer & Edmond, 1992). In consideration of these factors, the purpose of this study was to (1) analyze the Sr isotopic composition of two small rivers to assess the sources of Sr to the river water, (2) supplement existing Sr data for bedrock to evaluate if weathering has a significant impact on bedrock isotopic values, and (3) evaluate the influence of headwater geology on the Sr isotopic composition of the water delivered to the ocean.

The Neuse and Cape Fear Rivers in North Carolina were chosen for this study because both begin with groundwater flow, both traverse three distinct geologic provinces (from west to east, Precambrian and Paleozoic terranes of Gondwana affinity, Triassic rift basins, and coastal plain sedimentary rocks), and the two rivers are adjacent to one another, suggesting they should be subject to similar geologic influences (Figure 1). We present new Sr isotopic data for the rivers, groundwater in the headwaters region of the Neuse River, and limited samples of bedrock and saprolite to evaluate the sources of Sr into the rivers and the impact of headwater geology on the isotopic composition of the water that is introduced to the marine system.

2. Geologic Setting

The Neuse River and the Cape Fear River drain approximately 12% and 16% of the total land area of North Carolina, respectively. The United States Geological Survey (2017) has gauging stations located along the Neuse and Cape Fear Rivers which collect gauge height data daily. The rivers drain much of central and eastern North Carolina that are characterized by three generalized geologic provinces from west to east: Carolina Slate Belt (Late Proterozoic–Cambrian volcanic/plutonic rocks), the Durham basin (Triassic basaltic and sedimentary rocks), and the coastal plain (Cretaceous–Quaternary marine sedimentary rocks; Figure 1; Stewart & Roberson, 2007). Both the Neuse and Cape Fear River basins originate as groundwater flow in the Slate Belt and then traverse all three terranes and empty into the Atlantic Ocean along the North Carolina coast.

The Carolina Slate Belt exposes metamorphosed intrusive and volcanic rocks (Figure 1). It is thought to be one of several blocks of accreted Gondwanan terranes (Horton et al., 1989). Previous work on the Sr composition of granitic rocks in the Carolina Slate Belt has found relatively high modern $^{87}Sr/^{86}Sr$ ratios exceeding 0.706 (Fullagar & Butler, 1979). The Slate belt is dissected by Mesozoic rift basins formed during Gondwana breakup. The Durham Basin includes Mesozoic sedimentary rocks ranging from conglomerate to mudstone and Jurassic diabase dikes and sills. Although few of the dikes and sills are mapped, aeromagnetic data suggest that there are many unmapped dikes in the Triassic basin and surrounding Carolina Slate Belt (Ragland
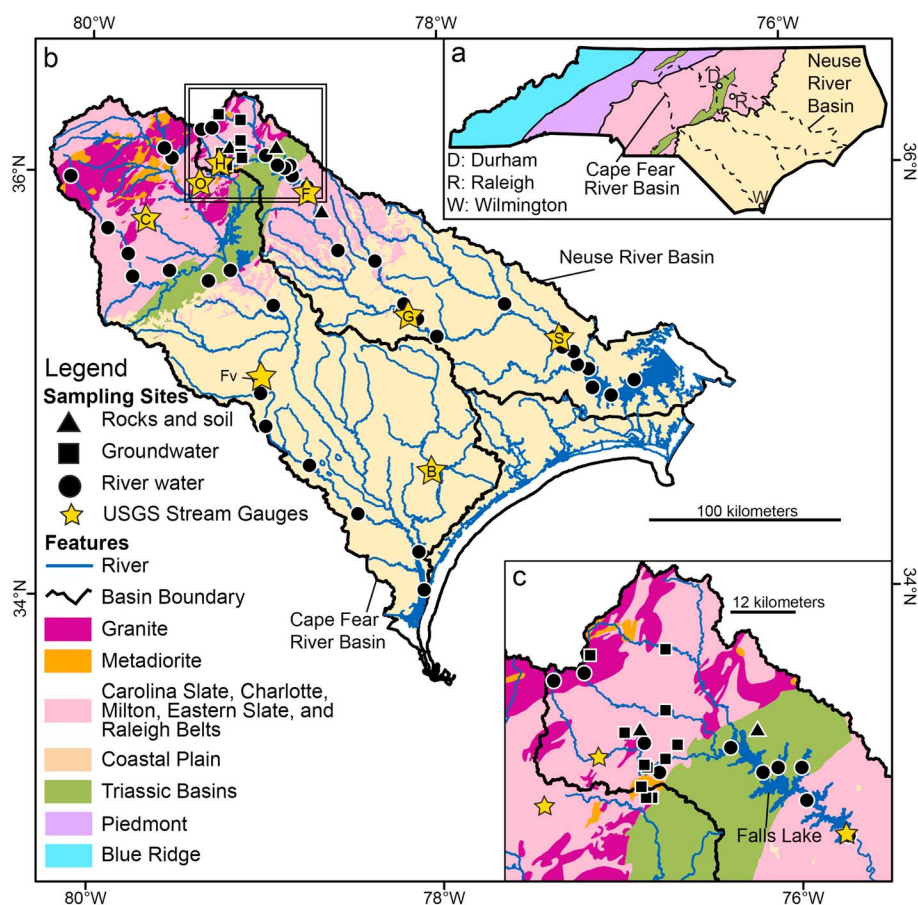
Figure 1. (a) Generalized geologic map of North Carolina, adapted from Stewart and Roberson (2007). The Neuse and Cape Fear River basins cut across three geologic units: the Gondwanan terranes, the Durham Triassic Rift basin, and the coastal plain. (b) Geologic map of the Neuse and Cape Fear River basins with sample sites and USGS gauge stations. Gauge station letters correspond to station names in Figure 2. On the Neuse River: (H) Hillsborough, (F) Falls Lake, (G) Goldsboro, and (S) Swift Creek. On the Cape Fear River: (O) Orange Grove, (C) Crutchfield, (Fv) Fayetteville, and (B) Burgaw. (c) Detail of the sampling sites in the headwaters of the Neuse River. River water samples were collected from the Neuse and Cape Fear Rivers, and rock, soil, and groundwater samples were collected from the Neuse River basin. The headwaters of the Neuse and Cape Fear Rivers lie in the Carolina Slate Belt, which primarily exposes metarhyolite, granite, and metadiorite. USGS = United States Geological Survey.

et al., 1983). The Raleigh Belt, east of the Durham Basin, is also hypothesized to be an accreted Gondwanan terrane (Figure 1; Horton et al., 1989). It includes Paleozoic metamorphic and igneous rocks, including Alleghanian granites with $^{87}Sr/^{86}Sr$ ratios ranging from 0.7071 to 0.7288 (Coler et al., 1997). The North Carolina coastal plain primarily exposes marine sedimentary rocks deposited between 38 and 2 Ma, which should have $^{87}Sr/^{86}Sr$ ratios similar to that of the ocean during the time of deposition (0.7080 to 0.7092; Brown et al., 1985; McArthur et al., 2001; Veizer, 1989).

The isotopic input of rainwater in the area is approximately 0.708–0.709 (Kiperwas, 2011; Surge et al., 2016; Tanner, 2014) and typically has concentrations ranging from less than 1 to 5 ppb, but can be as high as 16 ppb (Tanner, 2014). Tanner's (2014) analysis includes multiple storms that were terrestrial, marine, coastal, and mixed, and only one coastal storm was characterized by high $^{87}Sr/^{86}Sr$ (>0.710), but it was also characterized by low [Sr] (~1 ppb). In addition to natural geologic sources of Sr into the Neuse and Cape Fear Rivers, there are 16 wastewater treatment plants located along the Neuse River (Harned & Meyer, 1983), 46 along the Cape Fear River (North Carolina Department of Environment and Natural Resources (NCDENR): Division of Water Quality, 2009), and 48,000 farm operations in North Carolina as of 2017 (USDA & NASS, 2017). The impact of these anthropogenic inputs on fluvial Sr is not well understood, and no attempt was made to characterize these potential sources in this study.

3. Materials and Methods

In order to better know surface rock isotopic compositions and the impact of weathering on the isotopic compositions in the headwaters region of the Neuse River, three quarries were sampled. The furthest west quarry, in the Carolina Slate Belt, is in the granodiorite of the Buckwater Creek pluton, a late Proterozoic–Cambrian metamorphosed granite with diorite inclusions that intruded a sequence of inter-bedded felsic tuffs and volcaniclastic sedimentary rocks (Bradley et al., 2016). The second quarry, located within the Triassic Basin, exposes Jurassic diabase sills. The furthest east quarry lies in foliated to massive, Permian to Pennsylvanian granitic rock that is a part of the Rolesville batholith of the Raleigh Belt (Figure 1). Fourteen rock samples were collected from the three quarries (Figure 1). At each quarry, samples that had undergone varying degrees of weathering were collected. The less weathered samples required crushing with a Chipmunk, whereas the saprolite did not. Granitic rock samples were powdered using a mortar and pestle, and diabase samples were powdered using an Al-ceramic ball mill. Whole-rock powder was added to Teflon® Parr vessels with HF and HNO_3 and placed in an oven for 3 days for dissolution. The Sr concentrations of five rock samples (BQ-01, BQ-02, BQ-04, BQ-05, and SR-01) were determined using an inductively coupled plasma mass spectrometer at the University of North Carolina at Chapel Hill.

Sixty-two water samples were collected from the Neuse River and 18 from the Cape Fear River at accessible locations from the headwaters through the estuary. Twelve groundwater samples were collected from private wells near the headwaters of the Neuse River (Figure 1). To control for onsite variation during sampling, three Neuse River water samples were collected consecutively at the same site (EC02–EC04). In order to test the consistency of the results over time, several sites were sampled multiple times, and three Neuse River sites were sampled multiple times over the course of 2 years during different levels of flow. All river samples were collected using a Van Doorn sampler, and 60 ml of river water was filtered immediately after collection to remove particulates (>0.45 μm). To test the effect of removing particulate on $^{87}Sr/^{86}Sr$ ratios, samples collected at the same time from six sites (EEH, WEH, WFL, MFL, EFL, and EC) were split; half the sample was filtered using a 0.45-μm filter, and half was unfiltered. After filtering, all river water samples were immediately acidified to a pH of approximately 2 using ultrapure HNO_3. One liter of groundwater was collected from each private well and was acidified with 5 ml of HNO_3 on site and filtered (>0.45 μm) in the laboratory. All groundwater samples were collected during the week of 22 May 2017.

From each water sample, 10–12 ml was spiked with a tracer enriched in ^{84}Sr, dried down to a salt, and redissolved in 3.5-M nitric acid. Unfiltered water samples were treated the same as filtered samples after collection and were dissolved with 3.5-M nitric acid. Strontium was purified from water and rock samples using Sr-spec cation exchange resin after the methods of Lundblad (1994). $^{87}Sr/^{86}Sr$ ratios and Sr concentrations were measured by loading on Re-ribbon filaments with TaF_5 and analyzing using a VG Sector 54 thermal ionization mass spectrometer at the University of North Carolina at Chapel Hill. Data were collected with a three-cycle "peak-hopping" routine. Strontium isotope ratios were corrected for mass fractionation using an exponential law and normalized to $^{86}Sr/^{88}Sr = 0.1194$. Replicate analyses of the NBS-987 Sr standard yielded $^{87}Sr/^{86}Sr = 0.710265 \pm 0.000014$ (2σ; $n = 109$). Internal run precision exceeds external reproducibility of the standard; therefore, we accept ±0.000014 as the uncertainty in the analysis of the unknowns. A procedural blank for water samples was prepared using deionized water and was run through an identical procedure as filtered river water samples.

4. Results

4.1. River Gauging

United States Geological Survey (2017) river gauge data were collected from the gauging stations nearest sample sites on the date of sampling (Figure 1). The data show normal seasonal trends, excluding a hurricane event in October 2016 (Figure 2). At sites from which multiple samples were collected, normal and high flow episodes were sampled.

4.2. $^{87}Sr/^{86}Sr$ Compositions

Rock samples collected from the Carolina Slate Belt include intermingled granite (0.706323–0.707261; $n = 3$) and diorite (0.705233; $n = 1$). There is significant variation between the $^{87}Sr/^{86}Sr$ ratios of the weathered and unweathered rocks. The saprolite samples from this quarry have the highest $^{87}Sr/^{86}Sr$ ratios of any sample in
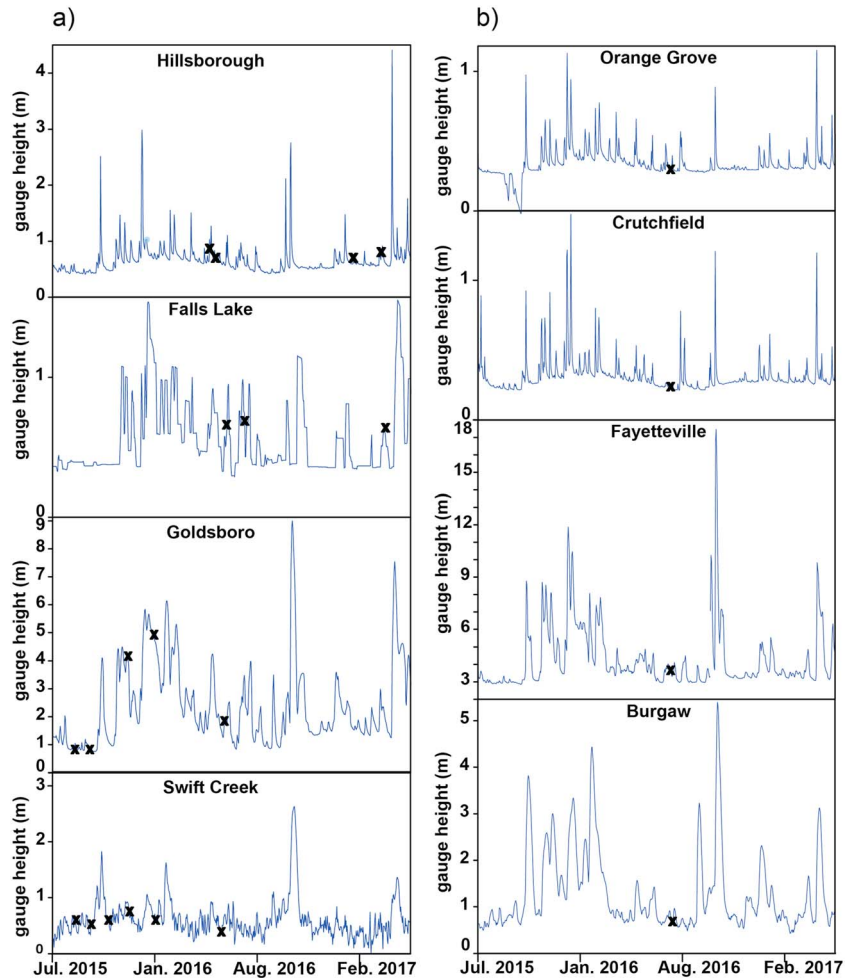
Figure 2. Mean daily gauge heights collected at four different gauging stations (Figure 1) from 1 July 2015 to 1 June 2017 on the (a) Neuse and (b) Cape Fear Rivers (United States Geological Survey, 2017). X's denote days that a sample was collected at or near the gauging station.

this study—up to 0.7191 ($n = 2$). From the Triassic Basin, fresh and weathered diabase samples were collected, and all yielded nearly identical $^{87}Sr/^{86}Sr$ ratios of 0.7048 ($n = 3$). Granitic samples from the Raleigh belt have consistent and radiogenic Sr compositions around $^{87}Sr/^{86}Sr = 0.7129$. There is no significant difference between the $^{87}Sr/^{86}Sr$ ratios of the bedrock and deeply weathered samples collected from the same location in the Raleigh Belt quarry (Figure 3a). Groundwater samples collected from the Neuse headwater catchment area have $^{87}Sr/^{86}Sr$ ratios ranging from 0.703835 to 0.710005 (Figure 3b). No discernible geographic pattern is evident in these data.

River water from the Neuse River ranges in $^{87}Sr/^{86}Sr$ ratios from 0.704456 to 0.711562 ($n = 64$; Table 1 and Figure 3b). Samples from within 25 km of the headwaters range from 0.704456 to 0.705375. Downstream, the $^{87}Sr/^{86}Sr$ ratios rise and eventually stabilize near the modern oceanic value of 0.7092. Notable exceptions to this trend are from the three sample sites in Falls Lake, which yield $^{87}Sr/^{86}Sr$ ratios ranging from 0.705642 to 0.710311 ($n = 15$). Sites that were sampled repeatedly are consistent through time (Figure 4d). Several sample sites have change in $^{87}Sr/^{86}Sr$ ratios over the course of approximately 11 months that exceed analytical uncertainty.

River water from the Cape Fear River ranges in $^{87}Sr/^{86}Sr$ ratios from 0.705561 to 0.709177 ($n = 17$; Figure 5). The headwaters have an $^{87}Sr/^{86}Sr$ ratio of 0.705152. Similar to the Neuse River, the isotopic composition of the Cape Fear River also rises toward oceanic $^{87}Sr/^{86}Sr$ from the headwaters to the estuary; however, it does not stabilize at oceanic Sr isotopic composition in the coastal plain as the Neuse does.
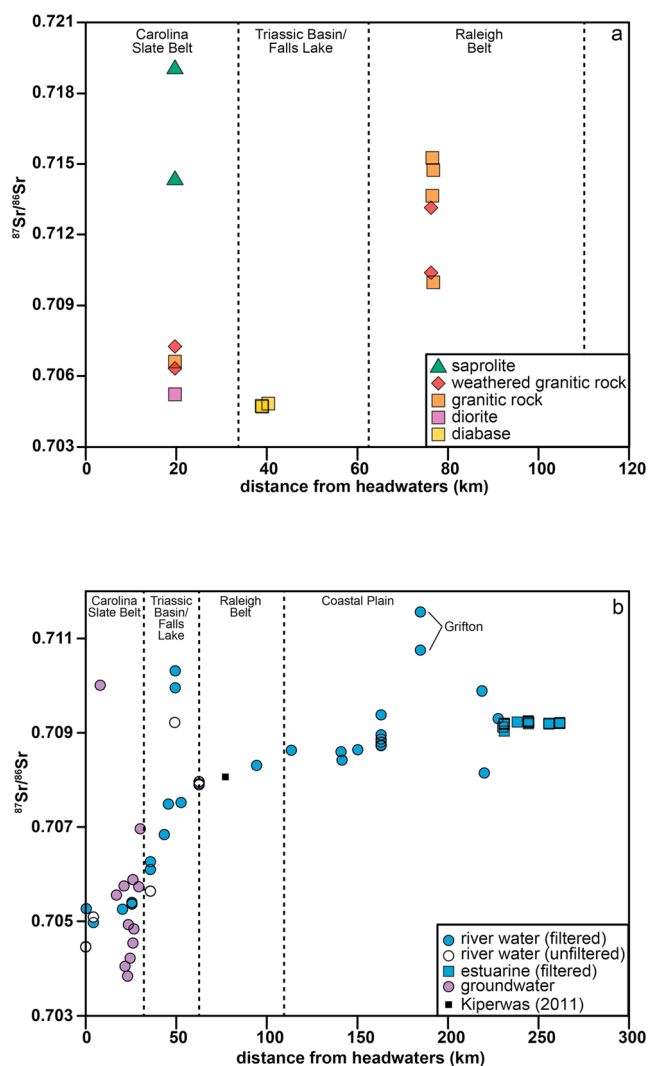
Figure 3. Sr isotopic ratios of (a) rock samples and (b) river and groundwater samples in the Neuse river basin as a function of distance from the headwaters (calculated as a straight-line distance between Universal Transverse Mercator coordinates of the headwaters and each sample). The isotopic compositions of bedrock and saprolite do not match the local river water nor do they change consistently with degree of weathering. River water samples begin low ($^{87}Sr/^{86}Sr = 0.705$) in the headwaters and steadily rise to 0.7092 in the estuary, with radiogenic outliers in Falls Lake (Triassic Basin) and at Grifton, North Carolina. Data from Kiperwas (2011) fit within the general trend of data from this study.

4.3. Sr Concentrations

Fresh river waters (nonestuarine) have consistently low Sr concentrations ranging from 4 to ~200 ppb ($n = 43$; Figure 6). River water near the estuary has Sr concentrations ranging from 104 to 2,658 ppb ($n = 19$). Groundwater samples have notably higher Sr concentrations than the headwaters of the Neuse River, ranging from 31 to 725 ppb ($n = 12$). The Cape Fear River shows a similar trend to Neuse, with low concentrations throughout most of the river, except at the estuary where concentrations increase by an order magnitude.

5. Discussion

The data set presented here integrate Sr concentrations and isotopic compositions for the Neuse and Cape Fear River basins. Representative samples of rock-type, saprolite, and groundwater lend further insight into the sources of fluvial Sr in the Neuse River basin. These data, combined with prior studies, better characterize isotopic variability of small streams that drain into the ocean.

5.1. Bedrock and Saprolite

The Bacon Quarry, the most upstream bedrock sample site located in the Carolina Slate belt, preserves a good weathering profile. There is minimal difference between the Sr compositions of the fresh and moderately weathered granodioritic rock samples, all of which are low for Precambrian silicic intrusions ($^{87}Sr/^{86}Sr$ 0.7067) but comparable to ratios measured by Fullagar and Butler (1979) elsewhere in the Carolina Slate Belt. In contrast, the saprolite samples yielded high $^{87}Sr/^{86}Sr$ ratios (>0.71). Some studies suggest that preferential removal of labile Sr during weathering may yield lower $^{87}Sr/^{86}Sr$ in the residuum as a result of removal of radiogenic ^{87}Sr (Blum et al., 1993; Blum & Erel, 1997; Brantley et al., 1998); however, this cannot account for the offset between fresh rock and saprolite observed here. Rather, the data can be explained if minerals with less radiogenic Sr (e.g., plagioclase) were preferentially weathered over minerals with more radiogenic Sr (e.g., biotite; Clow et al., 1997; Pett-Ridge et al., 2009; Stewart et al., 2001). Other possibilities for the isotopic offset between fresh/weathered rock and saprolite are that (1) there is a nonradiogenic mineral phase added to the saprolite as a result of soil formation (e.g., calcite cements; Jacobson & Blum, 2000) and (2) the saprolite sample was not derived directly from the sampled bedrock but has its origin in felsic metavolcanic or metasedimentary wall-rocks of the Buckwater Creek pluton (Bradley et al., 2016)—all of which would plausibly have high present-day $^{87}Sr/^{86}Sr$.

Jurassic diabase sill samples collected from the quarry in the Triassic basin are all either unweathered or only moderately weathered. No saprolite samples were collected from this site. All three sill samples are relatively low in radiogenic Sr as predicted by their age (~220 Ma) and low Rb/Sr ratios (<0.04; United States Geological Survey, 1984).

The samples collected from the easternmost quarry within the Rolesville batholith were all granitic and varied between bedrock and weathered granitic rock. The samples collected from this quarry show no consistent change in Sr isotopic composition with weathering. The $^{87}Sr/^{86}Sr$ ratios for the quarry overall ($^{87}Sr/^{86}Sr$ from 0.709991 to 0.715260, $n = 6$) were high, as expected for approximately 300-Ma granitic rocks (Fullagar & Butler, 1979), with a large range. This range is observed within unweathered samples, suggesting it is a result of differing isotopic evolution (i.e., Rb/Sr ratios) as opposed to systematic alteration from weathering. Weathered samples fall within the variation of unweathered samples.

Table 1

Sample Descriptions, Locations, and Sr Isotopic Compositions and Concentrations

Sample	Date	Type[a]	Latitude (°N)	Longitude (°W)	Downstream distance (km)	$^{87}Sr/^{86}Sr$	[Sr] (ppb)
Neuse River Basin							
WEH-02F	9-Apr-17	Water (F)	36.205	79.190	0	0.704456	52
WEH-02 U	9-Apr-17	Water (U)	36.205	79.190	0	0.704463	53
EW-WEH	1-Jun-16	Water (F)	36.205	79.190	0.25	0.705269	69
EW-EEH	1-Jun-16	Water (F)	36.191	79.150	4.08	0.704975	59
EEH-02F	9-Apr-17	Water (F)	36.191	79.150	4.08	0.705091	48
EEH-02 U	9-Apr-17	Water (U)	36.191	79.150	4.08	0.705094	49
BQ-07	17-Feb-17	Water (F)	36.106	79.005	20.2	0.705256	68
EC02	17-Jun-16	Water (F)	36.056	78.978	25.5	0.705371	78
EC03	17-Jun-16	Water (F)	36.056	78.978	25.5	0.705375	77
EC04	17-Jun-16	Water (F)	36.056	78.978	25.5	0.705365	77
EC05F	9-Apr-17	Water (F)	36.056	78.978	25.5	0.705370	50
EC05U	9-Apr-17	Water (U)	36.056	78.978	25.5	0.705403	52
EW-WFL	1-Jun-16	Water (F)	36.088	78.823	35.5	0.706099	60
EW-WFL02	7-Jul-16	Water (F)	36.088	78.824	35.5	0.706270	39
WFL-03F	9-Apr-17	Water (F)	36.088	78.824	35.7	0.705647	52
WFL-03 U	9-Apr-17	Water (U)	36.088	78.824	35.7	0.705642	51
EW-CRB	7-Jul-16	Water (F)	36.050	78.751	43.4	0.706837	45
EW-LRB	7-Jul-16	Water (F)	36.053	78.722	45.6	0.707489	50
EW-MFL	1-Jun-16	Water (F)	36.056	78.676	49.3	0.710311	39
EW-MFL02	7-Jul-16	Water (F)	36.056	78.676	49.3	0.709950	35
MFL-03F	9-Apr-17	Water (F)	36.056	78.676	49.0	0.709223	35
MFL-03 U	9-Apr-17	Water (U)	36.056	78.676	49.0	0.709221	36
EW-NLB	7-Jul-16	Water (F)	36.002	78.665	52.6	0.707518	50
EFL-03F	9-Apr-17	Water (F)	35.940	78.580	62.5	0.707958	
EFL-03 U	9-Apr-17	Water (U)	35.940	78.580	62.5	0.707963	41
EW-EFL	1-Jun-16	Water (F)	35.940	78.580	62.6	0.707895	44
EW-EFL02	7-Jul-16	Water (F)	35.940	78.580	62.6	0.707923	44
EW-RGS	1-Jun-16	Water (F)	35.646	78.406	94.4	0.708306	55
EW-LRGS	1-Jun-16	Water (F)	35.589	78.188	114	0.708628	56
EW-LRO	1-Jun-16	Water (F)	35.371	78.018	141	0.708597	48
EW-LRNM	1-Jun-16	Water (F)	35.350	78.032	142	0.708422	47
EW-PL	1-Jun-16	Water (F)	35.314	77.945	150	0.708640	48
SS-81215	12-Aug-15	Water (F)	35.229	77.846	163	0.708736	73
SS-91315	13-Sep-15	Water (F)	35.229	77.846	163	0.708868	66
SS-101515	15-Oct-15	Water (F)	35.229	77.846	163	0.709380	58
SS-112215	22-Nov-15	Water (F)	35.229	77.846	163	0.708956	27
SS-1916	9-Jan-16	Water (F)	35.229	77.846	163	0.708726	39
EW-SS	26-May-16	Water (F)	35.229	77.846	163	0.708801	49
G-81215	12-Aug-15	Water (F)	35.370	77.446	185	0.710750	55
EW-GFT2	26-May-16	Water (F)	35.370	77.446	185	0.711562	32
EW-SCOM	26-May-16	Water (F)	35.231	77.114	219	0.709887	62
EW-GC	26-May-16	Water (F)	35.179	77.132	220	0.708146	700
EW-SCM	26-May-16	Water (F)	35.141	77.062	228	0.709301	54
EW-TR	26-May-16	Water (F)	35.099	77.048	231	0.709114	180
NB-81215	12-Aug-15	Water (F)	35.104	77.035	232	0.709174	810
NB-91315	13-Sep-15	Water (F)	35.104	77.035	232	0.709173	870
NB-101515	15-Oct-15	Water (F)	35.104	77.035	232	0.709198	290
NB-112215	22-Nov-15	Water (F)	35.104	77.035	232	0.709031	35
NB-1916	9-Jan-16	Water (F)	35.104	77.035	232	0.709198	60
EW-FR	26-May-16	Water (F)	35.067	76.970	239	0.709223	390
EW-FB	26-May-16	Water (F)	34.985	76.950	245	0.709222	760
FB-91315	13-Sep-15	Water (F)	34.985	76.950	245	0.709187	2,300
FB-101515	15-Oct-15	Water (F)	34.985	76.950	245	0.709227	400
FB-112215	22-Nov-15	Water (F)	34.985	76.950	245	0.709251	110
FB-1916	9-Jan-16	Water (F)	34.985	76.950	245	0.709232	100
CR110FB	9-Oct-15	Water (F)	34.984	76.948	246	0.709213	
PC-91315	13-Sep-15	Water (F)	34.936	76.841	257	0.709181	2700
PC-101515	15-Oct-15	Water (F)	34.936	76.841	257	0.709195	1,100
PC-101615	16-Oct-15	Water (F)	34.936	76.841	257	0.709191	1,000

Table 1
(continued)

Sample	Date	Type[a]	Latitude (°N)	Longitude (°W)	Downstream distance (km)	$^{87}Sr/^{86}Sr$	[Sr] (ppb)
O-81215	12-Aug-15	Water (F)	35.018	76.705	263	0.709191	3,600
O-101515	15-Oct-15	Water (F)	35.018	76.705	263	0.709211	1,700
O-112215	22-Nov-15	Water (F)	35.018	76.705	263	0.709202	1,200
O-1916	9-Jan-16	Water (F)	35.018	76.705	263	0.709203	950
BQ-01	17-Feb-17	Saprolite	36.106	79.011	19.7	0.719074	15,000
BQ-02	17-Feb-17	Granitic soft rock	36.106	79.011	19.7	0.707261	2,300,000
BQ-03A	17-Feb-17	Granitic soft rock	36.106	79.012	19.7	0.706323	
BQ-04	17-Feb-17	Saprolite	36.106	79.012	19.7	0.714365	34,000
BQ-05	17-Feb-17	Granitic rock	36.105	79.012	19.7	0.706620	600,000
BQ-06	17-Feb-17	Dioritic rock	36.105	79.012	19.7	0.705233	
SR-03	3-Feb-17	Diabase rock	36.107	78.761	38.9	0.704750	
SR-05	3-Feb-17	Diabase rock	36.107	78.761	39.0	0.704711	
SR-01	3-Feb-17	Diabase rock	36.107	78.761	40.3	0.704845	85,000
WS-S01	16-Dec-16	Weathered granite	35.813	78.498	76.3	0.710392	
WS-S02	16-Dec-16	Weathered granite	35.813	78.498	76.3	0.713140	
WS-I01	16-Dec-16	Granitic soft rock	35.809	78.498	76.5	0.715260	
WS-I02	16-Dec-16	Granitic soft rock	35.809	78.498	76.5	0.713644	
WS-B01	16-Dec-16	Granitic rock	35.808	78.496	76.8	0.709991	
WS-B02	16-Dec-16	Granitic rock	35.808	78.496	76.8	0.714740	
W-10	22-May-17	Groundwater	36.243	79.115	7.97	0.710005	31
W-04	22-May-17	Groundwater	36.116	79.041	16.9	0.705559	100
W-08	22-May-17	Groundwater	36.251	78.963	21.2	0.705751	50
W-09	22-May-17	Groundwater	36.158	78.959	21.7	0.704045	230
W-11	22-May-17	Groundwater	36.069	79.000	23.1	0.703835	100
W-01	22-May-17	Groundwater	36.068	78.996	23.4	0.704929	730
W-02	22-May-17	Groundwater	36.056	78.994	24.4	0.704218	120
W-03	22-May-17	Groundwater	36.025	79.010	25.9	0.705887	84
W-07	22-May-17	Groundwater	36.071	78.956	26.0	0.704537	100
W-06	22-May-17	Groundwater	36.096	78.930	26.6	0.704842	270
W-05	22-May-17	Groundwater	35.999	78.992	29.2	0.705739	140
W-12	22-May-17	Groundwater	35.994	78.986	30.0	0.706958	190
Cape Fear River Basin							
ACR15	16-Jun-17	Water (F)	35.996	79.951	0	0.705561	85
ACR14	16-Jun-17	Water (F)	35.751	79.732	33.5	0.705679	68
ACR13	16-Jun-17	Water (F)	35.641	79.620	49.4	0.705691	69
ACR16	16-Jun-17	Water (F)	36.128	79.406	51.2	0.705152	68
ACR17	16-Jun-17	Water (F)	36.091	79.370	53.4	0.706787	67
ACR12	16-Jun-17	Water (F)	35.544	79.587	59.9	0.705830	70
ACR11	16-Jun-17	Water (F)	35.458	79.382	71.1	0.706218	68
ACR18	16-Jun-17	Water (F)	35.772	79.144	90.7	0.705798	59
ACR10	16-Jun-17	Water (F)	35.550	79.025	97.2	0.706746	68
ACR09	16-Jun-17	Water (F)	35.398	78.774	125	0.706801	67
ACR08	16-Jun-17	Water (F)	35.047	78.859	144	0.707020	58
ACR07	16-Jun-17	Water (F)	34.997	78.851	149	0.707033	56
ACR06	16-Jun-17	Water (F)	34.834	78.824	165	0.707314	50
ACR05	16-Jun-17	Water (F)	34.626	78.575	197	0.707671	38
ACR03	16-Jun-17	Water (F)	34.403	78.293	232	0.707408	45
ACR02	16-Jun-17	Water (F)	34.235	77.952	262	0.709120	470
ACR01	16-Jun-17	Water (F)	34.049	77.920	279	0.709177	2,800

[a]Samples are designated as water (river or lake), groundwater, and rock. Water samples are further designated as filtered (F) and unfiltered (U). All groundwater samples were filtered. Rock samples indicate broad rock type and relative state of weathering

The results from the unweathered versus weathered samples from both the Bacon and Rolesville batholith quarries support the possibility that the extremely radiogenic saprolite from the Bacon quarry was not derived from weathering of the sampled plutonic bedrock. It seems unlikely that breakdown of primary igneous minerals would yield no measurable isotopic change until formation of saprolite. However, we do not have data to fully evaluate this possibility. Because we did not attempt to isolate a carbonate
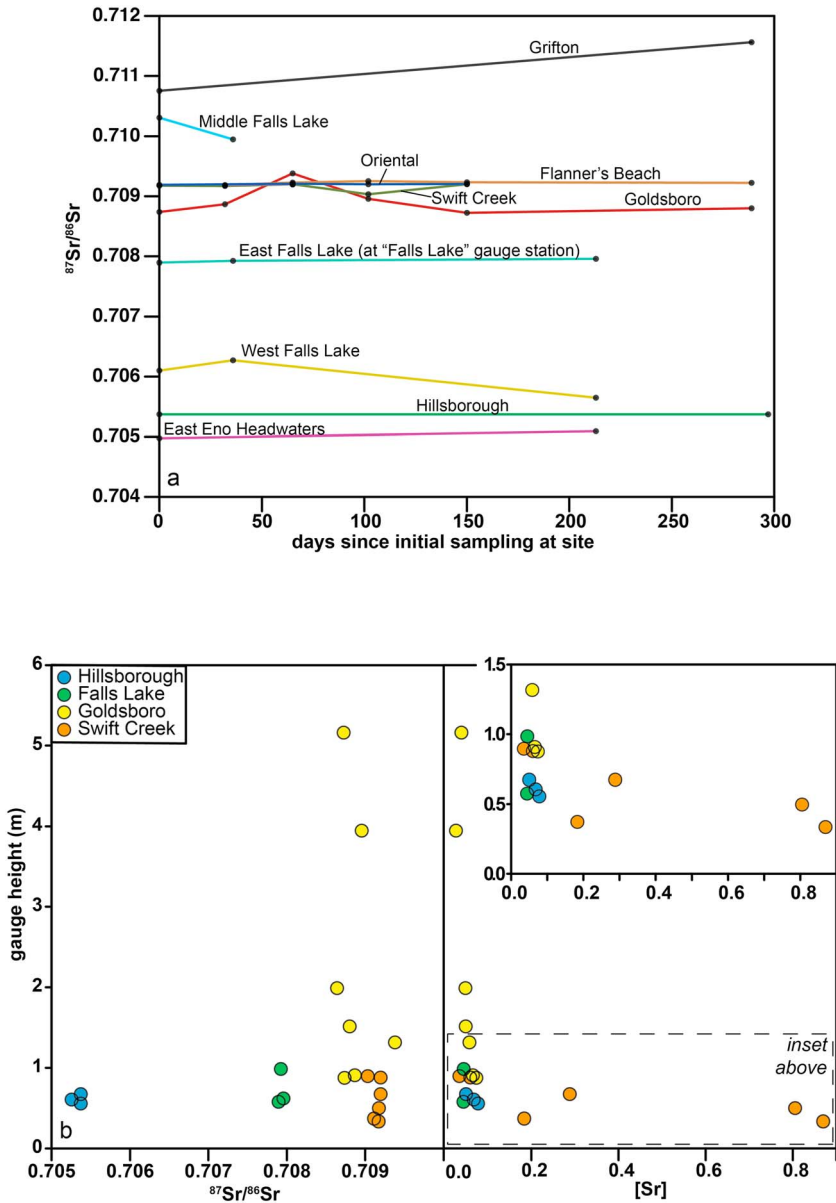
Figure 4. (a) Sr isotopic composition as a function of time for repeat samples at study sites along the Neuse River. The date of first sampling is variable between sites; thus, "day zero" is a different date for each sampling site (Table 1). Black dots indicate when samples were collected. Most sample sites have $^{87}Sr/^{86}Sr$ that is consistent over the duration of this study. Exceptions include the west and middle Falls Lake, Swift Creek, and Grifton sites. (b) Sr isotopic compositions and Sr concentrations against river gauge height of sample locations along the Neuse River (United States Geological Survey, 2017). Strontium isotopic compositions are consistent and independent of variation in gauge height. In contrast, Sr concentrations show some variation with gauge height, particularly for samples collected at the Swift Creek.

component in the saprolite, we cannot assess its impact on the measured isotopic ratio. If the saprolite at the Bacon quarry was not derived from the same rock as the unweathered and moderately weathered samples from that location, the data from all quarries seem to suggest that the impact of weathering on bulk rock isotopic compositions in the region is minimal. Therefore, we prefer the interpretation that published bedrock values are representative of the available bedrock Sr.

5.2. Groundwater

Groundwater samples collected in the headwaters of the Neuse River within the Carolina Slate Belt generally have low Sr isotopic ratios with a few high outliers (Figure 3b). Most measurements of groundwater
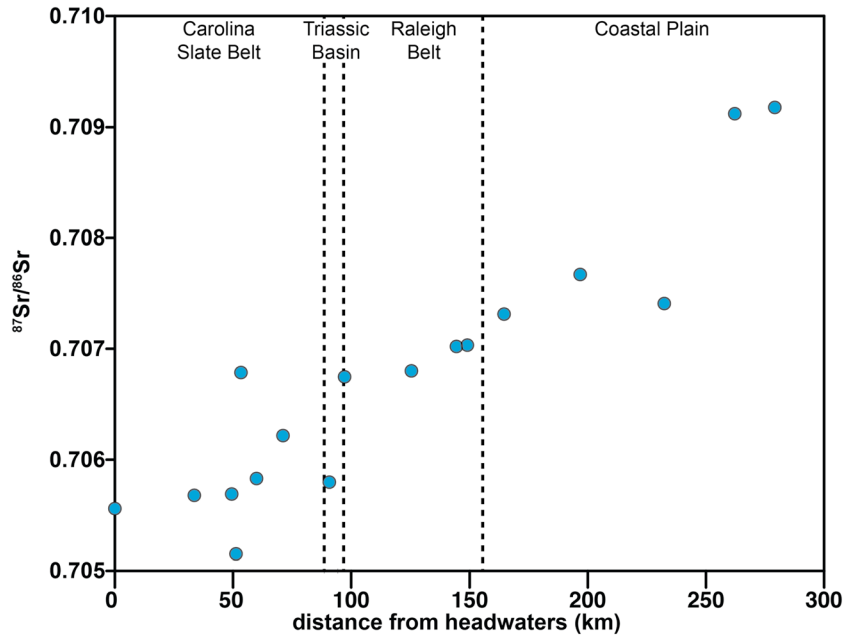
Figure 5. Sr isotopic composition of Cape Fear River water as a function of downstream distance. ^{87}Sr/^{86}Sr ratios begin low (0.705) in the headwaters and steadily rise to 0.7092 in the estuary. Whereas the Cape Fear does ultimately contribute ^{87}Sr/^{86}Sr that is isotopically similar to the modern ocean value (0.7092), it does not stabilize at this ratio as far inland as the Neuse River (cf. Figure 3b).
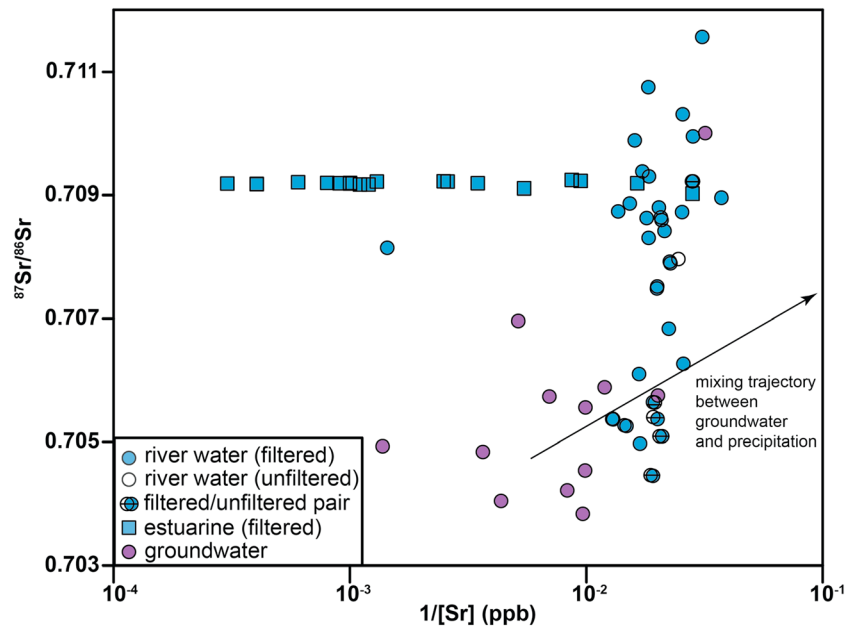

Figure 6. Sr isotopic compositions of Neuse River basin samples against 1/[Sr] (ppb), on a logarithmic scale. River water has consistently low Sr concentrations until it begins to mix with ocean water in the estuary. Note the significant increase in [Sr] (decrease in 1/[Sr]) at essentially constant ^{87}Sr/^{86}Sr in estuarine samples. Groundwater samples have high Sr concentrations relative to nonestuarine river waters; however, there is no apparent relationship between concentration and isotopic composition. A mixing trajectory is shown for average groundwater (this study; 0.7055 and 180 ppb) and average precipitation (Tanner, 2014; 0.7095 and 5 ppb). Mass balance estimates are difficult to make because of the variability of end member isotopic compositions and concentrations. Filtered and unfiltered pairs of samples were collected at the same sample sites at the same time.

^{87}Sr/^{86}Sr are between 0.7038 and 0.7059 ($n = 10$) with one sample yielding approximately 0.707 and another approximately 0.710. The low values suggest derivation of Sr from a source similar to the Triassic Basin diabase and/or the Precambrian diorite sampled in the Bacon Quarry, rather than the felsic metaigneous and metasedimentary rocks that dominate the surface exposures in the area sampled (Bradley et al., 2016). The groundwater samples in this study were all collected west of the Triassic Basin and are significantly less radiogenic than groundwater analyzed east of the basin in an area dominated by rocks similar to the Rolesville batholith (~0.707; Kiperwas, 2011). However, those groundwater values are also low in comparison to the dominant surficial rocks.

In the Triassic basin, the water table is low and difficult to access, and diabase dikes are targeted for well water drilling (Stoddard et al., 2016). Although none of the groundwater collected in this study is from the Triassic basin, diabase dikes are mapped throughout the Carolina Slate Belt (Bradley et al., 2016), and aeromagnetic data indicate that the dikes may be even more prevalent than outcrops suggest (Ragland et al., 1983). As in the rift basin, it seems possible that groundwater may preferentially flow near dikes throughout the Slate Belt as well. Boonstra and Boehmer (1986) suggest that dikes with contraction joints have high flow capacity and can form composite dike-aquifer systems. This may explain the apparent dominance of the Triassic rocks on groundwater Sr isotopic compositions despite their limited surface exposure in the area.

The low groundwater isotopic ratios in this study relative to those measured just to the east in the Slate Belt by Kiperwas (2011) suggest that the diabase dikes are the dominant bedrock influence on the isotopic composition of groundwater in the Neuse river headwaters. The increase in the ^{87}Sr/^{86}Sr of groundwater from west to east likely reflects the increase in ^{87}Sr/^{86}Sr reported for the bedrock into which the dikes intruded (Fullagar & Butler, 1979; this study). The measured Sr concentrations of diabase are relatively low (<90,000 ppb) relative to the granitic rocks ([Sr] > 230,000 ppb), but this could be compensated for by a strong correlation between diabase dikes and groundwater flow (Ragland et al., 1968; Stoddard et al., 2016; United States Geological Survey, 1984; Weigand & Ragland, 1970), and more significant weathering of the mafic dikes. Importantly, however, the hypothesized aquifer systems associated with the Triassic dikes have an influence on the groundwater isotopic composition disproportionate to their exposure. Thus, both structure and bedrock may have significant impact on the isotopic composition of the groundwater.

5.3. River Water

^{87}Sr/^{86}Sr ratios do not appear to be affected by filtration as conducted in this study, since the filtered and unfiltered samples have the same isotopic compositions within uncertainty. Moreover, the concentration of Sr in the unfiltered samples are not significantly higher than the filtered samples (Table 1). However, we made no attempt to dissolve suspended materials in the unfiltered samples. Because the unfiltered samples were acidified the same as filtered samples and redissolved in nitric acid in preparation for column chromatography, it is likely that some labile Sr could have been leached from suspended solids; however, the impact on the results is negligible. Consequently, we suggest that the bulk of the Sr analyzed is being carried in the dissolved load.

It was hypothesized that the ^{87}Sr/^{86}Sr ratios of the river water would roughly correlate to the age and Rb/Sr ratio of the underlying bedrock and thus begin relatively high in the Carolina Slate belt (Cambrian–Late Proterozoic), decrease in the Triassic basin, and stabilize toward oceanic ^{87}Sr/^{86}Sr ratios (0.7092) in the coastal plain (Cretaceous–Quaternary)—similar to results on larger rivers obtained in earlier studies (e.g., Palmer & Edmond, 1989). This hypothesis is not supported by the data collected from the headwaters through the Triassic basin (Figure 3b). Initial surface flow of the Neuse River at the headwaters appears to reflect the low ^{87}Sr/^{86}Sr of the groundwater—consistent with the headwaters of the rivers being sourced by groundwater flow. Samples collected from Falls Lake, which approximately spans the width of the Triassic basin, have higher ^{87}Sr/^{86}Sr ratios. Although there is a wide range of ^{87}Sr/^{86}Sr ratios found in the lake, they are overall higher than would be expected for the Triassic basin. The variation within the lake is worth further research, though it likely stems from variation within the numerous tributaries that feed into the lake and the poor mixing of lakes in general (Boehrer & Schultze, 2008).

After the Neuse River exits the Triassic Basin, the increase in ^{87}Sr/^{86}Sr continues. Our results are consistent with those reported by Kiperwas (2011) for samples collected in the Raleigh Belt (Figure 3b). The isotopic composition of the river water is more radiogenic than measured groundwater which Kiperwas (2011)

attributed to mixing with precipitation. However, mixing models between groundwater and precipitation can only produce some of the increase in the isotopic composition because the concentrations of Sr in the precipitation are generally too low to exert significant leverage on the isotopic composition (Figure 6). Within the coastal plain, the hypothesis that surface water should reflect surface geology is supported. In these samples, the surface waters match reported isotopic compositions for groundwater (0.7081–0.7092; Woods et al., 2000). This likely reflects the high solubility of carbonate minerals in the coastal plain sediments (Jacobson & Blum, 2000; Woods et al., 2000). In estuarine samples, the high concentration of Sr in seawater (~8 ppm) relative to the river water (<1 ppm) results in a rapid rise in [Sr] at essentially constant $^{87}Sr/^{86}Sr$, reflecting the tidal influence.

There is a single outlier to the simple trend in the coastal plain samples from the Neuse River at Grifton, North Carolina (185 km from the headwaters, $^{87}Sr/^{86}Sr$ 0.711562). This sample was collected from Contentea Creek, a tributary to the Neuse, and further study is needed to better understand the sources of Sr to this creek. It is possible that water in the creek is derived from deep groundwater that may have interacted with rocks similar to the Rolesville batholith or that anthropogenic sources (such as agricultural runoff) may contribute to this elevated $^{87}Sr/^{86}Sr$ ratio. It is unlikely that the origin of high ratios at Grifton is due to precipitation because the $^{87}Sr/^{86}Sr$ is higher than measured precipitation, [Sr] in the precipitation is low (Surge et al., 2016; Tanner, 2014), and it is unreasonable to suspect that only one site would be so profoundly impacted by precipitation. Regardless, this tributary has minimal impact on the Neuse River Sr isotopic composition as the isotopic composition downstream of Grifton is essentially the same as the nearest upstream samples. Ultimately, the Neuse River is contributing water with a Sr isotopic composition of approximately 0.7092 to the Atlantic Ocean.

The Cape Fear basin shows similar trends to the Neuse in terms of $^{87}Sr/^{86}Sr$ variation from the headwaters to the estuary (Figure 5). The two headwaters to the Cape Fear River sampled in this study have $^{87}Sr/^{86}Sr$ ratios of approximately 0.7052 and 0.7056. Whereas these are slightly higher than that of the Neuse ($^{87}Sr/^{86}Sr$ from 0.704456 to 0.705375, $n = 8$), they are lower than predicted on the basis of surface bedrock geology. This indicates that the results from the Neuse are not anomalous, and it is likely that the source of Sr to the headwaters of the Neuse is also the source to the Cape Fear River. The two rivers differ in isotopic composition in the coastal plain. Although the Neuse River's Sr isotopic composition quickly stabilizes toward 0.7092 in the coastal plain, the Cape Fear River steadily rises along the coastal plain and only reaches approximately 0.7092 near the estuary.

5.4. Temporal Variations in River Water

The temporal data collected show that at most locations, there is little change in the Sr isotopic composition of river water over the duration of this study. Samples that do show change include the west and middle Falls Lake, Goldsboro, and Grifton (Figure 4a). A variety of factors may influence the variability of Sr isotopic ratios at a single site; however, stream flow does not appear to be one of these factors (Figure 4b). Swift Creek is the only site that shows a significant correlation between [Sr] and gauge height (the higher the flow, the lower the Sr concentration of the water). However, there is no obvious correlation with $^{87}Sr/^{86}Sr$ and gauge height (Figure 4b and Table 1). As for the wide variation in the Sr isotopic composition of Falls Lake in general, the variations at a single site through time likely reflects poor mixing of the lake water (Boehrer & Schultze, 2008). Variability may reflect changes in individual stream influx, wind direction, and upwelling/overturn of the lake. The Goldsboro and Grifton sample sites are more difficult to explain. Goldsboro was sampled six times over the course of the study, including significant variation in stream gauge height (Figure 4b). It is likely that understanding the outlier isotopic composition of the water at Grifton may help explain the origin of the variation here and elsewhere. More detailed investigation is necessary to evaluate possibilities for temporal variations at these two sites, though some plausible factors are surface runoff and storm flow (Kirchner, 2003). Overall, however, the pattern on the Neuse is one of relatively constant isotopic composition at a single site through time.

5.5. Origin of the Sr Isotopic Variation

The results of this study indicate that there are five components influencing the Sr isoscape of the Neuse River: precipitation, granitic rock in the Carolina Slate and Raleigh Belts, diabase dikes in the Triassic basin and the older terranes, sediment from the coastal plain, and seawater. Kiperwas (2011) implicated

precipitation in drawing the isotopic compositions of Neuse River water up from measured groundwater values, which seems likely. However, the value used in that study (>0.710; Rose & Fullagar, 2005) from the Piedmont Province of Georgia is significantly more radiogenic than any of the measured values for more local precipitation (0.708–0.709; Surge et al., 2016; Tanner, 2014). That, and the low [Sr] of the precipitation relative to the river waters, suggests that the impact of precipitation is minimal. However, it likely accounts for the low [Sr] in the surface water relative to the groundwater as well as some of the elevation of the Sr isotopic composition above groundwater values (Figure 6). Because the variation in ^{87}Sr/^{86}Sr is similar between the Neuse and Cape Fear rivers and is easily explained by the geology, it seems unlikely that anthropogenic sources are a significant influence on the isotopic composition (except perhaps at the Grifton site, as noted above).

The data suggest that, at the headwaters of both the Neuse and Cape Fear Rivers, groundwater with a composition similar to that of the diabase dikes, their host granitic rocks, and precipitation begins to mix with low concentrations of dissolved granitic material with high ^{87}Sr/^{86}Sr ratios (Figure 6). Once water reaches the coastal plain, it begins to mix with water that has higher Sr concentrations and isotopic compositions similar to that reported for local groundwater (Woods et al., 2000), resulting in ^{87}Sr/^{86}Sr ratios which match coastal plain sediments (0.7092; Figure 3b). Woods et al. (2000) attributed the isotopic compositions of the groundwater to dissolution of aquifer minerals. Most likely, easily soluble carbonate minerals in the coastal plain account for both the rapid rise in [Sr] and buffering of the isotopic compositions near-seawater values. The observation that the Neuse River rapidly rises to near seawater values after entering coastal plain rocks whereas the Cape Fear River slowly rises to these values may indicate that the Cape Fear River has a lower groundwater gain than the Neuse River. Finally, at the estuary, freshwater mixes with salt water causing a spike in [Sr] concentration in both rivers but has little influence on isotopic composition (Figure 6).

There are several important implications of these results. The data from the headwaters emphasize that surficial geology may sometimes be a poor indicator of groundwater isotopic compositions. In the Neuse and Cape Fear River basins, we propose that Triassic mafic dikes have a disproportionate influence (relative to their exposure area) on the basin isoscape because groundwater flow is preferentially focused by the dikes and because, even though the dikes have lower [Sr] than surrounding host rocks, mafic dikes are more easily weathered than granitic rocks. Similarly, the carbonate rocks of the coastal plain have a stronger influence on the chemistry of the water delivered to the ocean than the igneous and metamorphic rocks upstream because they are significantly more soluble. Thus, in fluvial systems where there are young coastal plain sediments and sedimentary rocks that stretch sufficiently inland, the coastal plain may serve as a buffer for oceanic Sr isotopic compositions, even upstream of direct seawater influence in the estuary, by overwhelming the Sr isotopic signature from other geologic units with less labile Sr.

Large-scale efforts to characterize the global fluvial input of Sr to the ocean have focused on the isotopic composition of water at estuaries and assumed that the dominant surficial bedrock will control the isotopic composition of river water (Allegre et al., 2010; Palmer & Edmond, 1992). Brennan et al. (2016) suggested that fluvial isotopic compositions should be relatively homogenous within geologic units and heterogenous near geologic boundaries. The results of our study support the later, however, our results also show heterogeneity within geologic units (e.g., the Carolina Slate Belt and Triassic Basin; Figure 3b). We propose that this in-unit heterogeneity originates from variations in the weatherability of the rocks and structurally controlled groundwater flow, and that precisely predicting and modeling fluvial Sr compositions requires accounting for these factors.

Our data suggest that the discrepancy between quantitative estimates of Sr fluxes to the ocean and the modern Sr isotopic composition of seawater (Palmer & Edmond, 1989) may be partially explained by basins where mafic rocks exert an unanticipated influence. This, in addition to the impacts of island arc weathering (Allegre et al., 2010), reactivity of suspended volcanic sediment (Jones et al., 2014), and the proportion of evolved:unevolved rocks in the continental crust (Bataille et al., 2017), could result in incorrect global estimates of the Sr isotopic composition of fluvial input to the ocean.

6. Conclusions

The primary source of Sr to the headwaters of the Neuse and Cape Fear Rivers is not the dominant surficial bedrock and may instead be diabase dikes below the surface at the water table. Structurally-controlled

groundwater flow and preferential weathering of mafic rocks are, therefore, important components in controlling the basin isoscape. Thus, in some cases, the ^{87}Sr/^{86}Sr ratio of river water cannot be consistently approximated by the age and rock type of dominant surficial bedrock. Downstream, the coastal plain serves as a buffer for the Sr isotopic composition of the water ultimately delivered to the ocean in the Neuse and Cape Fear river basins. Consequently, the contributions of both rivers to seawater are poor indicators of the upstream surficial geology. Rather, the ultimate ^{87}Sr/^{86}Sr input from both the Neuse and Cape Fear rivers to the Atlantic Ocean is similar to near-modern oceanic Sr at ^{87}Sr/^{86}Sr 0.7092. The discrepancy between the previously estimated flux of Sr into the oceans and the Sr isotopic composition of the modern ocean may be, in part, a result of mischaracterizing the isotopic composition of the fluvial flux by assuming that dominant surficial bedrock and estuarine output are representative of a basin's Sr isotopic composition.

References

Allegre, C. J., Louvat, P., Gaillardet, J., Maynadier, L., Rad, S., & Capmas, F. (2010). The fundamental role of island arc weathering in the oceanic Sr isotope budget. *Earth and Planetary Science Letters*, *292*(1–2), 51–56. https://doi.org/10.1016/j.epsl.2010.01.019

Basu, A. R., Jacobsen, S. B., Poreda, R. J., Dowling, C. B., & Aggarwal, P. K. (2001). Large groundwater strontium flux to the oceans from the Bengal Basin and the marine Sr isotopic record. *Science*, *293*(5534), 1470–1473. https://doi.org/10.1126/science.1060524

Bataille, C. P., & Bowen, G. J. (2012). Mapping ^{87}Sr/^{86}Sr variations in bedrock and water for large scale provenance studies. *Chemical Geology*, *304-305*, 39–52. https://doi.org/10.1016/j.chemgeo.2012.01.028

Bataille, C. P., Brennan, S. R., Hartmann, J., Moosdorf, N., Wooller, M. J., & Bowen, G. J. (2014). A geostatistical framework for predicting variations in strontium concentrations and isotope ratios in Alaskan rivers. *Chemical Geology*, *389*, 1–15. https://doi.org/10.1016/j.chemgeo.2014.08.030

Bataille, C. P., Willis, A., Yang, X., & Liu, X.-M. (2017). Continental igneous rock composition: A major control of past global chemical weathering. *Science Advances*, *3*(3), e1602183. https://doi.org/10.1126/sciadv.1602183

Blum, J. D., & Erel, Y. (1997). Rb-Sr isotope systematics of a granitic soil chronosequence: The importance of biotite weathering. *Geochimica et Cosmochimica Acta*, *61*(15), 3193–3204. https://doi.org/10.1016/S0016-7037(97)00148-8

Blum, J. D., Erel, Y., & Brown, K. (1993). ^{87}Sr/^{86}Sr ratios of Sierra Nevada stream waters: Implications for relative mineral weathering rates. *Geochimica et Cosmochimica Acta*, *57*(21–22), 5019–5025. https://doi.org/10.1016/S0016-7037(05)80014-6

Boehrer, B., & Schultze, M. (2008). Stratification of lakes. *Reviews of Geophysics*, *46*, RG2005. https://doi.org/10.1029/2006RG000210

Boonstra, J., & Boehmer, W. (1986). Analysis of data from aquifer and well test in intrusive dikes. *Journal of Hydrology*, *88*(3–4), 301–317. https://doi.org/10.1016/0022-1694(86)90096-X

Bradley, P. J., Hanna, H. D., Gay, N. K., Stoddard, E. F., Bechtel, R., Phillips, C. M., & Fuemmeler, S. J. (2016). *Geologic map of Orange County,* North Carolina (1:50,000). Raleigh, NC: North Carolina Geological Survey.

Brantley, S. L., Chesley, J. T., & Stillings, L. L. (1998). Isotopic ratios and release rates of strontium measured from weathering feldspars. *Geochimica et Cosmochimica Acta*, *62*(9), 1493–1500. https://doi.org/10.1016/S0016-7037(98)00082-9

Brennan, S. R., Torgersen, C. E., Hollenbeck, J. P., Fernandez, D. P., Jensen, C. K., & Schindler, D. E. (2016). Dendritic network models: Improving isoscapes and quantifying influence of landscape and in-stream processes on strontium isotopes in rivers. *Geophysical Research Letters.*, *43*, 5043–5051. https://doi.org/10.1002/2016GL068904

Brown, P. M., Parker, J. M., & The State Geological Map Association (1985). *Geologic map of North Carolina (1:500,000)*. Raleigh, NC: North Carolina Geological Survey.

Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., & Otto, J. B. (1982). Variation of seawater ^{87}Sr/^{86}Sr throughout Phanerozoic time*Geology*, *10*(10), 516–519. https://doi.org/10.1130/0091-7613(1982)10<516:VOSSTP>2.0.CO;2

Christian, L. N., Banner, J. L., & Mack, L. E. (2011). Sr isotopes as tracers of anthropogenic influences on stream water in the Austin, Texas, area. *Chemical Geology*, *282*(3–4), 84–97. https://doi.org/10.1016/j.chemgeo.2011.01.011

Clow, D. W., Mast, M. A., Bullen, T. D., & Turk, J. T. (1997). Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado. *Water Resources Research*, *33*(6), 1335–1351. https://doi.org/10.1029/97WR00856

Coler, D. G., Samson, S. D., & Speer, J. A. (1997). Nd and Sr isotopic constraints on the source of Alleghanian granites in the Raleigh metamorphic belt and Eastern slate belt, southern Appalachians, U.S.A. *Chemical Geology*, *134*(4), 257–275. https://doi.org/10.1016/S0009-2541(96)00063-0

Crocket, K. C., Vance, D., Foster, G. L., Richards, D. A., & Tranter, M. (2012). Continental weathering fluxes during the last glacial/interglacial cycle: Insights from the marine sedimentary Pb isotope record at Orphan Knoll, NW Atlantic. *Quaternary Science Reviews*, *38*, 89–99. https://doi.org/10.1016/j.quascirev.2012.02.004

Fullagar, P. D., & Butler, J. R. (1979). 325 to 265 M.Y.-old granitic plutons in the Piedmont of the southeastern Appalachians. *American Journal of Science*, *279*(2), 161–185. https://doi.org/10.2475/ajs.279.2.161

Harned, D., & Meyer, D. (1983). Water quality of North Carolina streams, in US Geological Survey Water-Supply Paper, W-2185-E, E1-E71.

Horton, J. W., Drake, A. A. J., & Rankin, D. W. (1989). Tectonostratigraphic terranes and their Paleozoic boundaries in the Central and Southern Appalachians. *Special Paper – Geological Society of America*, *230*, 213–246. https://doi.org/10.1130/SPE230-p213

Jacobson, A. D., & Blum, J. D. (2000). Ca/Sr and ^{87}Sr/^{86}Sr geochemistry of disseminated calcite in Himalayan silicate rocks from Nanga Parbat: Influence on river-water chemistry. *Geology*, *28*(5), 463–466. https://doi.org/10.1130/0091-7613(2000)28<463:SASGOD>2.0.CO;2

Jones, M. T., Gislason, S. R., Burton, K. W., Reaves, C. R., Mavromatis, V., Pogge von Strandmann, P. A. E., & Oelkers, E. H. (2014). Quantifying the impact of riverine particulate dissolution in seawater on ocean chemistry. *Earth and Planetary Science Letters*, *395*, 91–100. https://doi.org/10.1016/j.epsl.2014.03.039

Kiperwas, H.R. (2011). Radium isotopes as tracers of groundwater-surface water interactions in inland environments (Ph.D. Dissertation). Retrieved from Duke University Libraries. (https://dukespace.lib.duke.edu/dspace/handle/10161/4971). Durham, NC: Duke University.

Kirchner, J. W. (2003). A double paradox in catchment hydrology and geochemistry. *Hydrological Processes*, *17*(4), 871–874. https://doi.org/10.1002/hyp.5108

Land, M., Ingri, J., Andersson, P. S., & Ohlander, B. (2000). Ba/Sr, Ca/Sr and ^{87}Sr/^{86}Sr ratios in soil water and groundwater: Implications for relative contributions to stream water discharge. *Applied Geochemistry*, *15*(3), 311–325. https://doi.org/10.1016/S0883-2927(99)00054-2

Lundblad, S. (1994). *Evolution of small carbonate platforms in the Umbria-Marche Apennines, Italy (Doctoral Dissertation)*. Chapel Hill, NC: University of North Carolina.

McArthur, J. M., Howarth, R. J., & Bailey, T. R. (2001). Strontium isotope stratigraphy: LOWESS version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *Journal of Geology*, *109*(2), 155–170. https://doi.org/10.1086/319243

North Carolina Department of Environment and Natural Resources (NCDENR): Division of Water Quality (2009). Cape Fear River Basin Basinwide Assessment Report Whole Effluent Toxicity Program 2004–2008

Palmer, M. R., & Edmond, J. M. (1989). The strontium isotope budget of the modern ocean. *Earth Planetary Science Letters*, *92*(1), 11–26. https://doi.org/10.1016/0012-821X(89)90017-4

Palmer, M. R., & Edmond, J. M. (1992). Controls over the strontium isotope composition of river water. *Geochimica et Cosmochimica Acta*, *56*(5), 2099–2111. https://doi.org/10.1016/0016-7037(92)90332-D

Pett-Ridge, J. C., Derry, L. A., & Kurtz, A. C. (2009). Sr isotopes as a tracer of weathering processes and dust inputs in a tropical granitoid watershed, Luquillo Mountains, Puerto Rico. *Geochimica et Cosmochimica Acta*, *73*(1), 25–43. https://doi.org/10.1016/j.gca.2008.09.032

Ragland, P. C., Hatcher, R. D., & Whittington, D. (1983). Juxtaposed Mesozoic diabase dike sets from the Carolinas: A preliminary assessment. *Geology*, *11*(7), 394–399. https://doi.org/10.1130/0091-7613(1983)11<394:JMDDSF>2.0.CO;2

Ragland, P. C., Rogers, J. J. W., & Justus, P. S. (1968). Origin and differentiation of Triassic dolerite magmas, North Carolina, U.S.A. *Contributions to Mineralogy and Petrology*, *20*(1), 57–80. https://doi.org/10.1007/BF00371066

Rose, S., & Fullagar, P. D. (2005). Strontium isotope systematics of base flow in Piedmont Province watersheds, Georgia (USA). *Applied Geochemistry*, *20*(8), 1571–1586. https://doi.org/10.1016/j.apgeochem.2005.04.015

Stewart, B. W., Capo, R. C., & Chadwick, O. A. (2001). Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils. *Geochimica et Cosmochica Acta*, *65*(7), 1087–1099. https://doi.org/10.1016/S0016-7037(00)00614-1

Stewart, K. G., & Roberson, M. R. (2007). *Exploring the geology of Carolinas: A field guide to favorite places from Chimney Rock to Charleston*. Chapel Hill, NC: University of North Carolina Press.

Stoddard, E. F., Clark, T. W., Kane, E. O., & Bolich, R. E. (2016). The relationship between groundwater availability and diabase dikes in the Deep River Triassic basin, North Carolina. *Geological Society of America Abstracts with Programs*, *48*(3), 7–7. https://doi.org/10.1130/abs/2016SE-273428

Surge, D., Schmidt, K. R., Moore, C., Coleman, D. S., & Mills, R. (2016). Tracing moisture sources of the extreme storm event impacting the Carolinas in October, 2015 using O, H, and Sr isotope ratios. *Geological Society of America Abstracts with Programs*, *48*(7), 116–118.

Tanner, M. (2014). *The Sr budget in the Croatan National Forest (BA Thesis)*. Retrieved from Carolina Digital Repository. Chapel Hill, NC: University of North Carolina. https://cdr.lib.unc.edu/record/uuid:f6eed215-33bd-4b6d-9e80-83b0e168599a

United States Geological Survey (1984). Dolerite, DNC-1|Certificate of Analysis|USGS Geochemical Reference Materials and Certificates, Available from: https://crustal.usgs.gov/geochemical_reference_standards/dolerite.html (Accessed 23 May 2017).

United States Geological Survey (2017). USGS Current Conditions for North Carolina, United States Geological Survey Available from: https://waterdata.usgs.gov/nc/nwis/current/?type=intro &group_key=NONE (Accessed 20 August 2017).

USDA, & NASS (2017). 2016 State Agriculture Overview for North Carolina, Available from: https://www.nass.usda.gov/Quick_Stats/Ag_Overview/stateOverview.php?state=NORTH CAROLINA (Accessed 28 July 2017).

Veizer, J. (1989). Strontium isotopes in seawater through time. *Annual Review of Earth and Planetary Sciences*, *17*(1), 141–167. https://doi.org/10.1146/annurev.ea.17.050189.001041

Veizer, J., & Compston, W. (1974). ^{87}Sr/^{86}Sr composition of seawater during the Phanerozoic. *Geochimica et Cosmochimica Acta*, *38*(9), 1461–1484. https://doi.org/10.1016/0016-7037(74)90099-4

Weigand, P. W., & Ragland, P. C. (1970). Geochemistry of Mesozoic dolerite dikes from eastern North America. *Contributions to Mineralogy and Petrology*, *29*(3), 195–214. https://doi.org/10.1007/BF00373305

West, J. B., Sobek, A., & Ehleringer, J. R. (2008). A simplified GIS approach to modeling global leaf water isoscapes. *PLoS ONE*, *3*(6), e2447. https://doi.org/10.1371/journal.pone.0002447

Woods, T. L., Beck, G., Tolen-Mehlhop, D. T., Troiano, R., & Whitley, J. K. (2000). *Geochemical tracers of groundwater movement between the Castle Hayne and associated coastal Plain aquifers, Water Resources Research Institute of the University of North Carolina, UNC-WRRI-2000-328*. Greenville, NC: East Carolina University.