ABSTRACT

E. Glynn Beck. **GROUNDWATER GEOCHEMISTRY OF THE CASTLE HAYNE AQUIFER SYSTEM IN THE NORTH CAROLINA COASTAL PLAIN** (Under the direction of Dr. Terri L. Woods) Department of Geology, October 1997.

Sixteen wells in southeastern North Carolina were sampled and analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Fe, Cl^{-}, SO_4^{2-}, SiO_2, HCO_3^{-}, O_2, NO_3^{-}, NO_2^{-}, PO_4^{3-}, NH_4^{+}, F^{-}, HS^{-}, TDS, pH, and Eh in order to characterize the major element chemistry of groundwater in the Castle Hayne Aquifer System. These data along with data collected by Sutton and Woods in the northern coastal plain were used to delineate regional chemical trends and to elucidate the major geochemical processes affecting water chemistry. Geochemical modeling programs, contour maps of ion concentrations, and Piper diagrams were used to analyze the chemical data. Waters from wells in the Lower Castle Hayne Aquifer and the northeasternmost wells in the Upper Castle Hayne Aquifer are all alkali and chloride rich and appear to be dominated by mixing with saline formation water. Waters from northwestern and southwestern wells of the Upper Castle Hayne Aquifer are calcium and bicarbonate rich due to dissolution of carbonate minerals in the aquifer. This water is also affected by dissolution of soil salts. Cation exchange appears to be a major geochemical process throughout the CHAS. Data from this investigation can be used by municipalities, fish farmers, and private citizens to better plan and develop water supplies in the North Carolina coastal plain.

GROUNDWATER GEOCHEMISTRY OF THE CASTLE HAYNE AQUIFER SYSTEM IN THE NORTH CAROLINA COASTAL PLAIN

A Thesis

Presented to

the Faculty of the Department of Geology

East Carolina University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Geology

by

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October 1997

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INTRODUCTION

Geologic and Hydrologic Framework

The Castle Hayne Aquifer System (CHAS) is the most extensively used aquifer in the North Carolina Coastal Plain (Figure 1), with a withdrawal rate of 146 million gallons per day (mgd) (Lyke and Treece, 1988). The aquifer ranges in thickness from zero at its feather edge in the west to over 1,100 feet in the east (Giese and others, 1991) where it extends beneath the Atlantic Ocean. It extends northeast about 160 miles from the middle of Brunswick County to the Virginia border, and underlies twenty-three coastal plain counties.

Gamus (1972) divided the CHAS into three hydrogeologic units (Figure 2); Upper Castle Hayne Aquifer (U-CHA), Lower Castle Hayne Aquifer (L-CHA), and Beaufort Aquifer. The Beaufort overlies strata of Late Cretaceous age. In the northern coastal plain (Figure 1) the U-CHA is predominantly moldic carbonates, mainly calcite and some dolomite, whereas the L-CHA is composed of calcareous sands interbedded with limestones (Gamus, 1972). Amsbaugh (1996) described the U-CHA in the central coastal plain as a quartz-rich (40-60%), fossiliferous biosparrudite, with minor glauconitic and phosphatic sand, while the L-CHA is composed of a quartz-rich (20-60%), fossiliferous biomicrudite, with minor glauconitic and phosphatic sand and lime mud. He used a well sorted, fine-grained, calcareous, muddy-limy quartz sand wedge as the boundary between the upper and lower CHAS units. The southern portion of the CHAS is characterized as a moldic and bryozoan-rich limestone, grading to calcareous fine-grained sandstone in the deeper subsurface (Lautier, 1994). The Beaufort Unit is mainly fine, glauconitic sand;

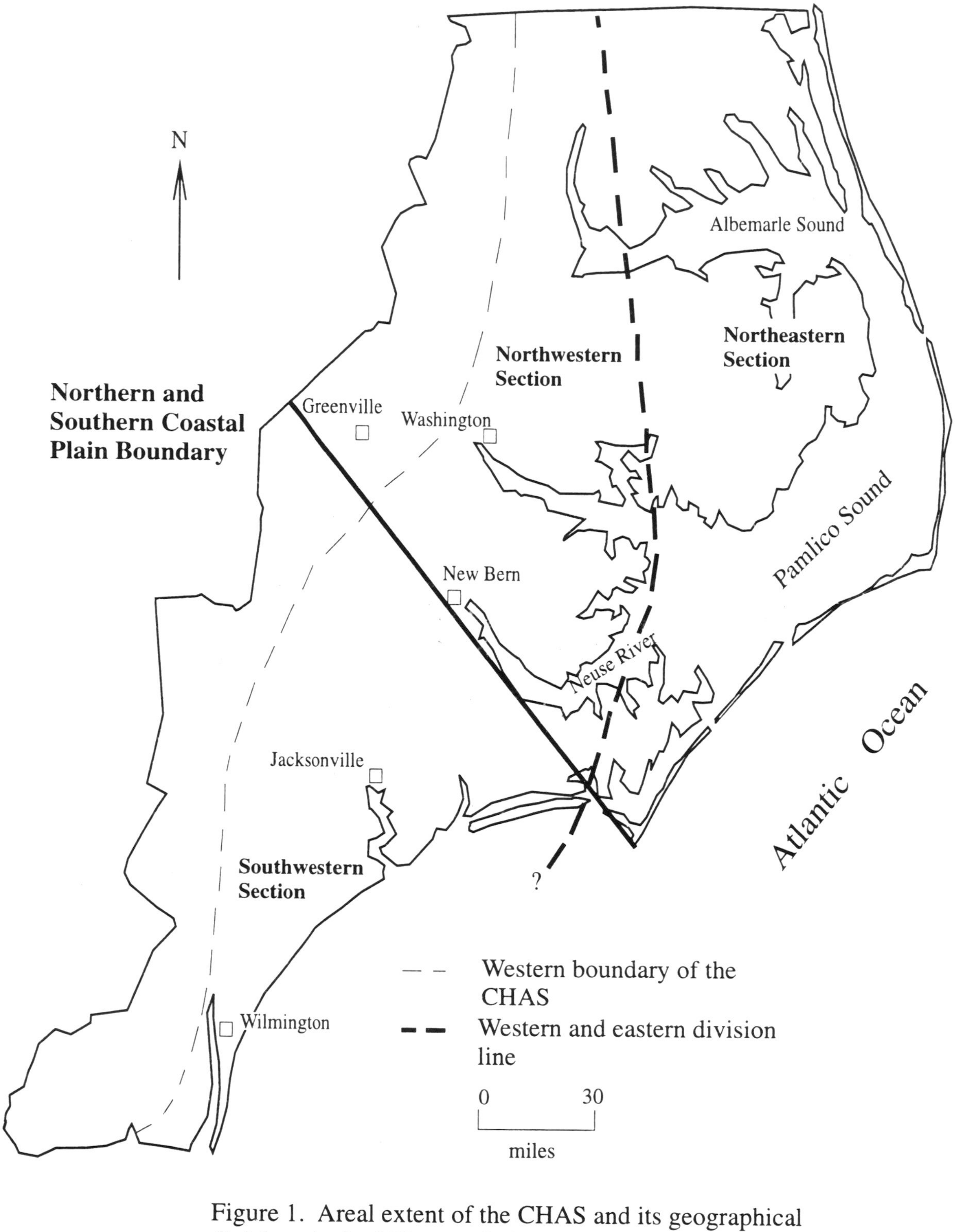


Figure 1. Areal extent of the CHAS and its geographical divisions in the NC coastal plain [modified from Giese and others (1991)].

System	Series	Stratigraphic Units	Hydrogeologic Units		Description
Quaternary	Recent Pleistocene	Undifferentiated Unnamed Unit	Surficial Unit		Sand, silt, shells, and some clay
Tertiary	Pliocene	Yorktown Formation	Yorktown Unit		Interbedded sand and clay with some shell beds
	Miocene	Pungo River Formation	Pungo River Unit		Phosphate & quartz sand, silt, clay, and limestones
	Oligocene	Belgrade Fm. River Bend Fm.	Castle Hayne Aquifer System	Upper Castle Hayne Unit	Permeable and porous shell limestone
	Eocene	Castle Hayne Limestone		Lower Castle Hayne Unit	Shell limestone interbedded with calcareous sands
	Paleocene	Beaufort Formation		Beaufort Unit	Fine glauconitic sand, silty and clayey in part
Cretaceous	Upper Cretaceous	Peedee Formation	Peedee Unit		Sand interbedded with clay and silt
		Black Creek Formation	Black Creek Unit		Laminated clay with interbedded sand
		Cape Fear Formation	Upper Cape Fear Unit		Alternating beds of sand and clay
			Lower Cape Fear Unit		Fine-grained sand
	Lower Cretaceous	Unnamed Formation	Lower Cretaceous Unit		Sand, shale, gravel and limestone
Basement					

Figure 2. Stratagraphic and hydrogeologic subdivisions of Coastal Plain Formations (Gamus, 1972, Lloyd and Daniel, 1988, and Winner and Coble, 1989).

Winner and Coble (1989) and Giese and others (1991) considered the Beaufort to be a separate aquifer. In the absence of data from wells penetrating the Beaufort Unit, it will be considered as part of the L-CHA. The CHAS contains a variety of minerals including; calcite, apatite, glaucony, zeolites, dolomite, quartz and chalcedony, pyrite, hematite, limonite, phosphates, and minor amounts of clay (Lyke and Treece, 1988; Moran, 1989; Otte, 1981).

The Pungo River, Yorktown, and Surficial Units overlie the U-CHA north and east of Jones and Craven Counties (Figure 3); to the south and west, the CHAS is overlain by the Surficial Aquifer (Figure 4) (Giese and others, 1991). Giese and others (1991) believe that the Surficial Aquifer affects recharge via leakage into the CHAS. About one inch of water or less per year moves down from the Surficial Aquifer into the deeper aquifers (Wilder and others, 1978). The Yorktown Formation is an aquifer itself but, together with the Pungo River Formation, it acts as an aquitard above the CHAS. The underlying Beaufort and Peedee Units may be sources of groundwater moving upward into the CHAS (Giese and others, 1991).

The CHAS has hydrologic conductivites from 15 to 300 ft/day and transmissivity ranges from 150 ft^2/day to 100,000 ft^2/day, depending on the local lithology (Giese and others, 1991). Amsbaugh (1996) determined that in Onslow County, the CHAS has a hydrologic conductivity of 32 to 309 ft/day and that the transmissivity ranges from 650 to 6,300 ft^2/day. In 1971 the North Carolina Board of Water and Air Resources, Texasgulf Corp., and the NC Phosphate Corporation published a report estimating that 89% of the water pumped from the CHAS is derived from the U-CHA (Joint Study, 1971).

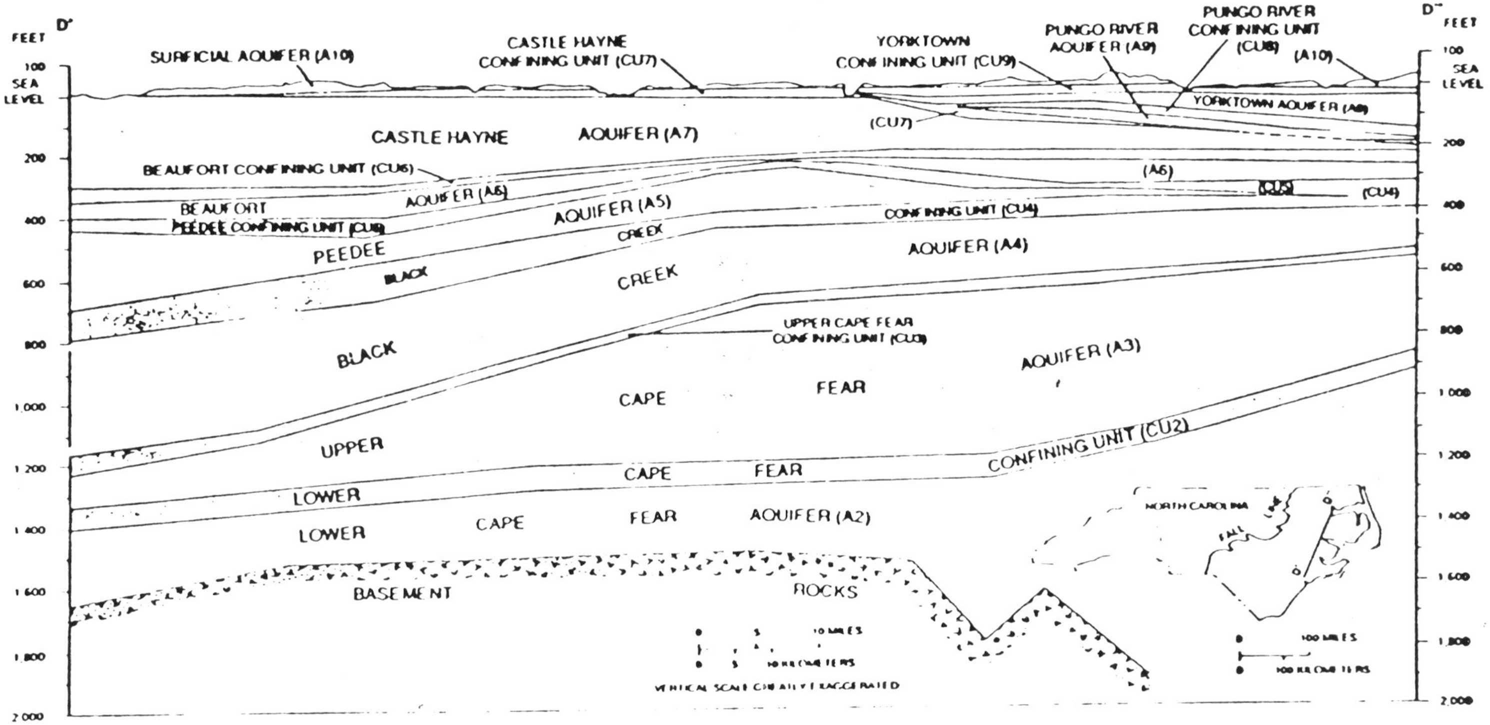


Figure 3. Hydrogeologic section D' - D'' from Onslow County to Chowan County [from Giese and others (1991)]

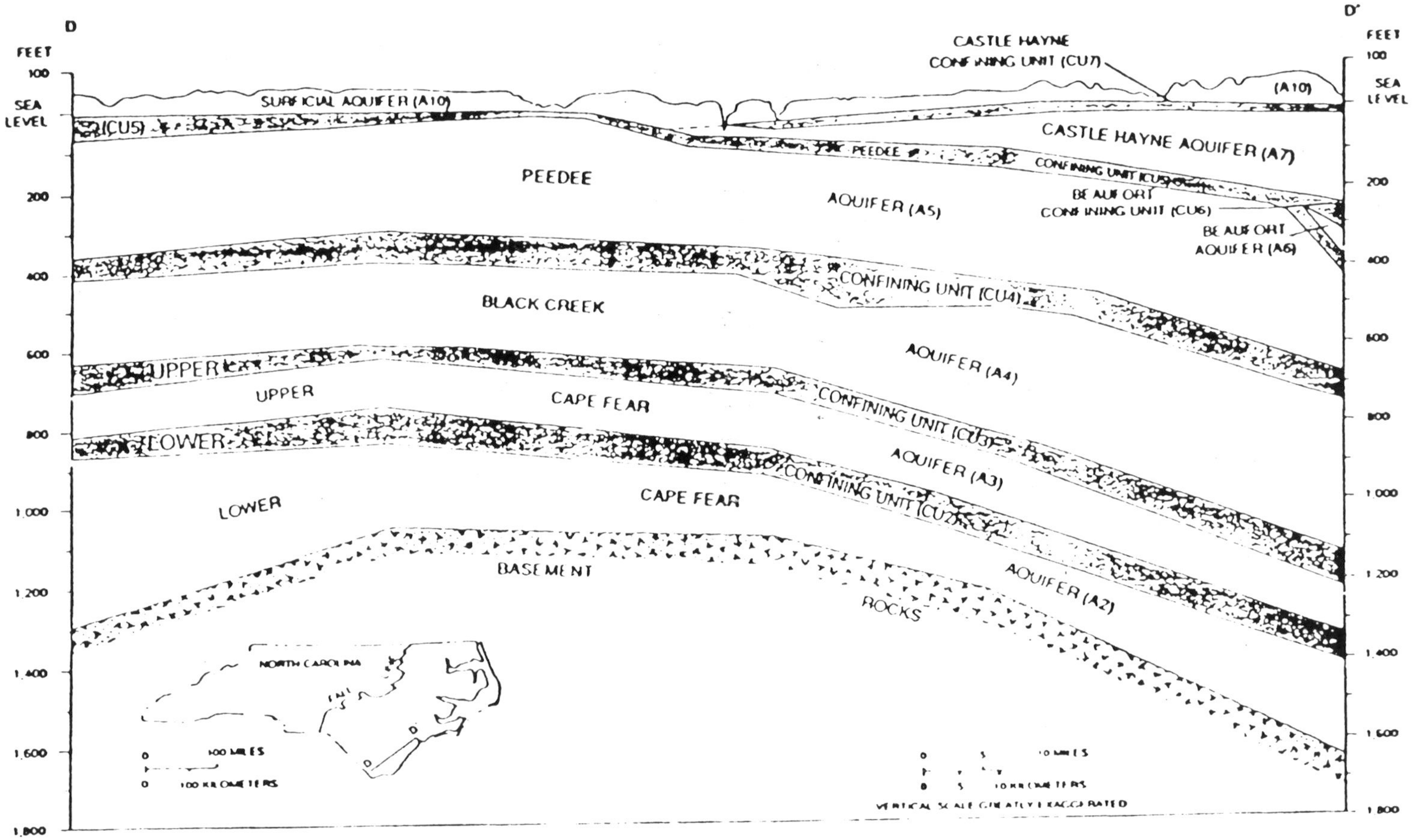


Figure 4 Hydrogeologic section D - D' from Brunswick County to Onslow County
[from Giese and others (1991)]

The CHAS is recharged, in the west, where the confining beds are thin, absent, or of higher hydraulic conductivity (Giese and others, 1991) and along the western edge where the aquifer is essentially unconfined or reaches the surface (Figure 5). Out crop locations (Otte, 1986) and areas of thin or absent confining units (Giese and others, 1991; DeWiest, 1969) were used to determine the approximate boundaries of the recharge area (Figure 5). The southern coastal plain recharge area extends out to sea which allows much more influx of saline water than in the northern coastal plain. Sherwani (1980) estimates that direct recharge to the aquifer is 20 mgd north of the Pamlico River and 45 mgd south of the Pamlico River. Dewiest (1969) suggested that the area of direct recharge covers approximately 290 square miles and roughly coincides with the subcrop pattern for the CHAS.

Groundwater from the CHAS discharges into streams, estuaries, and the sea (Sherwani, 1980; Lyke and Treece, 1988), but withdrawals "can alter the natural flow direction of groundwater, both horizontally and vertically" (Lyke and Treece, 1988, p. 472). Lowered pressures increase the potential for contamination by lower quality water from polluted surface water. Reversal of flow has already occurred at the U.S. Marine Corps Air Station at Cherry Point, NC (Lloyd and Daniel, 1988). Along the Pamlico River, excessive withdrawals threaten to initiate movement of water from the river directly into the aquifer (Lyke and Treece, 1988). Lautier (1994) proposes that overpumping of local aquifers and deepening the Wilmington shipping channel could alter the groundwater flow patterns in the area.

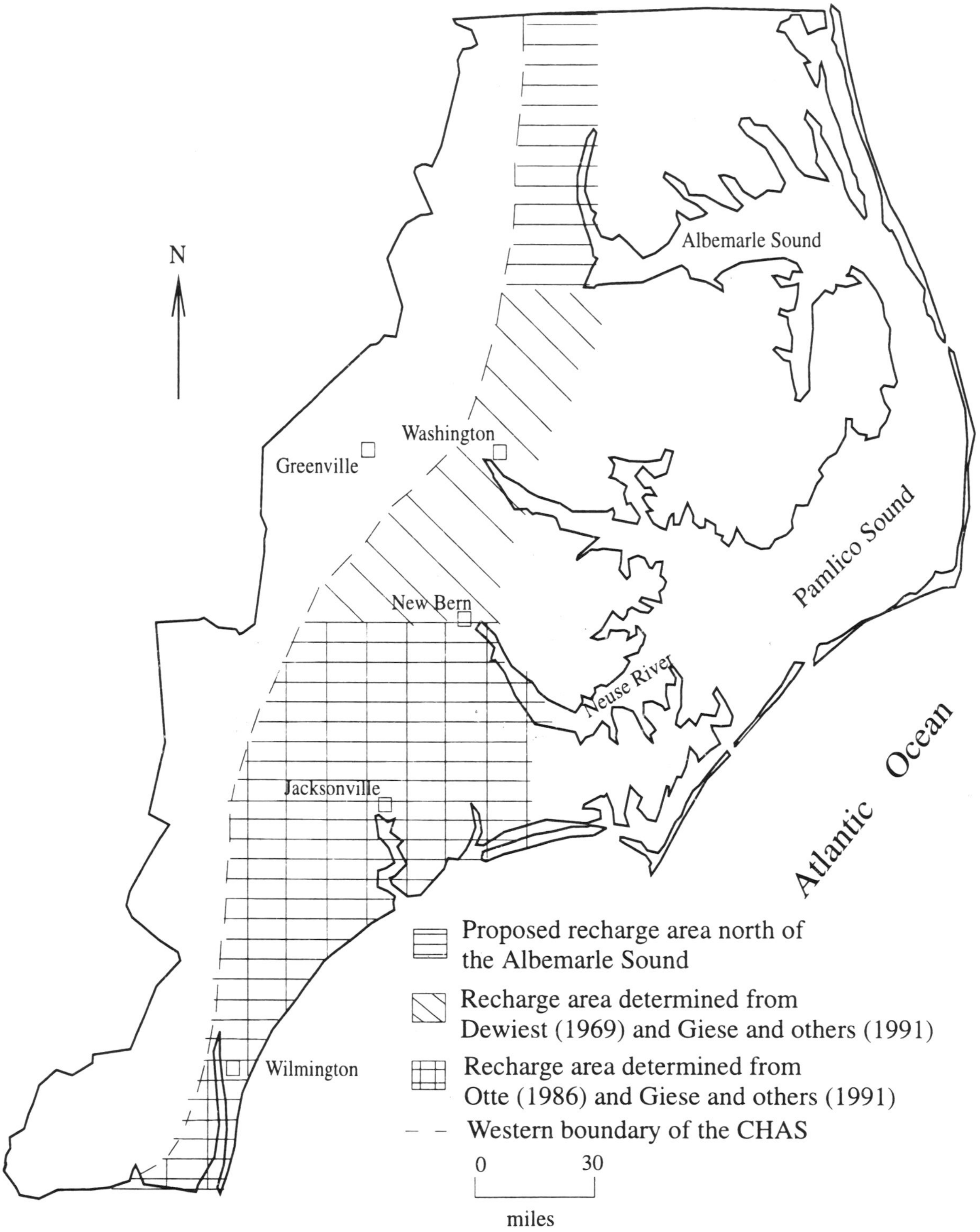


Figure 5. Proposed area of recharge to the CHAS

In the CHAS freshwater mixes with water containing dissolved salts (< 250 mg/L chloride) similar in composition to seawater (Figure 6). This water could be either connate or modern and will be termed saline formation water (SFW).

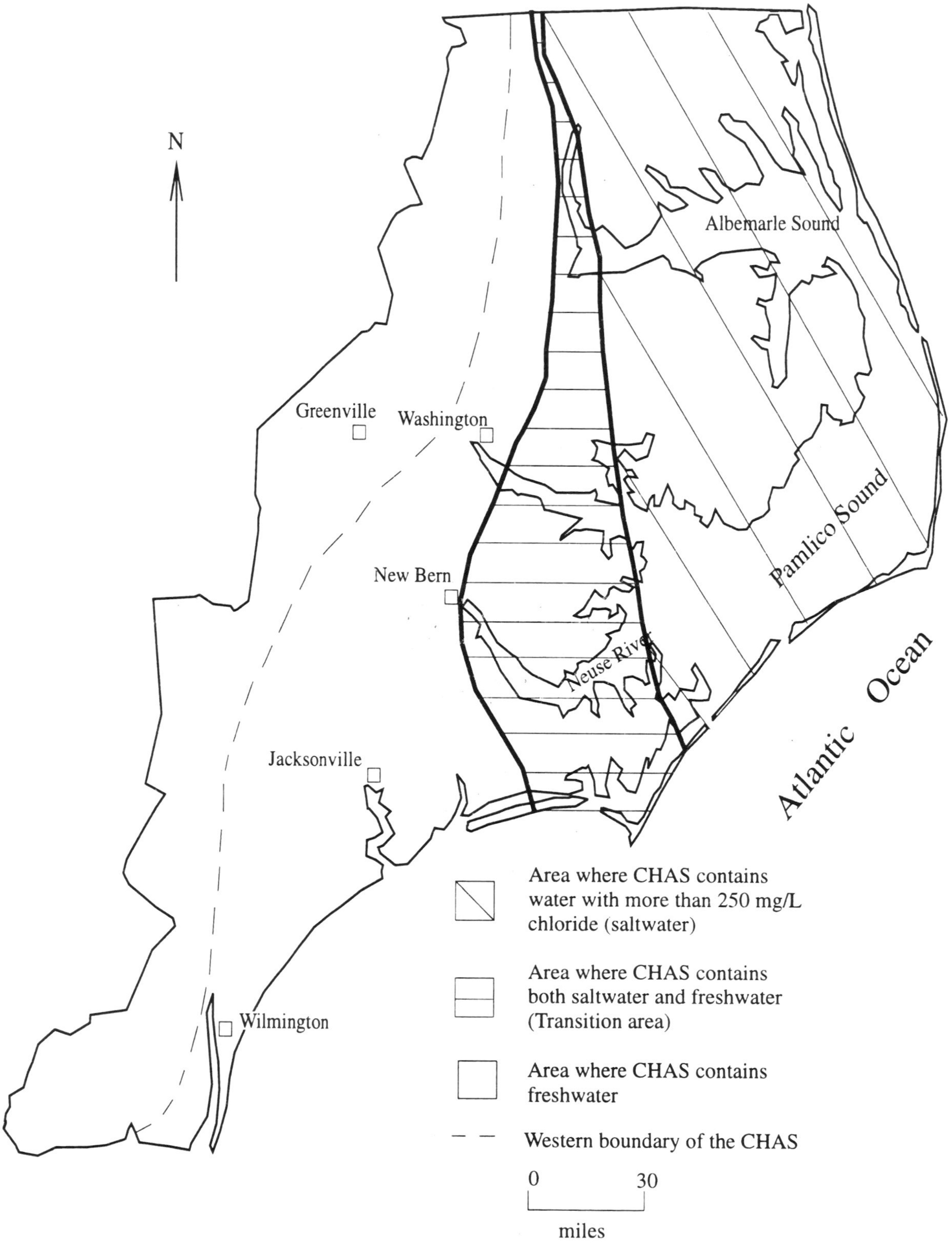


Figure 6. Freshwater and saltwater areas in the CHAS [modified from Harned and others (1989)].

Previous Investigations

The U-CHA contains good-quality water, but in the L-CHA the water is relatively brackish (Sherwani, 1980). According to Giese and others (1991), CHAS water is hard (120-180 mg/L as $CaCO_3$) to very hard (>180 mg/L as $CaCO_3$). Hardness is attributed to Ca^{2+} and Mg^{2+} dissolved from limestone and dolomite (Wilder and others, 1978). The hardness is lower near recharge areas and increases with residence time in the aquifer (Giese and others, 1987). CHAS water has a median dissolved-solids concentration of 300 mg/L and a median pH of 7.25 (Lloyd and Daniel, 1988).

High concentrations of dissolved iron typify the aquifer. In recharge areas, iron concentration often exceed the North Carolina Maximum Contaminant Level (MCL) of 0.3 mg/L (Giese and others, 1987). For example, water from wells in Onslow County has a median iron concentration of 1.07 mg/L (Amsbaugh, 1996). Dissolved iron precipitates when surface water enters the CHAS. Wilder and others (1978) believe that concentrations of iron-rich recharge water are highest near recharge areas because the water has not been in the aquifer long enough for significant iron to precipitate.

Wilder and others (1978) reported that silica usually ranges from 20-40 mg/L but occasionally approaches 80 mg/L. High concentrations of manganese (median concentration of 0.05 mg/L) have also been found in Onslow County (Amsbaugh, 1996).

Chloride concentration is an important measure of water quality and potability. Several wells in Brunswick County have been abandoned due to high chloride levels (L. Skipper, pers. commun., 1996). Sherwani (1980) suggests five possible sources of high chlorides in the U-CHA:

1) movement of water from farther east,
2) downward movement of brackish water from the Pamlico River,
3) downward movement of brackish water from the Yorktown hydrologic unit,
4) upconing of brackish water from the L-CHA and the Beaufort units, and
5) westward movement of the seawater-freshwater interface in the aquifer.

At Cherry Point chloride increased from 10 mg/L in 1942 to more than 40 mg/L in 1986 (Lloyd and Daniel, 1988). This increase is probably due to upward movement of water from the deeper parts of the CHAS induced by excessive pumping (Lloyd and Daniel, 1988).

Chemical analyses of water from wells in the coastal plain of North Carolina southwest of the Neuse River, tabulated by the North Carolina Department of Environment, Health, and Natural Resources (NCDEHNR, 1985-1995), Knobel (1985), and Lloyd and Daniel (1988) are given in Appendix L. Knobel (1985) has scanty information about location, well depth, and what section of the CHAS was sampled. Sutton and Woods (1995) sampled and analyzed waters from 29 wells in Capacity Use Area No.1 north and east of the Neuse River. All major, and 25 minor species concentrations, Eh, pH, O_2, and 87Sr/86Sr ratios were determined for waters from the Upper and Lower CHA (Appendix M). Sutton and Woods (1995) found that waters from the L-CHA and easternmost wells in the U-CHA are alkali- and Cl-rich, while waters from western wells in the U-CHA are Ca- and HCO_3-rich, and total dissolved solids (TDS) in both areas ranged from 310 to 10,900 mg/L. Sutton and Woods (1995) determined that concentration of major ions increase from west to east in the northern coastal plain and that they are affected by four dominant geochemical processes:

1) dissolution/precipitation of minerals,
2) mixing of groundwater with SFW,
3) chemical exchange between groundwater and aquifer ion exchange materials, and
4) dissolution of soil salts.

Objective

The major objective of this thesis is to characterize the chemical composition of water from the CHAS south and west of the Neuse River. This study expands upon work by Sutton and Woods (1995) in order to determine regional chemical trends in the CHAS and to elucidate the major geochemical processes affecting water chemistry. This main objective was addressed through a specific set of subobjectives that included the determination of:

1) concentrations of major and minor inorganic constituents,
2) speciation and behavior of inorganic constituents,
3) origin of inorganic constituents, and
4) minerals that are dissolving and/or precipitating along the flow path.

Chemical analyses were also used to study the:

1) differences between the U-CHA and the L-CHA, and
2) regional variability in the U-CHA and L-CHA.

STUDY AREA

The CHAS can be broken into four regions; the northeast, northwest, southeast, and southwest (Figure 1). Groundwater samples from 24 wells in the southwestern coastal plain of North Carolina were collected (Figure 7).

The field area encompasses eight counties; Brunswick, New Hanover, Pender, Onslow, Jones, Duplin, Craven, and Carteret. The North Carolina Department of Environment, Health, and Natural Resources (NCDEHNR), Brunswick County Water Corporation, Onslow County Water Corporation, and the cities of Bogue Banks, Atlantic Beach, Surf City, and Southport provided access to the wells. Ten wells have an open interval in the U-CHA, six in the L-CHA, five are open to both the Peedee and CHAS, and three are open to the Peedee. No L-CHA wells south of SFOW4 were sampled and no wells were sampled in Duplin County. Data from wells sampled during other studies, (NCDEHNR, 1989; Knobel, 1985; Sullivan's fish farm; Lloyd and Daniel,1988) were used in areas where wells were not available for sampling during the current study. These locations are identified by open triangles on Figure 7.

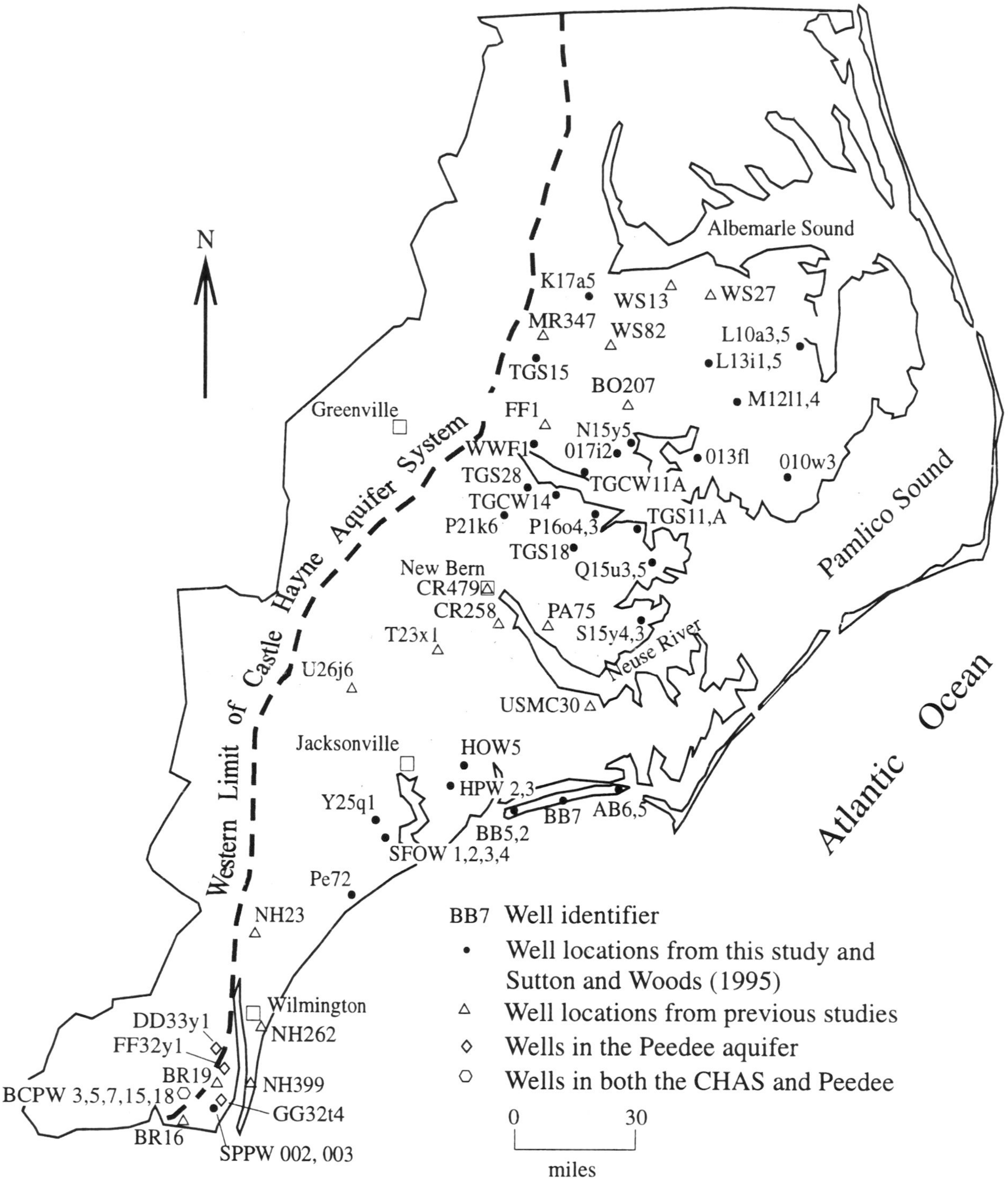


Figure 7. Sample Locations
[Previous studies are: Knobel (1985), NCDEHNR (1987), Sullivan's fish farm, and Lloyd and Daniels (1988).]

PROCEDURES

Field Procedures

In accordance with guidelines for the USGS pilot National Water-Quality Assessment Program (Hardy and others, 1989), wells were purged a minimum of three well volumes and up to as much as six well volumes until chemical stability (stable pH and Eh readings) was achieved. Proper purging insures that the sample collected is representative of the water in the aquifer not of standing water in the well. Three wells were purged and sampled using a 230 Volt 4" Grundfos submersible pump with a maximum flow rate of 7 gpm (Table 1). Six wells were purged and sampled using a 230 Volt 2" Grundfos Redi-Flo2 submersible pump with a maximum flow rate of 7 gpm (Table 1). The pump intake was placed between 5 to 10 feet below the drawdown water level within the well. Water from the well was routed through a T-fitting and pressure manifold, which controlled the flow rate into the sampling assembly and into the bottom of a one-liter plastic beaker equipped with pH and Eh probes. The water flowed out through a tube near the top of the beaker, providing constant circulation (flowthrough beaker). Chemical stability for all wells was monitored with the pH and Eh probes. The pH meter was calibrated using premixed pH buffers that were placed into a five gallon bucket filled with well water, equalizing the temperature of the buffers with that of the well water. When stability was reached, samples were collected after passing the water through an in-line filter (0.45 μm) and discarding the first 200 mL.

Fifteen of the sampled wells were municipal production wells equipped with permanent pumps (Table 1). Samples were collected after the wells had been running for approximately five minutes. After purging, a specially designed fitting was attached to the blow-off valve of the pump which allowed for sampling in the same manner as previously described.

Table 1. Sampling method used at each site

Well	Sampling Method
DD33y1(pd)	Grundfos 4" Low Flow Submersible Pump
FF32y1(pd)	Grundfos 4" Low Flow Submersible Pump
GG32t4(pd)	Grundfos 4" Low Flow Submersible Pump
SPPW 002(u)	Municipal Production Well
SPPW 003(u)	Municipal Production Well
BCPW 2(b)	Municipal Production Well
BCPW 5(b)	Municipal Production Well
BCPW 7(b)	Municipal Production Well
BCPW 15(b)	Municipal Production Well
BCPW 18(b)	Municipal Production Well
SFOW 1(l)	Grundfos Redi-Flo2 2" Submersible Pump
SFOW 2(l)	Grundfos Redi-Flo2 2" Submersible Pump
SFOW 3(l)	Grundfos Redi-Flo2 2" Submersible Pump
SFOW 4(l)	Grundfos Redi-Flo2 2" Submersible Pump
HPW 2(l)	Municipal Production Well
HPW 3(l)	Municipal Production Well
HOW 5(u)	Grundfos Redi-Flo2 2" Submersible Pump
Y25Q1(u)	Grundfos Redi-Flo2 2" Submersible Pump
ABPW 5(u)	Municipal Production Well
ABPW 6(u)	Municipal Production Well
BBPW 2(u)	Municipal Production Well
BBPW 5(u)	Municipal Production Well
BBPW 7(u)	Municipal Production Well
Pe 72(u)	Municipal Production Well

(u), U-CHA; (l), L-CHA; (pd), Peedee; (b), both the CHAS and Peedee

All samples, except those collected for O_2 analysis, were filtered. Concentrated nitric acid was added (to reduce oxidation) to a 250 mL sample for cation analysis by atomic absorption spectrophotometry (AA). Another 250 mL of sample was collected for fluoride and chloride analyses, fluoride by ion selective electrode and chloride by chloridometer. A 250 mL sample was collected for silica and sulfate analyses, silica by spectrophotometer and sulfate by turbidity meter. A 250-mL sample was frozen and later analyzed for ammonia, nitrate, nitrite, and phosphate using a colorimetric autoanalyzer. Samples were all placed in an ice chest after collection. Water for dissolved oxygen determinations was collected in Winkler flasks and two 50-mL samples were collected for alkalinity determinations. Both were titrated immediately. Twenty-five mL of sample were collected to determine sulfide in the field. An extra 500 mL were collected at each well. To evaluate analytical and sampling error, duplicate samples were collected at every third well.

Duplicate alkalinity titrations were performed in the field using a Hach digital titrator, which adds small increments (0.122 mL per 1 digit) of 1.6 N sulfuric acid (Appendix A). The pH of the sample was measured after each addition of acid, and the endpoint was taken as the value at which the maximum rate of change of pH per volume of titrant added occurred (Wood, 1976).

A dissolved oxygen titration was also performed in the field using the Winkler method (Appendix B). The titrant was added using a Gilmont buret, which can deliver as little as 0.001 mL of sodium thiosulfate (0.025 N) titrant solution. Each 0.001 mL increment is equivalent to an oxygen concentration of 0.001 mg/L if 200 mL of sample is titrated. Sulfide was determined in the field using a CHEMets sulfide test (Appendix C).

Laboratory Procedures

Spectrophotometry. Samples for silica analysis were kept refrigerated, then analyzed by the molybdosilicate method using a spectrophotometer within 48 hours of collection (Stainton and others, 1974). Six standards were used during each run and a correlation coefficient of at least 0.998 was obtained each time. All samples were diluted 1:50 before analysis (Appendix D).

Nitrate, nitrite, phosphate, and ammonia were analyzed on a spectrophotometer within 3 months of collection (Appendices E - G). The samples were slowly thawed in a cold room 18 hours before analysis. Nitrate was reduced to nitrite with cadmium powder, and a solution of sulfanilamide and N- (1-naphthyl) ethylenediamine dihydrochloride was added as the color agent (American Public Health Association, 1992). The same color reagent was added to untreated samples to determine the amount of nitrite only; this concentration was subtracted from the nitrate plus nitrite concentration to determine the concentration of nitrate. Phosphate was determined using an ascorbic acid method (American Public Health Association, 1992). Ammonia concentrations were determined by the phenolhypochlorite method (Solorzano, 1969).

Ion Selective Electrode. The ion activity of fluoride in solution was measured with an Orion combination fluoride electrode. TISAB III with CDTA was used as a buffer to provide a uniform ionic strength and background, adjust pH, and break up complexes. Use of the buffer allows the electrode to measure fluoride concentration (Appendix H). Samples were refrigerated and analyzed within one week of collection.

Chloridometer. A Buchler Digital Chloridometer measured the concentration of chloride in solution by passing a fixed current between a pair of silver electrodes immersed in a glacial acetic acid solution. The combination of silver ions and chloride ions results in an insoluble precipitate of silver chloride (Appendix I). Samples were refrigerated and analyzed within one week of collection.

Photometer. Sulfate ion is precipitated in an acetic acid medium with barium chloride so as to form barium sulfate crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve (Appendix J). Samples were analyzed within 48 hours of collection.

Atomic Absorption. Samples for cation analysis were preserved by adding 1 mL concentrated nitric acid to 250 mL of sample. Standards were made for each cation analyzed (calcium, potassium, magnesium, iron, and sodium). Flame atomic absorption spectrometry was used to determine cation concentrations (Appendix K).

RESULTS

Complete results of all analyses performed for this study are given in Appendix N. Sutton and Woods (1995) results for the northern coastal plain are given in Appendix M. Summaries of the concentrations of major and minor components determined in this study and previous studies used in the southern coastal plain are listed in Tables 2 and 3. Locations of U-CHA and L-CHA wells are shown on Figures 8 and 9, respectively. SFOW3 and BB5 were the only sites for which the electrical neutrality was not balanced within 10%. Electrical balance above 5% indicate possible sampling and/or analytical errors which produces unreliable data. Nineteen out of the twenty-four wells sampled balanced to within 5%.

Statistical Analysis of Analytical Results

Spectrophotometry was used to determine concentrations of silica, ammonia, nitrate, nitrite, and phosphate. Combined standard deviations of duplicate samples are in Table 4; calculated accuracies ranged from 89 - 98%.

Iron, calcium, magnesium, sodium and potassium were analyzed by Atomic Absorption. Table 5 shows the combined standard deviation of 8 duplicate samples. Percent recovery ranged from 82 - 97%.

The standard deviations for fluoride, chloride, and sulfate were 0.09, 4.83, and 5.73, respectively. There was a 98 percent recovery for chloride (Buchler Instruments, 1981) and an 85 - 91% recovery for sulfate (American Public Health Association, 1992).

Table 2. Concentration of major components in the CHAS groundwater.

WELL IDENTIFIER	Temp (°C)	pH	Eh (mV)	TDS ppm	HCO_3^- ppm	Cl^- ppm	SO_4^{2-} ppm	SiO_2 ppm	Mg^{2+} ppm	Na^+ ppm	K^+ ppm	Ca^{2+} ppm
SPPW 002(u)	20	7.5	170	408	203	76	4	9	4	31	10	71
SPPW 003(u)	20	7.5	146	386	217	50	3	12	4	26	8	66
SFOW 1(l)	18	7.4	149	398	266	19	0.3	13	4	12	7	77
SFOW 2(l)	18.5	7.4	144	376	243	20	0.2	13	4	12	8	76
SFOW 3(l)	19	7.2	-52	847	395	250	11	24	9	50	27	81
SFOW 4(l)	18	6.8	75	459	290	25	20	17	6	15	9	77
HPW 2(l)	19	7.2	136	386	245	31	3	8	2	12	5	80
HPW 3(l)	18.5	7.35	129	339	210	31	3	7	2	11	5	70
HOW 5(u)	18	7.28	129	372	244	24	1	9	2	9	5	78
Y25Q1(u)	18.5	7.3	60	407	253	31	7	24	3	15	4	70
AB 5(u)	19	7.14	206	486	317	26	4	17	6	13	13	90
AB 6(u)	21	7.1	37	545	358	28	4	20	14	16	15	90
BB 2(u)	20	7.23	34	453	293	28	4	14	5	14	10	85
BB 5(u)	19	7.18	-6	844	288	360	13	13	10	40	20	100
BB 7(u)	21	7.14	77	535	343	31	3	20	12	18	19	89
Pe 72(u)	19	7.36	124	340	200	33	5	8	6	16	6	66
BR-16(u)*	N/D	7.3	N/D	687	323	142	0.6	29	7	86	4	95
BR-19(u)*	19	7.6	N/D	354	206	24	3	38	3	16	2	62
T23x1(u)*	N/D	8.1	N/D	231	160	4	3	11	1	3	1	48
U26j6(u)*	N/D	7.6	N/D	283	200	6	5	7	1	3	0.7	60
NH-399(u)*	16.5	8	N/D	337	203	25	0.3	23	9	12	14	51
NH-23(u)*	N/D	7.1	N/D	583	305	84	2	41	9	58	N/D	84
USMC 30(u)*	18	7.27	N/D	320	330	9	8	35	3	19	4	79
NH-262(u)*	15.5	7.6	N/D	502	222	109	10	17	12	67	9	56

(u) = U-CHA
(l) = L-CHA
* = wells from previous studies
N/D = Not Determined

Table 3. Concentration of minor components in the CHAS groundwater.

WELL IDENTIFIER	Fe ppm	S^- ppm	F^- ppm	NH_4^+ ppm	PO_4^{3-} ppm	NO_3^- ppm
SPPW 002(u)	0.29	0.0	0.13	0.24	0.04	< 0.001
SPPW 003(u)	0.38	0.0	0.13	0.31	0.05	< 0.001
SFOW 1(l)	0.62	0.0	0.26	0.14	0.00	< 0.001
SFOW 2(l)	0.45	0.0	0.26	0.17	0.00	0.001
SFOW 3(l)	0.18	4.5	0.60	0.45	0.01	0.001
SFOW 4(l)	7.32	0.0	0.21	0.34	0.01	< 0.001
HPW 2(l)	0.87	0.0	0.11	0.06	0.12	0.002
HPW 3(l)	0.82	0.14	0.08	0.03	0.11	0.001
HOW 5(u)	1.07	0.0	0.19	0.06	0.10	0.001
Y25Q1(u)	4.06	0.0	0.12	0.17	0.22	0.027
AB 5(u)	0.1	0.0	0.26	0.70	0.01	< 0.001
AB 6(u)	0.05	0.0	0.37	0.77	0.01	< 0.001
BB 2(u)	0.1	0.1	0.37	0.38	0.01	< 0.001
BB 5(u)	0.3	1.5	0.24	0.42	0.01	< 0.001
BB 7(u)	0.05	0.05	0.19	0.56	0.01	< 0.001
Pe 72(u)	0.7	0.0	0.17	0.04	0.11	< 0.001
BR-16(u)*	N/D	N/D	N/D	N/D	N/D	1.8
BR-19(u)*	N/D	N/D	0.1	N/D	0.07	0.6
T23x1(u)*	0.9	0.0	0.2	0.11	0.07	N/D
U26j6(u)*	1.5	0.0	<0.1	0.09	0.17	N/D
NH-399(u)*	N/D	N/D	0.1	N/D	N/D	0.8
NH-23(u)*	N/D	N/D	0.1	N/D	N/D	0.7
USMC 30(u)*	1.3	N/D	0.2	N/D	0.01	N/D
NH-262(u)*	N/D	N/D	0.3	N/D	0.2	0.2

(u) = U-CHA
(l) = L-CHA
* = wells from previous studies
N/D = Not Determined

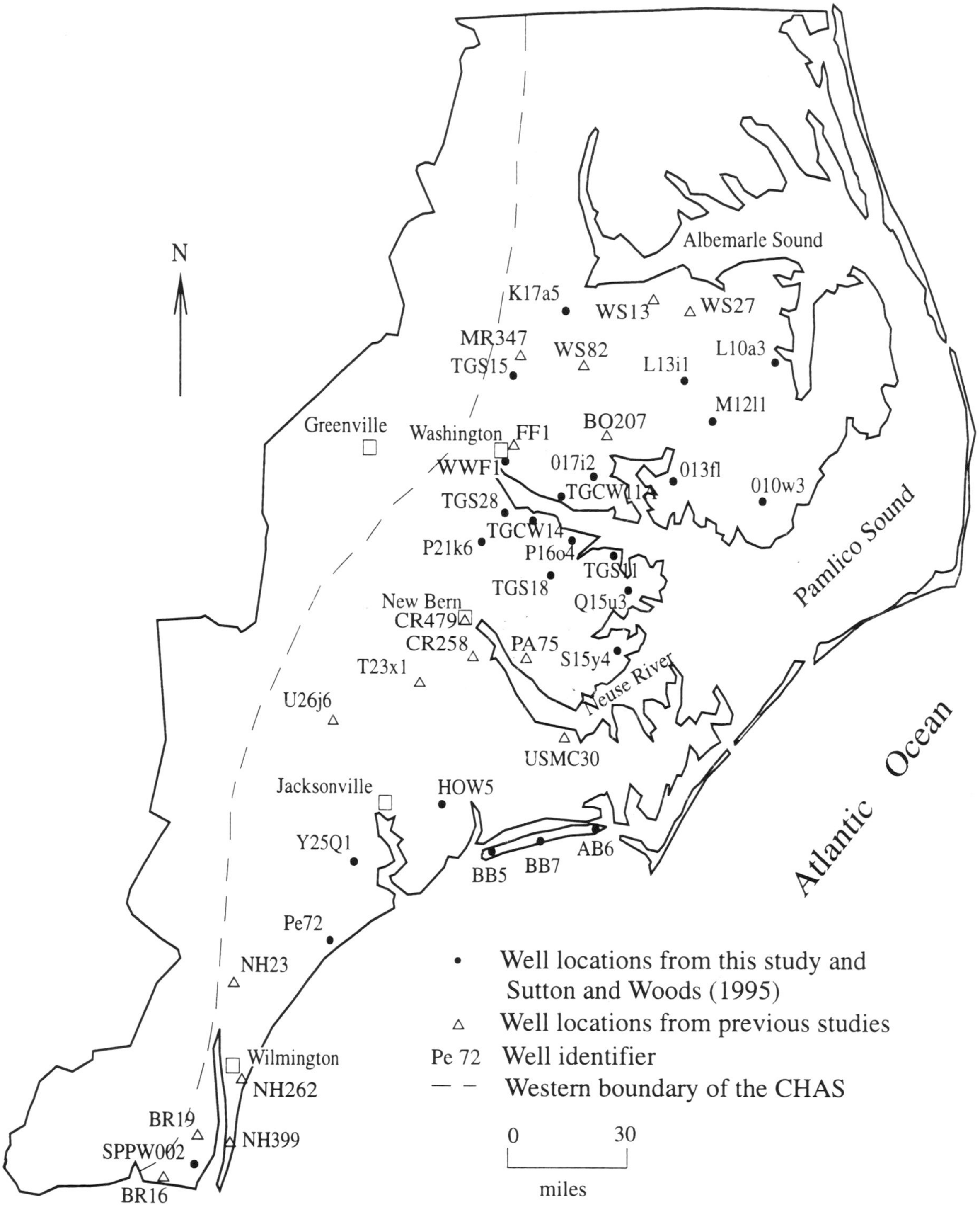


Figure 8. U-CHA Sample Locations
[Previous studies are: Knobel (1985), NCDEHNR (1987), Sullivan's fish farm, and Lloyd and Daniel (1988).]

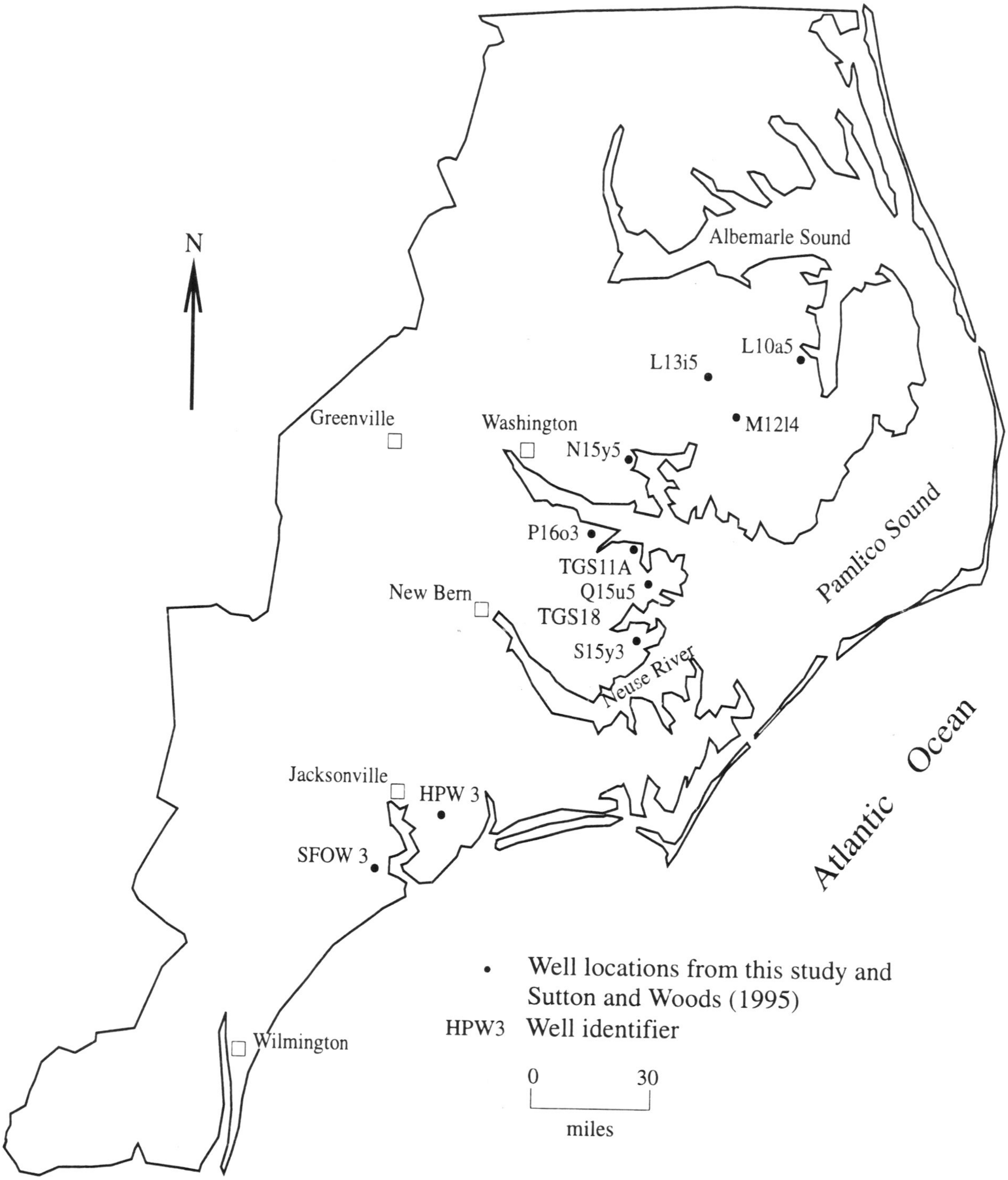


Figure 9. L-CHA Sample Locations

Table 4. Statistical analysis of spectrophotometric data. Precision is expressed as the combined standard deviation of "n" duplicate samples. Accuracy is expressed as % recovery of a known standard reference solution.

Ion	n	Combined sd ppm	Range of Concentrations (ppm)	% Recovery
Silica	8	±5.66	8.45 - 24	96%[1]
Ammonium	8	±0.21	0.16 - 0.772	94%[2]
Nitrate	8	±0.01	0 - 0.044	98%[3]
Nitrite	8	±0.001	0.0013 - 0.0033	98%[3]
Phosphate	8	±0.08	0 - 0.23	89-96%[4]

1) as reported by Stainton and others, 1974
2) as reported by Solorzano, 1969
3) as reported by Jones, 1984
4) as reported by American Public Health Association, 1992

Table 5. Statistical analysis of Atomic Absorbtion data. Precision is expressed as the combined standard deviation of "n" duplicate samples. Accuracy is expressed as % recovery of a known standard reference solution.

Ion	n	Combined sd ppm	Range of Concentrations (ppm)	% Recovery
Iron	4	±0.18	0.05 - 0.45	84%
	4	±1.23	1.61 - 4.23	
Magnesium	8	±4.35	1.65 - 13.54	97%
Sodium	7	±2.39	11.82 - 19.83	85%
	1	±0.08	30.93 - 31.04	
Potassium	8	±4.83	5.08 - 19.01	82%
Calcium	8	±9.78	70.25 - 94.62	98%

Concentrations of Ions

The concentration ranges of aqueous species for U-CHA and L-CHA waters and any seemingly anomalous values are listed in Table 6. The data of Sutton and Woods (1995) are included. A brief description of the chemical trends within the CHAS is given below.

TDS, chloride, and sulfate in the U-CHA north of the Neuse River generally increase from west to east. South of the Neuse River, TDS, chloride, and sulfate increase from northwest to southeast, except for Brunswick and New Hanover Counties where TDS values decrease and then increase again from southwest to northeast. TDS, chloride, and sulfate concentrations in the L-CHA are generally higher than those in the U-CHA at the same well site, and chloride is the main contributor to the TDS in the U- and L-CHA in the eastern wells. The concentrations of TDS, chloride, and sulfate in the L-CHA increase from west to east. Alkalinity in the U-CHA generally increases from southwest to northeast but no geographic trend for the L-CHA is obvious. Sutton and Woods (1995) found that L-CHA wells have higher sodium, potassium, calcium, and magnesium concentrations than U-CHA wells at the same location. Potassium and sodium concentrations in the U-CHA generally increase from west to east north of the Neuse River and from northwest to southeast south of the Neuse River. Calcium and magnesium follow the same general trend as potassium and sodium except that north of the Neuse River, both increase, decrease, and then increase again. This local minimum along a NW-SE profile seems to be associated with well L13i1. Silica concentrations increase, decrease, and then increase again between Albemarle Sound and Jacksonville. South of

Table 6. Concentration ranges of aqueous species

Dissolved species	Range of concentrations		Wells with anomalously low or high concentrations	
	U-CHA	L-CHA	Low	High
	ppm unless noted		Well ; Conc.	Well ; Conc.
TDS	170 - 4,693	340 - 10,600		SFOW3 (l) ; 854
				BB5 (u) ; 847
Cl^-	4 - 1,790	19 - 5,100	***L-13 (u) ; 55***	SFOW3 (l) ; 250
			L-13 (l) ; 510	BB5 (u) ; 360
				TGS 11a (l) ; 2,260
				M-12 (l) ; 5,100
SO_4^{2-}	0 - 336	0.3 - 1,120		***TGS 11a (l) ; 380***
				M-12 (l) ; 1,100
				Q-15 (l) ; 610
HCO_3^-	160 - 783	385 - 642	T23x1 (u) ; 160	***L-13 (u) ; 783***
F^-	0 - 3.2	0.08 - 1.71		***M-12 (l) ; 1.35***
				M-12 (u) ; 3.20
Na^+	3 - 1,690	11 - 3,360		SFOW3 (l) ; 50
				BB5 (u) ; 40
				TGS 11a (l) ; 1,470
				Q-15 (l) ; 920
K^+	0 - 82	5 - 124		SFOW3 (l) ; 27
Ca^{2+}	7 - 103	20 - 140		
Mg^{2+}	1 - 127	2 - 318		
Hardness	69 - 658	75 - 1,632		
SiO_2	7.0 - 78	7.0 - 26		
Iron	0.05 - 4.8	0.18 - 7.3		SFOW4 (l) ; 7.3
				Y25q1 (u) ; 4.1
NH_4^+	0.04 - 6.62	0.03 - 7.89		
S^{2-}	0 - 5.8	0 - 7.1		SFOW3 (l) ; 4.5
				BB5 (u) ; 1.5
				TGS 11a (u) ; 5.8
				P-16 (l) ; 7.1
NO_3^-	0 - 0.3	0 - 0.006		
PO_4^{3-}	0.003 - 0.22	0 - 0.12		
pH	6.92 - 8.2	6.8 - 7.67		T23x1 (u) ; 8.1
Eh (mV)	206 to -160	160 to -52	SFOW3 (l) ; -52	
			BB5 (u) ; -6	

(u), U-CHA sample (l), L-CHA sample

Hardness = mg equivalent CaCO3/L = 2.497 (Ca, mg/L) + 4.118 (Mg, mg/L) (American Public Health Association, 1992)

Bold = wells from Sutton and Woods (1995)

Jacksonville silica decreases generally from west to east.

Iron concentrations in the U-CHA and L-CHA generally decreased from west to east with a low concentration area, in the U-CHA, between the Neuse and Pamlico Rivers. In the northern coastal plain ammonia concentrations in the L-CHA were always higher than those of the U-CHA between wells from the two aquifers at the same site (Sutton and Woods, 1995), this did not hold true for the southern coastal plain. No significantly high nitrite, nitrate, or phosphate concentrations were found. There were no consistent differences between dissolved sulfide contents of waters from the Upper and Lower CHA.

pH for both the Upper and Lower CHA ranged from 6.8 to 8.2 with no consistent relationship observed between wells from the two aquifers at the same site. Eh values for the U-CHA are generally more positive than those for the L-CHA, suggesting that the U-CHA waters are more oxidizing.

DISCUSSION

Methodology

Contour maps were drawn showing the concentrations of major ions in the U-CHA and in the L-CHA. Wells from the Washington well field (WWF) draw water from both the U-CHA and L-CHA, but most of their water is derived from the U-CHA (Warner, 1993), and are included on the contour maps for calcium and iron. Because they were closely spaced, only one well from each of the Hubert and Sneads Ferry well fields was contoured. The wells with the overall highest ion concentration were used.

The computer program PHREEQE (Parkhurst and others, 1980) was used to determine the chemical speciation of solutes and to determine the saturation state of various phases. Another program, PHRQINPT, was used to create input files for PHREEQE. Any initial charge imbalance was maintained during the calculations. For each solution the solute concentrations, temperatures, pH, and pe (the negative log of the electron activity) measured at each well were entered into the data base. The following equation shows the relationship between pe and Eh:

$$pe = Eh * T / 2.3RT,$$

where R is the gas constant, T is temperature, and F is Faraday's constant. The extended Debye-Huckel equation was used to calculate activity coefficients for all species with an ion size parameter, and the Davies equation was used for all species with no ion size parameter.

Major Constituents

Calcium and Magnesium. Calcium is the most abundant cation in the dilute (low TDS) Ca-HCO_3 waters in the western parts of the study area, except for well NH 262 which is alkali rich (Figure 10). Rainfall (0.08 - 0.65 ppm of Ca; Table 7) is not a significant source of calcium in waters from the CHAS. Dissolution of calcite and dolomite in the U-CHA by acidic recharge water appears to be responsible for high calcium concentrations in the northwestern coastal plain (Figure 10). Concentrations reach a maximum near Washington and then decrease eastward. Ca^{2+} can be removed by:

Table 7. Average chemical composition of rainfall in the recharge area of the CHAS.

Ion	Concentration ppm	Ion	Concentration ppm
Na^+	0.27[3]-1[2]	Cl^-	2[2,4]
K^+	0.1[1]-0.2[2]	SO_4^{2-}	1.6-2[5]
Mg^{2+}	0.15 [1]	NO_3^-	0.4-4[3,5,6]
Ca^{2+}	0.08[3]-0.65[1]	NH_4^+	0.21-0.61[3,6]

1 from Gambell and Fisher, 1966
2 from Junge and Werby, 1958
3 from Willey and Kiefer, 1993
4 from Willey and Kiefer, 1990
5 from Willey et al., 1988
6 from D. Daniels, pers. comm, 1996

1) precipitation of calcite;

   $Ca^{2+} + 2\ HCO^-_3 \Leftrightarrow CaCO_3 + H_2CO_3$ Plummer and others (1983) and

2) chemical-exchange reactions with ion-exchange materials involving absorption of Ca^{2+} and release of Na^+; $Ca^{2+}_{(aq)} + 2Na^+ - EX \Leftrightarrow 2Na^+_{(aq)} + Ca^{2+} - EX$, where EX represents the exchanger (Sprinkle, 1989).

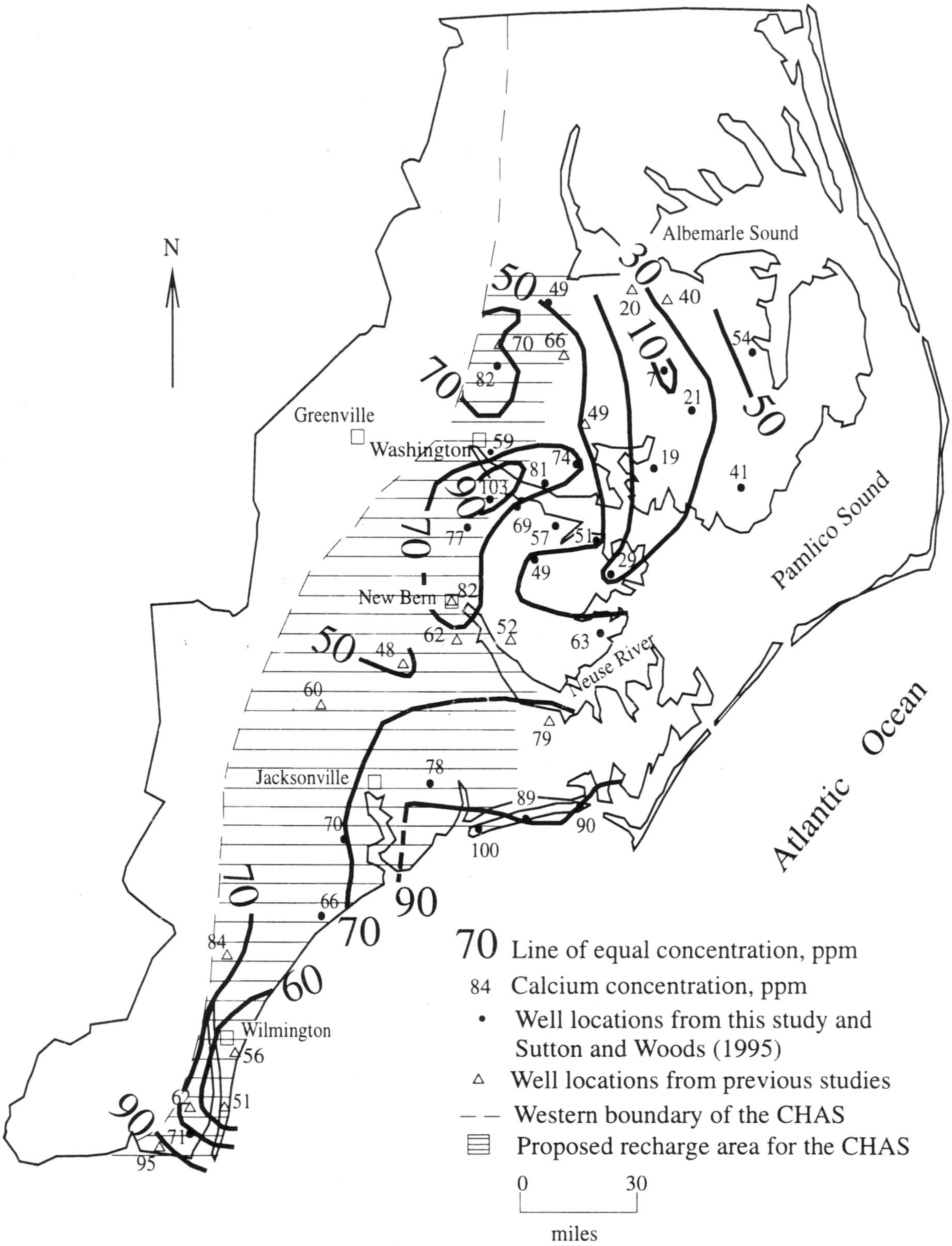


Figure 10. Calcium Concentrations in the U-CHA with the proposed area of recharge

Both processes may be occurring in the CHAS.

The effect of mixing SFW with freshwater in the aquifer can be seen in the area northeast of Jacksonville where in portions of the U-CHA calcium concentrations tend to increase from west to east. South of Wilmington, calcium values increase from northeast to southwest probably due to over pumping in the southwestern area.

Calcium is more abundant in wells that tap the L-CHA than wells in the same location that tap the U-CHA. This relationship can also be seen with other major cations and TDS, which suggests that the higher Ca^{2+} concentrations are due to mixing of SFW with freshwater in the deeper aquifer. Regional calcium trends in the L-CHA can't be fully delineated because of the lack of data (Figure 11).

The low concentration trough apparent on the calcium map at the L13i1 site occurs on other contour maps (i.e. Mg, alkalinity, Cl, etc.). A possible explanation may be leakage from overlying aquifers and through confining units into the U-CHA. The Ca^{2+} "tongue" seen on Figure 10 may be attributed to U-CHA waters rapidly recharging the heavily pumped region near the PCS phosphate mine. The tongue of low Ca^{2+} concentrations suggests that U-CHA waters are being recharged and discharged quickly, which doesn't allow the dissolution of large amounts of $CaCO_3$. East of the low Ca^{2+} concentration trough a steep concentration gradient can be seen in the U- and L-CHA, which indicates mixing of SFW with freshwater. This steep concentration gradient can also be seen on other CHAS maps (Mg^{2+}, SO_4^{2-}, Cl^-, etc.).

Magnesium shows a general increase from west to east with one low concentration trough at well L13i1 (Figure 12). Rainfall (0.15 ppm Mg^{2+}; Table 7) is not a significant

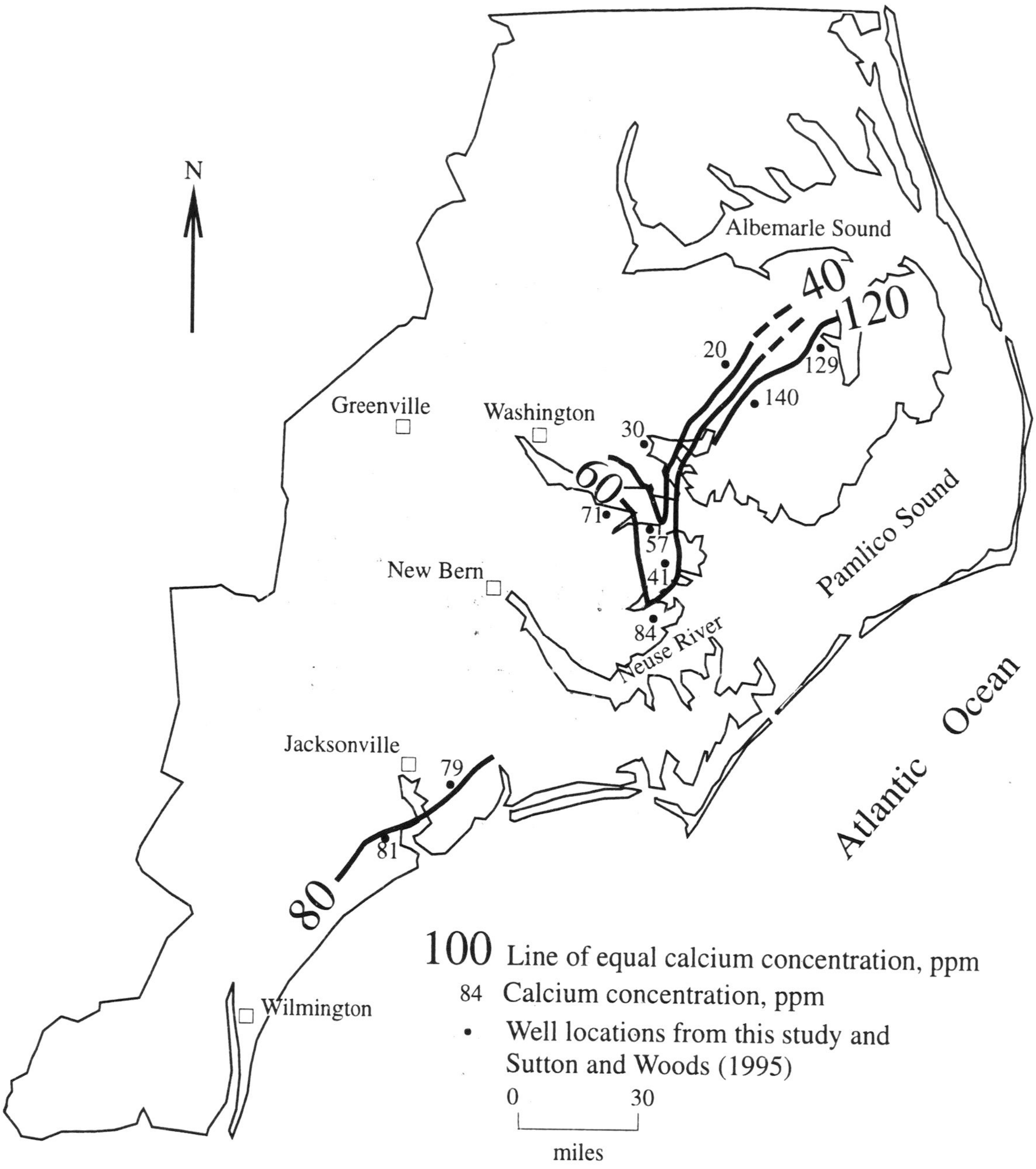


Figure 11. Calcium Concentrations in the L-CHA

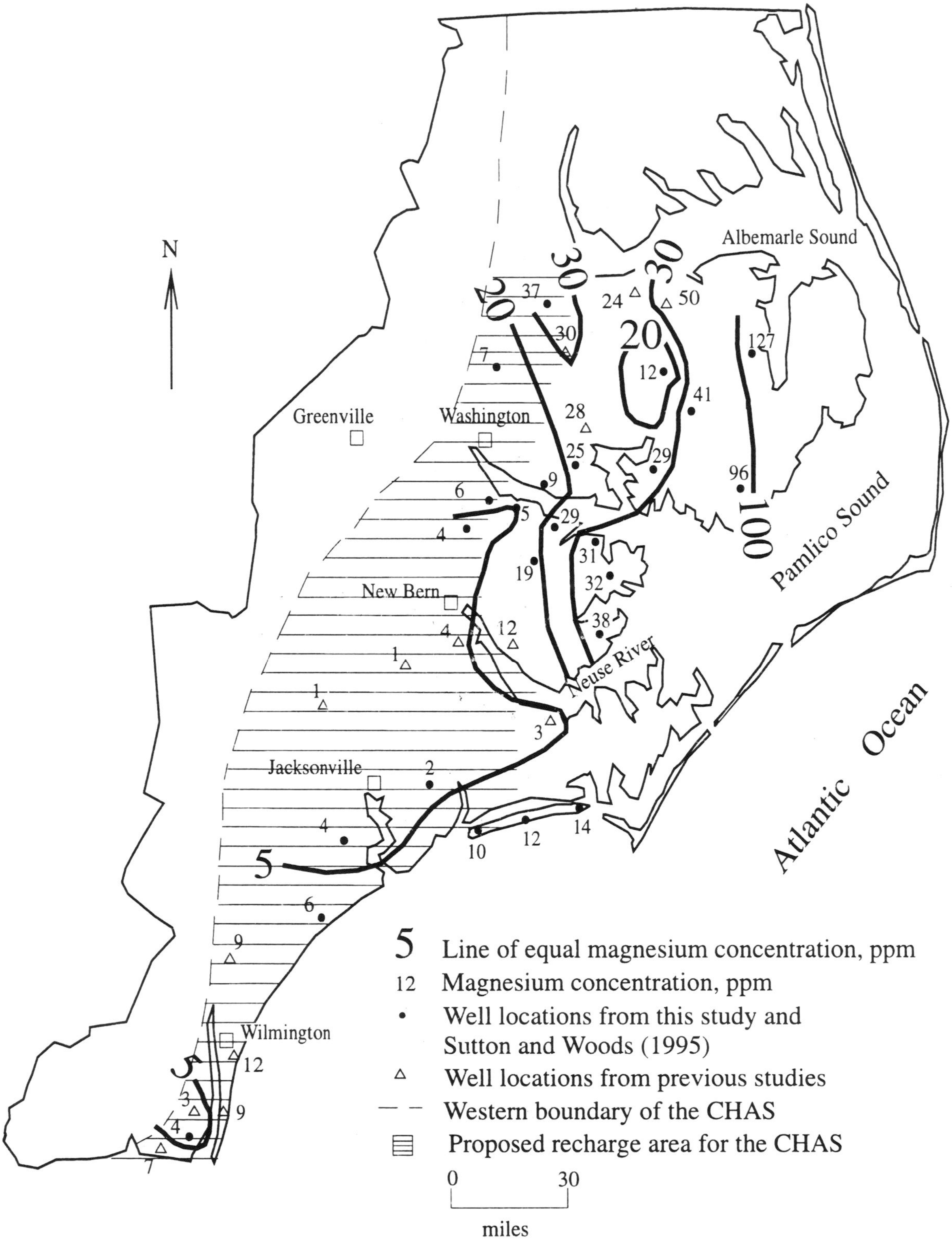


Figure 12. Magnesium Concentrations in the U-CHA with the proposed area of recharge

contributor to the magnesium concentrations. Magnesium concentrations in U-CHA waters north of the Neuse River are higher than those south of the river. Lawrence and Upchurch (1982) found that the concentration of Mg^{2+} in the Floridan aquifer increases as is the thickness of overlying units increases; postulating that Mg^{2+} is leached downward from Mg-rich clay minerals and dolomite (Scott, 1988). North of the Neuse River the CHAS is confined (Giese and others, 1991); in Onslow County it is confined to semiconfined (Amsbaugh, 1996); and in Brunswick County it is confined to locally unconfined (Lautier, 1994). The decreasing confinement may contribute to the decrease of Mg^{2+} seen in the southern coastal plain. However, another reason for higher Mg^{2+} in the northeast is that waters have been reacting with aquifer materials for a longer time as they are farther away from the recharge area; the southern coastal plain lacks the more evolved "downgradient" waters. Sutton and Woods (1995) found that wells in the L-CHA produce water with higher Mg^{2+} concentrations than U-CHA waters (Figure 13). Lateral intrusion of SFW may be a source of magnesium to eastern wells in the U-CHA and to most of the L-CHA wells.

Maps of the concentration ratio of Ca^{2+}/Mg^{2+} (by weight) show higher values to the west and lower values toward the coast (Figures 14 and 15). The high values in the recharge area could occur for several reasons:

1) the paucity of magnesium rich minerals, such as dolomite, which contribute Mg^{2+} to the water during dissolution, or
2) Mg^{2+} being adsorbed and $2Na^{+}$ being released into solution; a possible

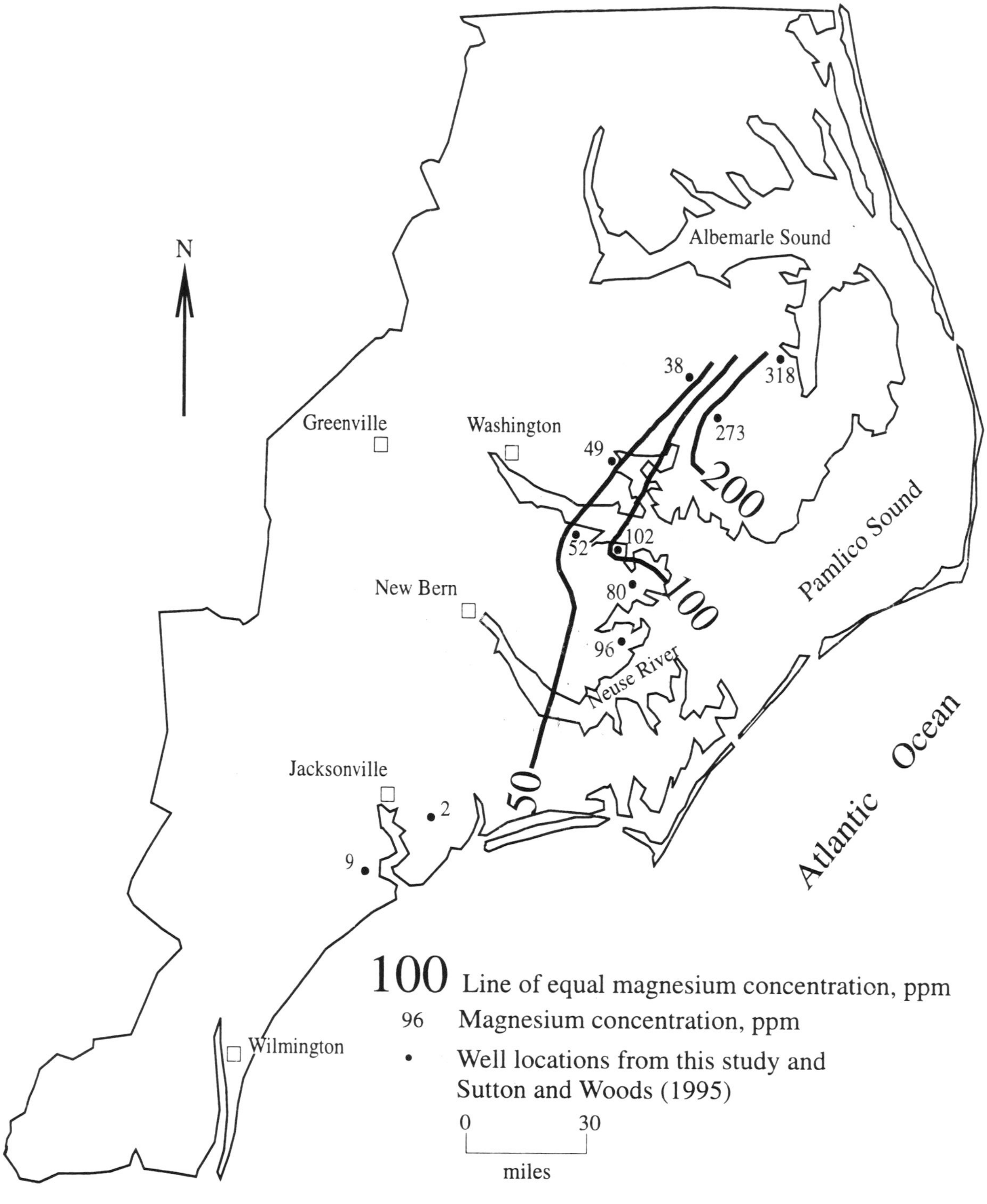


Figure 13. Magnesium Concentrations in the L-CHA

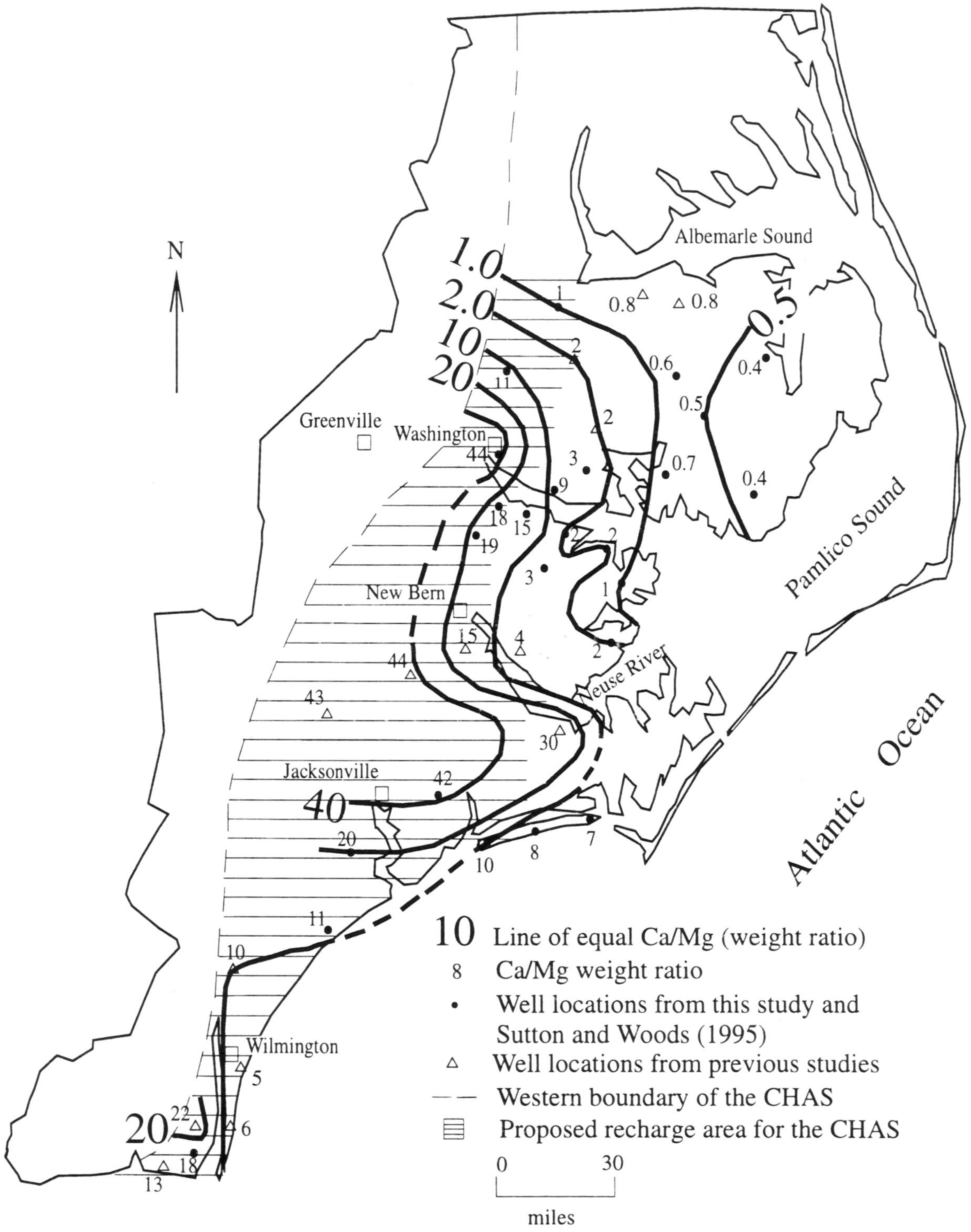


Figure 14. Weight Ratio of Ca/Mg in the U-CHA with the proposed area of recharge. Ca/Mg weight ratio of seawater is 0.32.

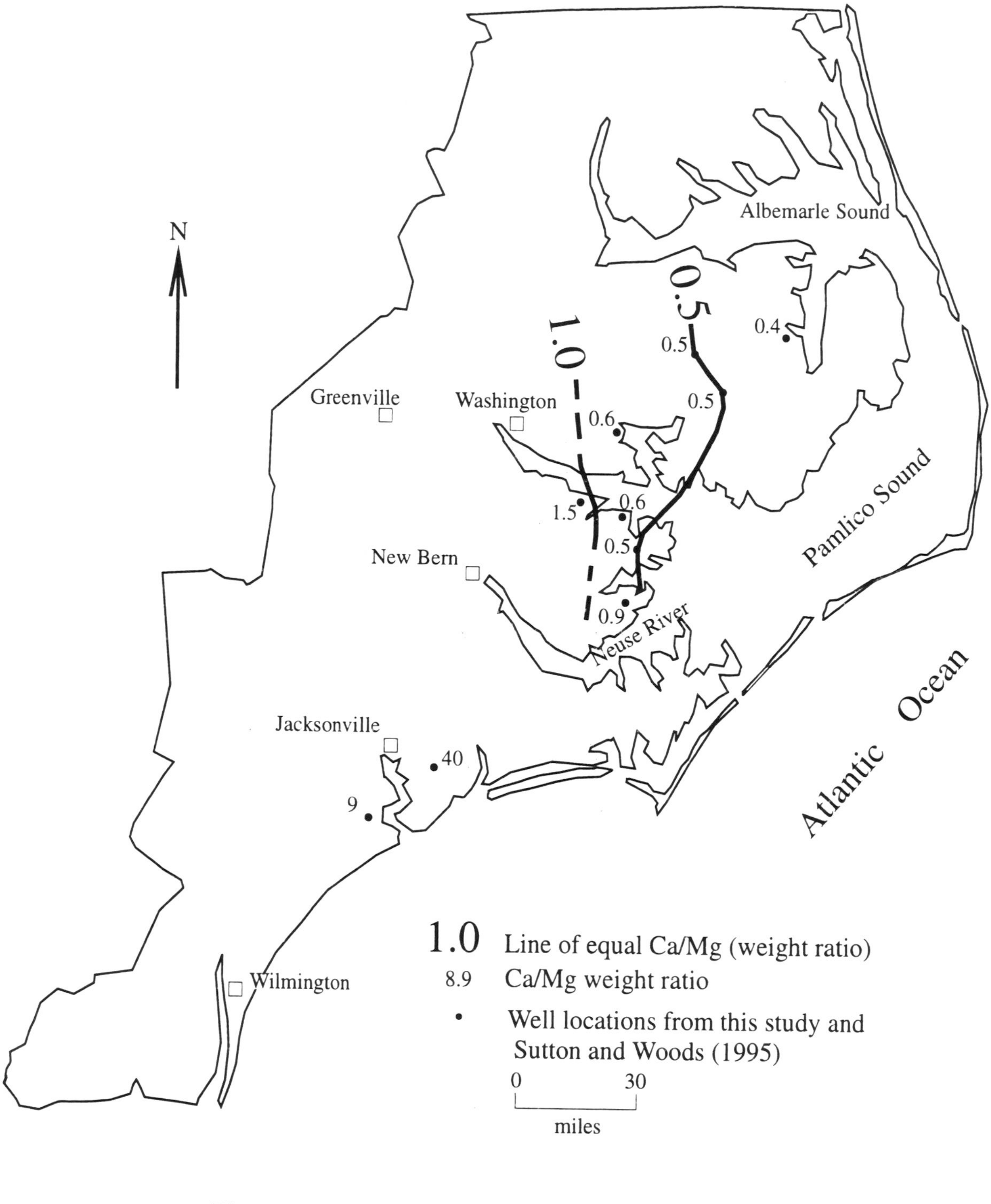


Figure 15. Weight Ratio of Ca/Mg in the L-CHA
Ca/Mg weight ratio for seawater is 0.32.

chemical reaction is $Mg^{2+} + 2Na^{+}\text{-EX} \Leftrightarrow Mg^{2+}\text{-EX} + 2Na^{+}$, where EX represents the exchanger (clays or other minerals) (Katz, 1992).

Ca^{2+}/Mg^{2+} values generally decrease from west to east throughout the coastal plain, with values as low as 0.4 evident in the northeastern portion of the study area. The Ca^{2+}/Mg^{2+} ratio in average seawater is 0.32 (Table 8). Wells WS-13 and WS-27 (Knobel, 1985), L13i1, L10a3, M12l1, O10w3, O13f1, and Q15u3 (Sutton and Woods, 1995) have Mg^{2+} concentrations that exceed their Ca^{2+} concentrations. This relationship between Mg^{2+} and Ca^{2+} concentrations is probably caused by mixing with SFW (Sprinkle, 1989).

Table 8. Chemical composition of seawater (salinity = $35^{0}/_{00}$).

Ion	Concentration ppm	Ion	Concentration ppm
Cl^-	19,354	HCO_3^-	120
Na^+	10,770	Br^-	66
Mg^{2+}	1,290	F^-	1-1.6
SO_4^{2-}	2,712	NO_3^-	0.60-2.4
Ca^{2+}	412	NO_2^-	0.004-0.170
K^+	399	NH_4^+	0.002-0.040
Ca^{2+}/Mg^{2+}	0.32	K^+/Cl^-	0.02
Na^+/Cl^-	0.86		

Sources: Wilson, 1975; Spencer, 1975; Brewer, 1975; and Williams, 1975

Bicarbonate. Bicarbonate is one of the principal anions found in the U-CHA. The predominance of Ca^{2+} and HCO_3^- in wells from the western part of the study area suggests that HCO_3^- is largely due to limestone dissolution, a process enhanced by dissolved CO_2 in recharge water. Alkalinities in this area are typical of waters whose composition is dominated by calcite dissolution (Sprinkle, 1989; Trainer and Heath, 1976). Carbonate buffering maintains the pH of the groundwater between 6.9 and 8.1, and HCO_3^- is the predominant carbonate species. North and east of Jacksonville alkalinity in the U-CHA generally increases from west to east, but then decreases again east of L13i1 (Figure 16). This pattern is largely a result of the very high values at L13i1 and M12l1 which could be due to vertical recharge through organic-rich swamps and pocosins (Sprinkle, 1989; Trainer and Heath, 1976). South of Jacksonville, in the U-CHA, as well as in the L-CHA (Figure 17) more data are needed to distinguish clear trends, although alkalinity appears to decrease from west to east near Wilmington. These decreases along the coast may be due to mixing with SFW of a lower alkalinity (Table 8).

Carbonate Saturation . The saturation index of a mineral is defined as

$$\text{saturation index} = \log\ (\text{IAP}/K_T),$$

where IAP is the ion activity product of the dissolved components in the solution, and K_T is the solubility product of the solid or gaseous phases at the specified temperature. The calcite saturation index ranged from -0.20 to 0.14 in the U-CHA and from -0.42 to 0.16 in the L-CHA (Figures 18 and 19). A saturation index of zero indicates saturation but because of the possibility of CO_2 outgassing and errors in measurements of pH and alkalinity, Sprinkle (1989) considered that a saturation index of -0.2 to +0.2 is indicative of calcite saturation in the Floridan aquifer. According to this criterion, all waters in this study, except for SFOW-4 and S15y3 (L-CHA), are saturated with calcite. The negative values of the saturation index occurred at the eastern and western edges of the study area, north of the Neuse River. The low values to the west suggest waters are less saturated in

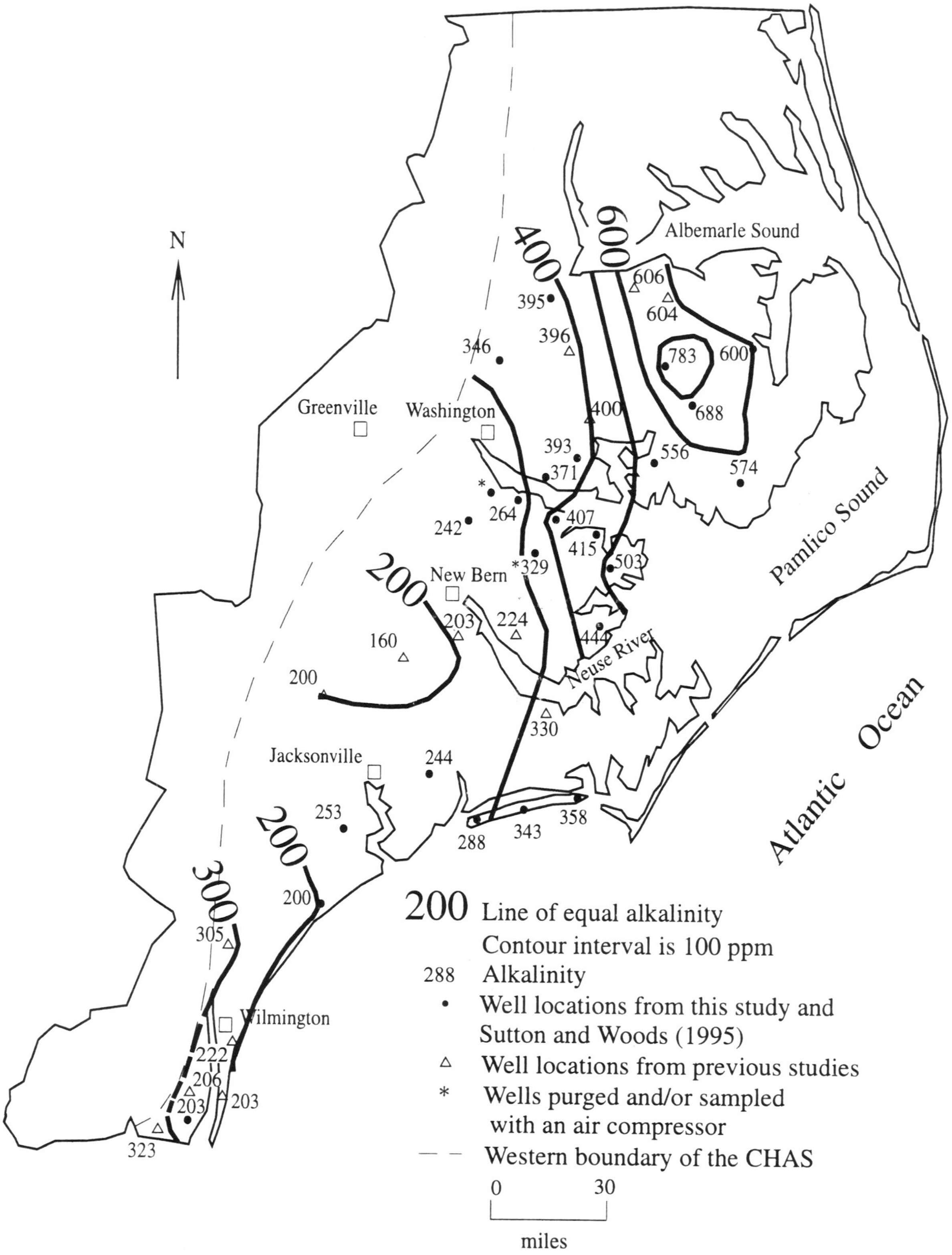


Figure 16. Alkalinity of the U-CHA in ppm of HCO_3^-. Concentrations were determined in the field.

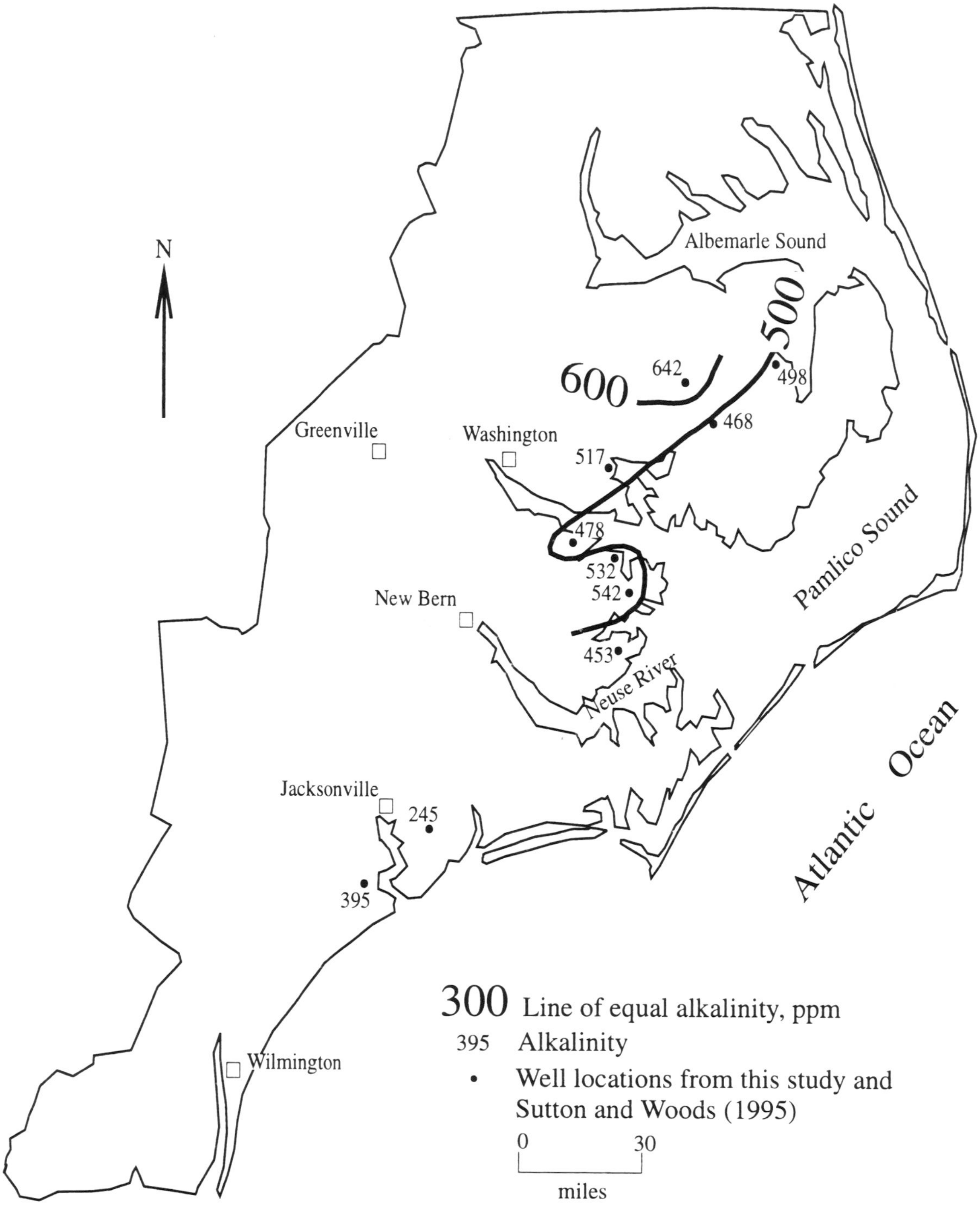


Figure 17. Alkalinity of the L-CHA in ppm of HCO_3^-
Concentrations were determined in the field.

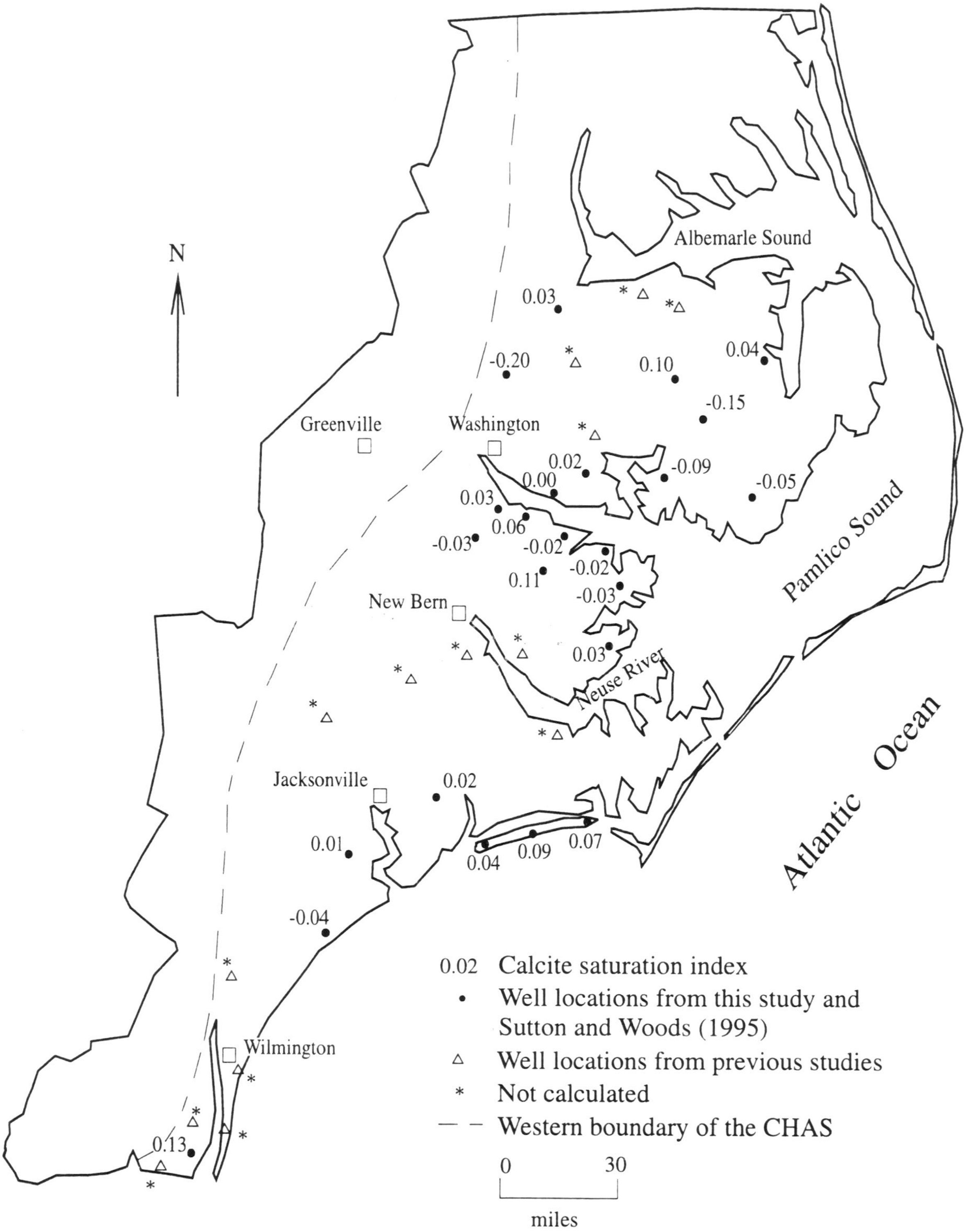


Figure 18. Calcite Saturation Index of the U-CHA
* Indicates that because of insufficient data the SI could not be determined. This was the case for most of the data from previous studies.

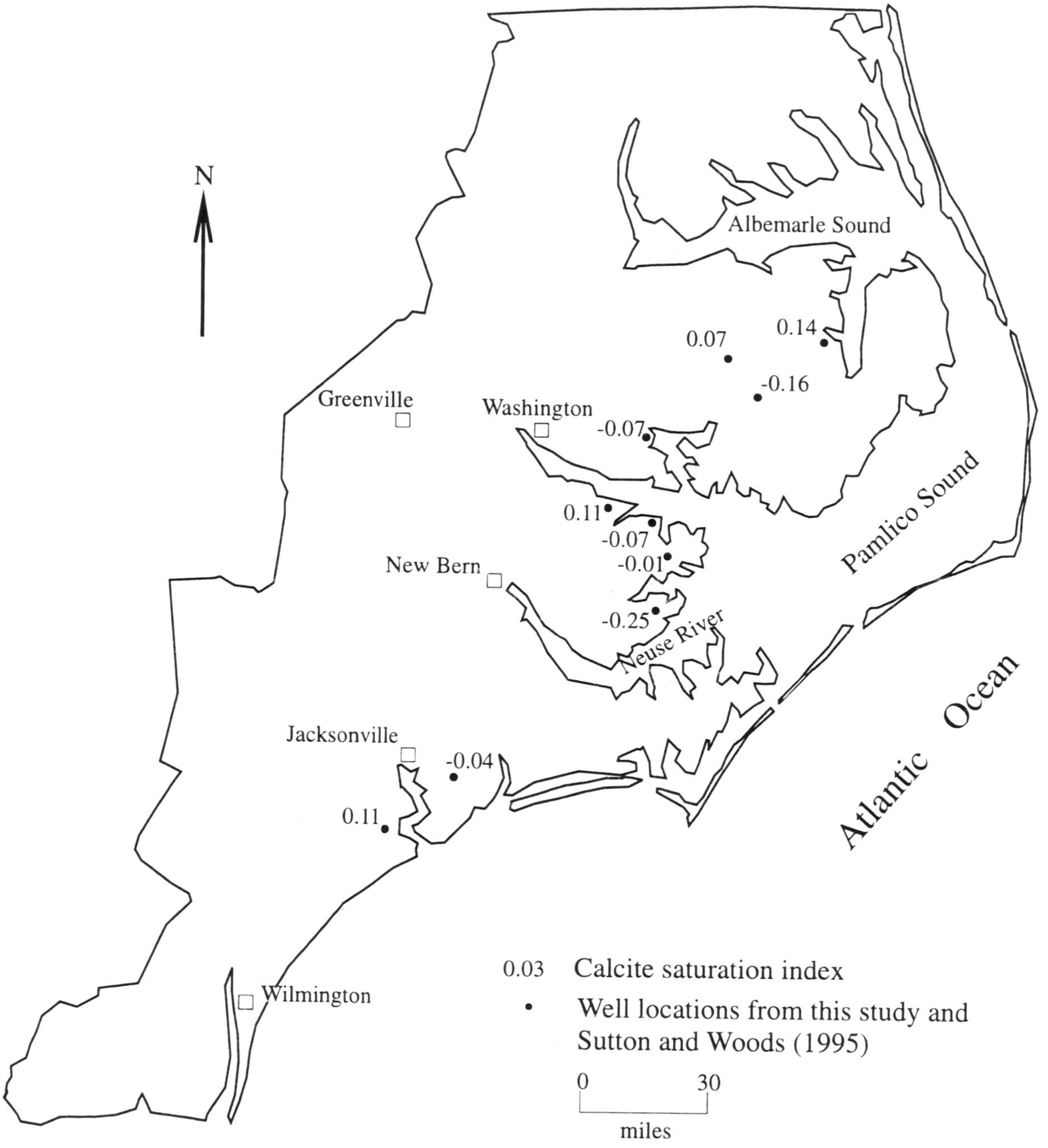


Figure 19. Calcite Saturation Index of the L-CHA

the recharge area (Figure 5). South of the Neuse River all values are positive except for Pe72. Katz (1992) stated that in semiconfined and confined parts of the Floridan aquifer the median calcite SI is near zero indicating that calcite is controlling the concentrations of Ca^{2+} in water from the aquifer.

The dolomite saturation index ranged from -1.60 to +0.78 in the U-CHA and from -1.66 to +0.99 in the L-CHA (Figures 20 and 21). Sprinkle (1989) considered that a saturation index of -0.4 to +0.4 indicates saturation. Sutton and Woods (1995) found that at the same site, the degree of dolomite saturation was generally higher in the L-CHA than in the U-CHA. The dolomite saturation index increases from west to east in the U-CHA, north of Y25Q1. Dolomite was oversaturated (> +0.4) in the northeastern part of the study area in both the U-CHA and L-CHA. Sutton and Woods (1995) theorized that Mg^{2+} is being introduced from SFW and the accompanying increase in sulfate inhibits dolomite precipitation leaving the waters saturated or oversaturated with dolomite. South of the Neuse River all waters were undersaturated (< -0.4).

Sulfate. North of the Neuse River sulfate concentrations increase from west to east in both the U-CHA and L-CHA (Figures 22 and 23). No sulfate was found in water in the northern recharge area, so rainfall concentrations (2 ppm of SO_4^{2-}) are being removed from solution. South of the Neuse River all concentrations are below 10 ppm, except BB-5 and NH-262 (mixing of SFW), which suggests that rain could be a significant source of sulfate.

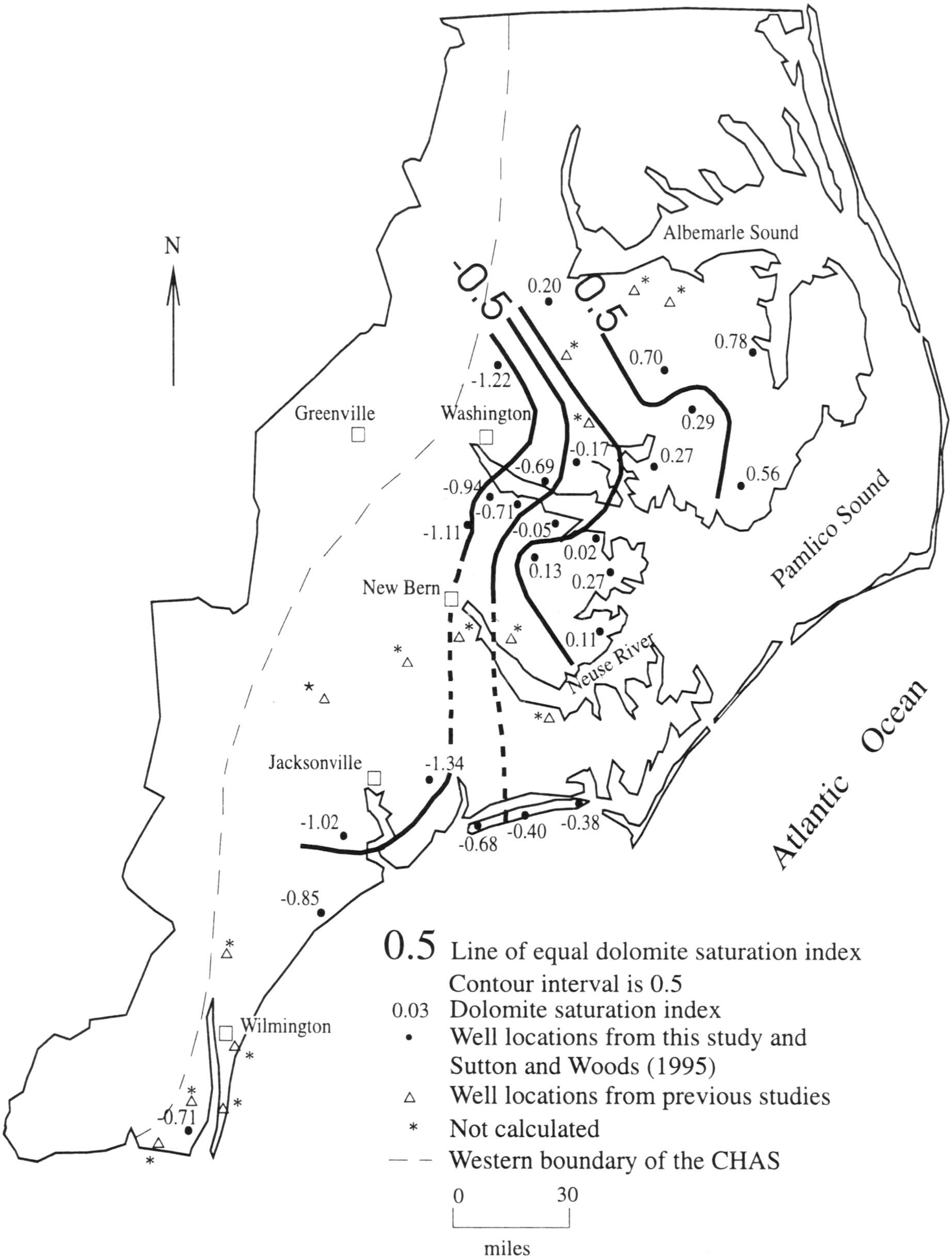


Figure 20. Dolomite Saturation Index of the U-CHA
* Indicates that because of insufficient data the SI could not be determined.

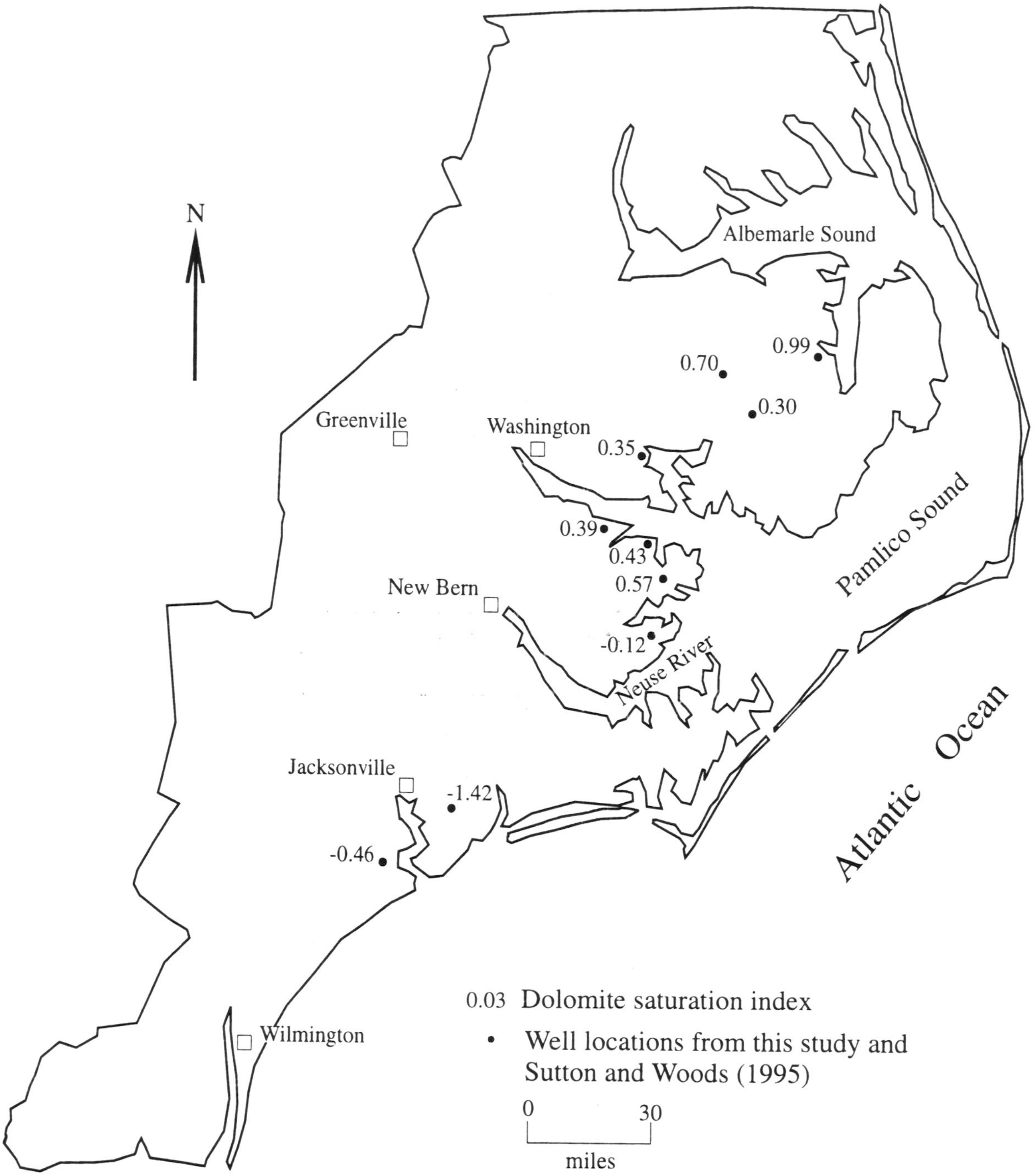


Figure 21. Dolomite Saturation Index of the L-CHA

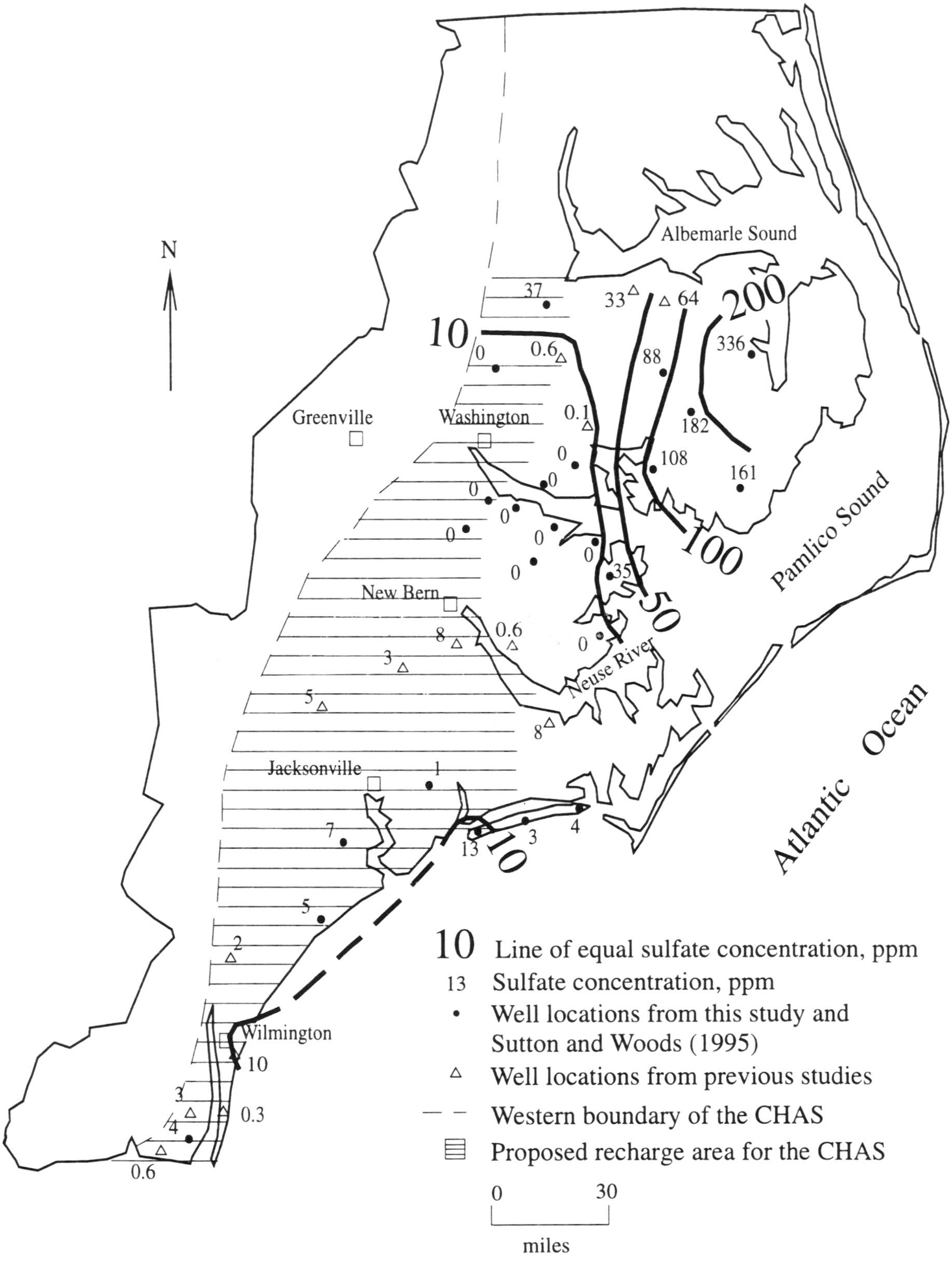


Figure 22. Sulfate Concentrations in the U-CHA with the proposed area of recharge. North Carolina MCL is 250 ppm (NCDEHNR, 1989).

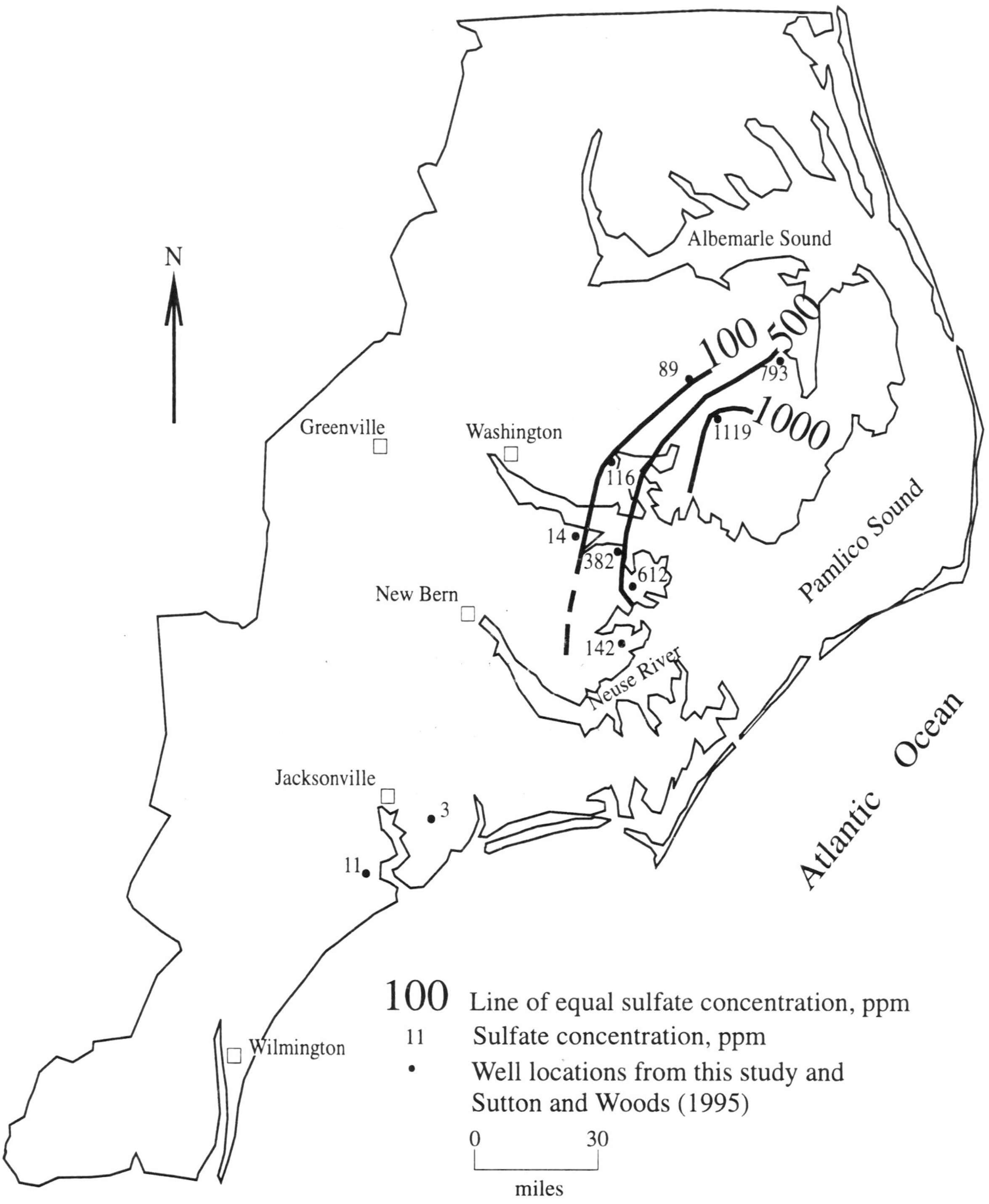


Figure 23. Sulfate Concentrations in the L-CHA
North Carolina MCL is 250 ppm (NCDEHNR, 1989).

No sulfate minerals have been reported in the CHAS. Figure 24 (modified from Rightmire and others, 1974) shows a gypsum trend and a seawater trend on a graph of sulfate concentrations versus SO_4^{2-}/Cl^- ratio. These trends may be used to identify the sources of SO_4^{2-} in a groundwater sample. Points A and C represent the SO_4^{2-} and Cl^- concentrations found in dilute groundwater, with point C representing a more mineralized starting point. Analyses that plot near line A-B or C-D indicate that gypsum is the primary source of SO_4^{2-}, and analyses that plot along line A-E or C-E represent a mixing trend with seawater (E). All samples taken south of the Neuse River, as well as those north of the river (Sutton and Woods, 1995), fall along the seawater trend, except T23x1, U26j6, SFOW4, and L13i1. This indicates that seawater is the primary source of SO_4^{2-}. T23x1 and U26j6 lie within the recharge area which has very dilute water and the source of SO_4^{2-} is probably rainfall. The L13i1 sulfate/chloride ratio is probably skewed due to the explanation given earlier in the calcium and magnesium section. The high ratio in SFOW4 may be influenced by the upward movement of waters from the Cretaceous Aquifer System caused by a leaky confining bed (Amsbaugh, 1996).

Gypsum is undersaturated over the entire study area, but the saturation index increases from west to east (Figures 25 and 26). The gypsum saturation trend appears to be very similar to the dolomite saturation trend (Figures 20 and 21), but more data in the southeastern coastal plain would be very useful.

Chloride. In the U-CHA wells in the northeastern coastal plain and the Wilmington area have high chloride concentrations (Figure 27). The major source of chloride in these areas is SFW which is mixing with freshwater in the aquifer.

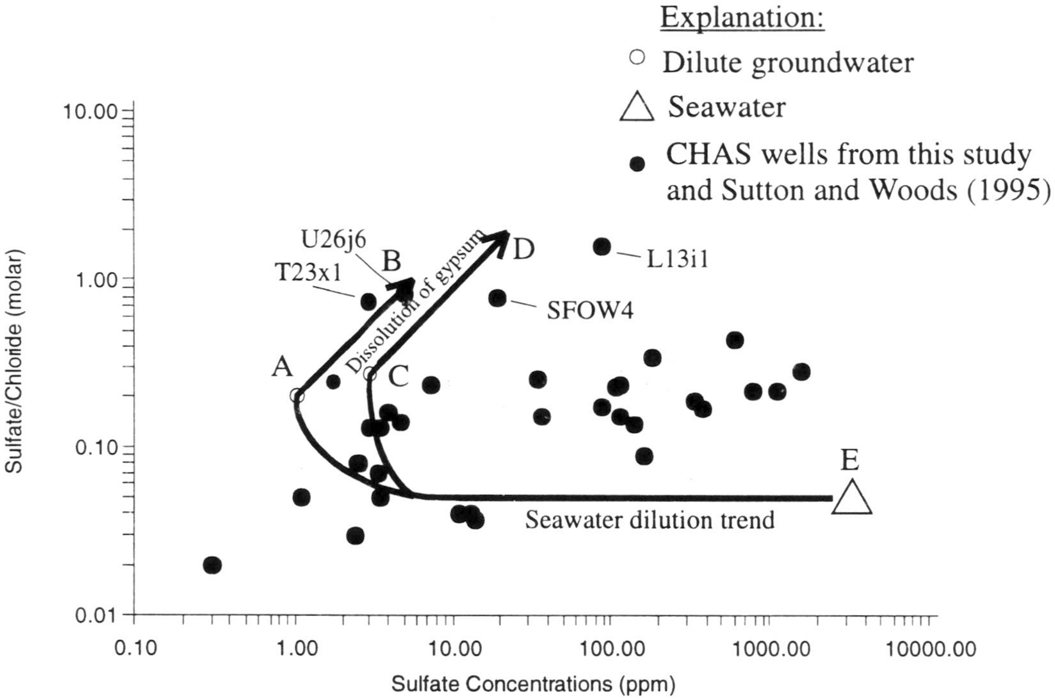


Figure 24. Graph of Sulfate-to-Chloride Ratios Versus Sulfate Concentrations.

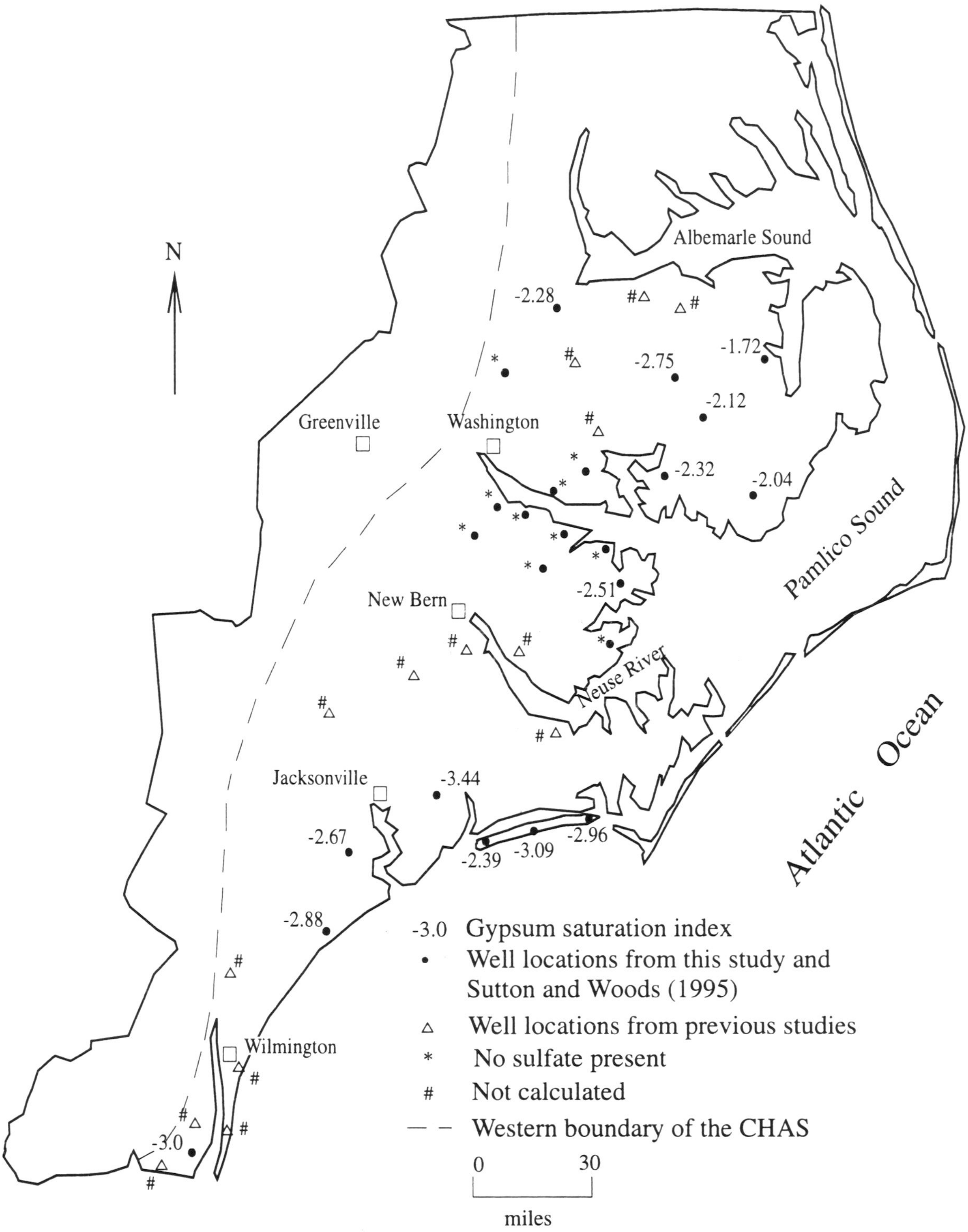


Figure 25. Gypsum Saturation Index of the U-CHA
* Iindicates that sulfate is absent or below the detection limit.
\# Indicates that because of insufficient data the SI could not be determined.

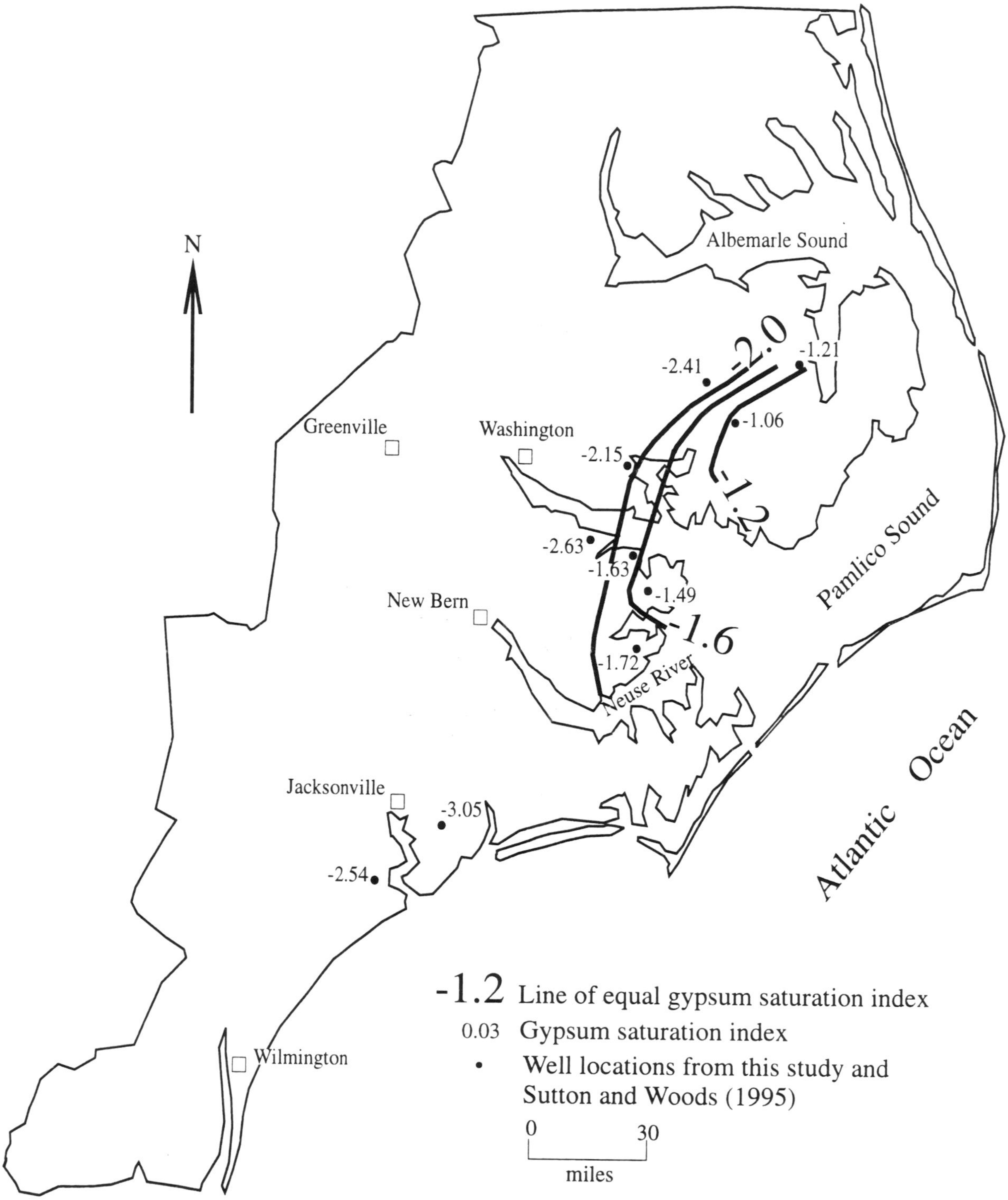


Figure 26. Gypsum Saturation Index of the L-CHA

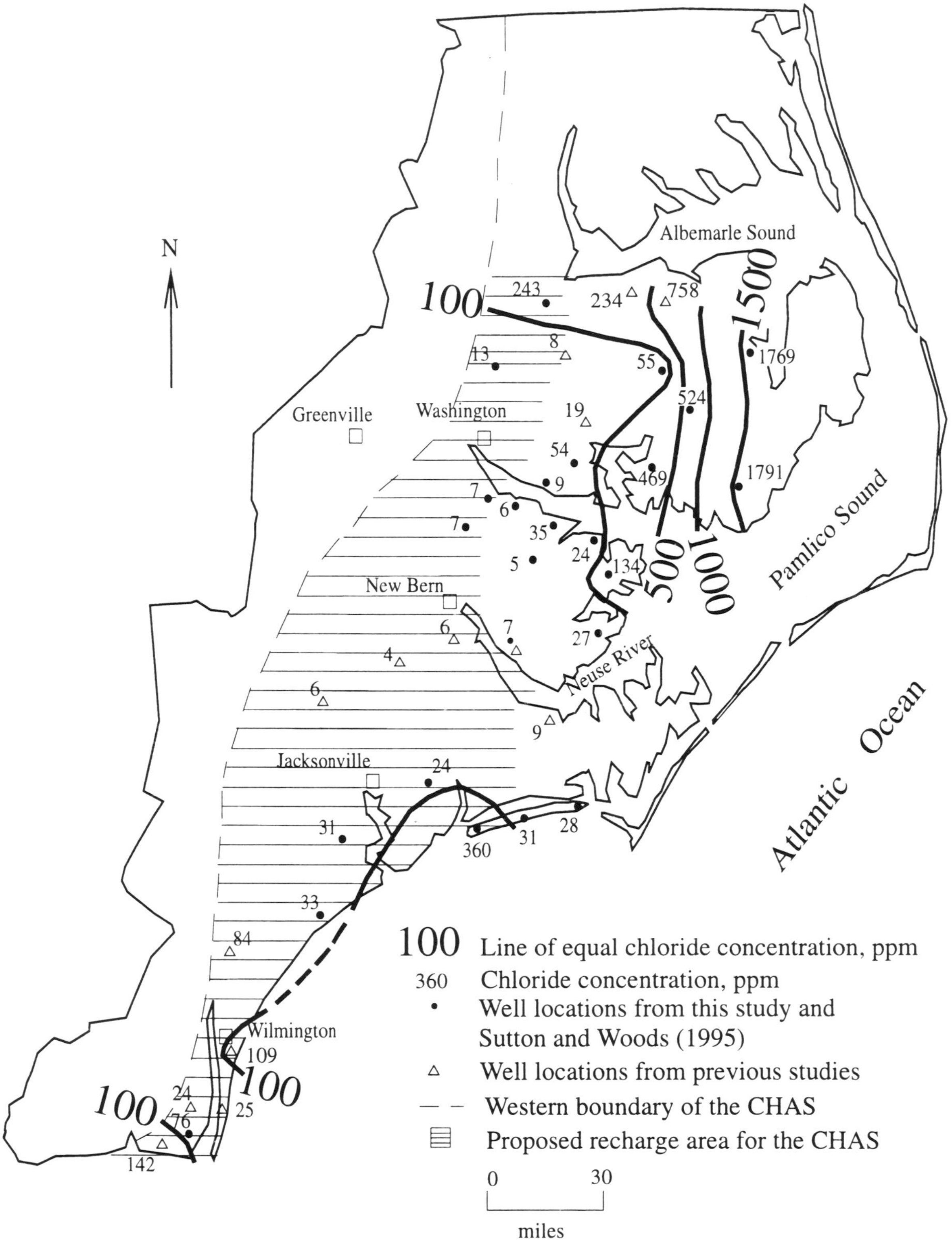


Figure 27. Chloride Concentrations in the U-CHA with the proposed area of recharge. North Carolina MCL is 250 ppm (NCDEHNR, 1989).

Well BB5 at the southwest tip of Bogue Banks has a chloride concentration of 360 ppm which is ten times higher than surrounding wells. The source of this chloride is probably seawater migrating landward within the White Oak River paleochannel. This paleochannel ranges in depth from 20 m on the landward side of Bogue Banks to over 40 m on the inner continental shelf and cuts through Quaternary sediments into Tertiary units (Hine and Snyder, 1985).

The chloride content of waters in western areas, although low, also appears to have been acquired in the subsurface because the chloride content of local rainfall is only about 2 ppm (Table 7). Transpiration and evaporation are very active within capillary fringes and above the water table (Nesbitt and Cramer, 1993). Therefore, salt contents of soil and shallow groundwater may increase during dry seasons (July to September) and cause chloride to reach levels where it is adsorbed or exchanged onto organic materials or minerals. Data from Trainer and Heath (1976) suggest that a tenfold increase in the concentration of chloride in shallow groundwater is easily and routinely reached in most eastern North American groundwaters during dry seasons.

Chloride is the dominant anion in the L-CHA (Figure 28), and dominates the anion concentration of the U-CHA in the northeastern coastal plain. The source of chloride in the L-CHA is SFW, as the CHAS does not contain sufficient Cl-rich minerals to account for such high chloride concentrations by dissolution. Seawater trapped when these marine sediments were deposited, or introduced during high sea level stands, has probably since been flushed out with freshwater. Amsbaugh (1995) stated that the higher chloride concentrations within the Sneads Ferry Well Field in Onslow County (SFOW 1, 2, 3, and

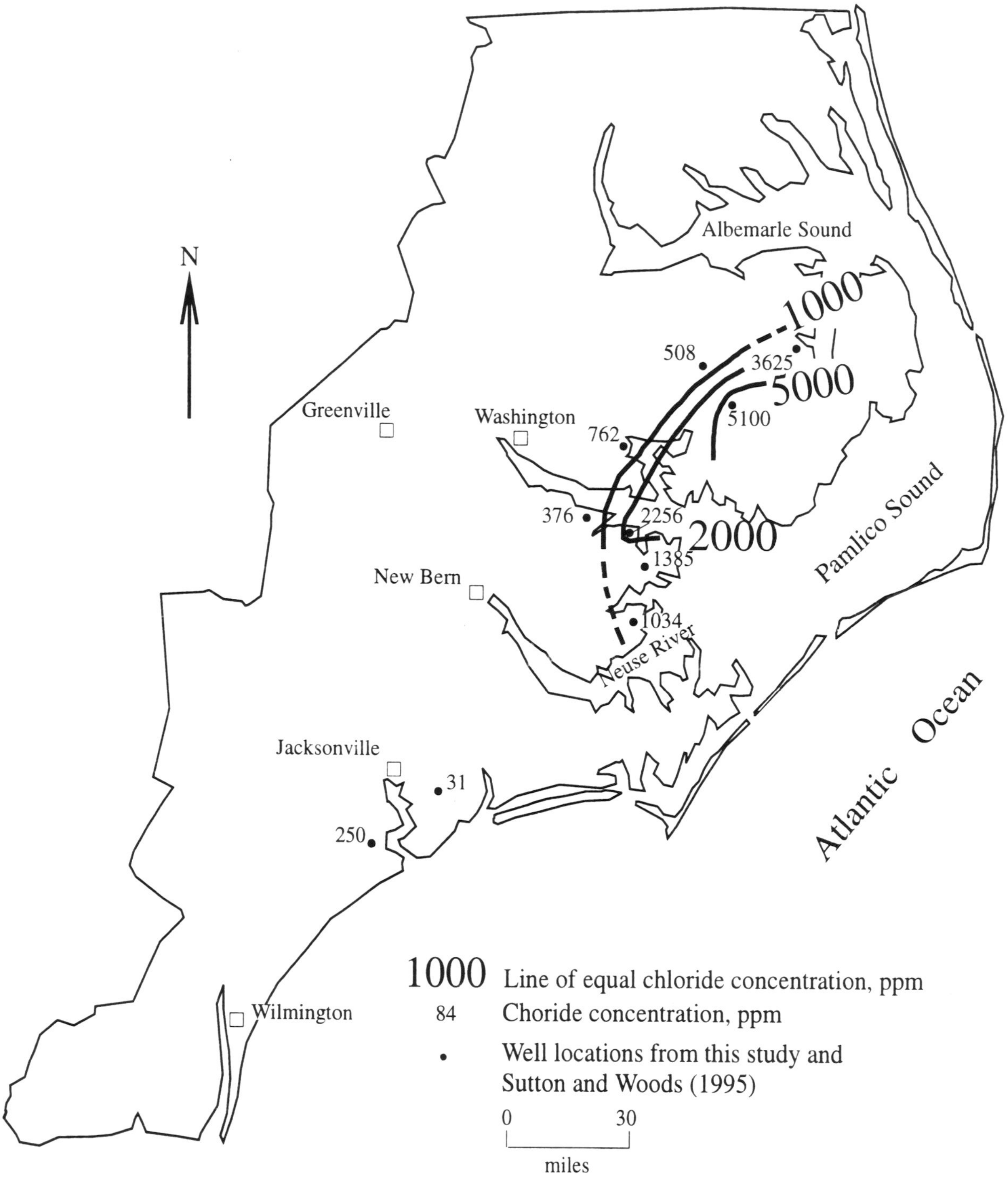


Figure 28. Chloride Concentrations in the L-CHA
North Carolina MCL is 250 ppm (NCDEHNR, 1989).

4) could be related to a leaky upper confining bed in the Cretaceous Aquifer System which directly underlies the CHAS. In the area around the PCS Phosphate (formerly Texasgulf Corp.) mine, the chloride content has increased due to the lateral encroachment of chloride-rich water from beneath Pamlico Sound, and upconing of SFW from underlying units (Reynolds, 1992; Sutton and Woods, 1995). This upconing is suggested by the 2000 ppm contour line around well TGS11A (Figure 28).

Sodium and Potassium. Sodium concentration generally increases from west to east in the U- and L-CHA, north of Wilmington (Figures 29 and 30). In this area the greatest concentrations are in the northeast section. U-CHA sodium data from Knobel (1985) were compared to Sutton and Woods (1995) data to see if there were any noticeable changes due to pumping at PCS Phosphate. Wells sampled prior to pumping (1965) didn't show an increase in sodium concentration when sampled by Sutton and Woods in 1993 (Knobel average 38 ppm; Sutton and Woods average 22 ppm). This pattern is disrupted near Wilmington due to extensive pumping for municipal water supplies. Potassium exhibits the same trend as sodium (Figures 31 and 32), although the deflections in contour lines around PCS Phosphate are less pronounced for K^+.

North and south of the Neuse River, potassium and sodium concentrations in the western part of the study area are low but still too high to be due to rainfall (0.15 ppm K^+; 0.64 ppm Na^+). The high concentrations can probably be explained by:

1) dissolution of soil salts (as discussed in the previous section),

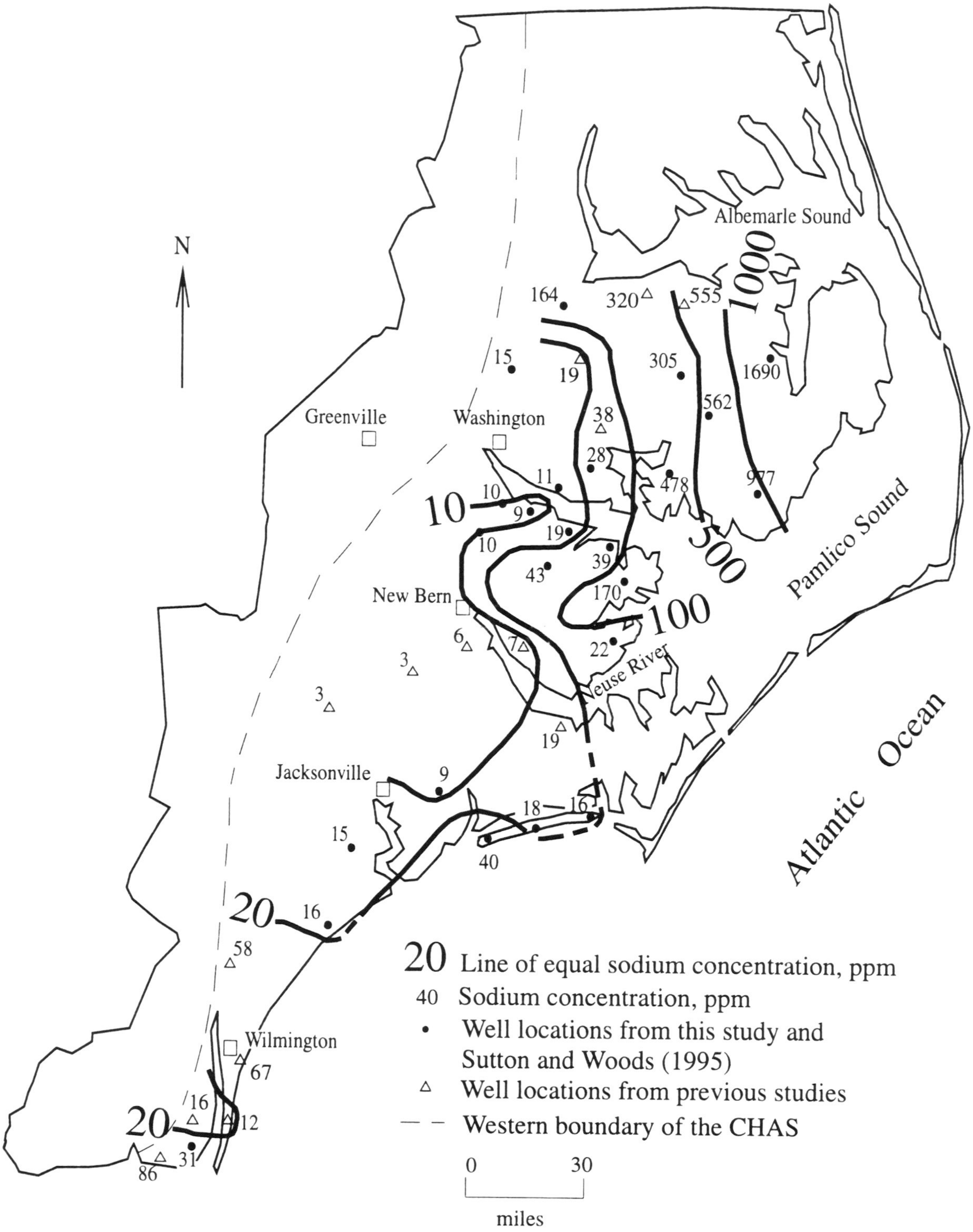


Figure 29. Sodium Concentrations in the U-CHA

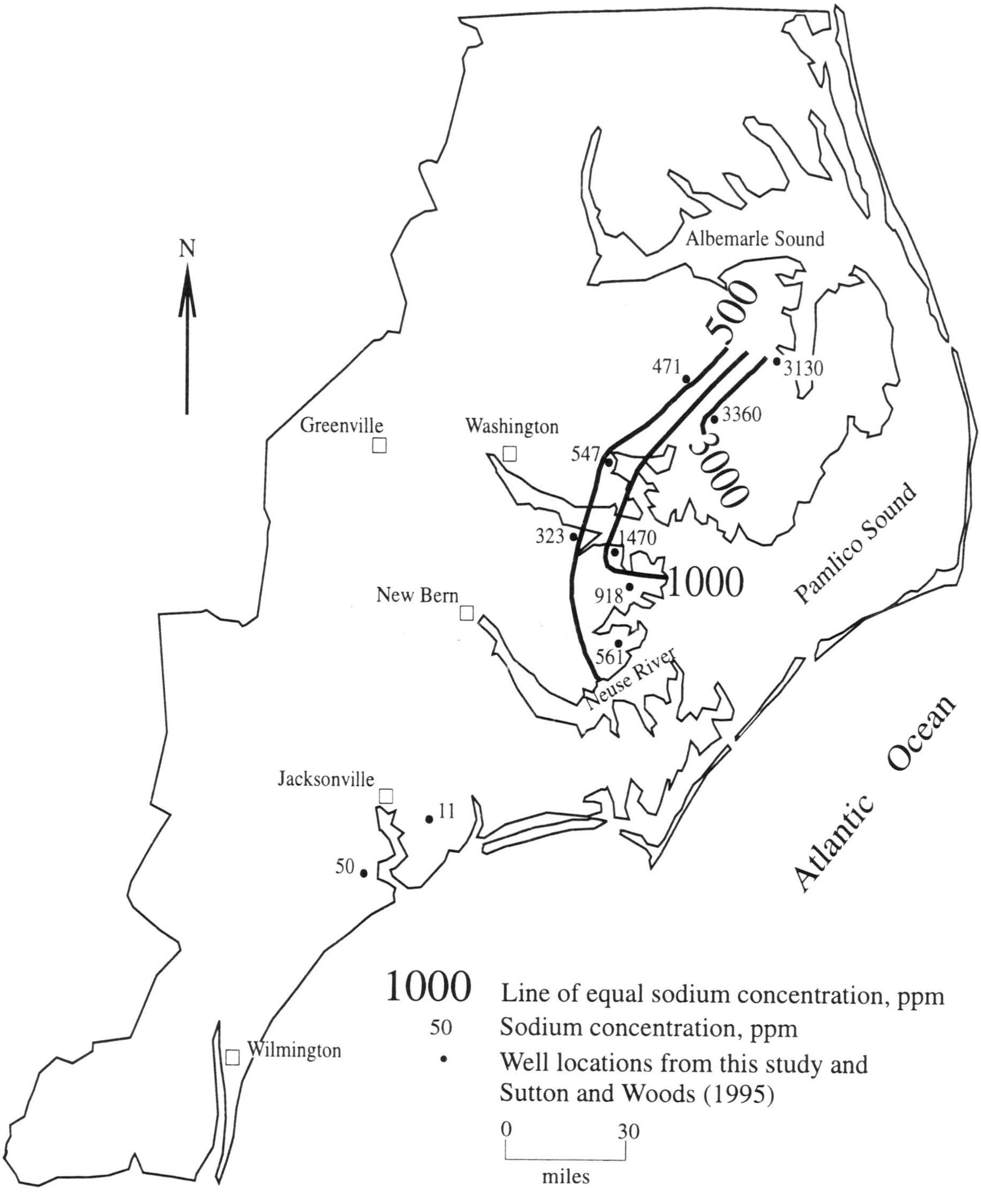


Figure 30. Sodium Concentrations in the L-CHA

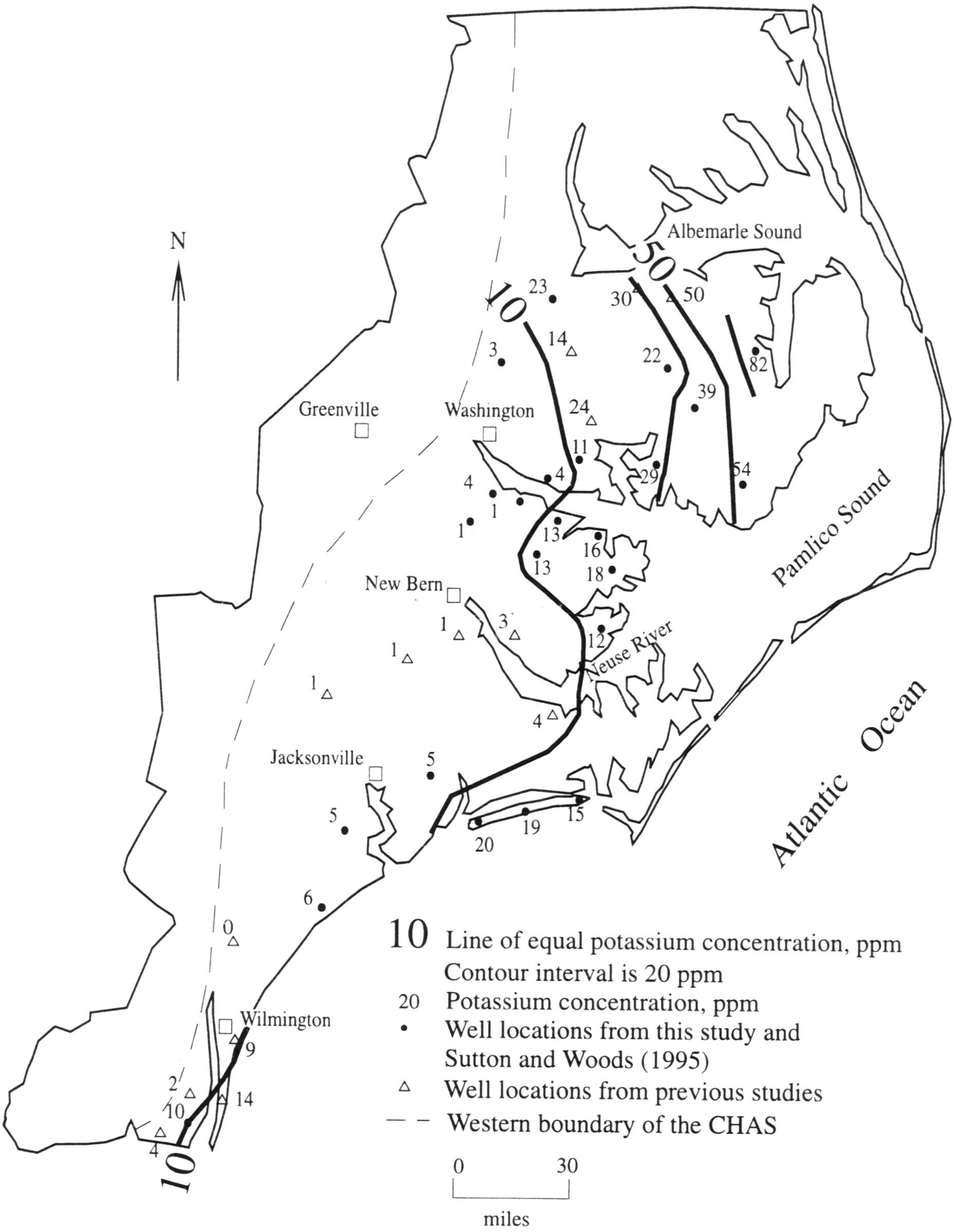


Figure 31. Potassium Concentrations in the U-CHA

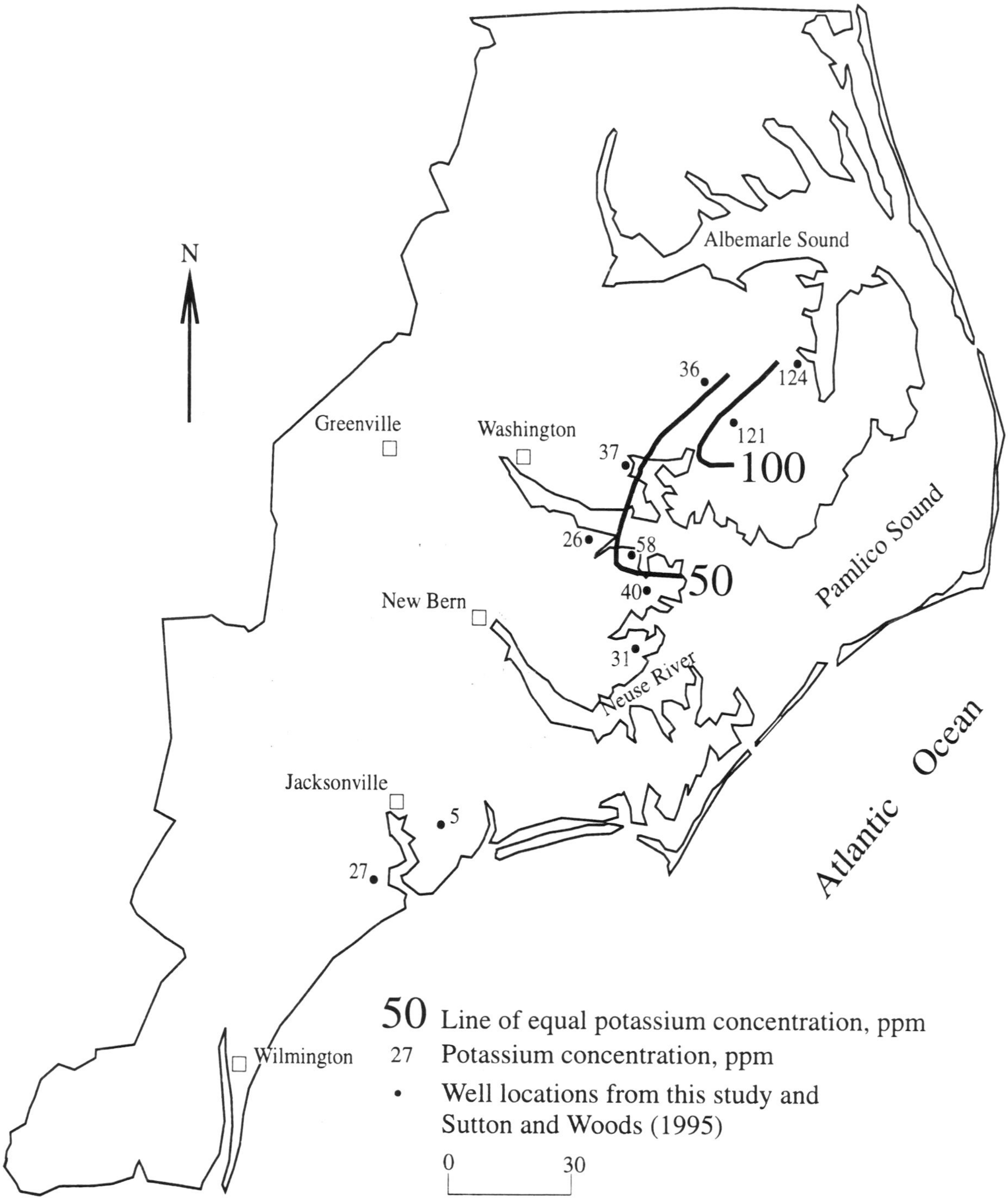


Figure 32. Potassium Concentrations in the L-CHA

2) cation exchange reactions, where $2Na^+$ and $2K^+$ in clays are exchanging for Ca^{2+} in water from the aquifer (Katz, 1992), and
3) leaching of K^+ and Na^+ from fertilizers applied to soils (Bohlke and Denver, 1995).

North and south of the river, increasing Na^+ and K^+ concentrations to the east are due to mixing with SFW.

The Na^+/Cl^- molar ratios range from 0.17 to 9.04 and 0.31 to 0.99 for the U-CHA and L-CHA, respectively (Figures 33 and 34). Ratios much higher than the seawater ratio (0.86), which occur in areas where clay minerals are known to be present, were used as evidence for exchange of $2Na^+$ for Ca^{2+} by Sprinkle (1989). Evaporated precipitation recharging the system may also have caused the elevated ratios to the west. The cause for the low ratio seen in well BB5 is not fully understood. In L-CHA wells, the Na^+/Cl^- ratios are less than those in the U-CHA and all but four are less than or equal to the seawater ratio.

The K^+/Cl^- molar ratio of seawater is 0.02. U-CHA ratios approach this value in most of the easternmost wells, and all L-CHA waters approximate this ratio except for wells in the SF and HB well fields (Figures 35 and 36). The potassium and chloride in the SF and HB wells may be contributed by rainwater, which has a K^+/Cl^- ratio of 0.11 in eastern North Carolina (Willey and Kiefer, 1993). The concentrations, however, are higher than those in the rainwater, indicating that some K^+/Cl^- ratios in the CHAS may have originated by evaporation of rainwater. Most western wells in the U-CHA have ratios in the range of the rainwater ratio (0.11). Where the K^+/Cl^- ratios are high, K^+ could

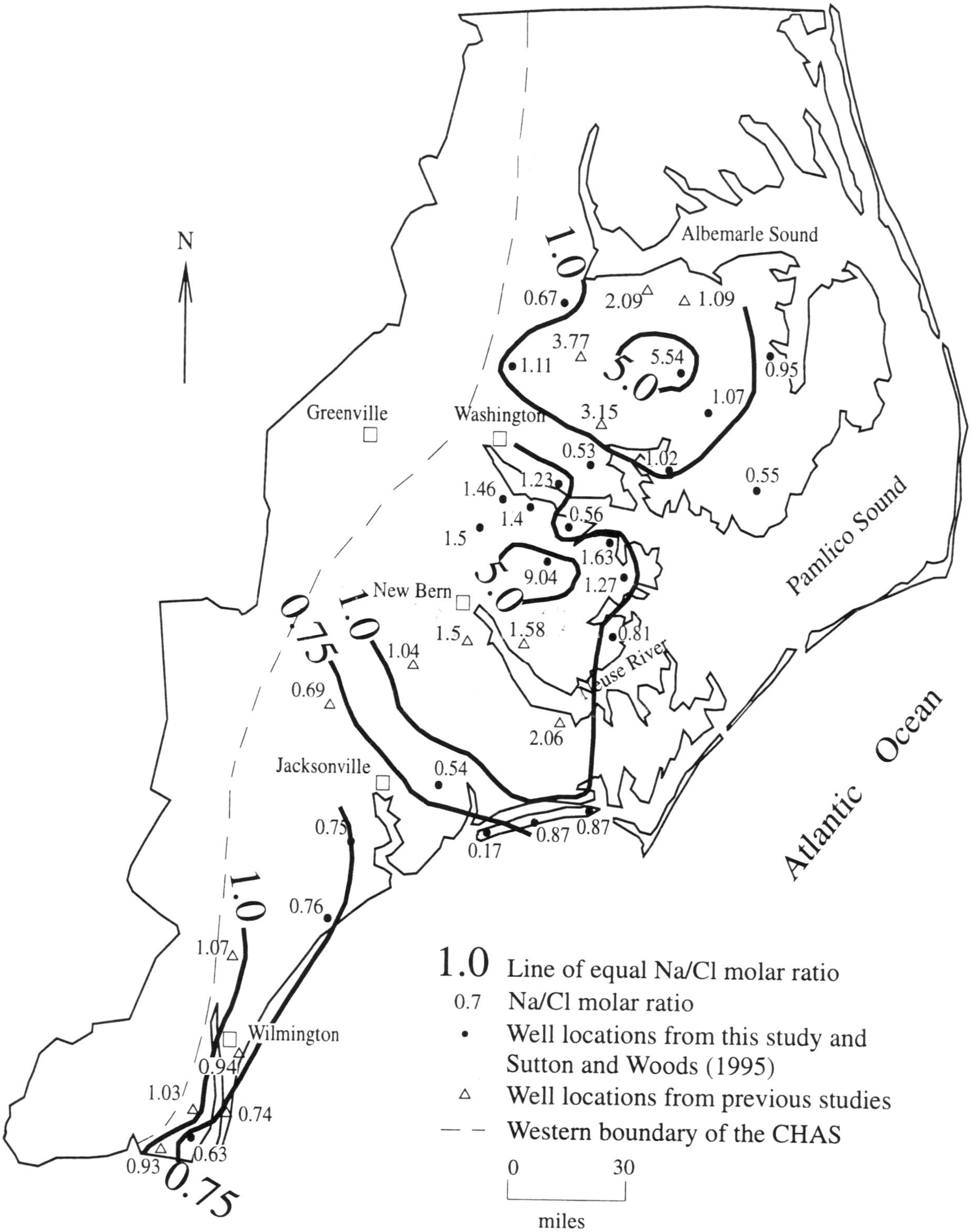


Figure 33. Molar Ratio of Na/Cl in the U-CHA
The molar ratio for seawater is 0.86.

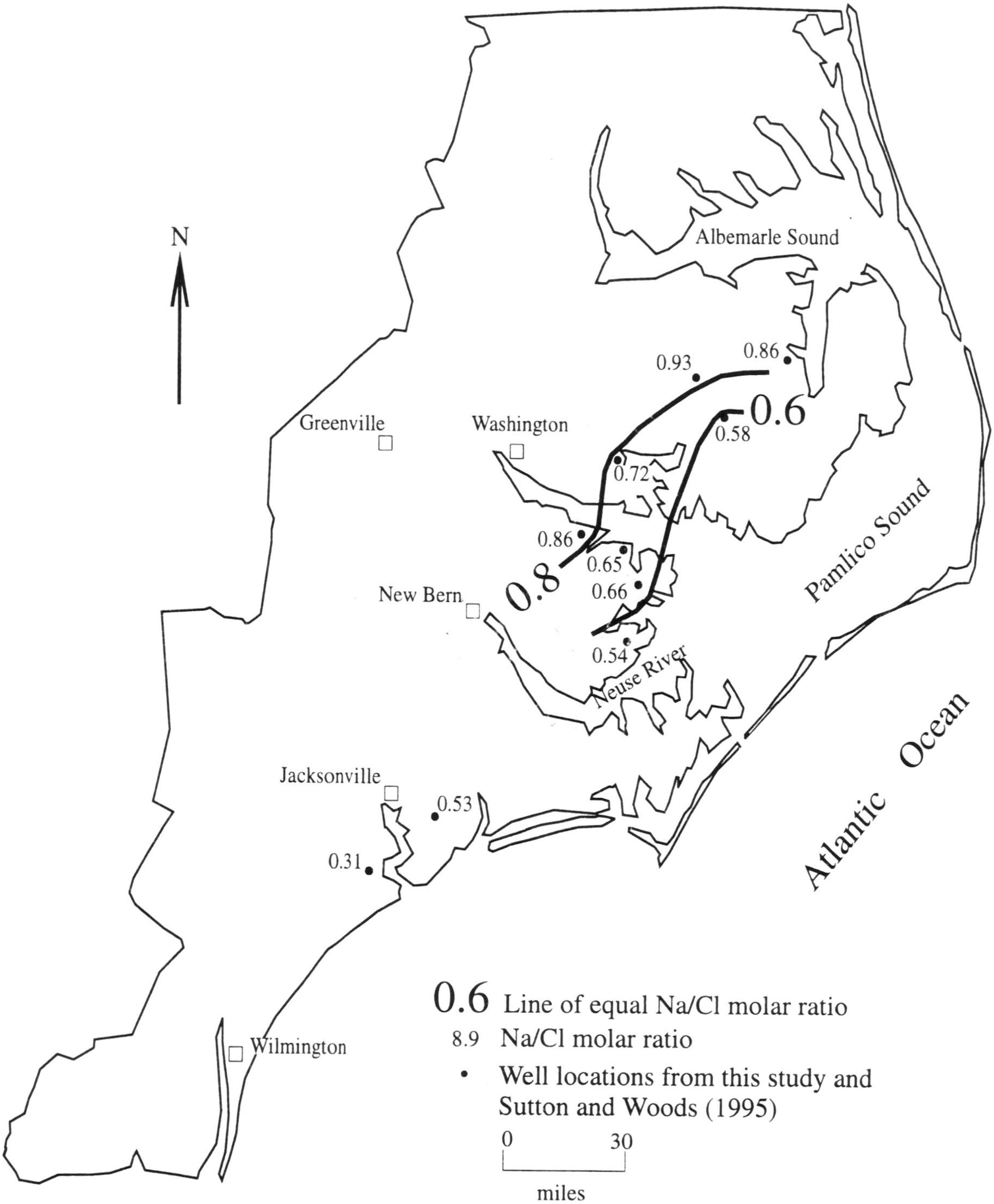


Figure 34. Molar Ratio of Na/Cl in the L-CHA
The molar ratio for seawater is 0.86.

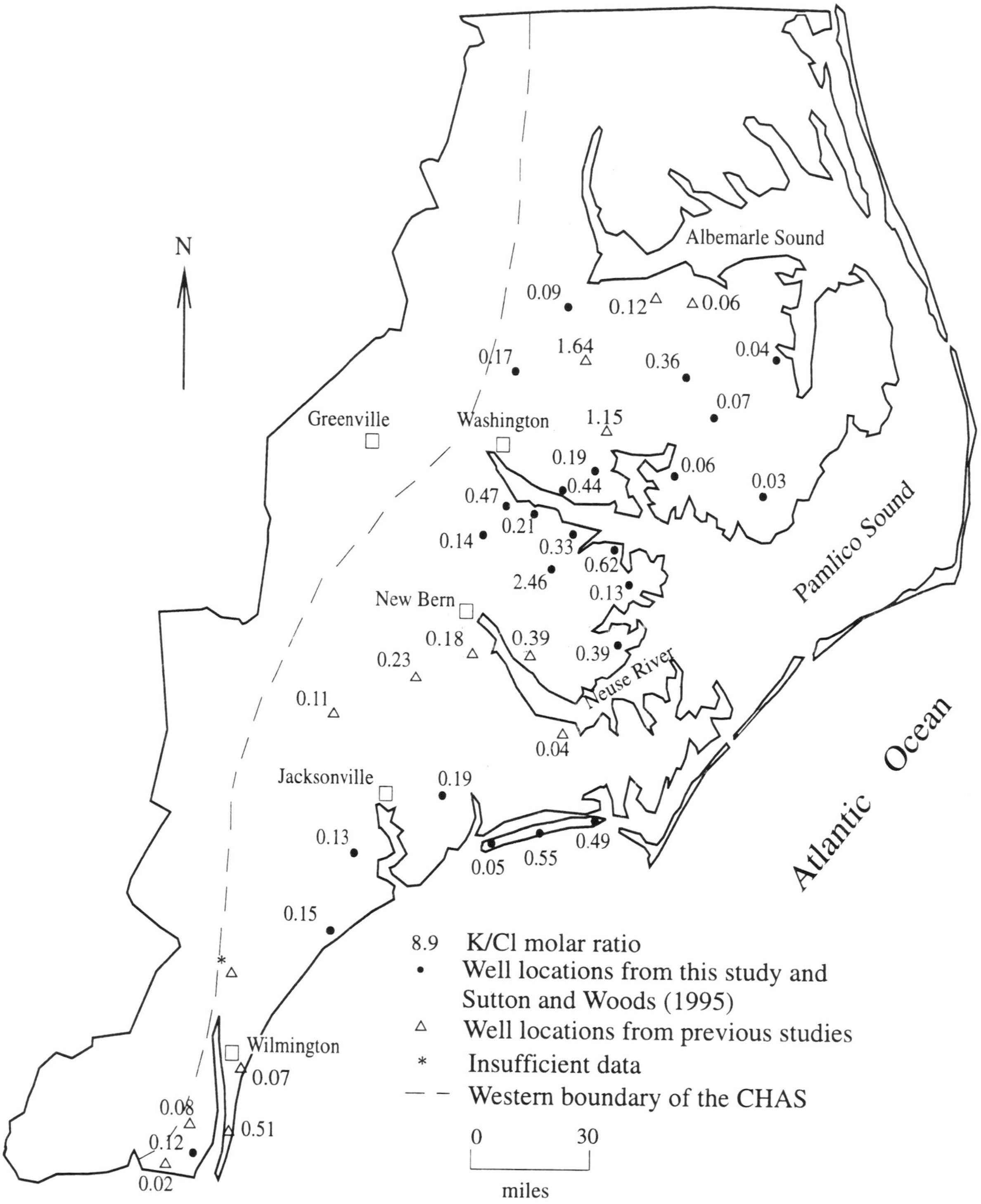


Figure 35. Molar Ratio of K/Cl in the U-CHA
* Indicates that potassium data were not available.
The molar ratio for seawater is 0.02.

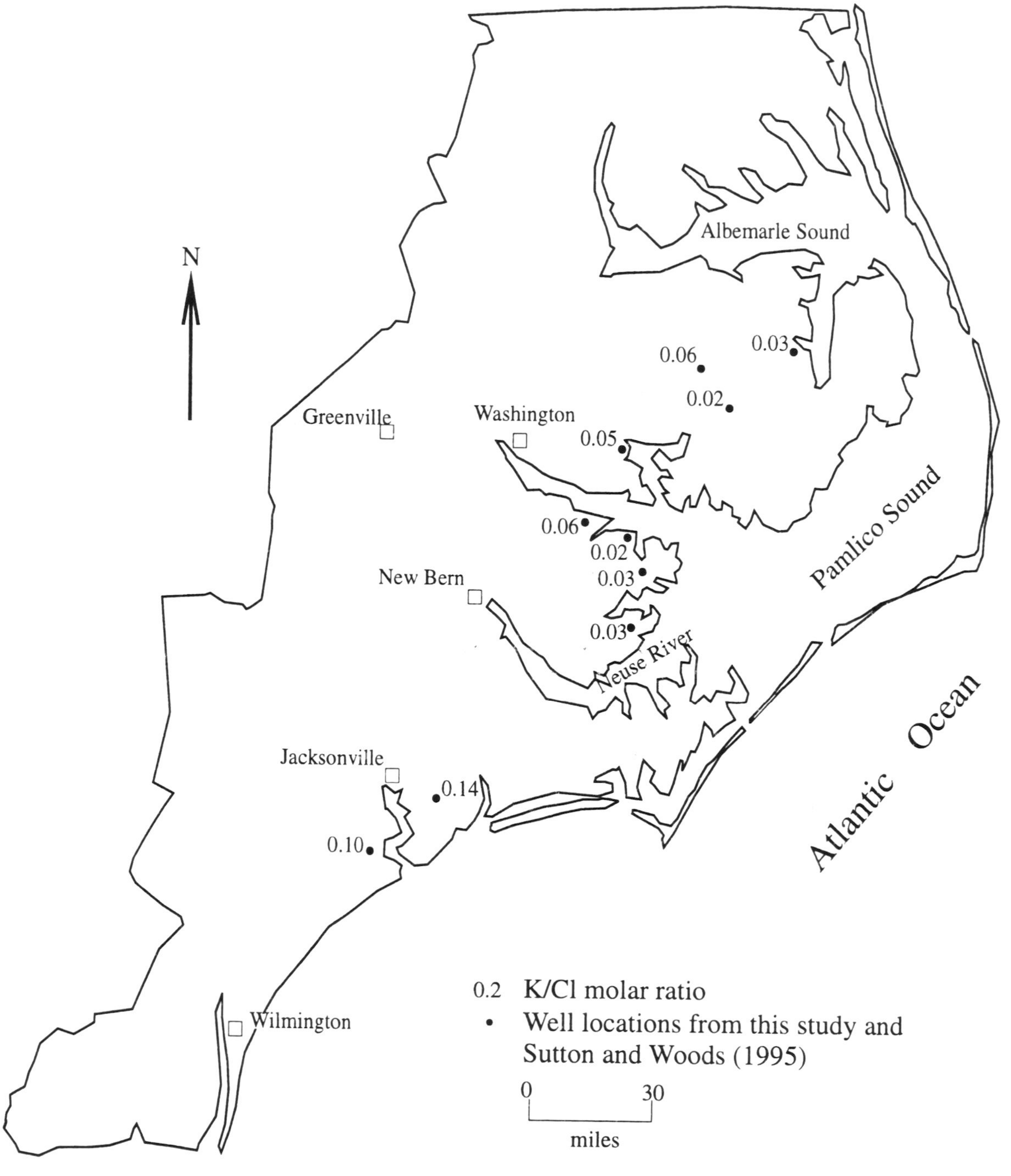


Figure 36. Molar Ratio of K/Cl in the L-CHA
The molar ratio for seawater is 0.02.

come from dissolution of K^+-bearing minerals (glauconite), ion exchange ($2K^+$ for Ca^{2+} or Mg^{2+}), or leaching of fertilizers (Chapelle and Knobel, 1983; Bohlke and Denver, 1995; Katz, 1992). Sodium and potassium concentrations both increase from west to east while calcium seems to decrease; therefore, ion exchange could be an important process influencing the water chemistry.

Silica. Except around Jacksonville, the easternmost wells in the U-CHA are generally lower in silica than wells in the western part of the study area (Figure 37). The silica concentration in seawater is 6 ppm; which partially explains the decrease from west to east. Areas with high silica concentrations occur northeast of Washington and southeast of New Bern (Figure 37). These high areas may be due to local variations in the abundance of amorphous silica in the CHAS. Concentrations up to 50 ppm are observed in the Floridan aquifer where chalcedony and aluminosilicate minerals appear to be more abundant, however Sprinkle (1989, p. I65) states, "Concentrations of dissolved silica higher than 40 mg/L may be the result of local contamination, dissolution of local sources of highly soluble silicate phases (diatom tests), or water sampling and analytical errors." The high-SiO_2 "bullseyes" (Figure 37) are centered on older data points and may reflect analytical error. Only a few determinations are available from the L-CHA (Figure 38).

Total Dissolved Solids. Throughout the study area, TDS generally increase from west to east in the Upper and Lower CHA (Figures 39 and 40), with the highest concentrations in the northeastern section. In New Hanover and Brunswick Counties TDS values decrease and then increase

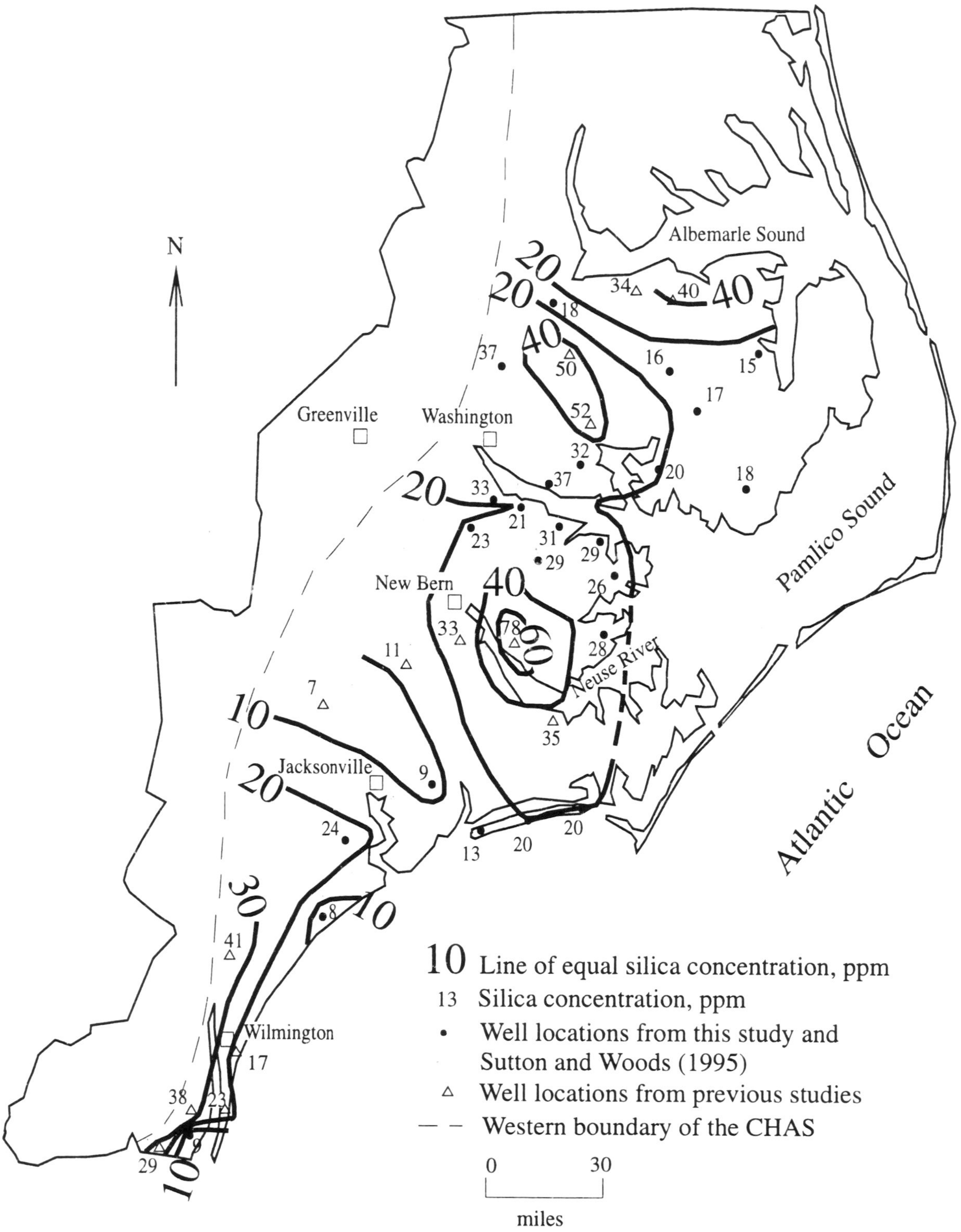


Figure 37. Silica Concentrations in the U-CHA

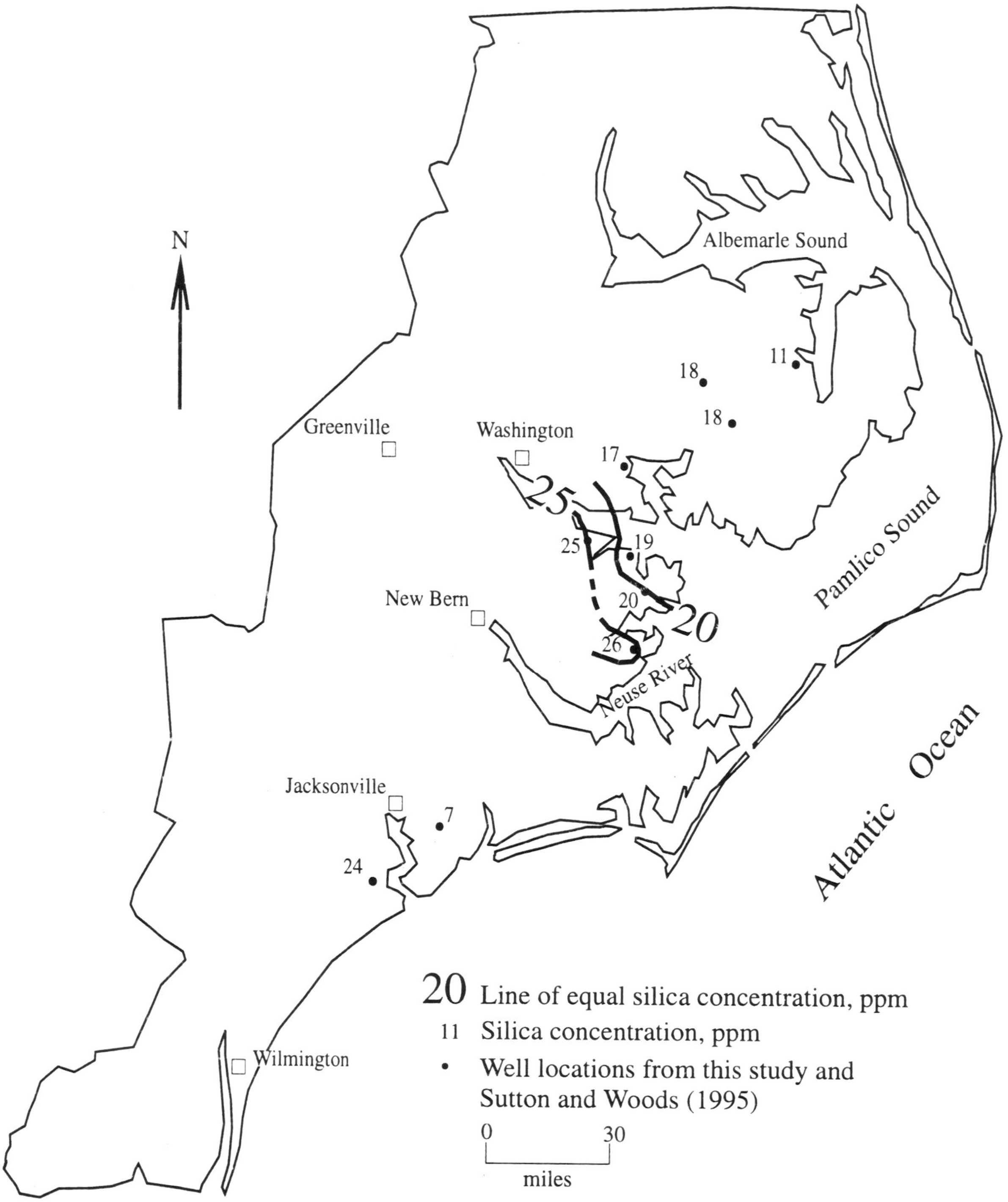


Figure 38. Silica Concentrations in the L-CHA

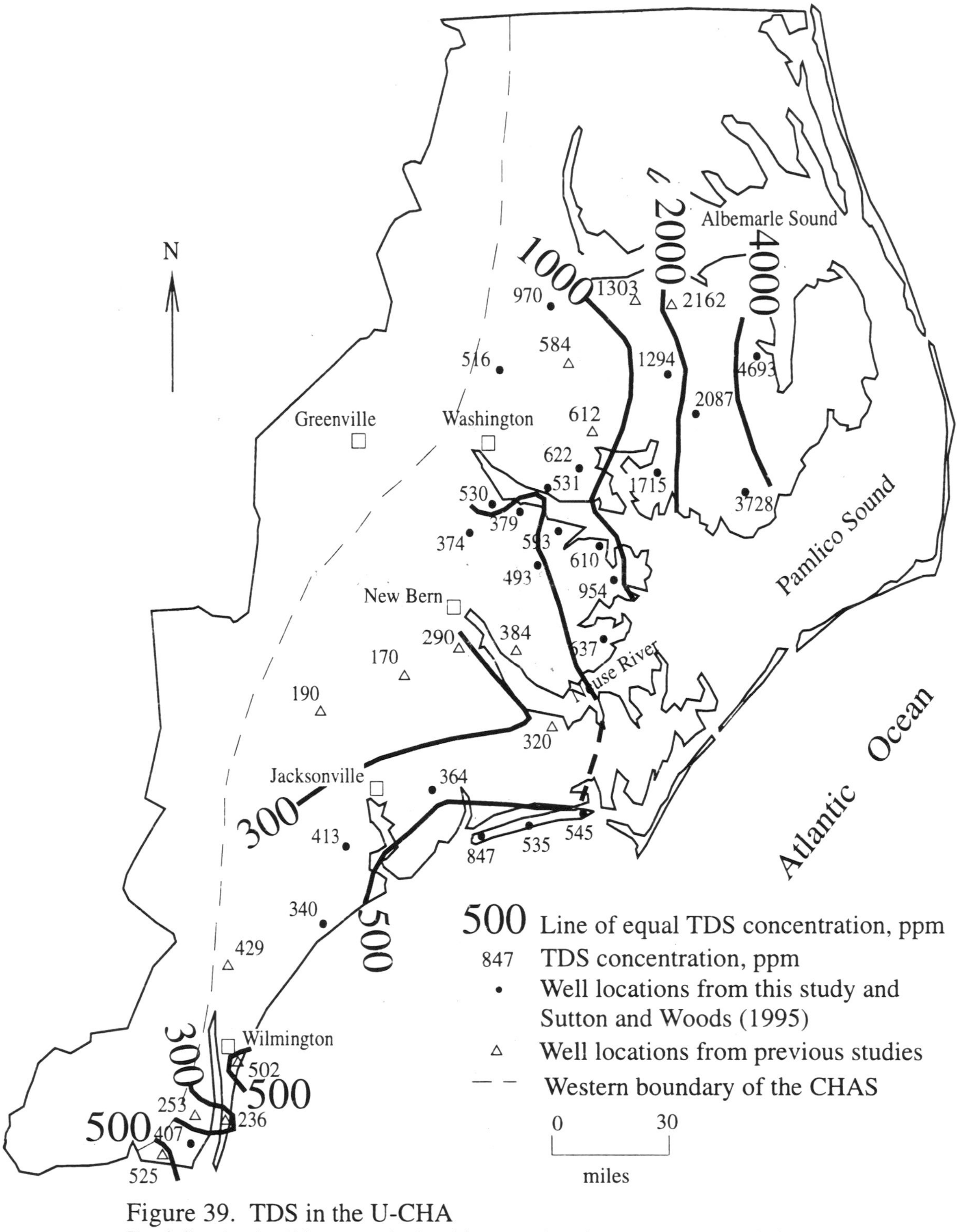


Figure 39. TDS in the U-CHA

Total dissolved solids were calculated by summing the concentrations of all ions.
The national drinking water standard is 500 ppm (Driscoll, 1986).
Water with a TDS concentration less than 1,000 is considered fresh, and water with a TDS concentration of 1,000 - 10,000 is considered brackish (Driscoll, 1986).

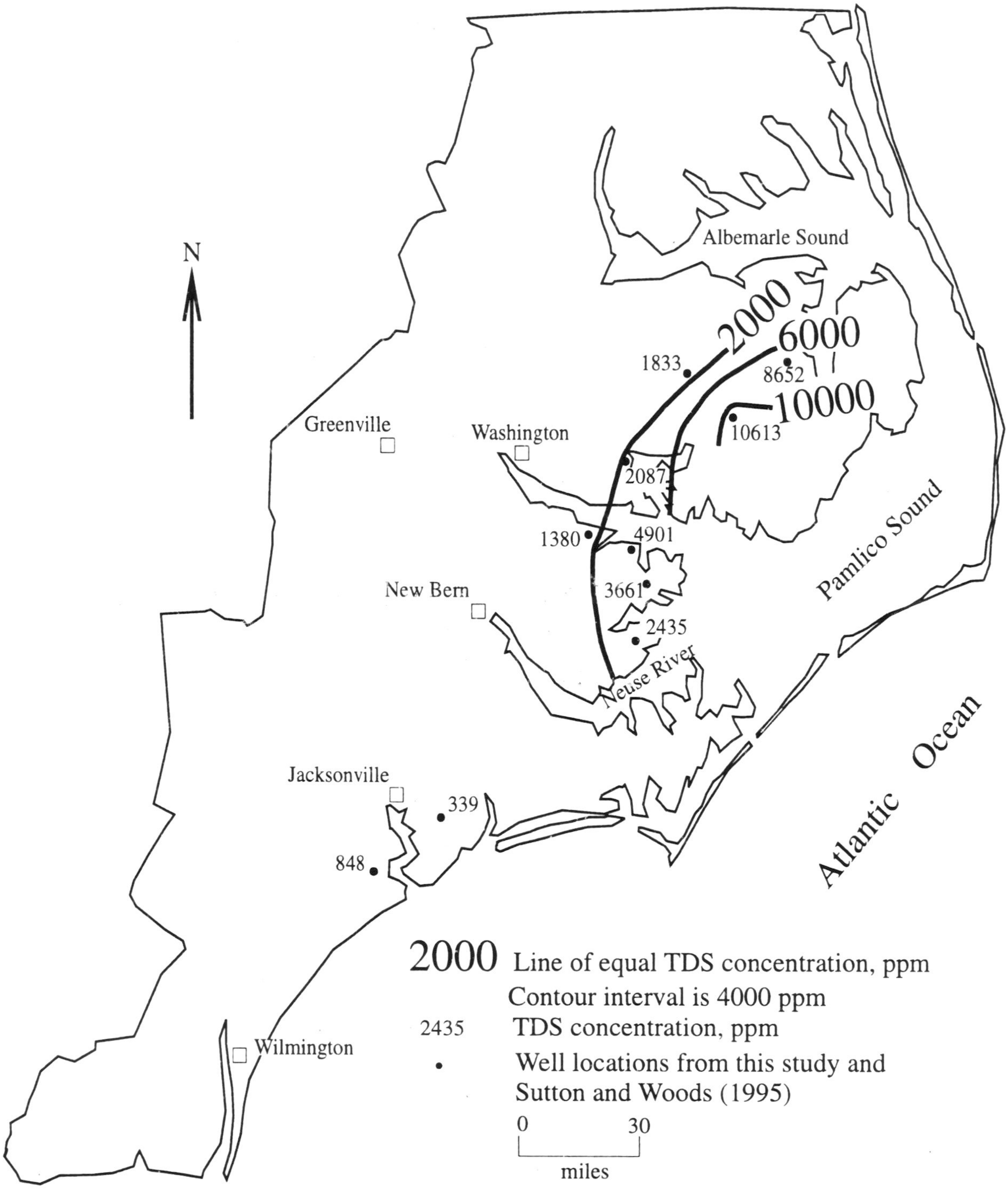


Figure 40. TDS in the L-CHA
Total dissolved solids were calculated by summing the concentrations of all ions.
The national drinking water standard is 500 ppm (Driscoll, 1986).
Water with a TDS concentration of 1,000-10,000 is considered brackish,
and water with a TDS concentration of 10,000-100,000 is considered saline (Driscoll, 1986).

again from southwest to northeast. Excessive pumping of municipal wells near Wilmington may explain the variations in that area. The contour pattern is very similar to those for chloride, sodium, and sulfate. The eastward increase in TDS is due to mixing with SFW, derived from seawater (TDS; 34,500 ppm).

Minor Constituents

Fluoride. Fluoride concentrations generally increase from west to east in the U-CHA (Figure 41); U-CHA wells in the northeast corner generally have higher concentrations than L-CHA wells (Figure 42). Upper and Lower CHA wells north of the Neuse River have higher concentrations than wells south of the Neuse River. This could be due to carbonate fluorapatite in the CHAS or Pungo River Formation which is not present south of the Neuse River except in eastern Craven and Carteret Counties (Giese and others, 1991; Riggs, 1979, 1984). In wells L13i1 and M12l1, fluoride concentrations are higher than in surrounding wells. The high fluoride seen at these wells could be caused by acidic recharge waters dissolving fluorapatite, but phosphate levels don't indicate dissolution. The fluoride concentration of seawater is 1.3 ppm, which could be a source of fluoride to these waters, but ion exchange is believed to be the major geochemcial process affecting fluoride levels.

Iron and Sulfide. Iron enters groundwater in recharging surface waters which dissolve iron compounds in the soil largely mediated by microbial processes (Chapelle, 1993; Wilder and others, 1978). Dissolved iron in groundwater is ferrous (Fe^{2+})

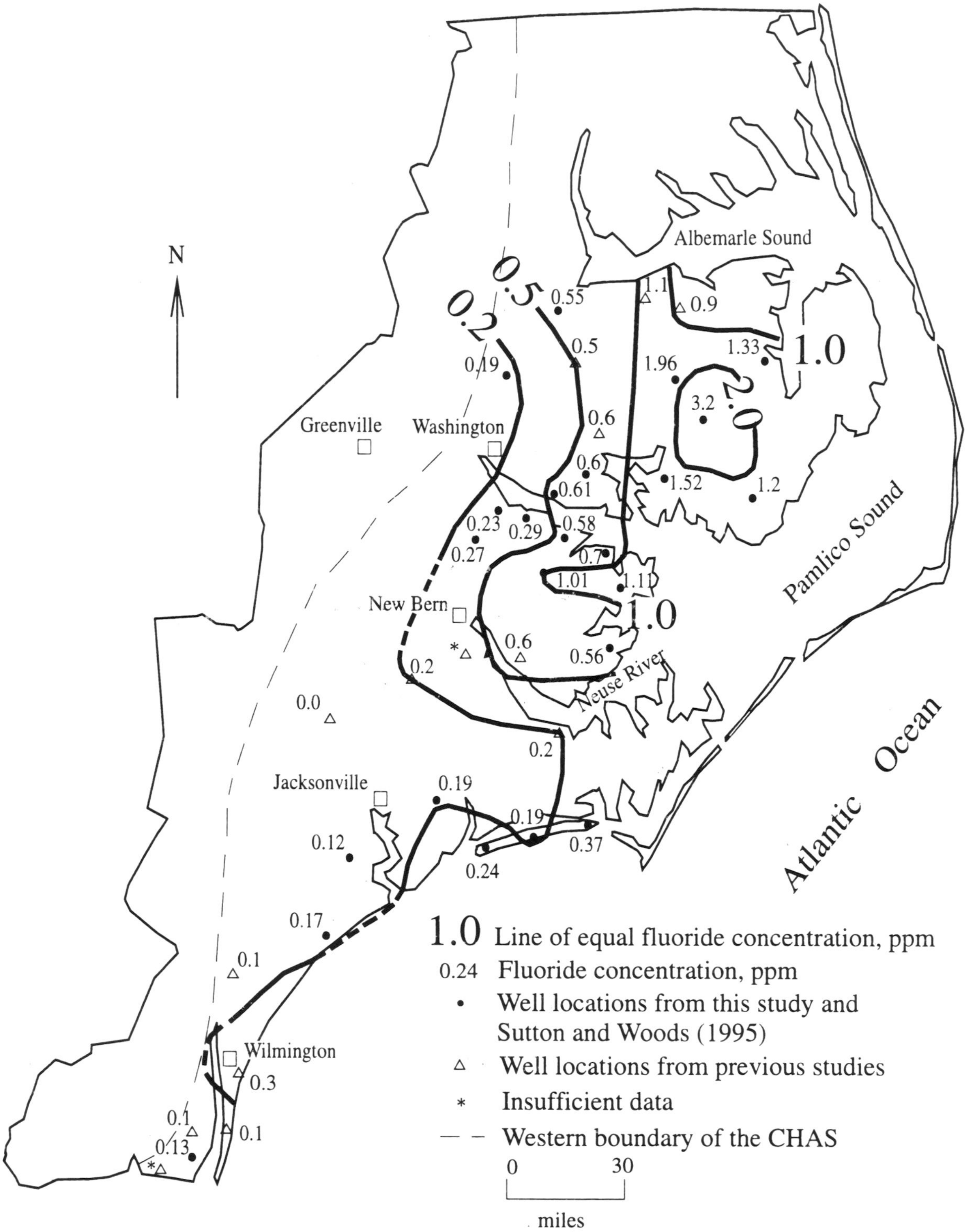


Figure 41. Fluoride Concentrations in the U-CHA
* Indicates that fluoride data were not available.
North Carolina MCL is 2.0 ppm (NCDEHNR, 1989).

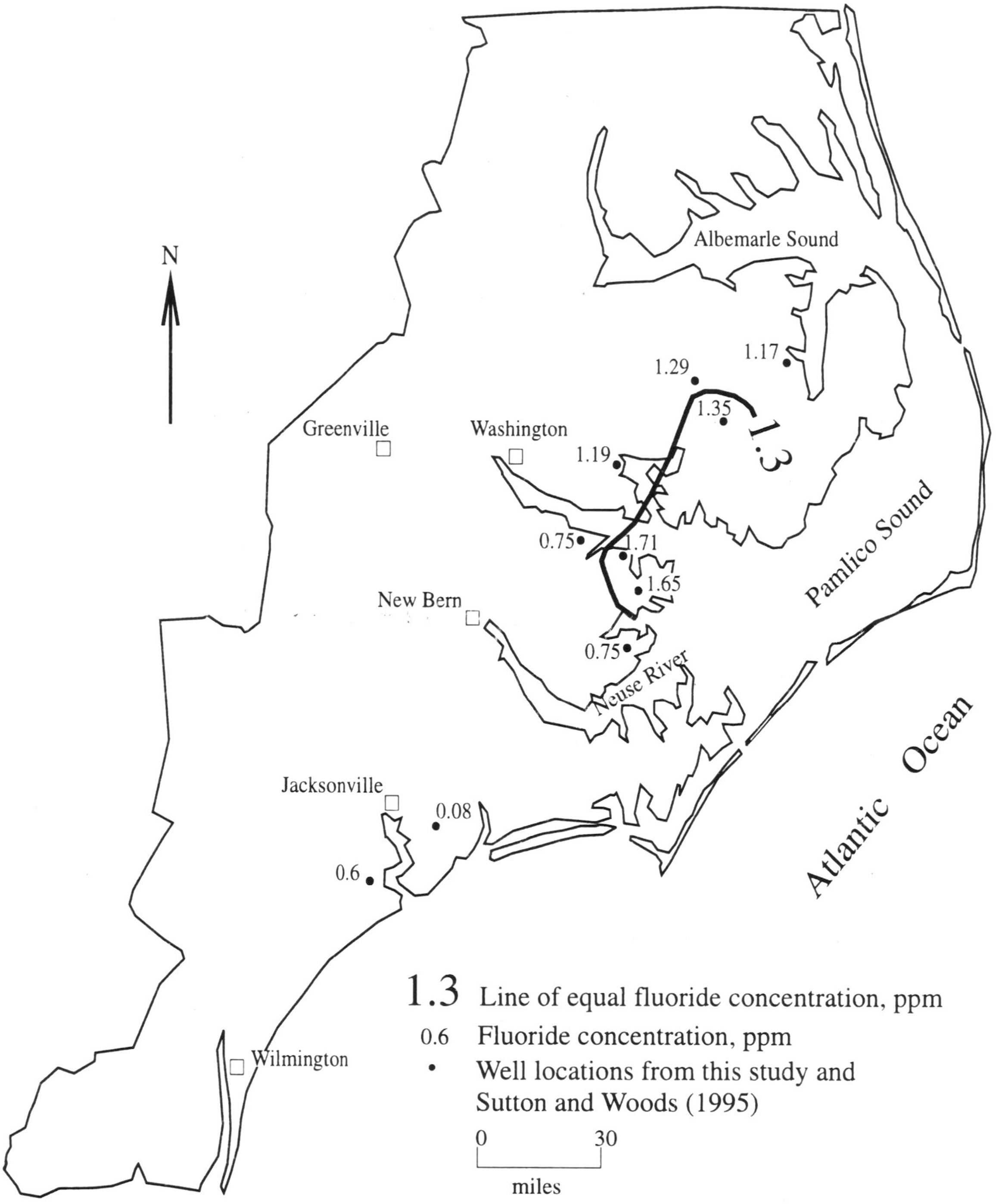


Figure 42. Fluoride Concentrations in the L-CHA
North Carolina MCL is 2.0 ppm (NCDEHNR, 1989).

and/or ferric (Fe^{3+}) ions (Chapelle, 1993). Ferric is highly insoluble and mobile only in strong acidic environments, while ferrous is much more soluble and mobile under a wide range of pH conditions (Chapelle, 1993). Once iron enters the groundwater it can undergo oxidation and reduction; both are microbially catalyzed.

Iron concentrations are highest in the western wells of the U-CHA (Figure 43). The reason for the high iron in the western wells is probably contributed to acidic recharge waters reducing Fe(III) hydroxide compounds ($Fe(OH)_3$) that are present in the surficial sediments. Amsbaugh (1996) noted the presence of iron rich sand between 15 and 30 feet below land surface in Onslow County. Along with acidic recharge waters microrganisms can reduce Fe(III) to Fe(II) within anaerobic environments (Chapelle, 1993). The reduced Fe(II) is more mobile which allows it to flow down gradient in the aquifer. There is no evidence of Fe(II) oxidation in the CHAS, therefore another geochemcial process must be responsible for the decreasing iron eastward. This process is probably cation exchange, where the Fe(II) is adsorbed by the aquifer materials and other cations (Na, Mg, and Ca) are released into solution. Abundant iron-rich glauconite is observed in core samples from the CHAS in the northern coastal plain (Tolen, in progress). Limited data inhibit clarification of the trend in iron concentrations in the L-CHA (Figure 44).

The ferrihydrite saturation index ranged from -3.90 to +1.77 and -5.11 to +1.48 in the Upper and Lower CHAS, respectively (Figures 45 and 46). Ferrihydrite ($Fe(OH)_3$), was chosen as the most likely phase controlling iron concentration because of its abundance in natural environments (Matsunaga and others, 1993) and its higher solubility

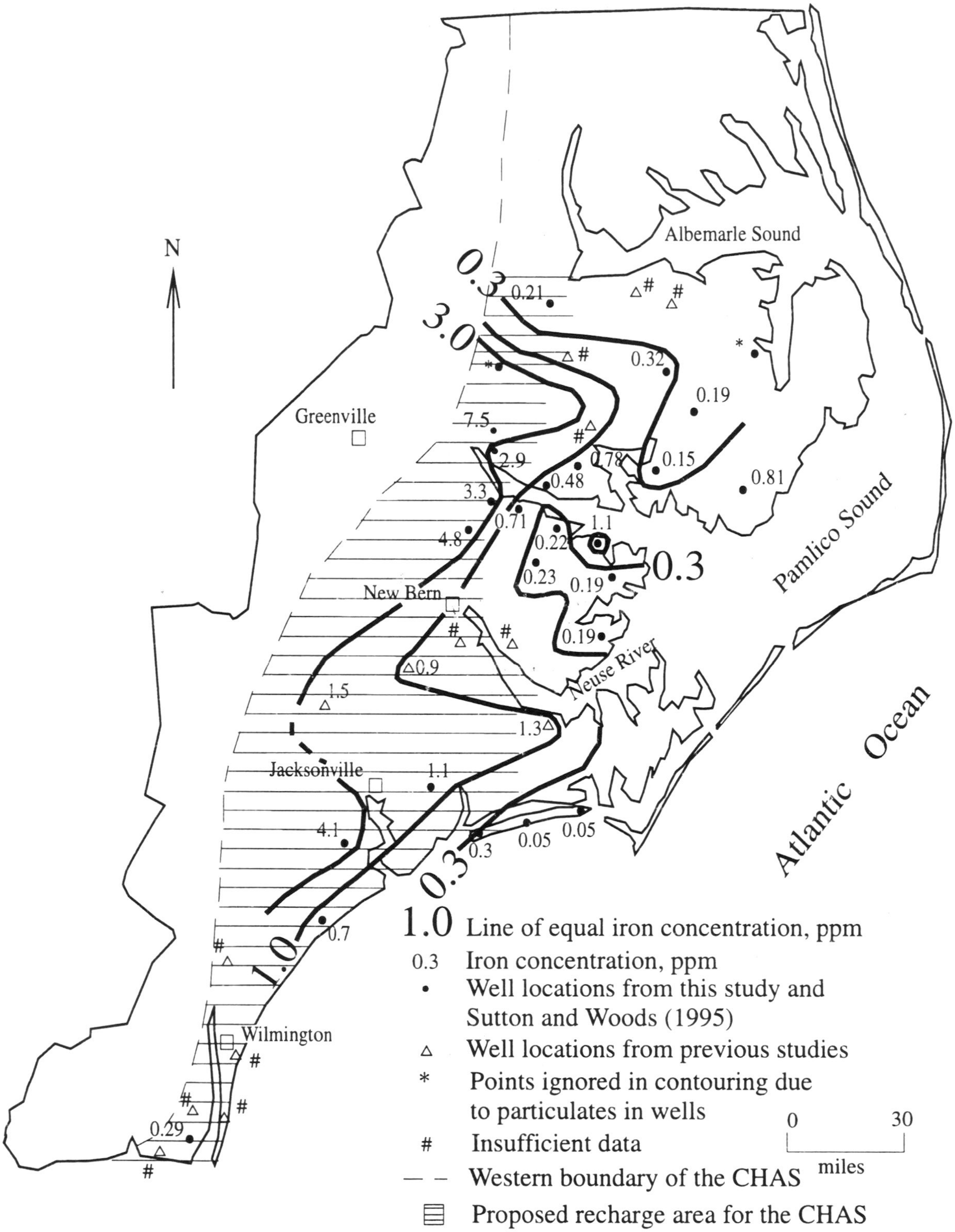


Figure 43. Iron Concentrations in the U-CHA
* Indicates that iron data were not available.
North Carolina MCL is 0.3 ppm (NCDEHNR, 1989).

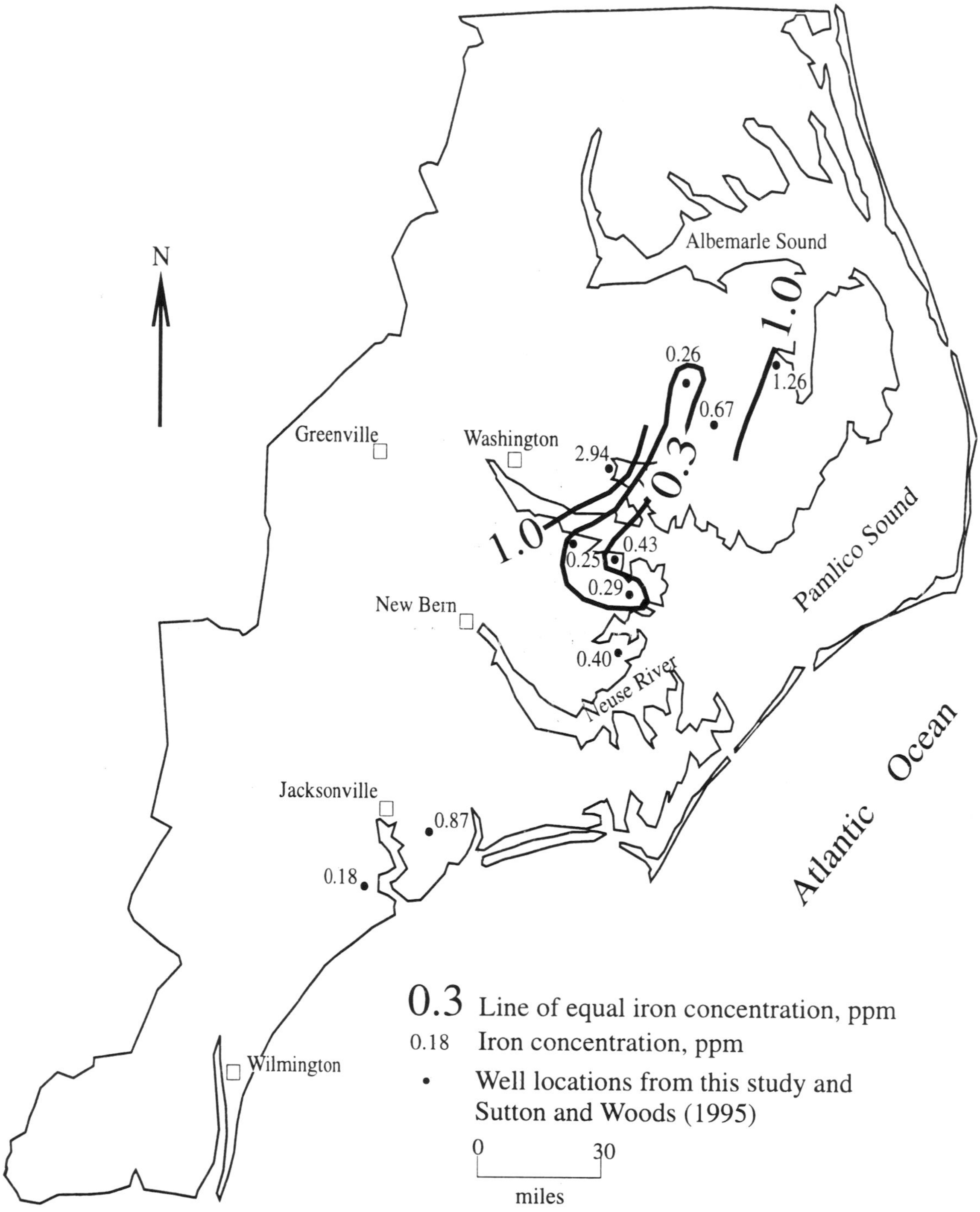


Figure 44. Iron Concentrations in the L-CHA
North Carolina MCL is 0.3 ppm (NCDEHNR, 1989).

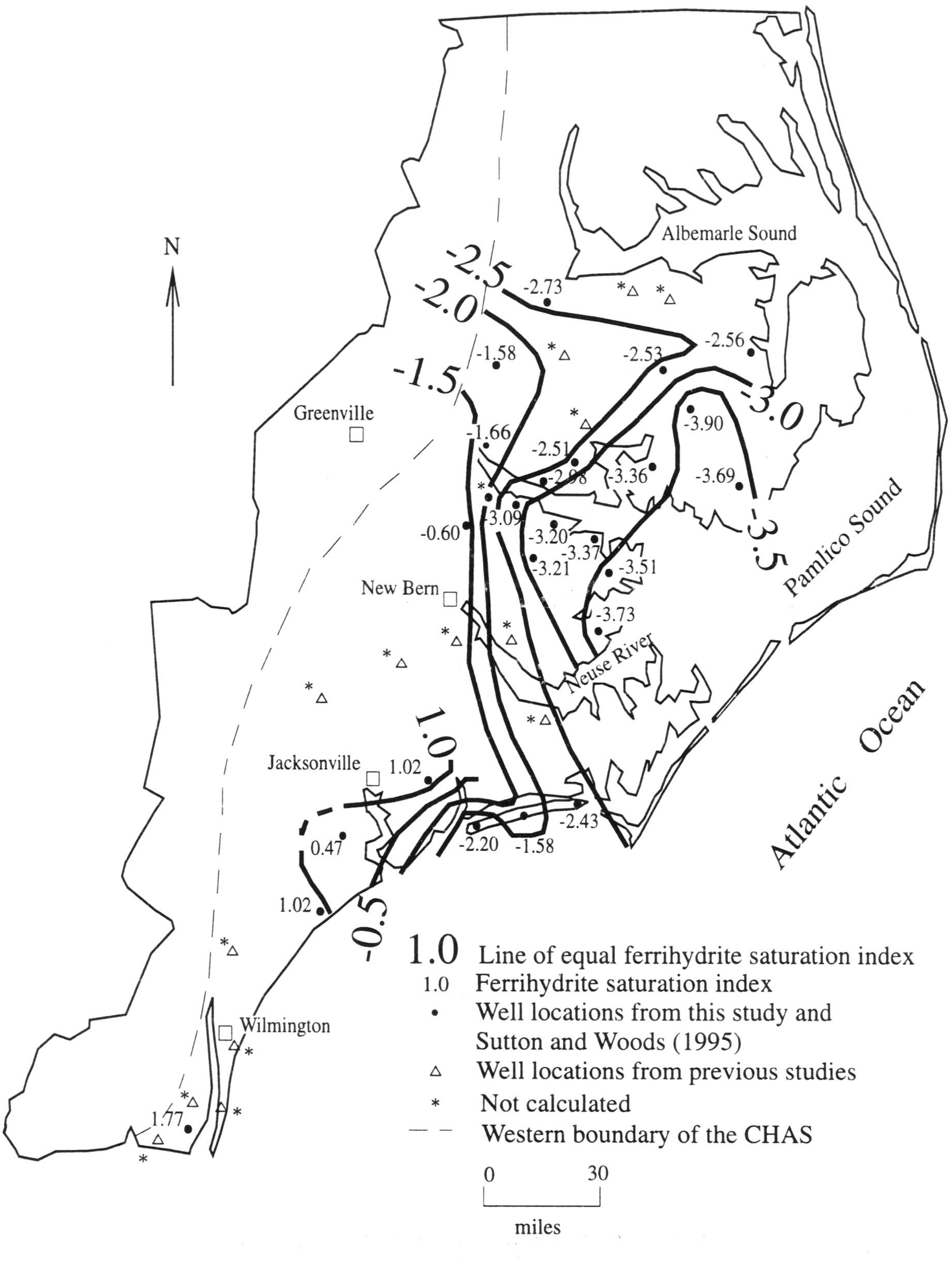


Figure 45. Ferrihydrite Saturation Index of the U-CHA
* Indicates that because of insufficient data the SI could not be determined.

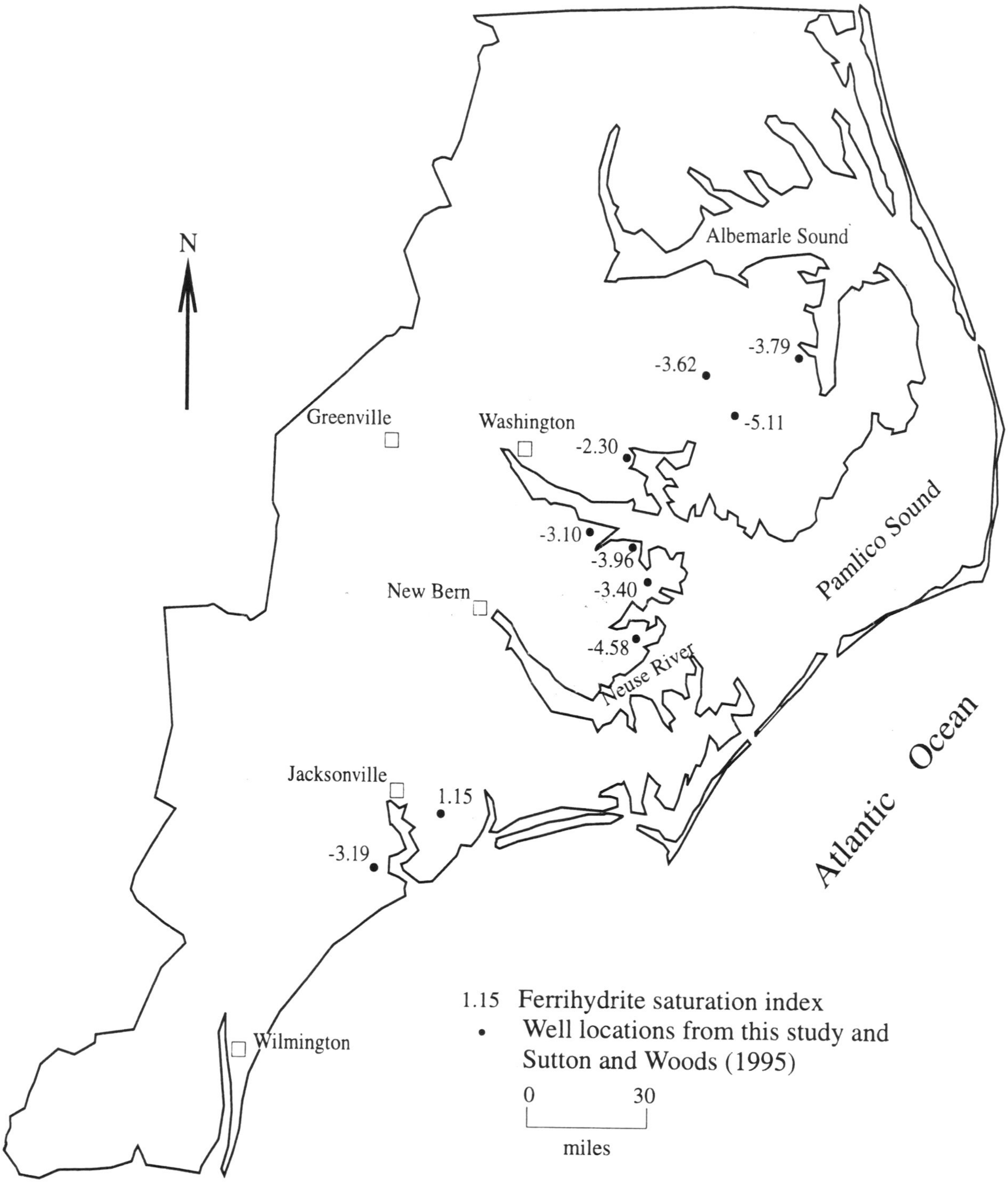


Figure 46. Ferrihydrite Saturation Index of the L-CHA

than goethite and hematite (Langmuir, 1997). Ferrihydrite also dissolves significantly faster than other Fe-oxides (goethite and hematite) (Postma, 1993). The oxidation of ferrous iron and the precipitation of ferrihydrite is shown by the following reactions:

$$Fe^{2+} + H^{+} + \tfrac{1}{4}\,O_2 \rightarrow Fe^{3+} + \tfrac{1}{2}\,H_2O$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+}$$

(Chapelle, 1993). Wells in the U-CHA north of the Neuse River are undersaturated with ferrihydrite while several wells south of the Neuse are oversaturated. The undersaturated ferrihydrite in the north supports cation exchange in the CHAS because of the unlikely hood of iron precipitating with such low SI.

Sulfide concentrations were very low; those in western wells in the U-CHA were generally lower than in eastern wells, except for TGCW-11A (5.8 ppm) (Figure 47). The average sulfide concentration in L-CHA waters is generally higher than in U-CHA waters (Figure 48). Sulfide can be generated when sulfate undergoes bacterial reduction, $SO_4^{2-} + 2C_{(org)} + 2H_2O \rightarrow H_2S + 2HCO_3^{-}$ (Drever, 1997), but the sulfide is probably rapidly removed from solution by reaction with Fe^{2+} to produce iron sulfides (Chapelle, 1993).

Ammonia and Nitrate. Ammonia concentrations show a general increase from west to east in both CHAS units (Figures 49 and 50). At locations where wells penetrated both units, concentrations in the L-CHA exceeded those in the U-CHA. Concentrations in average seawater do not exceed 0.04 ppm, so intermixing of SFW is not a likely source of the ammonia unless the saline water contains significant amounts of organic matter.

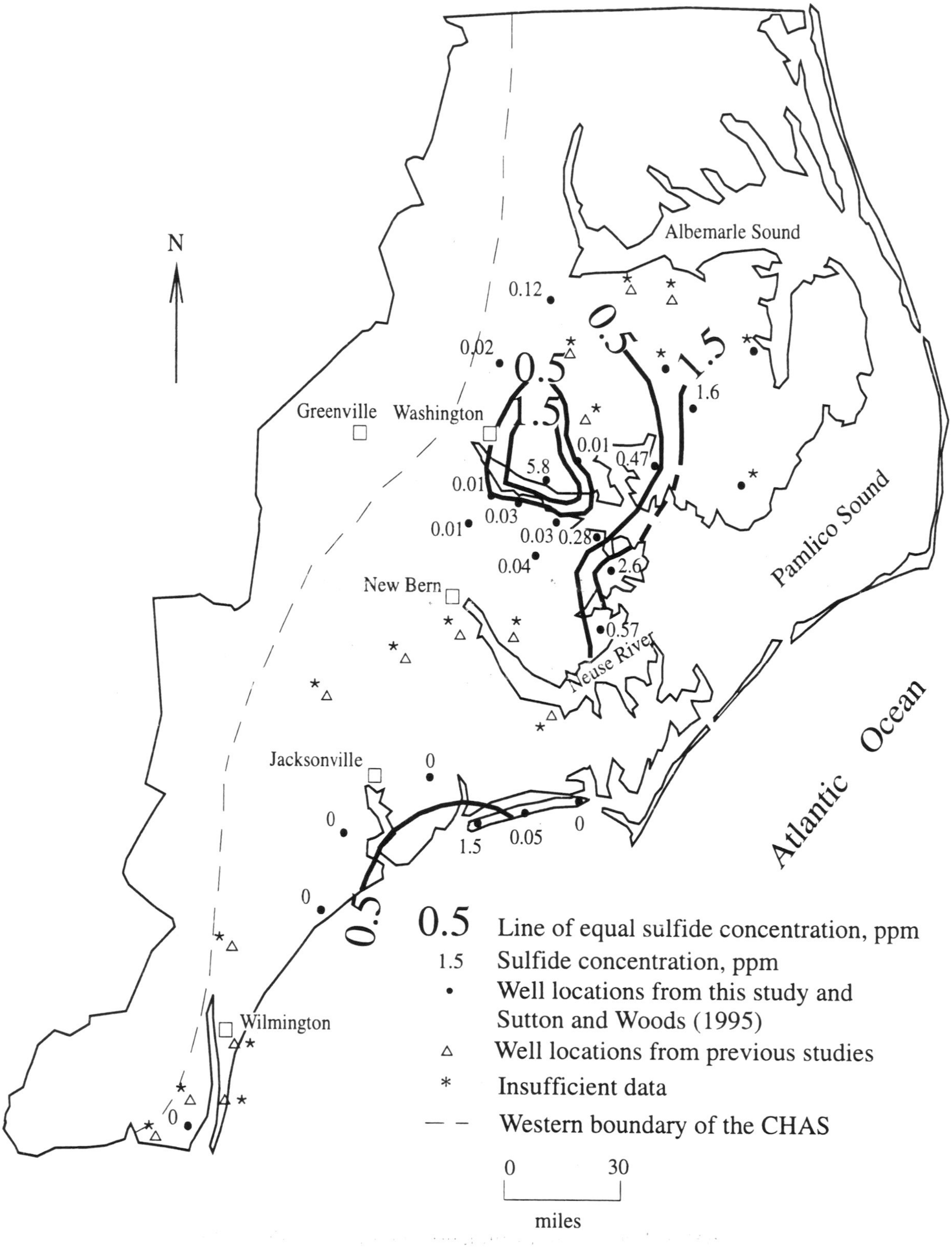


Figure 47. Sulfide Concentrations in the U-CHA
* Iindicates that sulfide data were not available.

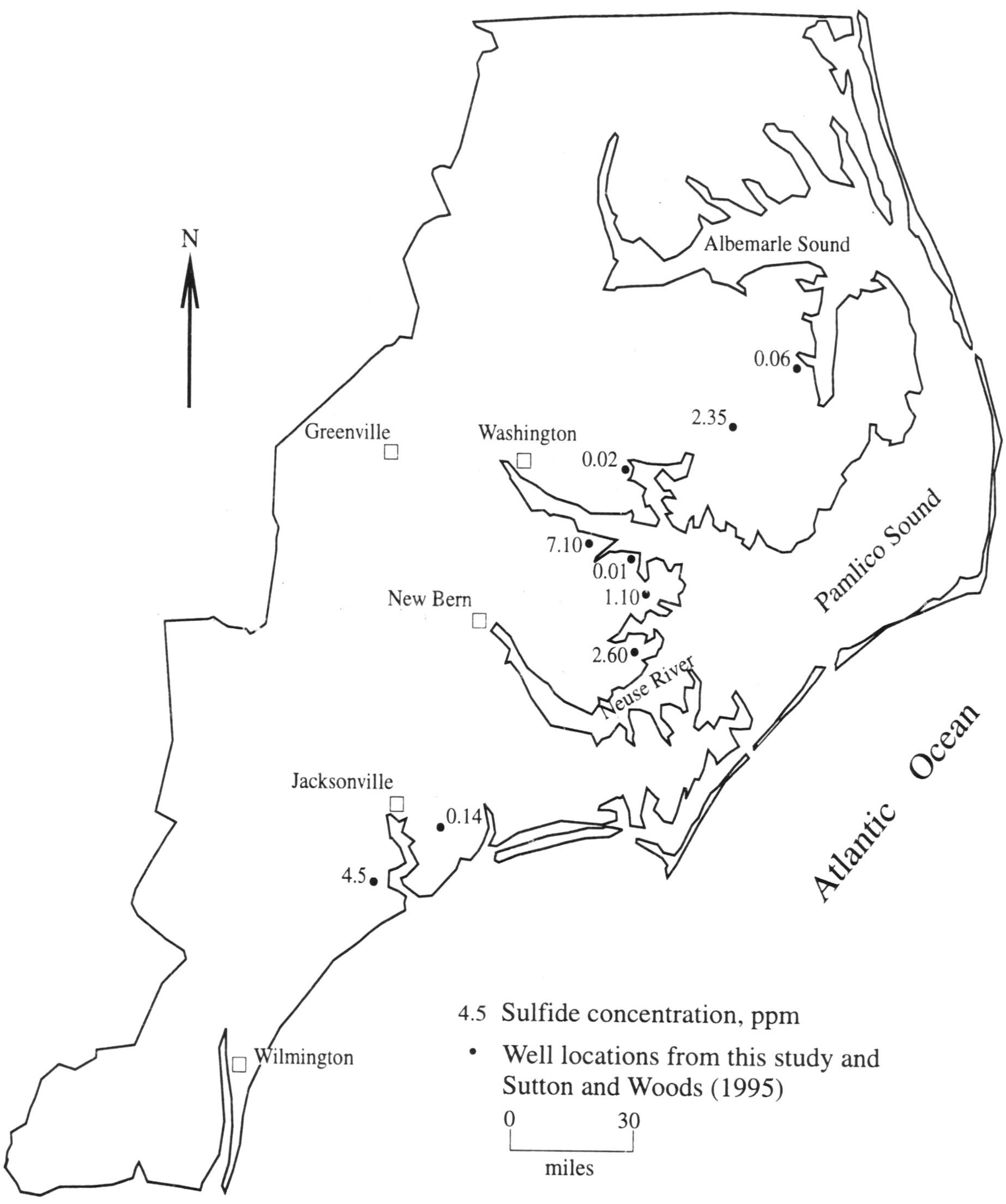


Figure 48. Sulfide Concentrations in the L-CHA

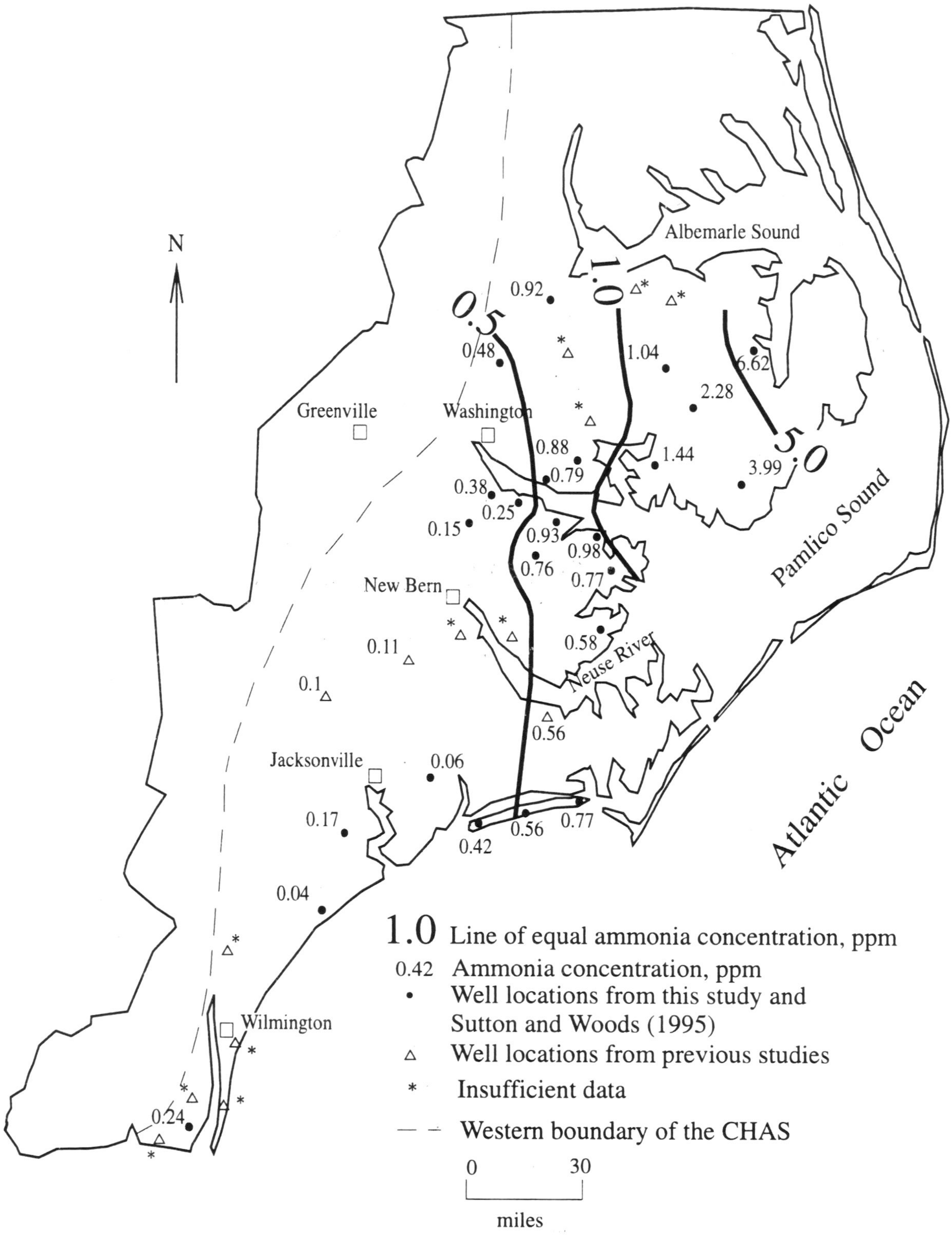


Figure 49. Ammonia Concentrations in the U-CHA
* Iindicates that ammonia data were not available.

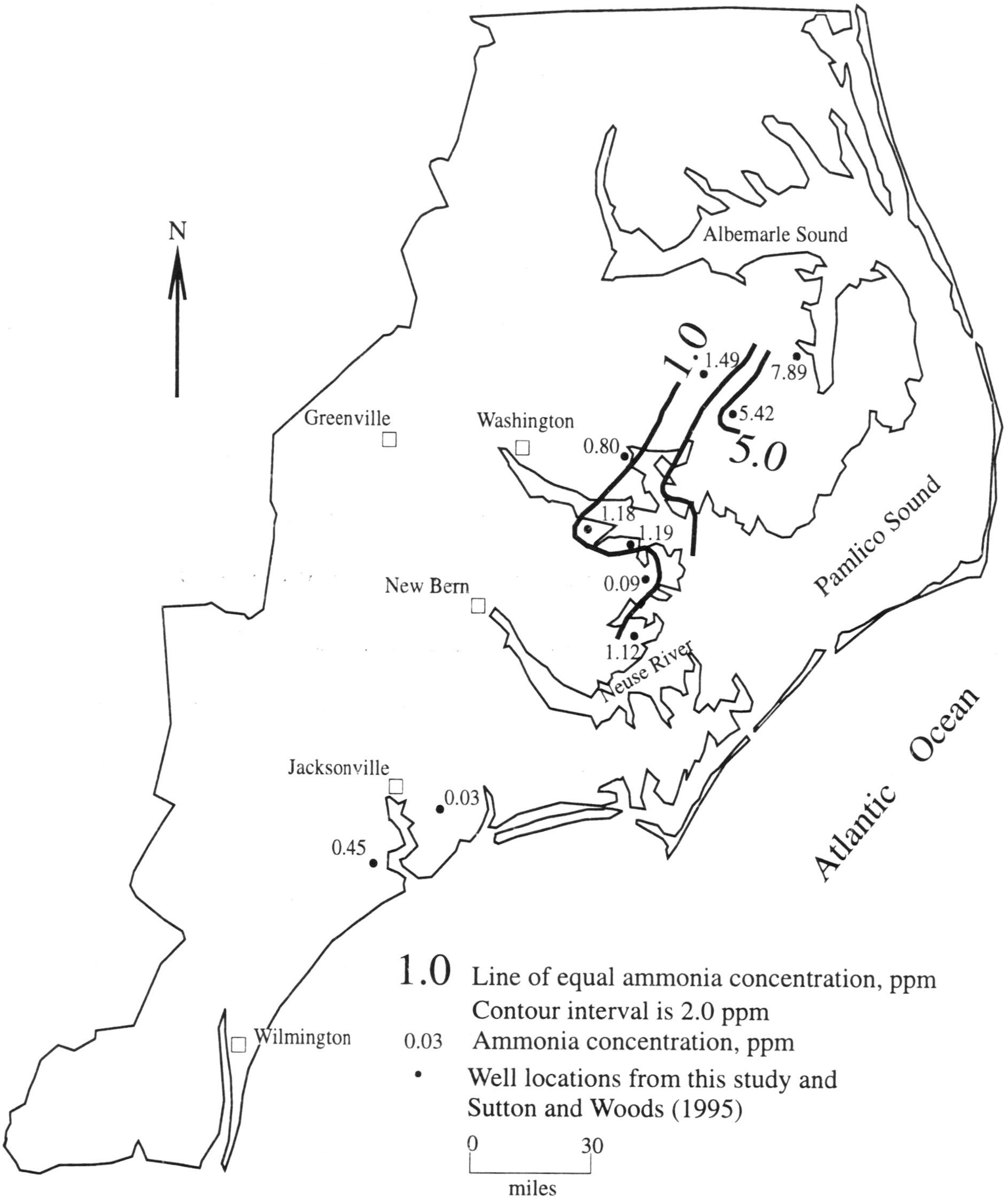


Figure 50. Ammonia Concentrations in the L-CHA

A possible explanation for the high concentrations of ammonia is decomposition of amino acids in organic matter in the aquifer or in the SFW that intrudes the aquifer from the east. Under certain anaerobic conditions (present in the downdip portion of the CHAS), this process may release ammonia into groundwater (Drever, 1997).

Based on data from this report and that of Sutton and Woods (1995) nitrate in the Upper and Lower CHA waters were just above maximum detection limits (Table 3).

pH and Eh. There are two distinct trends in pH in the U-CHA (Figure 51). North of Jacksonville in two different areas separated by the Pamlico River, values generally increase and then decrease from west to east. A different pattern is evident south of Wilmington where pH increases from southwest to northeast but this difference may be due to the lack of samples in the downdip part of the aquifer in the Wilmington area. The two high pH centers are probably related to acidic waters from overlying pocosins recharging through confining units and progressively neutralized by reaction with aquifer carbonates (Sutton and Woods, 1995). Generally the U-CHA pH values are higher than those found in the L-CHA (Figure 52).

As pointed out by Stumm and Morgan (1991) and Drever (1997) measurements of Eh in natural waters using platinum electrodes represent mixed potentials not appropriate for quantitative interpretation. Such measurements can, however, be useful for identifying reducing and oxidizing (redox) zones. Eh values in the Upper and Lower CHA, north of the Neuse River, generally become more negative from west to east (Figures 53 and 54)

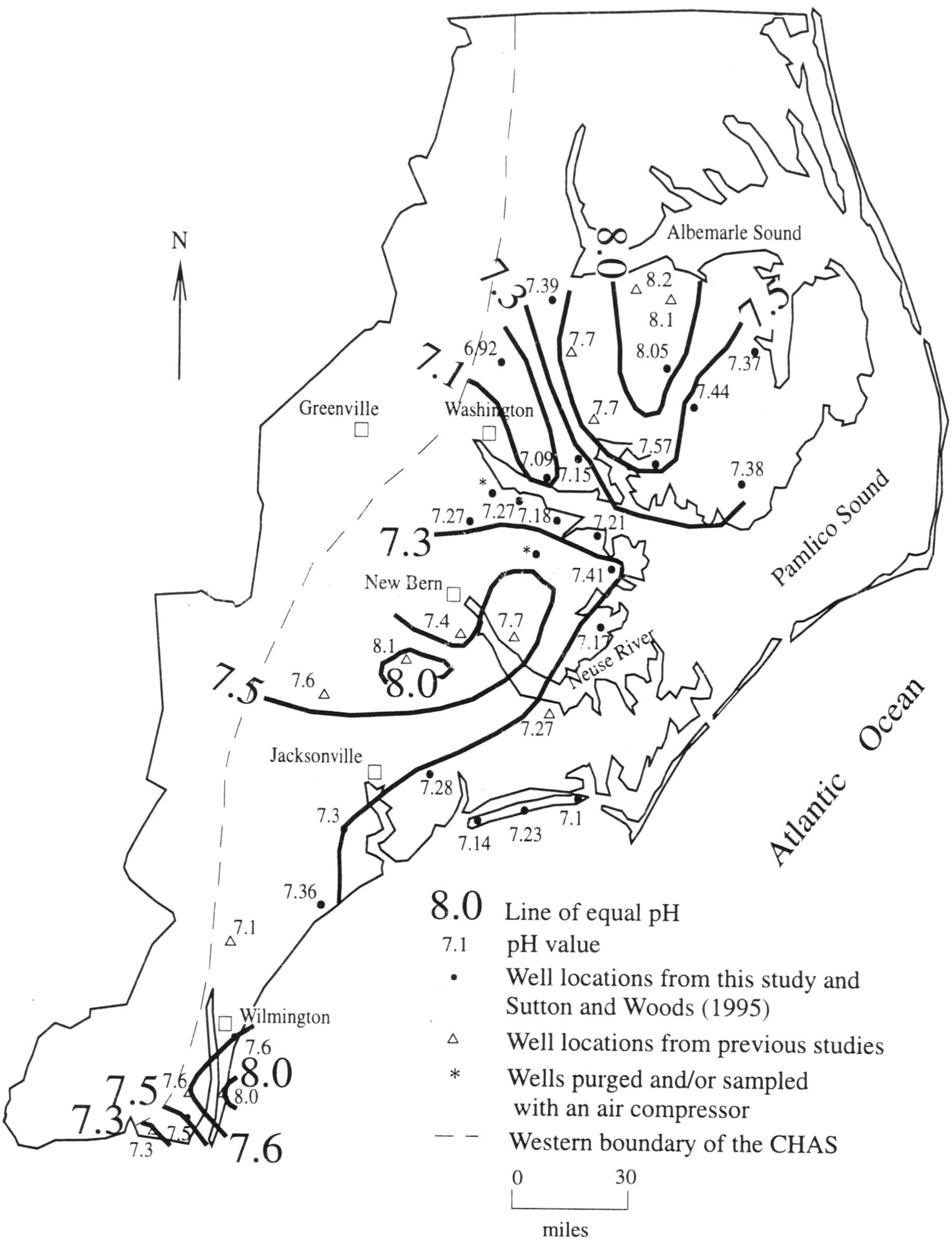


Figure 51. pH Values in the U-CHA

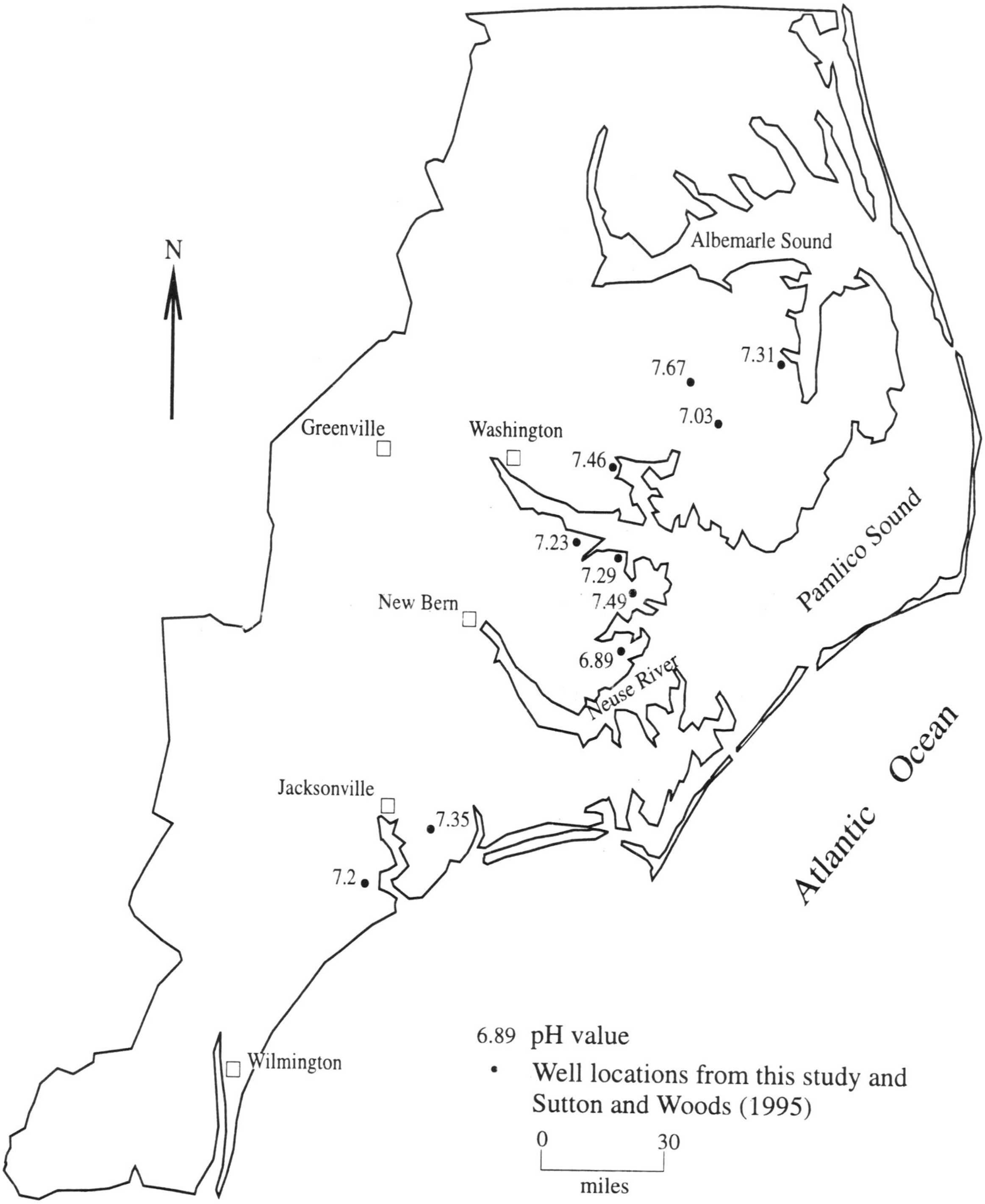


Figure 52. pH Values in the L-CHA

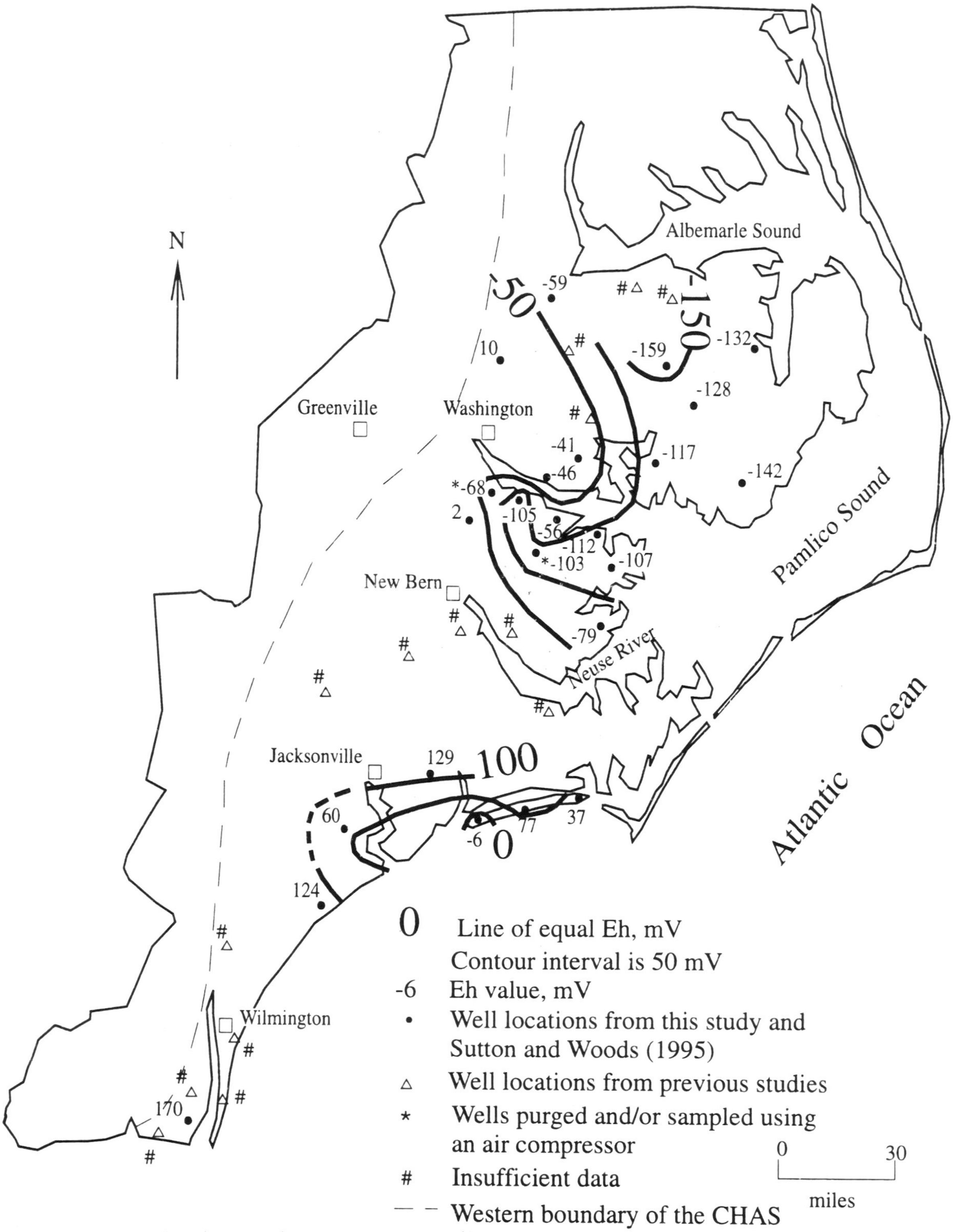


Figure 53. EhValues in the U-CHA in millivolts (mV)
# Indicates that Eh data were not available.

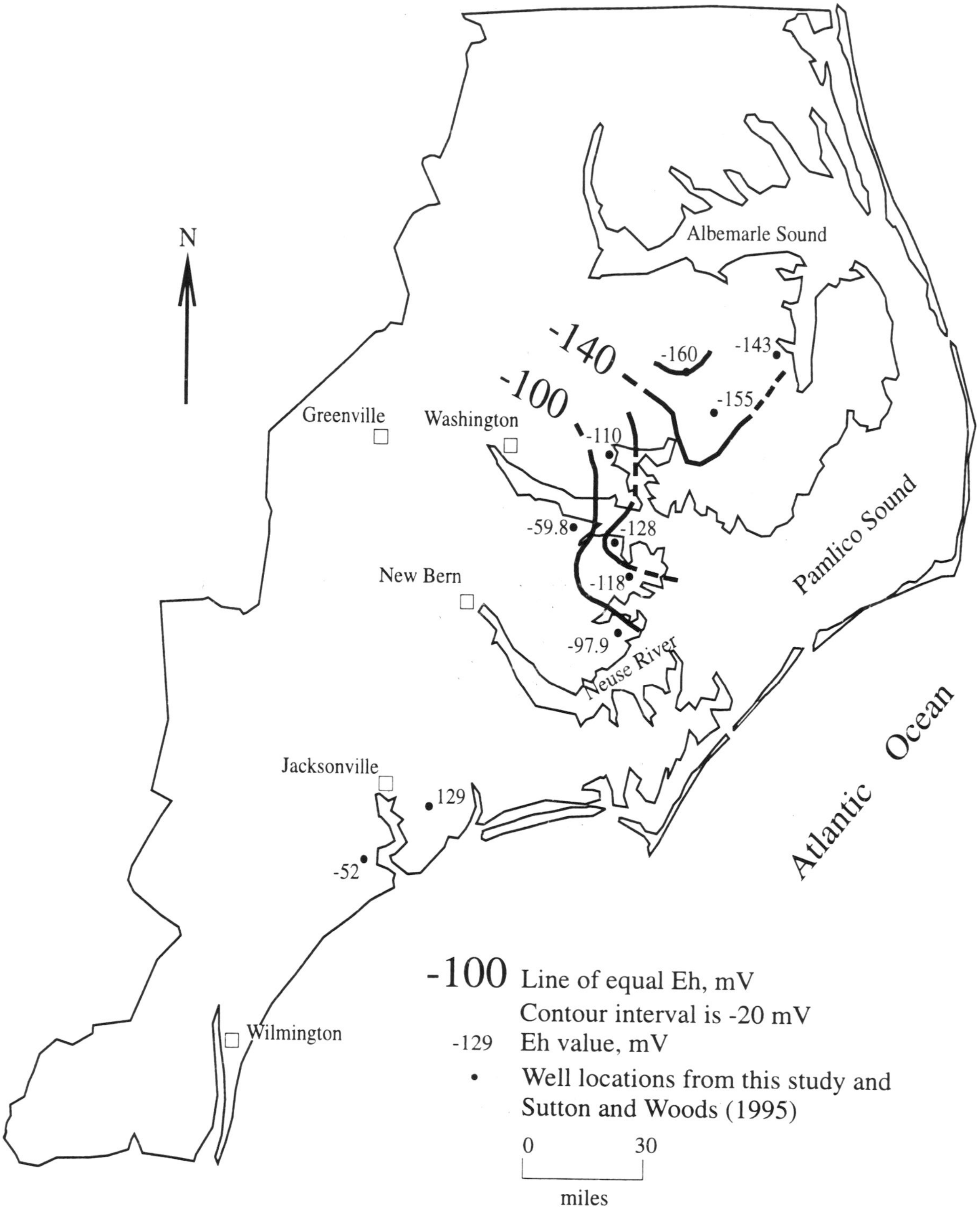


Figure 54. Eh Values in the L-CHA in millivolts (mV)

indicating that aquifer waters are becoming less oxidizing. Recharge down through overlying organic-rich surface deposits might provide waters with lowered redox potentials, as would gradual O_2 depletion as groundwater flows down gradient away from an atmospheric source (Sutton and Woods, 1995). Except for BB5 (-6 mV), all values in the U-CHA south of the Neuse are positive, indicating that aquifer waters are oxidizing.

Comparison of Groundwater Chemistry with MCL's

Table 9 presents the Maximum Contaminant Levels (MCL's) for constituents analyzed in this study. In the northern coastal plain all L-CHAS waters and water from 15 U-CHA wells exceeded the TDS limit of 500 ppm (Figures 39 and 40). In the southern coastal plain water from 8 U-CHA wells and one L-CHA well exceeded the MCL for TDS. In the northern coastal plain (Figures 27 and 28), L-CHA waters and most U-CHA waters (except for those in the west) exceeded the chloride limit of 250 ppm. Whereas in the southern coastal plain, water from one U-CHA well and one L-CHA well exceeded the chloride limit. In the northern and southern coastal plain, most waters in the U-CHA were over the MCL for iron, especially in the western portion of the study area (Figure 43). Five L-CHA wells in the southern coastal plain and 3 L-CHA wells in the northern coastal plain contained waters which were over the MCL for iron. High iron concentrations are by far the most common water quality problem associated with groundwater withdrawal (Chapelle, 1993).

Groundwater from M12l1, an U-CHA well, exceeds the MCL for fluoride (Figure 41). Several U-CHA waters (located in the extreme northeast and northwest) were above the MCL for manganese and water from one northern L-CHA well was above the MCL.

Table 9. Maximum Contaminant Levels (MCL's) for drinking water (NCDEHNR, 1989).

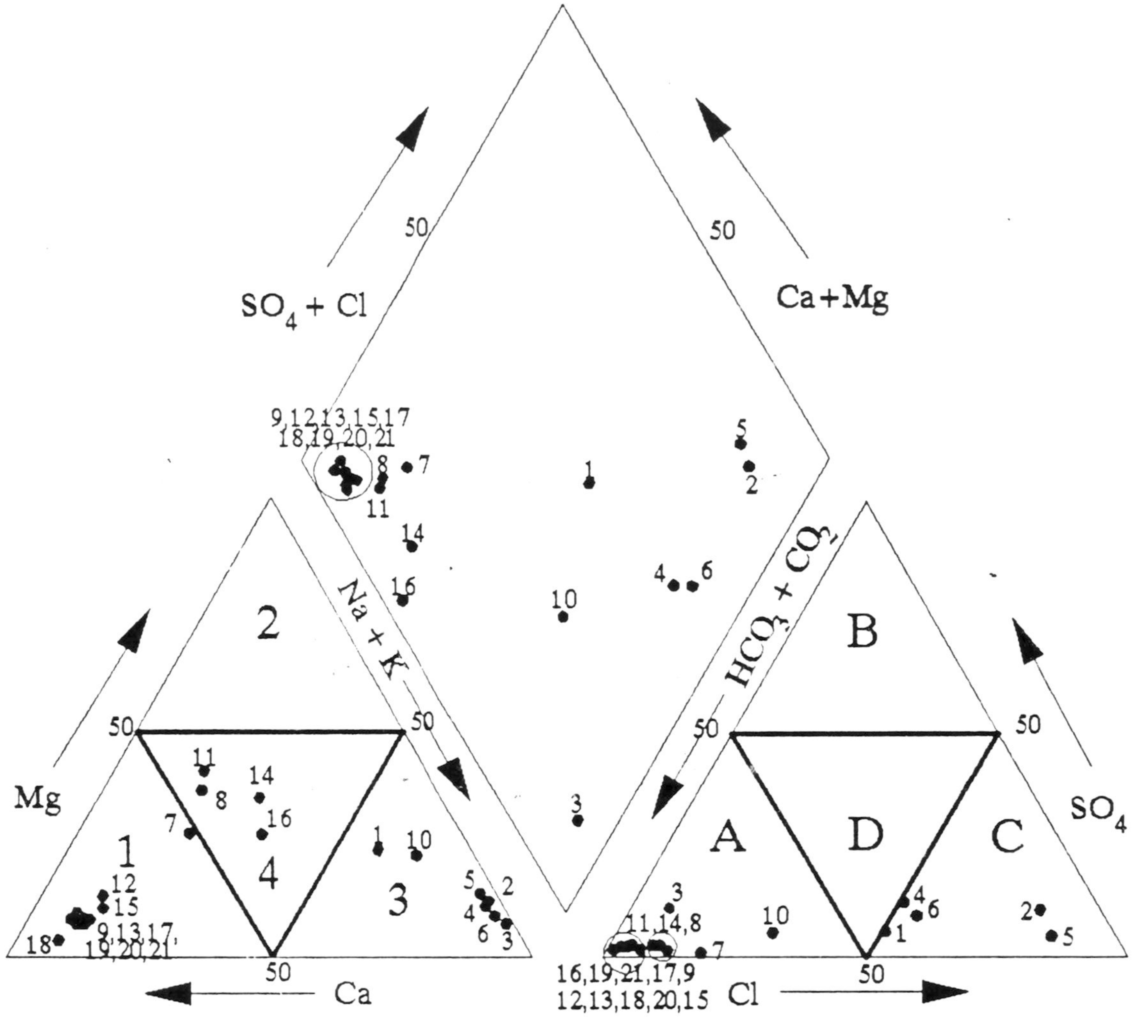
Constituent	Standard mg/L	Constituent	Standard mg/L
chloride	250	manganese	0.05
dissolved solids (TDS)	500	nitrate	10
		nitrite	1
fluoride	2	pH	6.5-8.5
iron	0.3	sulfate	250

Hydrochemical Facies

Piper diagrams (1944) were used to delineate hydrochemical facies in the northern (Figures 55 and 56) and southern (Figures 57 and 58) coastal plains. In the western area all waters are calcium rich (1) and bicarbonate rich (A), except wells BB5 and NH262 (Figure 59). A strong correlation can be seen between:

1) TDS,
2) calcium,
3) the U-CHA hydrochemical facies and
4) the recharge area (Figure 5).

This correlation shows that reaction with aquifer carbonates is the major hydrochemical process affecting water chemistry within the western U-CHA. Sutton and Woods (1995) found that waters near PCS Phosphate are composed of a mixture of cations and are HCO_3^- rich and northeasternmost waters in the U-CHA become alkali rich (3) and chloride rich (C), just like waters in the L-CHA (Figure 60). This probably reflects the mixing of fresh groundwater and SFW. Wells L13i1, WS13, and NH262 contain waters that are alkali rich (3) and bicarbonate rich (A) because local recharge through confining layers may dilute chloride, add bicarbonate, and enhance alkali concentrations by cation exchange. NH262 is a municipal production well for Wrightsville Beach (Knobel, 1985). The alkali- and bicarbonate-rich conditions here could have been induced by pumping. Well BB5 water is probably calcium rich (1) and chloride rich (C) because of the dissolution of calcite and the migration of chloride through the paleochannel located beneath the barrier island.

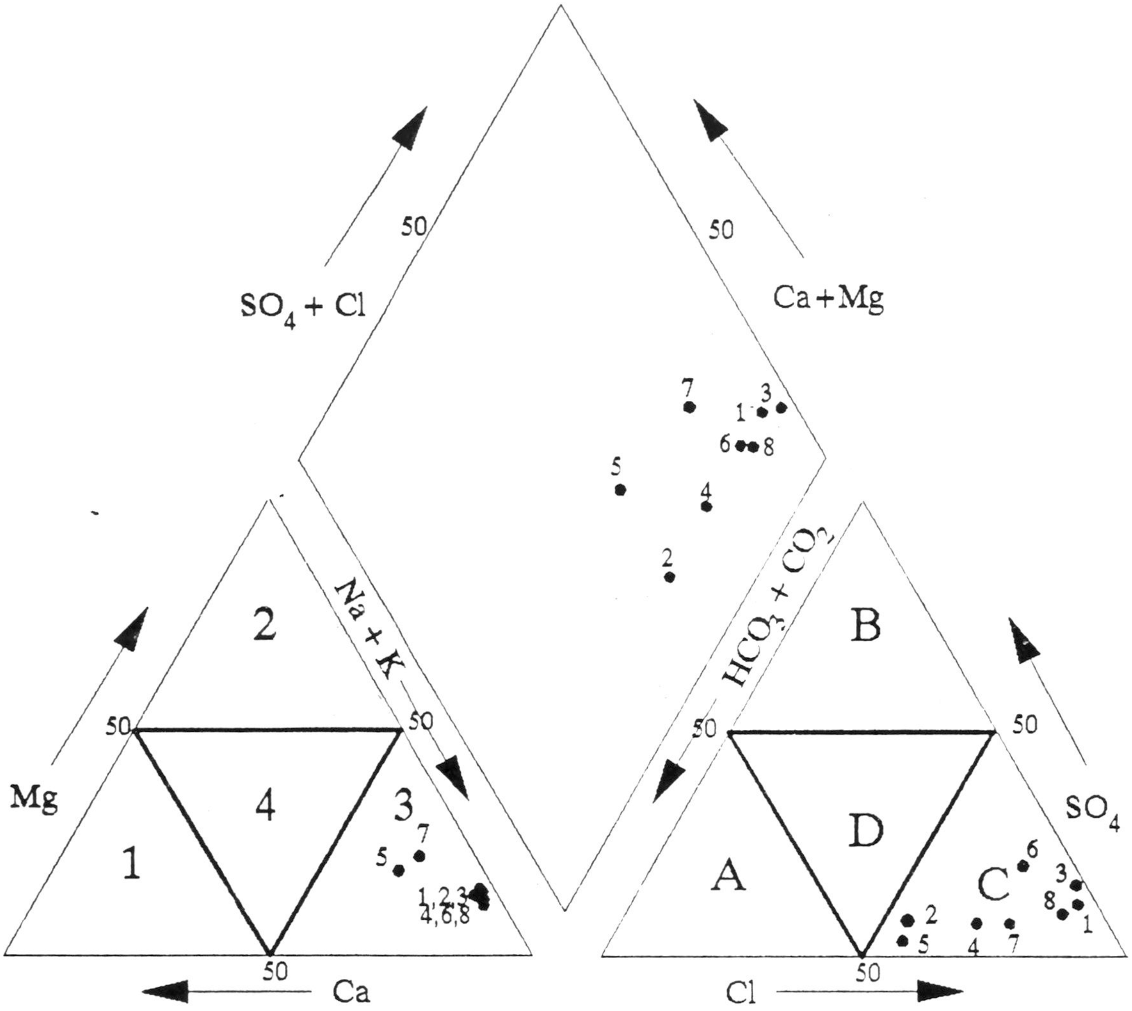


1. K-17 a-5
2. L-10 a-3
3. L-13 i-1
4. M-12 l-1
5. O-10 w-3
6. O-13 f-1
7. O-17 i-2
8. P-16 o-4
9. P-21 k-6
10. Q-15 u-3
11. S-15 y-4
12. TGCW-11A
13. TGCW-14
14. TGS-11
15. TGS-15
16. TGS-18
17. TGS-28
18. WWF-1
19. WWF-2
20. WWF-3
21. WWF-4

1. Ca-rich
2. Mg-rich
3. alkali-rich
4. mixed cations

A. bicarbonate-rich
B. sulfate-rich
C. chloride-rich
D. mixed anions

Figure 55. Piper Diagram for the U-CHA in the Northern Coastal Plain

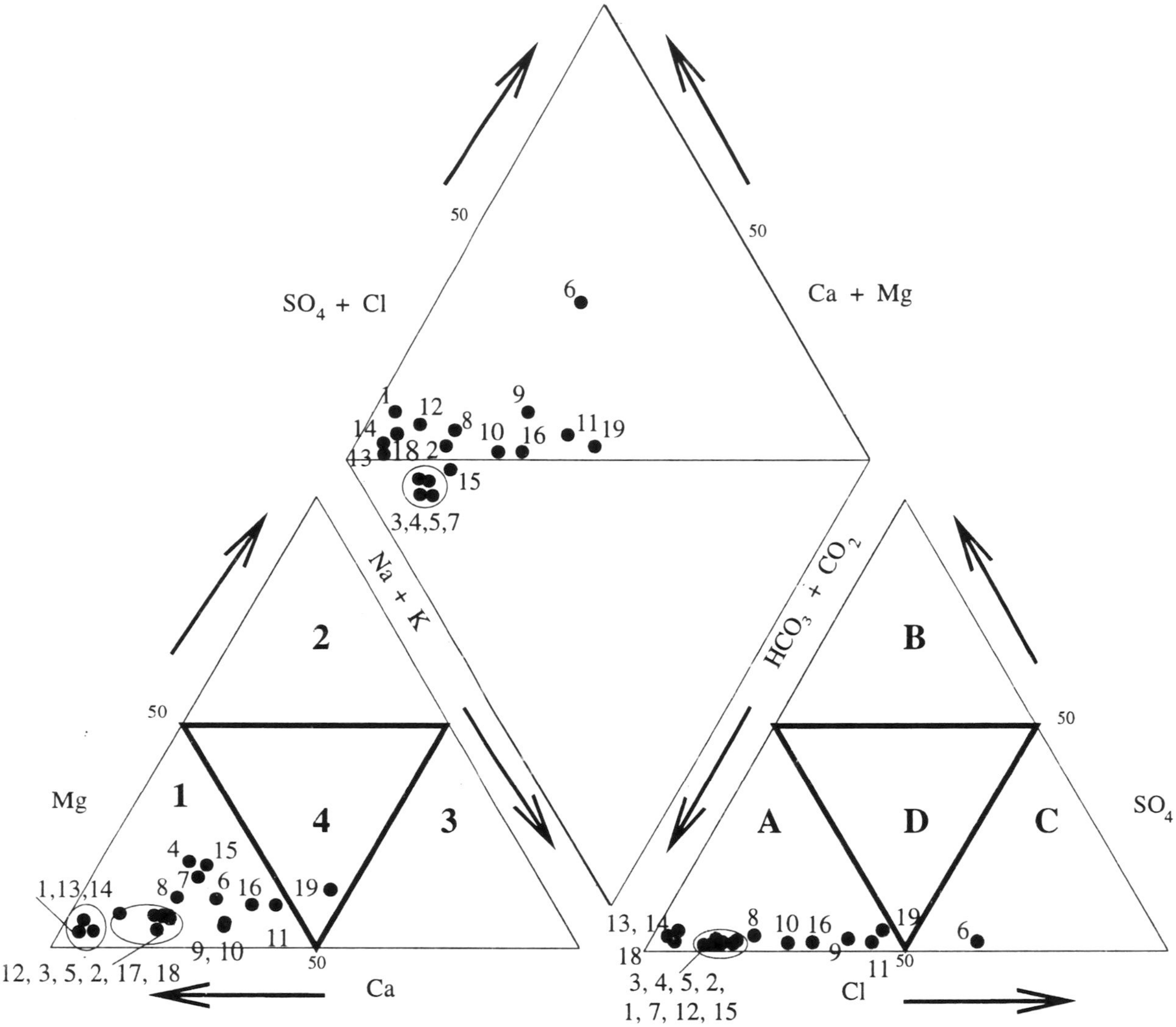


1. L-10 a-5
2. L-13 i-5
3. M-12 l-4
4. N-15 y-5
5. P-16 o-3
6. Q-15 u-5
7. S-15 y-3
8. TGS-11A

1. Ca-rich
2. Mg-rich
3. alkali-rich
4. mixed cations

A. bicarbonate-rich
B. sulfate-rich
C. chloride-rich
D. mixed anions

Figure 56. Piper Diagram for the L-CHA in the Northern Coastal Plain

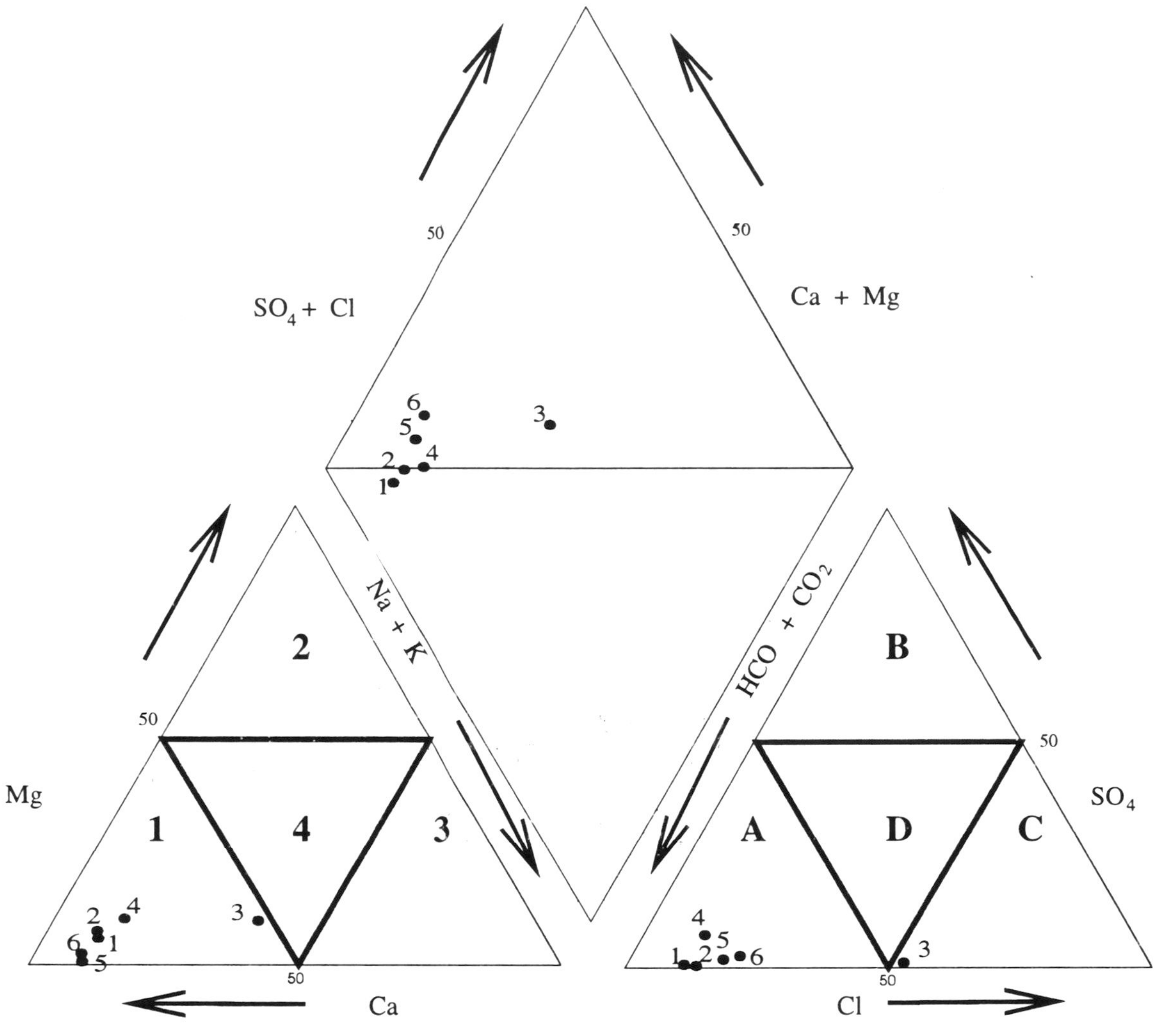


1. HOW 5
2. Y25Q1
3. ABPW 5
4. ABPW 6
5. BBPW 2
6. BBPW 5
7. BBPW 7
8. Pe 72
9. SPPW 002
10. SPPW 003
11. BR 16
12. BR 19
13. T23x1
14. U26j1
15. NH 399
16. NH 23
17. USMC 30
18. CR 258
19. NH 262

1. Ca-rich
2. Mg-rich
3. alkali-rich
4. mixed cations

A. bicarbonate-rich
B. sulfate-rich
C. chloride-rich
D. mixed anions

Figure 57. Piper Diagram of the U-CHA in the Southern Coastal Plain.



1. SFOW 1
2. SFOW 2
3. SFOW 3
4. SFOW 4
5. HPW 2
6. HPW 3

1. Ca-rich
2. Mg-rich
3. alkali-rich
4. mixed cations

A. bicarbonate-rich
B. sulfate-rich
C. chloride-rich
D. mixed anions

Figure 58. Piper Diagram of the L-CHA in the Southern Coastal Plain.

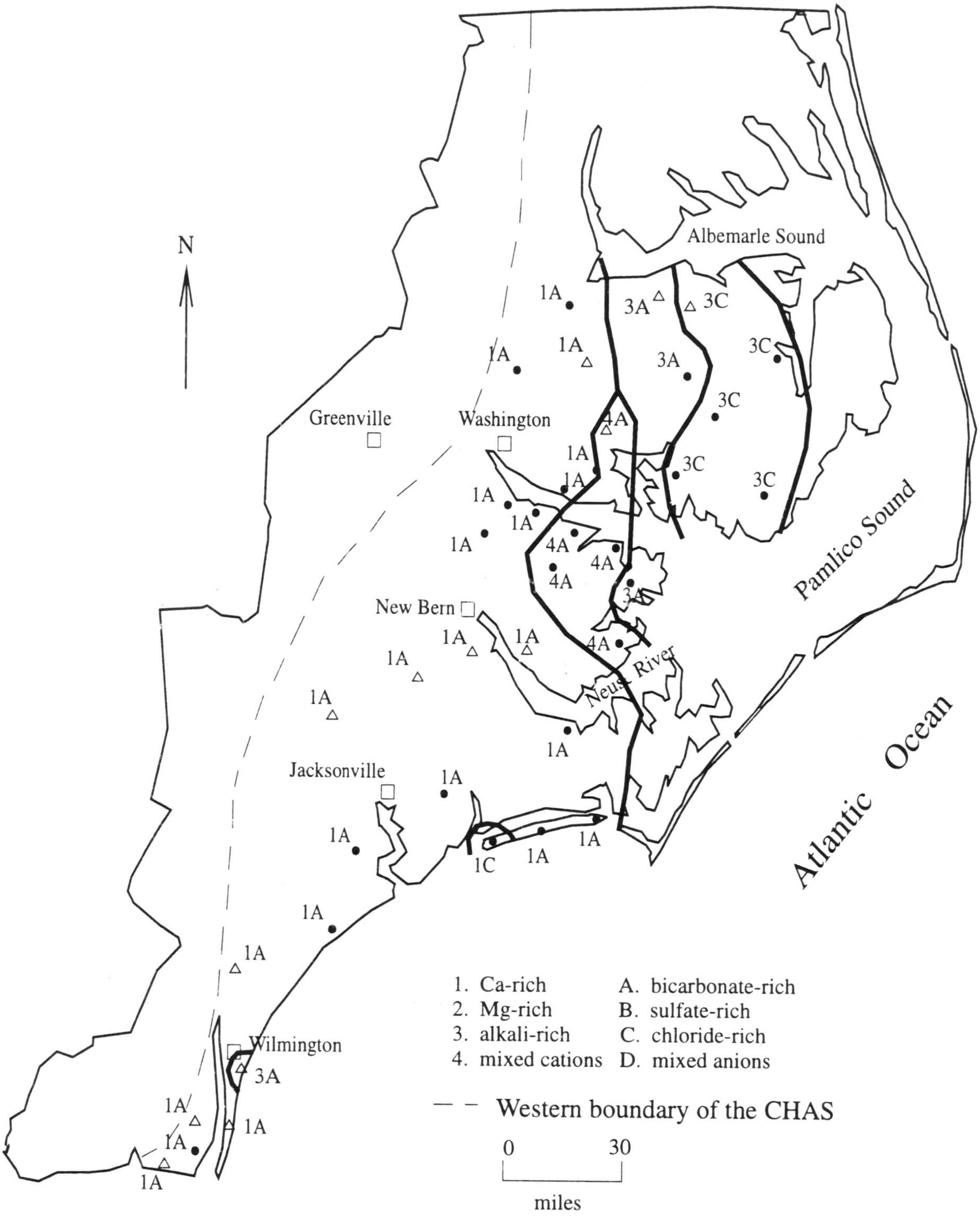


Figure 59. U-CHA Hydrochemical Facies from Piper Diagram

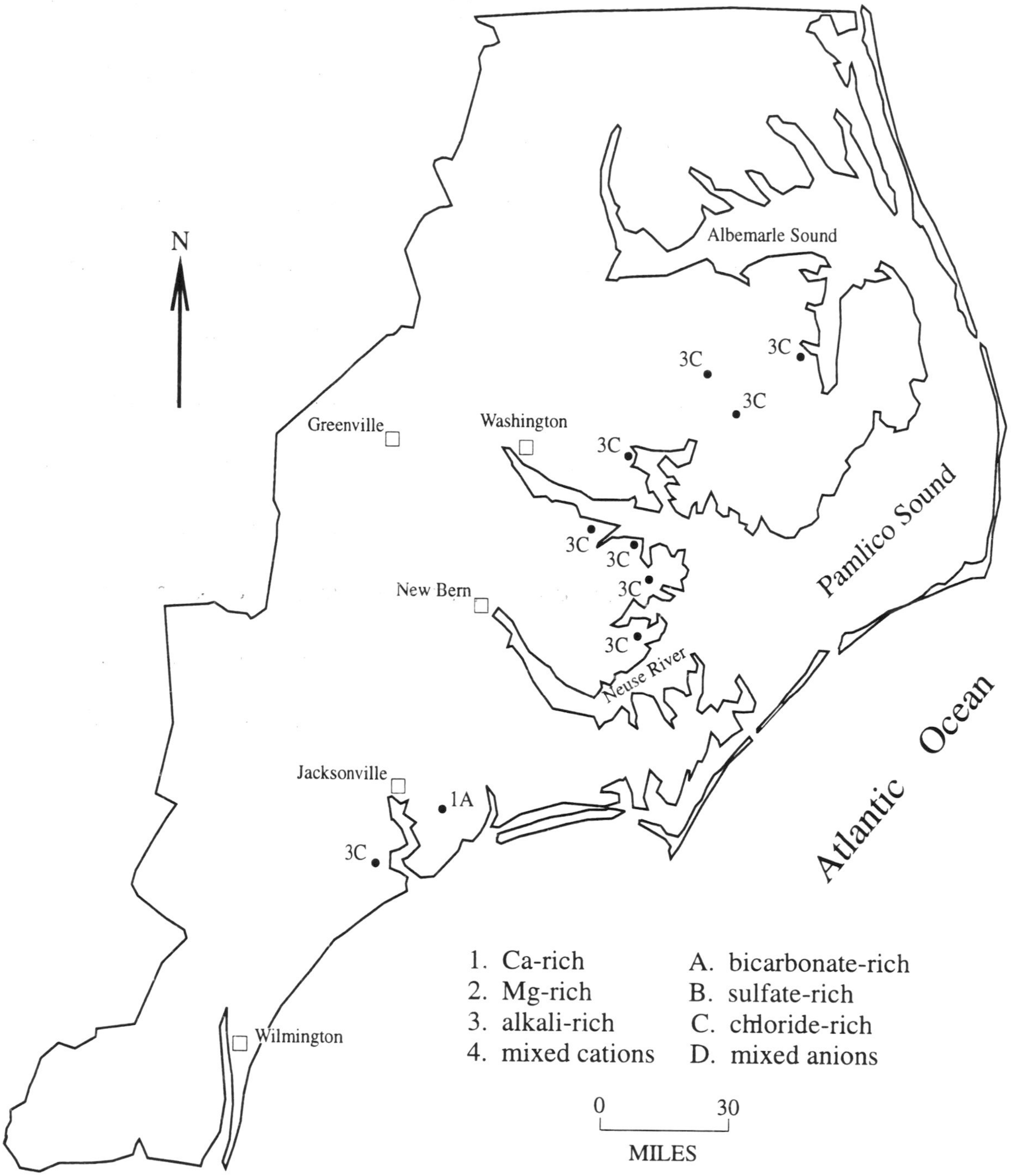


Figure 60. L-CHA Hydrochemical Facies from Piper Diagram

Trapp and Meisler (1992) studied the regional aquifer system underlying the Northern Atlantic Coastal Plain and found that the hydrochemical facies of each aquifer follows a general down-dip sequence from (1) water of variable composition, to (2) calcium and magnesium bicarbonate water, to (3) sodium bicarbonate water, to (4) sodium chloride water. In the U-CHAS, northern coastal plain, the following hydrochemical facies are seen from west to east:

1) calcium and bicarbonate waters,
2) mixed cations and bicarbonate waters/alkali and bicarbonate waters, and
3) alkali and chloride waters.

In the southern coastal plain the calcium and bicarbonate water is the only hydrochemical facies seen, except for NH262 and BB5. This is due to the fact that southeastern portions of the CHAS extend beneath the Atlantic Ocean.

Comparison of Northern and Southern Geochemistry

The CHAS in the northern coastal plain (NCP) is overlain by the Surficial, Yorktown, and Pungo River units which act as confining units to impede recharge. In the southern coastal plain (SCP) only the Surficial unit overlies the CHAS, so that the recharge area is larger than in the NCP and extends all the way to the coast in most areas. Throughout the SCP pH values are lower and Eh values are more positive than in the NCP due to acidic and oxidizing recharge waters entering the U-CHA in the west. TDS, Cl^-, SO_4^{2-}, K^+, Na^+, and Mg^{2+} concentrations increase from west to east throughout the coastal plain, but are higher in the northeastern coastal plain caused by a greater influx of saline formation water. Chloride is higher in the southern recharge area than in the northern area because the southern recharge area is closer to the Atlantic Ocean and is influenced by pumping along the coast. Chloride values gradually increase to the south, in the SCP, towards a heavily pumped region near Wilmington.

Calcium concentrations in the SCP are similar to those in the northern recharge area as acidic recharge waters dissolve $CaCO_3$. In the NCP calcium values tend to first increase and then decrease from west to east and then increase again east of well L1311. Available data from the SCP show only an initial decrease, followed by an increase along the coast east of Jacksonville. Bicarbonate increases from west to east north of Jacksonville and decreases from west to east south of Jacksonville. Calcite is saturated throughout the coastal plain whereas dolomite is undersaturated in the SCP and the northern recharge area.

Fluoride concentrations are higher in the NCP than in the SCP. Higher fluoride values in the NCP may be attributable to recharge through the Pungo River formation which overlies the U-CHA, only in the NCP, and contains an abundance of fluorapatite.

Iron values in the U-CHA decrease from west to east throughout the coastal plain. The SCP values are similar to those in the northern recharge area, again indicating that acidic recharge waters are entering the U-CHA throughout the SCP. The decreasing iron concentrations are probably controlled by cation exchange.

NETPATH

The computer model NETPATH (Plummer and others, 1994) was used to identify net geochemical mass-balance reactions that could account for chemical differences between an initial and final water along a hydrologic flow path. The program will also compute the mixing proportions of two initial waters and the resultant net geochemical reactions that can account for the observed composition of a final water. Running NETPATH requires creation of two essential files; DB and NETPATH. The NETPATH program uses DB files, but also requires input of "constraints" and "phases". A constraint is a chemical element included in the model to constrain the masses of selected minerals and gases that can enter or leave the aqueous solution between the initial and final wells. A phase is any mineral or gas that can enter or leave the aqueous solution along the flow path (Plummer and others, 1994).

The geochemical processes possibly occurring along two flow paths in the southern coastal plain were investigated using NETPATH. Evolution of groundwater from HOW5 to AB6 and SPPW003 to SPPW002 (Figure 61) were delineated. Reactions with aquifer minerals and intermixing of seawater were considered.

In the first model HOW5 to AB6, the constraints are carbon, iron, magnesium, sodium, and calcium, and phases are organic matter (CH_2O), CO_2, FeII-Na exchange, calcite, and low-Al glauconite. The low-Al glauconite formula used is:

$$K_{(1.036)}\ Al_{(0.521)}\ Fe^{3+}_{(2.410)}\ Mg_{(1.626)}\ Si0_{2\,(6.919)}\ Al_{(1.081)}\ .$$

Carbon dioxide and CH_2O were used as phases to delineate the interaction of surface waters with CHAS waters and to determine their effects on Eh.

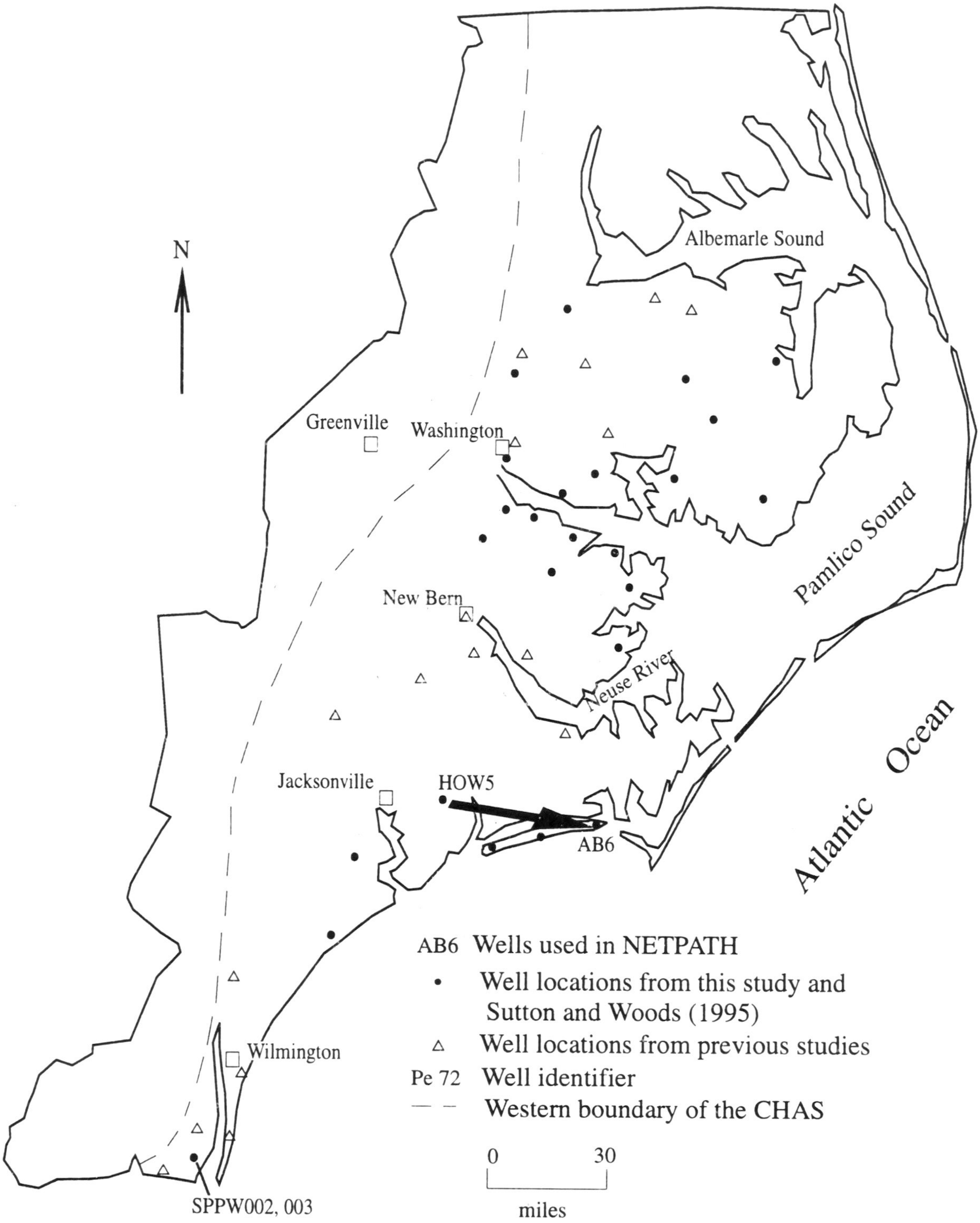


Figure 61. NETPATH wells

Dolomite was not included in the final model because of the large amount needed, which is not believed to be present in the CHAS, to produce significant Mg,. The following analytes increase from HOW5 to AB6; Na, Ca, Mg, and K. The model accounts for the increase in these analytes by the following reactions:

1) dissolution of calcite,
2) dissolution of low-Al glauconite, and
3) FeII-Na exchange in which Fe is adsorbed by aquifer materials and Na is released.

This model suggests that CH_2O goes into solution accounting for the increase in HCO_3 and the decrease in Eh and pH. In other models seawater was also added to HOW5 and it was found that mixing of seawater is not a logical scenario to explain the water chemistry in AB6.

The second model involved mixing SPPW003 water with seawater to obtain the observed chemistry in SPPW002. Seawater was suspected to be entering the U-CHA at well SPPW002 because of the increase of chloride (50 to 76 ppm) seen from SPPW003 to SPPW002. Two possible models were constructed that most likely delineate the evolution of SPPW003 into SPPW002. Both models utilize the same constraints (calcium, iron, carbon, chloride) and phases (calcite, FeII-Na exchange, CO_2 or CH_2O). The mixing ratio for both models is the same; 99.83% of the water being mixed is derived from SPPW003 whereas 0.17% is derived from seawater. The mixing ratio is driven by the increase of Cl^- from SPPW003 to SPPW002. Carbon dioxide precipitates in both models which probably accounts for the decrease in HCO_3. Calcite dissolves and iron is adsorbed into clays and

Na is released into solution accounting for the increase in Ca and Na and the decrease in Fe. The two models do show that the mixing of seawater with water from SPPW003 helps explain the water chemistry observed in SPPW002.

CONCLUSIONS

In the western coastal plain calcium is the most abundant cation in the Upper and Lower CHA, with concentrations ranging from 7 to 140 ppm. In the northeastern coastal plain Na^+ dominates. The concentration of Ca^{2+} is controlled primarily by calcite saturation, but is modified by cation exchange and mixing with SFW. The concentrations of Mg^{2+} in the CHAS range from 1 to 318 ppm; they generally increase from west to east and are much higher northeast of the Neuse River. These high concentrations are caused by mixing of SFW and longer residence times of water in the aquifer.

Sodium and potassium concentrations range from 3 to 3360 ppm and 0 to 124 ppm, respectively, and increase from west to east with the highest concentrations seen north of the Neuse River. Na^+ and K^+ are influenced by rainfall, dissolution of soil salts, cation exchange, leaching of fertilizers, upconing of saltwater from underlying aquifers, and SFW.

Silica concentrations range from 7 to 78 ppm and are probably derived from dissolution of amorphous silica or other silicate minerals in the CHAS and overlying units. The two areas with concentrations greater than 40 ppm exist because of data from previous studies, which may have significantly overestimated the silica concentrations. However, those two areas do have higher SiO_2 than surrounding regions. South of Jacksonville silica decreases from west to east.

The two major anions are HCO_3^- and Cl^-; concentrations range from 160 to 783 ppm and 4 to 5100 ppm, respectively. The HCO_3^- concentration is controlled by dissolution of calcite by CO_2-rich recharge waters and possibly by recharge from overlying organic-rich surface water. In the northern coastal plain bicarbonate increases from west to east to well L13i1, east of L13i1 bicarbonate begins to decrease. Bicarbonate in the southern coastal plain generally decreases from west to east. The Cl^- concentration is largely controlled by mixing of SFW and dissolution of soil salts; concentrations increase from west to east in both the U- and L-CHA.

Sulfate concentrations generally increase from west to east in both Castle Hayne units and range from 0 to 1120 ppm. SFW is the primary source of SO_4^{2-}. Fluoride concentrations increase from west to east in both the U- and L-CHA; ranging from 0 to 3.2 ppm. Iron concentrations range from 0.05 to 7.3 ppm and decrease from west to east. The source of the iron in the CHAS is reduction of Fe^{3+} compounds in the overlying sediments within the recharge area. The iron decrease to the east is probably controlled by cation exchange.

The major geochemical processes that occur in the northern and southern coastal plains are:

1) dissolution/precipitation of minerals,
2) mixing of groundwater with SFW,
3) chemical exchange between groundwater and aquifer ion exchange materials, and
4) dissolution of soil salts.

In the western portions of the study area , the concentrations of ions are determined primarily by rainfall, dissolution of soil salts, and dissolution of aquifer minerals toward equilibrium. In the southwestern portion, groundwater near the ocean is influenced by

SFW. In the eastern portions of the study area, mixing of groundwater with SFW increases the concentrations of many ions. Ion exchange appears to be occurring at several localities in the northern and southern coastal plain.

Calcite, dolomite, and ferrihydrite are the only minerals tested that are saturated in waters from the CHAS. Ferrihydrite was saturated in only four wells, in the southern coastal plain. The gypsum saturation index increased from west to east due to an increase in sulfate, but never reached positive values.

The L13i1 site appears to be an area of recharge. The TDS, chloride, sulfate, and calcium concentrations are low when compared to surrounding wells. A possible explanation is the leakage of surface waters from overlying aquifers and through confining units into the U-CHA.

Water in the northeastern U- and L-CHA exceeds the MCL for chloride and sulfate. In the northern and southern coastal plain most wells in the U-CHA were over the MCL for iron.

In the U-CHA, northern coastal plain, the following hydrochemical facies are seen from west to east:

1) calcium- and bicarbonate-rich waters,
2) mixed cations and bicarbonate-rich waters,
3) alkali- and bicarbonate-rich waters, and
4) alkali- and chloride-rich waters.

In the southern coastal plain calcium-rich and bicarbonate-rich water is the only hydrochemical facies seen in the U-CHA, except at wells BB5 and NH262 where influx of

SFW influences water chemistry. The L-CHA, northen coastal plain, water is alkali and chloride rich. Most L-CHA waters in the southern coastal plain are calcium and bicarbonate-rich.

The computer modeling program NETPATH showed that observed groundwater chemistries can be produced by:

1) dissolution of calcite,
2) dissolution of low-Al glauconite,
3) FeII-Na exchange in which Fe is adsorbed by aquifer materials and Na is released, and
4) fresh aquifer water mixing with SFW.

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APPENDIX A
Alkalinity Titration

PRINCIPLE OF THE METHOD

Alkalinity is produced by several dissolved carbon dioxide species, but in this study alkalinity is reported in terms of an equivalent amount of carbonate and bicarbonate. Ions are determined by titration of the samples with a standard solution of strong acid. The following reactions are involved:

$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-$ (Complete near pH 8.3)
$HCO_3^- + H^+ \Leftrightarrow H_2O + CO_2$ (Complete near pH 4.5)

REAGENT

1.6 N Sulfuric acid

STANDARD

Bake Na_2CO_3 at 250°C for approximately 3 hours. Cool in a desiccator overnight. Place 0.3371 g of Na_2CO_3 in a 500 mL volumetric and fill to the mark. This will produce a solution that is 636 mg/L Na_2CO_3.

PROCEDURE

1. Assemble the Hach digital titrator.

2. Obtain a filtered sample.

3. Pour 50 mL of sample into a 100 mL beaker using a 50 mL plastic volumetric flask.

4. Record the initial pH of the sample. Using the data sheet, record the number of digits of titrant, the pH of the sample, and the change in pH divided by the volume of titrant added.

5. Inflection points should be noted around pH values of 8.3 and 4.5.

CALCULATIONS

0.122025625 x # of digits = mL of acid for the following equations when using 1.6 N acid as the titrant.
CO_3^{2-} in mg/L = $[1000/mL_{(s)}] \times [mL_{(a)}$ to end point near pH 8.3$] \times (0.9835)$

HCO_3^- in mg/L = $[1000/mL_{(s)}] \times ([mL_{(a)}$ between end points near 8.3 and 4.5] - $[mL_{(a)}$ to end point near 8.3])

where $mL_{(s)}$ = volume of sample
$mL_{(a)}$ = volume of titrant

REFERENCE

Wood, W. W. 1976. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 1, Chapter D2, 24 p.

APPENDIX B

Dissolved Oxygen Titration

PRINCIPLE OF THE METHOD

Manganous chloride and an alkaline iodide solution are added to the sample. The manganous ions combine with the hydroxide ions to precipitate manganous hydroxide. The manganous hydroxide reacts with the dissolved oxygen, and the manganese is oxidized to a higher oxidation state. The sample is acidified, and the manganic ion oxidizes the iodide ions to iodine. Sodium thiosulfate is used to titrate the liberated iodine.

REAGENTS

Manganous chloride solution Add 60 g of $MnCl_2 \bullet 4H_2O$ to a 100-mL beaker with 50-mL of water and stir until dissolved on a magnetic stirrer. Pour the solution into a 100-mL volumetric flask and bring to volume with water.

Alkaline-iodide solution Add 32 g of NaOH to a 100 mL beaker with 70 mL of water and stir until dissolved on a magnetic stirrer. Add 60 g of NaI to the beaker and continue stirring until dissolved. Pour the solution into a 100 mL volumetric flask and bring to volume with water.

Sulfuric acid H_2SO_4, concentrated.

Starch indicator Prepare a slurry of 1 g of starch-soluble and add to 100 mL of boiling water. Boil the solution for 2 minutes and then cool.

Sodium thiosulfate titrant Fisher sodium thiosulfate solution N/140 (0.0248-0.0252 N).

PROCEDURE

1. Insert tubing to bottom of glass oxygen flask.

2. Flush 2 flask volumes then fill to brimful with no air bubbles.

3. Add 1 mL of $MnCl_2 \bullet 4\ H_20$ as far down in the flask as possible.

4. Add 1 mL of NaI/NaOH as far down in the flask as possible.

5. Insert stopper without introducing air bubbles and shake vigorously for 1 minute.

6. Allow precipitate to settle to the lower half of the flask.

7. Shake flask for 1 minute.

8. Allow precipitate to settle to the lower third of the flask.

9. Unstopper the flask and immediately add 1 mL of sulfuric acid.

10. Stopper and shake for one minute.

11. Measure out 203 mL of the solution in a specially calibrated 203-mL plastic volumetric flask.

12. Place a stir bar in a 250 mL plastic beaker and pour in the solution.

13. Stir very gently. Do not create a vortex.

14. Titrate with sodium thiosulfate solution if a yellow color is visible. Titrate until color is pale straw yellow and then add 1 mL of starch indicator.

15. Add 1 mL of starch indicator if the solution does not show any yellow coloration and begin titration.

16 For solutions that contain less than 2 mg/L dissolved oxygen titrate by adding sodium thiosulfate with a 2-mL Gilmont buret until the blue color is completely gone. If solution contains more than 2 mg/L dissolved oxygen refill Gilmont buret and continue titration until the blue color is completely gone.

17 The amount of titrant added is equal to the amount of dissolved oxygen in the sample because 200 mL of original solution are used.

REFERENCE

Strickland, J. D. H., and T. R. Parsons. 1972. A practical handbook of seawater analyses: Fisheries Research Board of Canada, Canada, 311 p.

APPENDIX C
Determination of Sulfide

PRINCIPLE OF METHOD

In an acidic solution sulfide reacts with ferric chloride and N,N-dimethyl-p-phenylene diamine to produce methylene blue. This test measures hydrogen sulfide and total acid-soluble sulfides. The blue color formed is directly proportional to the sulfide concentration in the sample. Concentration is determined visually.

PROCEDURE

1. Fill sample cup to the 25 mL mark.

2. Add 3 drops of A-9500 Activator Solution.

3. Stir briefly and immediately snap the tip of the CHEMet ampoule in the sample.

4. Mix the contents of the CHEMet ampoule.

5. After 5 minutes, compare with color standards by placing the ampoule next to the best matching color standard.

REFERENCE

CHEMetrics Inc. 1995. CHEMetrics Sulfide Instruction Manual, Model K-9510. CHEMetrics, Inc. Calverton, Va.

APPENDIX D
Determination of Silica

PRINCIPLE OF THE METHOD

Ammonium molybdate reacts with silica and phosphate to produce heteropoly acids. Tartaric acid is added to prevent phosphate interference. The molybdosilicic acid is reduced to silicomolybdenum blue with stannous chloride and read colorimetrically at 820 nm.

Operating range: 5 - 1500 μg Si/liter

REAGENTS

Ammonium molybdate   Place 5 g of ammonium paramolybdate $(NH_4)_6Mo_7O_{24} \bullet H_2O$ in a 100-mL volumetric flask and dissolve with distilled, deionized water.

1 N Hydrochloric acid

Mixed Molybdate   Measure 20 mL of the ammonium molybdate solution with a 25-mL graduated cylinder and pour into a 125-mL erlenmeyer flask. Measure 30 mL of 1 N HCl with the graduated cylinder, pour into the flask, and swirl to mix. Prepare this solution fresh each time.

Tartaric acid   Place 7 g of tartaric acid into a 100-mL volumetric. Measure 70 mL of water with a 100-mL graduated cylinder, pour the water into the volumetric containing the tartaric acid, and mix.

Stannous chloride   Add 5 mL of 1 N HCL and 5 mL of water to a 125-mL erlenmeyer flask. Dissolve 0.4 g of stannous chloride $(SnCl_2 \bullet 2H_2O)$ in the flask and then pour into a 100 mL graduated cylinder. Fill the cylinder to the 70-mL mark and pour back into the 125-mL flask. Prepare this solution fresh each time.

Silica standard   Fisher silica reference solution, 1000 ppm.

STANDARDS

Prepare silica standards using the Fisher silica reference solution. Dilute 1 mL of the 1000 ppm standard solution in a 100 mL plastic volumetric flask to create a 10,000 μg/L stock solution. Use this stock solution to make 100-, 200-, 500-, 1,000-, and 1,500-μg/L standard solutions. Store these solutions in plastic volumetric flasks.

PROCEDURE

1. If the silica concentrations of your samples are high (>1500 µg), dilute the samples 2:100 by adding 2 mL of sample to a 100-mL plastic volumetric flask and fill to the mark with distilled deionized water. Multiply final reading by 50.

2. Add 0.6 mL of the mixed molybdate reagent to each 25-mL flask.

3. Add 20 mL of sample by using a 10-mL plastic pipette twice. Rinse the pipette with distilled, deionized water twice and once with the sample before measuring the sample. Swirl the flask to mix.

4. Wait 15 minutes and then add 0.4 mL of tartaric acid. Mix well.

5. Wait 2 minutes and then add 0.2 mL of stannous chloride. Mix well.

6. Between 5 minutes and 1 hour later, measure the samples at an absorbance of 820 nm on a spectrophotometer.

REFERENCES

Stainton, M. P., M. J. Capel, and F. A. J. Armstrong. 1974. The chemical analysis of fresh water. Environment Canada Miscellaneous Publ. No. 25, Research and Development Directorate, Freshwater Institute, Winnipeg, Canada, 119 p.

APPENDIX E
Determination of Nitrate/Nitrite

PRINCIPLE OF THE METHOD

This procedure for the determination of nitrate and nitrite utilizes the procedure whereby nitrate is reduced to nitrite by a copper-cadmium reductor column. The nitrite ion then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-napthylethylenediamine dihydrochloride to form a reddish-purple azo dye. If the reduction column is not utilized, only nitrite is analyzed.

Operating range: 1 - 1.0 mg NO_2-N/L + NO_3-N/L

REAGENTS

Color Reagent A: Dissolve 50 g of ammonium chloride and 10 g of sodium tetraborate in deionized water and dilute to 500 mL. Add 0.5 mL of Brig-35.

Color Reagent B: To approximately 350 mL of distilled water and 50 mL of concentrated phosphoric acid add 5 g of sulfanilamide. Dissolve completely (heat gently if necessary). Add 0.25 g of N-1-napthylethylenediamine dihydrochloride, and dissolve. Dilute to 500 mL. Add 0.5 mL of Brig-35. Store in a cold, dark place.

STANDARDS

Nitrate Stock: Dissolve 1.011 g potassium nitrate in 1 liter of deionized water. Add 2-mL chloroform as a preservative. This makes a stock solution that is 10,000 μM nitrate nitrogen.

Nitrite Stock: Dissolve 0.6900 g of sodium nitrite in 1000-mL deionized water. This makes a stock solution that is 10,000 μM nitrite nitrogen.

Intermediate Stock Standard: Dilute 1 mL of stock standard to 1000 mL using deionized water. This makes an intermediate standard that is 100 μM.

Working Standards: Dilute the intermediate standard to make working standards of 0.5, 1.0, 2.0, 3.0, and 5.0 μM.

PROCEDURE

The nitrate is reduce to nitrite by a copper-cadmium reductor column and measured with a Scientific Instruments Autoanalyzer Model CFA-200. The samples are analyzed without using the reductor column to determine the amount of nitrite in the samples.

REFERENCES

American Public Health Association. 1992. Standard methods for the examination of water and wastewater, 18th ed. : Washington, D.C.

Environmental Protection Agency. 1979. Methods for chemical analysis of water and wastes, EPA-600/4-79-020, pp. 365.1 and 365.3-4.

Grasshoff, K., M. Erhardt, and K. Kremling (eds.). 1983. Methods of seawater analysis, 2nd edition : Verlag Chemie, Weinheim, West Germany.

Jones, M. 1984. Nitrate reduction by shaking with cadmium: alternative to cadmium columns: Water Res., v. 18, no. 5, pp. 643-646.

Orion Scientific Instruments Corporation, no date, Nitrite or nitrate and nitrite in water or seawater, Product Information Pamphlet for Modular Continuous Flow Analyzer (M/CFA).

Stanley, D. W. 1987. Water quality in the Pamlico River Estuary. Institute for Coastal and Marine Resources Technical Report 87-01, East Carolina University, Greenville, NC, 77 p.

APPENDIX F
Determination of Phosphate

PRINCIPLE OF THE METHOD

Ammonium molybdate and antimony potassium tartrate react with orthophosphate to form a phosphomolybdenum complex. Ascorbic acid is used as a reductant and yields an intense blue color which is read colorimetrically at 880 nm.

Operating range: 0 - 1 mg P/L

REAGENTS

SLS Wetting Reagent: Dissolve 15 g of SLS (sodium lauryl sulfate) in 87 mL of deionized water. Add 5 drops of concentrated sulfuric acid and mix.

Color Reagent A: Dissolve 1.5 g of ammonium molybdate in 150-mL deionized water, add 0.03 g of antimony potassium tartrate, and 17 mL of concentrated sulfuric acid. Add 0.2-mL SLS wetting reagent. Dilute to 200 mL.

Color Reagent B: Dissolve 6.0 g of ascorbic acid in 90 mL of deionized water, add 5 mL of acetone and 0.5-mL SLS wetting reagent. Dilute to 100 mL.

STANDARDS

Orthophosphate Stock: Dissolve 1.3609 g potassium dihydrogen phosphate (dried one hour at 105°C) in 1 liter of deionized water. This makes a stock solution that is 10,000 μM orthophosphate phosphorus.

Intermediate Stock Standard: Dilute 1 mL of stock standard to 1000 mL using distilled, deionized water.

Working Standards: Dilute the intermediate standard to make working standards of 0.5, 1.0, 3.0, 5.0, and 10.0 μM.

PROCEDURE

A Scientific Instruments Autoanalyzer is used to determine the concentration of the phosphomolybdenum blue complex which is read colorimetrically at 880 nm.

REFERENCES

American Public Health Association. 1992. Standard methods for the examination of water and wastewater, 18th ed. : Washington, D.C.

Environmental Protection Agency. 1979. Methods for chemical analysis of water and wastes, EPA-600/4-79-020, pp. 365.1 and 365.3-4.

Grasshoff, K., M. Erhardt, and K. Kremling (eds.). 1983. Methods of seawater analysis, 2nd edition : Verlag Chemie, Weinheim, West Germany.

Orion Scientific Instruments Corporation, no date, Orthophosphate in water and seawater, Product Information Pamphlet for Modular Continuous Flow Analyzer (M/CFA).

Stanley, D. W. 1987. Water quality in the Pamlico River Estuary. Institute for Coastal and Marine Resources Technical Report 87-01, East Carolina University, Greenville, NC, 77 p.

APPENDIX G
Determination of Ammonia

PRINCIPLE OF THE METHOD

The blue color of indophenol is obtained by the reaction at high pH of ammonia, phenol and hypochlorite. Sodium nitroprusside is used to catalyze the reaction. The samples are read colorimetrically at 640 nm.

Operating range: 0.1 to 10 μg/liter N

REAGENTS

Phenol reagent: Dissolve 11.1 mL of 90% phenol in 95% ethanol and make to 100 mL with 95% ethanol. This reagent separates at low temperature. Shake well before dispensing.

Sodium nitroprusside reagent: Dissolve 0.5 g sodium nitroprusside in 100-mL deionized water.

Hypochlorite (Clorox) : 5.5% available chlorine. Discard within 2 months of date opened.

Alkaline stock solution: Dissolve 100 g sodium citrate and 10 g 50% NaOH (or 5 g NaOH pellets) in deionized water. Dilute to 500 mL.

Oxidizing reagent: Prepare fresh daily in a ratio of 100 mL of alkaline stock to 25 mL of Clorox.

STANDARDS

Ammonium standard stock: Dissolve 0.5349 g of dry ammonium chloride and dilute to 1000 mL with deionized water. This produces a stock solution of 10,000 μM ammonia.

Intermediate standard stock: Dilute 10 mL of stock to 1000 mL which yields a concentration of 100 μM ammonia.

Working standards: Dilute the intermediate standard stock to make working standards of 0.5, 1.0, 2.0, 3.0, 5.0, 10.0, 20.0, and 40.0 μM ammonia nitrogen.

PROCEDURE

1. Prepare a blank and standards.

2. Place 25 mL of sample in 50-mL erlenmeyer flask.

3. Add 1 mL of phenol reagent and swirl.

4. Add 1 mL of nitroprusside reagent and swirl.

5. Add 2.5 mL of oxidizing reagent and swirl.

6. Allow color to develop for at least 1 hour. Read absorbance at 640 nm within hours. (Note: If the concentrations are high, the samples may be diluted with blanks.)

REFERENCES

American Public Health Association. 1992. Standard methods for the examination of water and wastewater, 18th ed. : Washington, D.C.

Environmental Protection Agency. 1979. Methods for chemical analysis of water and wastes, EPA-600/4-79-020, pp. 365.1 and 365.3-4.

Koroleff, F. 1976. Determination of ammonia, *in Grasshoff*, K. (ed.), Methods of seawater analysis, 2nd edition : Verlag Chemie, Weinheim, pp. 126-133.

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenol hypochlorite method: Limnol. Oceanogr., v. 14, pp. 799-801.

Stanley, D. W. 1987. Water quality in the Pamlico River Estuary. Institute for Coastal and Marine Resources Technical Report 87-01, East Carolina University, Greenville, NC, 77 p.

APPENDIX H
Determination of Fluoride

PRINCIPLE OF THE METHOD

Fluoride activity is measured with a fluoride electrode. The fluoride ion activity depends on the pH and ionic strength of the solution, and on fluoride complexing. TISAB III with CDTA is used as a buffer to adjust ionic strength and pH so that, in effect, the electrode measures concentration.

STANDARDS

Stock Solution: Add 0.4199 g of NaF to 1 liter of water to create a stock solution of 190 ppm F^-.

Working Standards: Dilute the stock solution to create working standards of 1.9 ppm F^- and 0.19 ppm F^-.

PROCEDURE

Use an Orion model 96-09 combination fluoride electrode and a Corning ion analyzer 250 meter to analyze the samples. Add 20 mL of TISAB III to 20 mL of each working standard and use the two standards to calibrate the meter. Add 20 mL of TISAB III to 20 mL of each sample and read the concentrations directly from the meter.

REFERENCES

American Public Health Association. 1992. Standard methods for the examination of water and wastewater, 18th ed. : Washington, D.C.

APPENDIX I

Determination of Chloride

PRINCIPLE OF THE METHOD

The combination of silver ions and chloride ions is a quantitative reaction that results in an insoluble precipitate of silver chloride (AgCl). This reaction is carried out at a constant rate by passing a fixed direct current between a pair of silver electrodes immersed in an acid solution. As the equivalence point of the reaction is reached, the current flowing between a pair of separate indicator electrodes increases and is detected by the sense circuitry. At a preset indicator current, the instrument automatically stops the incremental counter and the generation of silver ions. Since the generator current is constant, the total titration time is proportional to the number of chloride ions that are introduced into the sample vial. The instrument displays this relative time in units of milliequivalents (mM) chloride per liter.

Operating range:	high range	100 μL sample
	low range	10 μL sample

REAGENTS

Acid solution: Add 6.4 ml concentrated nitric acid and 100 mL glacial acetic acid to 900 mL deionized water.

Gelatin reagent (Buchler 4-2028): Heat one liter of deionized water to boiling. Slowly add the contents of one vial of Buchler dry gelatin mix (6.2 g) to the water while stirring until the powder is dissolved. When mixture has cooled slightly, divide it among 10-20 screw-cap centrifuge tubes. The gel may be refrigerated for up to 6 months and may be used at room temperature for 8 hours.

Standard stock: 1000 mM NaCl. Dissolve 5.845 g dried NaCl in 100-mL volumetric flask, and dilute to volume.

PROCEDURE

1. With the instrument off, check that the generator electrode (silver wire spool) is the same length as the other electrodes and is thicker than the shaft of an ordinary pin.

2. Clean all 4 electrodes with silver polish, rinse, and buff with tissue. Avoid getting skin oils on the electrodes.

3. Place a vial containing 4 mL acid solution and 4 drops gelatin in the vial holder. Set range switch to LOW, titration switch to AUTO, and BLANK ADJUST to 00.0.

Raise the holder to immerse the electrode and start the stirrer. If a reading is not displayed after 30 seconds rinse and buff again, then titrate a new vial.

4. To run standards place 1 mL acid solution, 4 drops gelatin, and 3 mL standard in a vail. Place the vial in the vial holder and raise until stirrer begins. Run each standard until replication is reached.

5. To run samples place 1 mL acid solution, 4 drops gelatin, and 3 mL sample in a vial. Place the vial in the vial holder and raise until stirrer begins. Run each sample until replication is reached.

REFERENCE

Buchler Instruments, Inc. 1981. Buchler Digital Chloridometer Instruction Manual, Model 4-2500. Buchler Instruments, Inc. Fort Lee, NJ. 10 p.

APPENDIX J
Determination of Sulfate

PRINCIPLE OF METHOD

Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

Minimum detectable concentration: Approximately 1 mg SO_4^{2-}/L.

REAGENTS

Buffer solution A: Dissolve 30 g magnesium chloride, $MgCl_2 \bullet 6H_2O$, 5 g sodium acetate, $CH_3COONa \bullet 3H_2O$, 1.0 g potassium nitrate, KNO_3, and 20 mL acetic acid, CH_3COOH (99%), in 500 mL distilled water and make up to 1000 mL.

Buffer solution B: (required when the SO_4^{2-} concentration is less than 10 mg/L): Dissolve 30 g $MgCl_2 \bullet 6H_2O$, 5 g $CH_3COONa \bullet 3H_2O$, 1.0 g KNO_3, 0.111g sodium sulfate, Na_2SO_4, and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.

Barium chloride ($BaCl_2$): crystals, 20 to 30 mesh. In standardization, uniform turbidity is produced with this mesh range and the appropriate buffer.

Standard sulfate solution: Prepare a standard sulfate solution with 1.00 mL = 100 µg SO_4^{2-}. Dissolve 0.1479 g anhydrous Na_2SO_4 in distilled water and dilute to 1000 mL.

PROCEDURE

1. Measure 100 mL sample into a 250-mL erlenmeyer flask. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for 60 ± 2 sec at constant speed.

2. After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 5 ± 0.5 min.

3. Estimate SO_4^{2-} concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying SO_4^{2-} standards through the entire procedure. Space standards at 5 mg/L increments in the 0 to 40 mg/L SO_4^{2-} range. Above 40 mg/L accuracy decreases and $BaSO_2$ suspensions lose stability. Check reliability of calibration curve by running a standard with every three or four samples.

REFERENCE

Rossum, J. R., and P. Villarruz. 1961. Suggested methods for turbidimetric determination of sulfate in water. Jour. Amer. Water Works Assoc. 53:873.

Sheen, R. T., H. L. Kahler, and E. M. Ross. 1935. Turbidimetric determination of sulfate in water. Ind. Eng. Chem., Anal. Ed. 7:262.

Thomas, J. F., and J. E. Cotton. 1954. A turbidimetric sulfate determination. Water Sewage Works 101:462.

APPENDIX K

Determination of Cations by Atomic Absorption Spectrometry

PRINCIPLE OF THE METHOD

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range.

STANDARDS

Calcium standard: Fisher calcium reference solution, 1000 ppm. Dilute reference solution to make working standards of 1.0, 5.0, 10.0, 25.0, 50.0, 75.0, and 100.0 ppm. To every 1 L of standard add 1.0 g $LaCl_3 \bullet 7 H_20$ and 4 mL of 69% nitric acid.
Example: Add 100 mL of 1000 ppm reference solution to 1 L of deionized water, which gives 100 ppm Ca solution.

Potassium standard: Fisher potassium reference solution, 1000 ppm. Dilute reference solution to make working standards of 0.5, 2.5, 5.0, 12.0, 25.0, 40.0, and 50.0 ppm. To every 1 L of standard add 1.0 g $LaCl_3 \bullet 7 H_2O$ and 4 mL of 69% nitric acid.

Magnesium standard: Fisher magnesium reference solution, 1000 ppm. Dilute reference solution to make working standards of 0.5, 2.5, 5.0, 12.0, 25.0, 40.0, and 50.0 ppm. To every 1 L of standard add 1.0 g $LaCl_3 \bullet 7 H_2O$ and 4 mL of 69% nitric acid.

Iron standard: Fisher iron reference solution, 1000 ppm. Dilute reference solution to make working standards of 0.25, 0.5, 1.0, 2.5, 5.0, 7.0, and 10.0 ppm. To every 1 L standard add 1.0 g $LaCl_3 \bullet 7 H_2O$ and 4 mL of 69% nitric acid.

NOTE: Ca, K, Mg, and Fe standards can be made as one solution.

Working blank for Ca, K, Mg, and Fe: Add 1.0 g $LaCl_3 \bullet 7 H_2O$ and 4 mL of 69% nitric acid to 1 L deionized water. The working blank is used as the zero concentration standard.

Sodium standard: Fisher sodium reference solution, 1000 ppm. Dilute reference solution to make working standards of 0.5, 1.0, 3.0, 5.0, 7.0, 10.0, 15.0, 25.0, and 50.0 ppm. To every 1 L standard add 200 mL potassium chloride and 4 mL of 69% nitric acid.

Working blank for Na: Add 200 mL potassium chloride and 4 mL of 69% nitric acid to 1 L deionized water. The working blank is used as the zero concentration standard.

Cleaning blank: Add 4 mL of 69% nitric acid to 1 L deionized water. The cleaning blank is used to clean the burner head between aspirations.

SAMPLES

10 % Lanthanum solution: Add 10 g $LaCl_3 \bullet 7 H_2O$ to 100 mL deionized water.

When analyzing for Ca, K, Mg, and Fe: Add 1 mL of 10% $LaCl_3 \bullet 7 H_20$ solution to 100 mL of sample. This gives 0.1% La in solution. This concentration of La is within working range of all cations being tested. All samples should have 1 mL of 69% nitric acid per 250 mL.

Potassium chloride solution: Dilute 7.455 g potassium chloride to 100 mL with deionized water to give a 10, 000 ppm solution. Add 100 mL of stock solution to a 500 mL volumetric flask and fill to volume to make a 2000 ppm solution.

When analyzing for K: Add 20 mL of potassium chloride solution to 80 mL sample to make a 2000 ppm solution.

PRE-START CHECK LIST

1) ABS display toggle on lower right side of machine should always be on ABS, unless computer is connected to AA.

2) Regulator pressure gauge should be off.

START UP MACHINE

1) Push "Power" button.

2) Check lamp amp (Amp knob should be turned to the left and meter should read zero).

3) Turn "Restart/Stdby" knob to "Operate". This turns lamp on if it's plugged in.

4) Open gas valve on the tank completely. **Absolute: check to ensure tank contains at least 100 psi of gas.**

5) Turn hood "On" (AA exhaust fan). **Position hood over burner before igniting.**

6) Turn "Off" knob to "Air". **Aspirator should not be in solution.**

7) Check air gauge (it should be set on 50 psi)

8) Turn "Air" to "Air/Fuel".

9) Push the "Pilot" button to ignite the burner.

10) Place the aspirator in distilled water after the burner is ignited.

11) Immediately check gas gauge (it should be set on 15 psi, gauge reads 0-100 psi).

12) Open the oxidant valve completely and the silver bubble should be set between 12 and 14.

13) Set the fuel bubble between 4 and 5. This should give a lean flame. If there are brakes in the flame the burner head needs to be cleaned (see Manual).

14) Log in (what lamp(s) was used, users name, date, and time in and out).

Running Standards and Samples in Absorption Mode

1) Let burner and lamp warm up for at least 45 minutes before running standards.

2) If the flame is not even then the burner head needs to be cleaned of accreted particulate matter in the burner slot (follow cleaning procedure in the Operator's Manual).

3) Before running standards the machine needs to be standardized, with the flame off, by the following methods:
    - A) Turn flame off, follow shut down procedures listed below.
    - B) Focus the lamp beam in the center of the burner slot with a straight line drawn on an index card and by turning the focus knob next to the lamp. The beam should be in the center of the burner and burner slot and should have a small, clear focal point.
    - C) Set the correct wavelength for the desired element (see the IL Atomic Absorption Methods Manual).
    - D) Set the correct bandwidth (see IL AA Methods Manual).
    - E) Set the correct lamp amp (see IL AA Methods Manual or the lamp label if not an IL lamp).
    - F) Set the I/I_o toggle switch to the I position.

G) Set the H.C./D_2 toggle switch to the H.C. position.

H) Set appropriate voltage (determined by the energy needle being within the green area).

I) Press the following keyboard buttons:
   1) "Auto" (light should come on).
   2) "INT" (integration time of reading on LED).
      Enter desired time (1 sec).
      "Enter".
   3) "Abs" (this puts machine in absorbance mode). Display should read 1.000. Press "Enter" and light should come on.
   4) "Zero".
   5) "Read" (0.000 should appear on LED).

J) Use screened slide to fix the burner height. Center slide over beam window and adjust wavelength knob until display reads near 0.484 (no lower than 0.471). Adjustment of burner head may be needed to reach optimum absorbance.

K) Ignite burner again and zero machine using the cleaning blank (back to page 1 step 6).

4) Set the "INT" to 10 seconds (close burner door and put burner cover in place).

5) Zero the machine with the working blank (if you get a non-zero blank then check blank).

6) Shake standard bottle and begin aspirating the lowest concentrated standard.

7) When the aspirating tube is in the standard push "Read".

8) Record the LED reading that appears after the first 20 seconds (don't use first reading).

9) Push "Read" and remove aspirating tube from standard and place in working blank.

10) Continue this until all standards have been run.

11) Determine a regression. If the regression is below 0.9 run standards again and check machine parameters.

12) If regression is good begin running samples by starting with your standards as outlined below.

13) Zero machine with working blank.

14) Run standards as described above, steps 5-12, check regression.

15) After the last standard run the first sample without zeroing the machine.

16) After every 3 samples run standards that correlate with absorbance of samples.

17) If duplicate readings are desired take the first reading after 20 seconds and the second reading after 40 seconds.

To change lamp to run another element (while aspirating working blank).

1) Turn "Amp" to zero and "Operate" to "Restart/Stdby".
2) Go to FLAME SHUTDOWN section.
3) Unplug lamp and remove from clamp.
4) Place new lamp in clamp and plug in lamp.
5) Go to START UP MACHINE section.

Running Standards and Samples in the Emission Mode

1) Follow intructions for START UP MACHINE, but unplug lamp when running emission (no lamp is needed).

2) Press "A.E." on keyboard.

3) Press "Abs" to turn off absorbance.

4) Set "INT" as described above.

5) Press "Auto".

6) Set wavelength to the approximate emission line (see IL AA Methods Manual).

7) Set bandwidth (see IL Manual). Burner should be lit. Set I/I_o toggle switch to I.

8) Aspirate the working blank.

9) Press "Zero" and then press "Read" (0.000 should appear on LED).

10) Aspirate the highest standard first. While aspirating use the wavelength selector, voltage control, bandwidth, and adjust the burner height so that the emission reading is approximately 0.900.

11) Aspirate the following standards and samples as described above in the absorption section. Make sure the regression is checked.

FLAME SHUTDOWN

1) Aspirate cleaning blank for 2 minutes, then distilled water for 30 seconds. If burner head is dirty take off and clean.

2) Turn "Fuel/Air" knob to "Air" and wait for flame to disappear, then remove aspirator from distilled water.

3) Wait 15 seconds then turn the "Air" knob to "Off".

4) When the air has shut off completely, place the aspirator in distilled water.

MACHINE SHUTDOWN

1) Close regulator valve and gas valve on tank completely.

2) Turn the lamp amp knob completely to the left.

3) Turn the "Operate" knob to "Restart/Stdby".

4) Push "Power" button.

5) Turn hood "Off".

REFERENCES

American Public Health Association. 1995. Standard methods for the examination of water and wastewater, 19th ed. : Washington, D.C.

Instrumentation Laboratory Inc. 1981. Operator's manual for models IL357 and 457 AA/AE spectrophotometers : Wilmington, MA.

Sotera, J. J., and Stux, R. L., 1979. Instrumentation Laboratory, Inc. Atomic Absorption Methods Manual. v.1, Wilmington, MA.

APPENDIX L: CHEMICAL ANALYSES FROM PREVIOUS STUDIES

Appendix B1: Chemical Analyses from Knobel (1985), NCDEHNR (1987), Lloyd and Daniel (1988), and Sullivan's fish farm.

LOCATION NAME	WELL IDENTIFIER	COUNTY	DATE SAMPLED
SOUTHPORT MUNICIPAL	BR-16*	BRUNSWICK	6/8/58
US ARMY TERMINAL	BR-19*	BRUNSWICK	12/12/69
OLIVERS CROSS ROADS	T23x1[#]	JONES	3/30/87
COMFORT RESEARCH STATION	U26j5[#]	JONES	3/30/87
CAROLINA BEACH MUNICIPAL	NH-399*	NEW HANOVER	12/4/58
WILMINGTION PACKING CO.	NH-23*	NEW HANOVER	5/20/52
USMC CHERRY POINT	USMC 30[%]	CRAVEN	10/20/86
USGS WELL	CR-258*	CRAVEN	6/19/63
GG BRINSON (PRIVATE)	PA-75*	PAMLICO	8/24/61
WRIGHTSVILLE BEACH	NH-262*	NEW HANOVER	4/21/65
JW ALLEN (PRIVATE)	WS-82*	WASHINGTON	8/20/63
C FURLOUGH (PRIVATE)	WS-13*	WASHINGTON	9/1/63
CRESWELL MUNICIPAL	WS-27*	WASHINGTON	8/20/63
O JONES (PRIVATE)	BO-207*	BEAUFORT	3/18/55
SULLIVAN FISH FARM	FF 1^	BEAUFORT	4/30/91
NEW BERN	CR-479*	CRAVEN	11/19/52
C. J. ROBERSON	MR-347*	MARTIN	3/10/59

* = Wells from Knobel (1985)
# = Wells from NCDEHNR (1987)
% = Well from Lloyd and Daniel (1988)
^ = Richard Spruill (pers. comm.)

WELL IDENTIFIER	pH	TEMP °C	TEMP K	AKALINITY as HCO_3^- ppm	HARDNESS mg eq $CaCO_3$/L	TDS ppm	Cl^- ppm
BR-16	7.3	ND	ND	323	267	525	142
BR-19	7.6	19	292	206	166	253	24
T23x1	8.1	ND	ND	160	124	170	4
U26j6	7.6	ND	ND	200	156	190	6
NH-399	8	16.5	289.5	203	165	236	25
NH-23	7.1	ND	ND	305	245	429	84
USMC 30	7.3	18	291	330	208	489	9
CR-258	7.4	ND	ND	203	171	290	6
PA-75	7.7	ND	ND	224	179	384	7
NH-262	7.6	15.5	288.5	222	189	502	109
WS-82	7.7	21	294	396	288	584	8
WS-13	8.2	22.5	295.5	606	149	1303	234
WS-27	8.1	ND	ND	604	306	2162	758
BO-207	7.7	ND	ND	400	238	612	19
FF 1	7.1	ND	ND	189	188	293	11
CR-479	7.3	ND	ND	249	ND	ND	7.5
MR-347	8.7	ND	ND	360	ND	ND	10

ND = Not Determined

WELL IDENTIFIER	**F^- ppm**	**SO_4^{2-} ppm**	**SiO_2 ppm**	**NH_4^+ ppm**	**PO_4^{3-} ppm**	**Mg^{2+} ppm**	**Na^+ ppm**	**K^+ ppm**
BR-16	ND	0.6	29	ND	ND	7	86	4
BR-19	0.1	3	38	ND	0.07	3	16	2
T23x1	0.2	3	11	0.11	0.07	1	3	1
U26j6	<0.1	5	7	0.09	0.17	1	3	0.7
NH-399	0.1	0.3	23	ND	ND	9	12	14
NH-23	0.1	2	41	ND	ND	9	58	ND
USMC 30	0.2	8	35	0.564	0.009	3	19	4
CR-258	ND	8	ND	ND	ND	4	6	1
PA-75	0.6	0.6	78	ND	ND	12	7	3
NH-262	0.3	10	17	ND	0.2	12	67	9
WS-82	0.5	0.6	50	ND	ND	30	19	14
WS-13	1.1	33	34	ND	0.1	24	320	30
WS-27	0.9	64	40	ND	ND	50	555	50
BO-207	0.6	0.1	52	ND	ND	28	38	24
FF 1	0.35	ND	ND	ND	ND	4.2	ND	ND
CR-479	0.1	7.7	17	ND	ND	1.8	ND	ND
MR-347	ND	3.5	10	ND	ND	29	ND	ND

WELL IDENTIFIER	Ca^{2+} ppm	LATITUDE	LONGITUDE	Na/Cl MOL RAT	K/Cl MOL RAT	Ca/Mg WEIGHT RAT
BR-16	95	33 54 41	78 07 28	0.93	0.02	13
BR-19	62	33 59 34	77 58 29	1.03	0.08	21
T23x1	48	35 00 14	77 17 43	1.04	0.23	44
U26j6	60	34 58 10	77 30 11	0.69	0.11	43
NH-399	51	34 01 47	77 53 57	0.74	0.51	6
NH-23	84	34 20 33	77 54 09	1.07	0	9
USMC 30	79	34 54 49	76 54 05	3.19	0.42	26
CR-258	62	35 05 44	77 09 08	1.5	0.18	16
PA-75	52	35 08 30	76 55 30	1.58	0.39	4
NH-262	56	34 11 18	77 48 37	0.94	0.07	5
WS-82	66	35 43 60	76 45 00	3.77	1.64	2
WS-13	20	35 55 15	76 32 15	2.09	0.12	1
WS-27	40	35 52 00	76 23 30	1.09	0.06	1
BO-207	49	35 39 22	76 41 05	3.15	1.15	2
FF 1	57	ND	ND	ND	ND	ND
CR-479	82	35 07 54	77 05 39	ND	ND	ND
MR-347	70	35 42 27	76 59 11	ND	ND	ND

APPENDIX M: Chemical Analyses from Sutton and Woods (1995).

LOCATION NAME	WELL IDENTIFIER	COUNTY	DATE SAMPLED	pH
PLYMOUTH	K-17 a-5 (u)	Washington	5/23/93	7.39
GUM NECK	L-10 a-3 (u)	Tyrrell	5/11/93	7.37
GUM NECK	L-10 a-5 (l)	Tyrrell	5/11/93	7.31
LAKE PHELPS	L-13 i-1 (u)	Washington	5/7/93	8.05
LAKE PHELPS	L-13 i-5 (l)	Washington	5/7/93	7.67
NEW LAKE	M-12 l-1 (u)	Hyde	7/9/93	7.44
NEW LAKE	M-12 l-4 (l)	Hyde	5/5/93	7.33
NEW LAKE	M-12 l-4 (l)	Hyde	7/9/93	7.03
HUBS REC	N-15 y-5 (l)	Beaufort	5/10/93	7.46
HYDELAND	O-10 w-3 (u)	Hyde	5/6/93	7.38
SLADESVILLE	O-13 f-1 (u)	Hyde	5/10/93	7.67
SLADESVILLE	O-13 f-1 (u)	Hyde	7/8/93	7.57
RESEARCH STATION #3	O-17 i-2 (u)	Beaufort	5/17/93	7.15
FERRY LANDING	P-16 o-3 (l)	Beaufort	5/24/93	7.23
FERRY LANDING	P-16 o-4 (u)	Beaufort	5/27/93	7.18
WILMAR	P-21 k-6 (u)	Beaufort	5/17/93	7.27
HOBUCKEN	Q-15 u-3 (u)	Pamlico	5/18/93	7.41
HOBUCKEN	Q-15 u-5 (l)	Pamlico	5/27/93	7.49
TINGLEROAD	S-15 y-3 (l)	Pamlico	5/18/93	6.89
TINGLEROAD	S-15 y-4 (u)	Pamlico	5/18/93	7.17
TEXASGULF	TGCW11A (u)	Beaufort	5/20/93	7.09
TEXASGULF	TGCW14 (u)	Beaufort	6/21/93	7.27
TEXASGULF	TG S-11 (u)	Beaufort	6/21/93	7.21
TEXASGULF	TG S-11A (l)	Beaufort	6/21/93	7.29
TEXASGULF	TG S-15 (u)	Beaufort	5/20/93	6.92
TEXASGULF	TG S-18 (u)	Beaufort	6/21/93	7.41
TEXASGULF	TG S-28 (u)	Beaufort	6/22/93	7.03
WASHINGTON WELL FIELD #1	WWF #1 (b)	Beaufort	5/2/93	7.34
WASHINGTON WELL FIELD #2	WWF #2 (b)	Beaufort	5/26/93	7.64
WASHINGTON WELL FIELD #3	WWF #3 (b)	Beaufort	5/25/93	7.3
WASHINGTON WELL FIELD #4	WWF #4 (b)	Beaufort	5/22/93	7.2

(l) = L-CHA
(u) = U-CHA
(b) = Within both U- and L-CHA

WELL IDENTIFIER	TEMP °C	TDS ppm	Cl^- ppm	F^- ppm	SO_4^{2-} ppm	SiO_2 ppm	Fe^{2+} ppm
K-17 a-5 (u)	18	970	243	0.55	37	17.6	0.21
L-10 a-3 (u)	22	4690	1770	1.33	340	14.8	*7.60
L-10 a-5 (l)	21	8650	3630	1.17	790	10.6	*1.26
L-13 i-1 (u)	18	1290	55	1.96	90	16.3	0.32
L-13 i-5 (l)	20	1830	510	1.29	90	17.7	0.26
M-12 l-1 (u)	20	2090	520	3.2	180	16.8	0.19
M-12 l-4 (l)	20	10900	5500	1.31	1600	17.3	*3.12
M-12 l-4 (l)	22	10600	5100	1.35	1100	17.8	0.67
N-15 y-5 (l)	20	2090	760	1.19	120	17.4	*2.94
O-10 w-3 (u)	20	3730	1790	1.2	160	18.1	0.82
O-13 f-1 (u)	20	1700	470	1.49	110	20.2	*1.61
O-13 f-1 (u)	20	1720	470	1.52	110	19.5	0.15
O-17 i-2 (u)	18	620	54	0.6	0	32.2	0.78
P-16 o-3 (l)	21	1380	380	0.75	14	25.3	0.25
P-16 o-4 (u)	20	590	35	0.58	0	31	0.22
P-21 k-6 (u)	16	370	7	0.27	0	22.8	4.75
Q-15 u-3 (u)	20	950	134	1.11	35	26.4	0.19
Q-15 u-5 (l)	20	3660	1390	1.65	610	20.3	0.29
S-15 y-3 (l)	22	2440	1030	0.75	140	26	0.4
S-15 y-4 (u)	19	640	27	0.56	0	27.8	0.19
TGCW11A (u)	18	530	9	0.61	0	37.1	0.48
TGCW14 (u)	23	380	6	0.29	0	20.8	0.71
TG S-11 (u)	20	610	24	0.7	0	29.3	1.08
TG S-11A (l)	22	4900	2260	1.71	380	18.5	0.43
TG S-15 (u)	17	520	13	0.19	0	37.4	*9.29
TG S-18 (u)	22	490	5	1.01	0	29.1	0.23
TG S-28 (u)	18	530	7	0.23	0	32.6	3.3
WWF #1 (b)	17	310	7	0.15	1	17.3	2.93
WWF #2 (b)	17	360	4	0.19	0	27.8	2.89
WWF #3 (b)	17	380	8	0.4	0	21.2	1.2
WWF #4 (b)	17	390	5	0.27	0	32.3	1.13

* Inaccurate due to particulates

WELL IDENTIFIER	Mg^{2+} ppm	Na^{+} ppm	K^{+} ppm	Ca^{2+} ppm	HCO_3^{-} ppm	Br^{-} ppm	S^{2-} ppm
K-17 a-5 (u)	37	164	23	49	395	0	0.12
L-10 a-3 (u)	127	1690	82	54	600	3	ND
L-10 a-5 (l)	318	3130	124	129	498	8	0.06
L-13 i-1 (u)	12	305	22	7	783	0	ND
L-13 i-5 (l)	38	470	36	20	642	7	ND
M-12 l-1 (u)	41	560	39	21	688	3	1.55
M-12 l-4 (l)	251	3190	103	131	468	5	ND
M-12 l-4 (l)	273	3360	121	140	468	4	2.35
N-15 y-5 (l)	49	550	37	30	517	5	0.02
O-10 w-3 (u)	96	980	54	41	574	9	ND
O-13 f-1 (u)	25	450	27	18	570	3	0.06
O-13 f-1 (u)	28	480	29	19	556	2	0.47
O-17 i-2 (u)	25	28	11	74	393	0	0.01
P-16 o-3 (l)	52	323	26	71	478	4	7.1
P-16 o-4 (u)	28	19	13	57	407	0	0.03
P-21 k-6 (u)	4	10	1	77	242	0	0.01
Q-15 u-3 (u)	32	170	18	29	503	0	2.6
Q-15 u-5 (l)	80	920	40	41	542	16	1.1
S-15 y-3 (l)	96	560	31	84	453	0	2.6
S-15 y-4 (u)	38	22	12	63	444	0	0.57
TGCW11A (u)	9	11	4	81	371	0	5.8
TGCW14 (u)	5	8	1	69	264	0	0.02
TG S-11 (u)	30	39	16	51	415	0	0.28
TG S-11A (l)	102	1470	58	57	532	23	0.01
TG S-15 (u)	7	15	2	82	346	0	0.02
TG S-18 (u)	19	43	13	49	329	0	0.04
TG S-28 (u)	6	10	4	103	361	0	0.01
WWF #1 (b)	1	6	1	59	215	0	ND
WWF #2 (b)	3	10	1	63	249	0	0
WWF #3 (b)	4	7	2	62	273	0	0
WWF #4 (b)	4	9	2	65	273	0	0.01

ND = Not Determined

WELL IDENTIFIER	PO_4^{3-} ppm	Al^{3+} ppm	Li^{+} ppm	Mn^{2+} ppm	Zn ppm	NH_4^{+} ppm	NO_3^{-} ppm
K-17 a-5 (u)	0.009	0.03	0.03	<0.01	0.06	0.92	<0.001
L-10 a-3 (u)	0.012	0.07	0.08	0.05	0.01	6.62	0.001
L-10 a-5 (l)	0.016	0.03	0.11	0.02	0.01	7.89	<0.001
L-13 i-1 (u)	0.064	0.09	0.02	0.01	0.01	1.04	0.001
L-13 i-5 (l)	0.017	0.09	0.03	0.01	<0.01	1.49	0.001
M-12 l-1 (u)	0.0009	0.02	0.05	0.01	0.01	2.28	0.004
M-12 l-4 (l)	<0.001	0.03	0.09	0.07	<0.01	5.07	0.003
M-12 l-4 (l)	0.003	0.09	0.1	0.01	0.21	5.42	0.006
N-15 y-5 (l)	0.015	0.06	0.04	0.02	0.02	0.8	0.002
O-10 w-3 (u)	0.023	0.11	0.06	0.05	<0.01	3.99	0.002
O-13 f-1 (u)	0.039	0.09	0.03	0.03	0.02	1.03	0.002
O-13 f-1 (u)	0.012	0.01	0.03	<0.01	0.02	1.44	0.004
O-17 i-2 (u)	0.004	0.03	0.03	0.03	0.01	0.88	0.002
P-16 o-3 (l)	0.015	0.02	0.03	<0.01	0.09	1.18	0.001
P-16 o-4 (u)	0.028	<0.01	0.01	<0.01	0.03	0.93	<0.001
P-21 k-6 (u)	0.086	0.17	0.01	0.09	0.01	0.15	0.002
Q-15 u-3 (u)	0.04	0.02	0.02	0.01	<0.01	0.77	0
Q-15 u-5 (l)	0.017	0.03	0.04	0.01	0.06	0.9	0.002
S-15 y-3 (l)	0.003	0.22	0.03	<0.01	<0.01	1.12	0.004
S-15 y-4 (u)	0.006	0.02	0.01	0.01	<0.01	0.58	0
TGCW11A (u)	0.023	0.01	0.03	0.01	0.01	0.79	0.002
TGCW14 (u)	0.004	0.01	0.01	0.01	0.16	0.25	0.001
TG S-11 (u)	0.004	<0.01	0.02	0.01	<0.01	0.98	0.002
TG S-11A (l)	0.003	0.1	0.06	0.02	1.88	1.19	0.005
TG S-15 (u)	0.042	0.05	0.04	0.34	0.02	0.48	0.006
TG S-18 (u)	0.003	0.16	0.02	<0.01	1.51	0.76	0.005
TG S-28 (u)	0.004	0.06	0.03	0.15	1.04	0.38	0.002
WWF #1 (b)	0.076	0.04	0.01	0.08	0.01	0.06	<0.001
WWF #2 (b)	0.025	0.07	0.02	0.13	0.06	0.21	0.003
WWF #3 (b)	0.037	<0.01	0.02	0.06	0.09	0.34	0.001
WWF #4 (b)	0.025	0.05	0.03	0.07	0.16	0.33	<0.001

APPENDIX N: RESULTS OF CHEMICAL ANALYSES FROM THIS STUDY

LOCATION NAME	WELL IDENTIFIER	COUNTY	DATE SAMPLED
TOWN CREEK	DD33y1(pd)	BRUNSWICK	7/17/95
BOILING SPRINGS	FF32y1(pd)	BRUNSWICK	7/18/95
SOUTHPORT	GG32t4(pd)	BRUNSWICK	7/17/95
SOUTHPORT	SPPW 002(u)	BRUNSWICK	6/17/96
SOUTHPORT	SPPW 003(u)	BRUNSWICK	6/17/96
BRUNSWICK CO. WELL FIELD	BCPW 3(b)	BRUNSWICK	6/18/96
BRUNSWICK CO. WELL FIELD	BCPW 5(b)	BRUNSWICK	6/18/96
BRUNSWICK CO. WELL FIELD	BCPW 7(b)	BRUNSWICK	6/18/96
BRUNSWICK CO. WELL FIELD	BCPW 15(b)	BRUNSWICK	6/18/96
BRUNSWICK CO. WELL FIELD	BCPW 18(b)	BRUNSWICK	6/18/96
SNEADS FERRY WELL FIELD	SFOW 1(l)	ONSLOW	2/13/96
SNEADS FERRY WELL FIELD	SFOW 2(l)	ONSLOW	2/12/96
SNEADS FERRY WELL FIELD	SFOW 3(l)	ONSLOW	1/27/96
SNEADS FERRY WELL FIELD	SFOW 4(l)	ONSLOW	2/12/96
HUBERT WELL FIELD	HPW 2(l)	ONSLOW	3/5/96
HUBERT WELL FIELD	HPW 3(l)	ONSLOW	3/5/96
HUBERT WELL FIELD	HOW 5(u)	ONSLOW	2/27/96
DIXON FIRE TOWER	Y25Q1(u)	ONSLOW	3/5/96
ATLANTIC BEACH WELL FIELD	ABPW 5(u)	CARTERET	6/20/96
ATLANTIC BEACH WELL FIELD	ABPW 6(u)	CARTERET	6/20/96
BOGUE BANKS WELL FIELD	BBPW 2(u)	CARTERET	6/21/96
BOGUE BANKS WELL FIELD	BBPW 5(u)	CARTERET	6/21/96
BOGUE BANKS WELL FIELD	BBPW 7(u)	CARTERET	6/21/96
SURF CITY	Pe 72(u)	PENDER	6/20/96

(u) = U-CHA
(l) = L-CHA
(pd) = Peedee
(b) = within both CHAS and Peedee

WELL IDENTIFIER	pH	Eh mV	Eh corrected	Eh V	pe	TEMP °C	TEMP K
DD33y1	7.3	-152	92	0.092	1.6	18	291
FF32y1	6.9	-127	117	0.117	2.03	19	292
GG32t4	7.4	-148	96	0.096	1.66	20	293
SPPW 002	7.5	-74	170	0.17	2.92	20	293
SPPW 003	7.5	-98	146	0.146	2.51	20	293
BCPW 3	7.1	-110	124	0.124	2.32	17.5	290.5
BCPW 5	7.26	-150	94	0.094	1.62	19	292
BCPW 7	7.25	-130	114	0.114	1.97	19	292
BCPW 15	7.1	-184	60	0.06	1.03	19	292
BCPW 18	7.14	-102	142	0.142	2.45	19	292
SFOW 1	7.4	-95	149	0.149	2.6	18	291
SFOW 2	7.4	-100	144	0.144	2.51	18.5	291.5
SFOW 3	7.2	-296	-52	-0.052	-0.9	19	292
SFOW 4	6.8	-169	75	0.075	1.31	18	291
HPW 2	7.2	-108	136	0.136	2.36	19	292
HPW 3	7.35	-115	129	0.129	2.25	18.5	291.5
HOW 5	7.28	-115	129	0.129	2.23	18	291
Y25Q1	7.3	-184	60	0.06	1.04	18.5	291.5
ABPW 5	7.14	-38	206	0.206	3.55	19	292
ABPW 6	7.1	-207	37	0.037	0.64	21	294
BBPW 2	7.23	-210	34	0.034	0.58	20	293
BBPW 5	7.18	-250	-6	-0.006	-0.1	19	292
BBPW 7	7.14	-167	77	0.077	1.37	21	294
Pe 72	7.36	-120	124	0.124	2.14	19	292

WELL IDENTIFIER	AKALINITY as HCO_3^- ppm	HARDNESS mg eq $CaCO_3$/L	DO ppm	TDS ppm	Cl^- ppm
DD33y1	215	173	0.000	333	21
FF32y1	371	247	0.000	567	29
GG32t4	268	198	0.000	487	71
SPPW 002	203	194	0.412	409	76
SPPW 003	217	181	0.040	387	50
BCPW 3	325	227	0.000	484	24
BCPW 5	244	190	0.000	376	22
BCPW 7	249	188	0.000	384	25
BCPW 15	320	228	0.000	474	21
BCPW 18	337	237	0.000	501	21
SFOW 1	266	209	0.032	399	19
SFOW 2	243	206	0.350	377	20
SFOW 3	395	239	0.000	853	250
SFOW 4	290	217	0.000	467	25
HPW 2	245	208	0.000	387	31
HPW 3	210	183	0.000	340	31
HOW 5	244	203	0.000	373	24
Y25Q1	253	191	0.000	413	31
ABPW 5	317	249	0.048	487	26
ABPW 6	358	278	0.020	545	28
BBPW 2	293	233	0.154	454	28
BBPW 5	288	291	0.000	846	360
BBPW 7	343	272	0.130	536	31
Pe 72	200	192	0.024	342	33

WELL IDENTIFIER	S^- ppm	F^- ppm	SO_4^{2-} ppm	SiO_2 ppm	NH_4^+ ppm	PO_4^{3-} ppm	NO_3^- ppm
DD33y1	0.00	0.08	13	3	0.040	0.013	0.002
FF32y1	0.00	0.14	22	16	0.220	0.020	0.001
GG32t4	0.00	0.18	8	8	0.520	0.013	0.002
SPPW 002	0.00	0.13	4	9	0.242	0.043	< 0.001
SPPW 003	0.00	0.13	3	12	0.310	0.045	< 0.001
BCPW 3	0.00	0.09	5	15	0.300	0.158	< 0.001
BCPW 5	0.00	0.12	5	9	0.255	0.161	< 0.001
BCPW 7	0.00	0.12	4	10	0.229	0.134	< 0.001
BCPW 15	0.00	0.09	9	10	0.240	0.130	< 0.001
BCPW 18	0.00	0.12	4	22	0.453	0.145	< 0.001
SFOW 1	0.00	0.26	0.3	13	0.140	0.000	< 0.001
SFOW 2	0.00	0.26	0.2	13	0.170	0.002	0.001
SFOW 3	4.50	0.60	11	24	0.450	0.008	0.001
SFOW 4	0.00	0.21	20	17	0.340	0.005	< 0.001
HPW 2	0.00	0.11	3	8	0.060	0.120	0.002
HPW 3	0.14	0.08	3	7	0.030	0.110	0.001
HOW 5	0.00	0.19	1	9	0.060	0.096	0.001
Y25Q1	0.00	0.12	7	24	0.170	0.220	0.027
ABPW 5	0.00	0.26	4	17	0.697	0.009	< 0.001
ABPW 6	0.00	0.37	4	20	0.769	0.008	< 0.001
BBPW 2	0.10	0.37	4	14	0.376	0.006	< 0.001
BBPW 5	1.50	0.24	13	13	0.415	0.012	< 0.001
BBPW 7	0.05	0.19	3	20	0.564	0.009	< 0.001
Pe 72	0.00	0.17	5	8	0.036	0.108	< 0.001

WELL IDENTIFIER	NO_2^- ppm	Fe^{2+} ppm	Mg^{2+} ppm	Na^+ ppm	K^+ ppm	Ca^{2+} ppm	LATITUDE	LONGITUDE
DD33y1	0.001	1	2	8	4	66	34 10 18	78 09 56
FF32y1	0.002	4	3	20	8	94	34 00 52	78 04 58
GG32t4	0.001	0.7	8	40	17	66	33 56 37	78 00 38
SPPW 002	0.003	0.3	4	31	10	71	33 55 34	78 01 02
SPPW 003	0.003	0.4	4	26	8	66	33 55 41	78 01 42
BCPW 3	0.003	3	3	16	6	86	33 58 20	78 05 10
BCPW 5	0.003	2	3	14	5	71	33 57 10	78 05 05
BCPW 7	0.003	2	2	15	5	72	33 56 40	78 05 37
BCPW 15	0.003	2	2	16	6	88	33 59 00	78 06 09
BCPW 18	0.003	2	3	16	5	90	33 58 55	78 03 55
SFOW 1	0.001	0.6	4	12	7	77	34 34 32	77 29 05
SFOW 2	0.002	0.5	4	12	8	76	34 34 05	77 29 24
SFOW 3	0.001	0.2	9	50	27	81	34 33 34	77 29 38
SFOW 4	0.001	7	6	15	9	77	34 32 56	77 29 55
HPW 2	0.003	0.9	2	12	5	80	34 43 10	77 13 57
HPW 3	0.003	0.8	2	11	5	70	34 43 32	77 14 03
HOW 5	0.001	1	2	9	5	78	34 44 16	77 14 24
Y25Q1	0.003	4	4	15	4	70	34 36 39	77 28 59
ABPW 5	0.003	0.1	6	13	13	90	34 42 05	76 44 30
ABPW 6	0.003	0.1	13	16	15	90	34 42 05	76 42 31
BBPW 2	0.003	0.1	5	14	10	85	34 40 02	77 01 36
BBPW 5	0.003	0.3	10	40	20	100	34 39 24	77 04 09
BBPW 7	0.003	0.1	12	18	19	89	34 41 21	76 52 36
Pe 72	0.003	0.7	6	16	6	67	34 26 40	77 33 33

WELL IDENTIFIER	CALCIUM SAT. INDEX	FERRIHYDRITE SAT. INDEX	GYPSUM SAT. INDEX	DOLOMITE SAT. INDEX	Na/Cl MOL RAT
DD33y1	-0.08	0.57	-2.42	-1.49	0.61
FF32y1	-0.14	0.22	-2.14	-1.55	1.05
GG32t4	0.11	0.65	-2.69	-0.43	0.86
SPPW 002	0.13	1.77	-3	-0.71	0.63
SPPW 003	0.14	1.52	-3.03	-0.66	0.81
BCPW 3	-0.02	0.94	-2.82	-1.24	1.05
BCPW 5	-0.03	0.66	-2.87	-1.24	1.03
BCPW 7	-0.03	1.01	-2.91	-1.29	0.92
BCPW 15	0.00	-0.55	-2.53	-1.45	1.22
BCPW 18	0.07	1.14	-2.83	-1.09	1.16
SFOW 1	0.16	1.48	-4.03	-0.67	0.99
SFOW 2	0.13	1.27	-4.23	-0.76	0.91
SFOW 3	0.11	-3.19	-2.54	-0.46	0.31
SFOW 4	-0.42	-0.53	-2.24	-1.66	0.91
HPW 2	-0.04	0.84	-3.09	-1.42	0.59
HPW 3	-0.01	1.15	-3.05	-1.36	0.53
HOW 5	0.02	1.02	-3.44	-1.34	0.54
Y25Q1	0.01	0.47	-2.67	-1.02	0.75
ABPW 5	0.04	0.85	-2.87	-0.8	0.81
ABPW 6	0.07	-2.43	-2.96	-0.38	0.87
BBPW 2	0.09	-1.79	-2.94	-0.79	0.78
BBPW 5	0.04	-2.2	-2.39	-0.68	0.17
BBPW 7	0.09	-1.58	-3.09	-0.4	0.87
Pe 72	-0.04	1.02	-2.88	-0.85	0.76

WELL IDENTIFIER	K/Cl MOL RAT	Ca/Mg WEIGHT RAT
DD33y1	0.16	33
FF32y1	0.25	31
GG32t4	0.22	8
SPPW 002	0.12	18
SPPW 003	0.15	17
BCPW 3	0.22	29
BCPW 5	0.21	24
BCPW 7	0.17	36
BCPW 15	0.28	44
BCPW 18	0.23	30
SFOW 1	0.32	19
SFOW 2	0.37	19
SFOW 3	0.1	9
SFOW 4	0.32	13
HPW 2	0.16	40
HPW 3	0.14	35
HOW 5	0.19	39
Y25Q1	0.13	18
ABPW 5	0.45	15
ABPW 6	0.49	7
BBPW 2	0.34	17
BBPW 5	0.05	10
BBPW 7	0.55	7
Pe 72	0.15	11