CCR Alternative Source Evaluation Process for Aquifers at an Electric Power Facility Using δD, δ^{18}O, δ^{11}B, δ^{34}S, ^{87}Sr/^{86}Sr and Chemical Composition

by Edward Muller[1], R.L. Bassett[2], and Nicholas K. Furse[3]

[1] Corresponding author: Tetra Tech, Inc., 3801 Automation Way, Suite 100, Fort Collins, CO, 80525
[2] Geochemical Technologies Corporation, 208 Casa Verde Dr., Georgetown, TX 78633
[3] Tetra Tech, Inc., 8911 Capital of Texas Hwy, Suite 2310, Austin, TX 78759

ABSTRACT

In response to the federal Coal Combustion Residual (CCR) rule, power utilities are evaluating intra-well differences in concentrations of groundwater constituents specified in Appendix III of the rule. Changes in constituent concentrations may be due to sources beyond site facilities, and the rule allows the demonstration of alternative sources other than the CCR facility for these concentration changes. Chemical concentration and distribution of groundwater constituents alone may not be sufficient to identify a source, primarily because the monitored constituents are commonly present in groundwater. Distinguishing the constituents by source becomes critically important if the origin is off-site, and the isotopic values of indicator elements can provide this independent information. Stable isotope analyses for δ^{11}B and δ^{34}S directly relate to monitored constituents; δD and δ^{18}O of water becomes useful if landfill materials experience evaporation, or multiple aquifer assessment is needed; and ^{87}Sr/^{86}Sr provides additional information as a co-migrating constituent. At the Sutton Energy Complex, New Hanover County, North Carolina, evaluation of δ^{11}B, ^{87}Sr/^{86}Sr, and δ^{34}S in the surficial aquifer and underlying Pee Dee Aquifer confirmed the Pee Dee values were consistent with marine water influence and are unrelated to CCR waste sources; furthermore the δD and δ^{18}O range was narrowly confined compared to the surficial aquifer, also indicating hydraulic separation of the two aquifers. The isotopic results provide independent data supporting separation of the Pee Dee Aquifer from the surficial aquifer and the CCR source leachate. This evaluation identifies a marine water influence as an alternative source for elevated Appendix III constituents, specifically B and SO_4.

INTRODUCTION

Surface water and groundwater at the Duke Energy L.V. Sutton Energy Complex, New Hanover County, North Carolina, is being evaluated for the status of chemical constituents potentially associated with CCR material stored in waste piles and impoundments (Figure 1). The Site is a former coal-fired electrical power generation facility located on a peninsula, adjacent to the Cape Fear River on the west, and the Northeast Cape Fear River one mile east (Figure 1). The Sutton Energy Complex is approximately 3,300 acres (13.35 km^2) and contains power plant structures, ash basins, a 1,100-acre (4.45 km^2) cooling pond (Lake Sutton), and associated canals. Ash generated from coal combustion was initially stored in an ash disposal area; since 1971, ash has been stored in two locations, the 1971 and 1984 Ash Basins (Figure 1). The two principal aquifers at the Site and the focus of this study are the Pee Dee Aquifer and overlying surficial aquifer (Figure 2). The Site ceased burning coal in November of 2013, and the facility no longer generates coal ash.

Discharges from the cooling ponds and ash basins are permitted by the North Carolina Department of Environmental Quality (NCDEQ) under the National Pollution Discharge Elimination System (NPDES) permit NC0001422. Under that permit, Duke Energy has been performing groundwater monitoring since 1990. Groundwater monitoring has revealed concentrations of several constituents of interest (COI), among them boron (B) and total dissolved solids (TDS), in excess of the North Carolina Administrative Code (NCAC) Title 15A groundwater quality standards or the Interim Maximum Allowable Concentrations (IMAC) in groundwater samples collected in ash pore water wells (SynTerra, 2015a).

The NCDEQ has additionally required Duke Energy to initiate several interim corrective actions. Recommendations have included collection of additional samples beyond those from the shallow surficial aquifer to include the underlying Pee Dee Aquifer. Such a study could identify potential sources of elevated B concentrations within the Pee Dee Aquifer at the site, alternative sources might exist to CCR such as sea water intrusion, or other unidentified sources, as well as provide an updated site conceptual model. The objectives of this study are: 1) determine the intrinsic isotopic signature of dissolved constituents of background, Site, and downgradient groundwater as well as coastal ocean water; 2) evaluate potential mixing of native groundwater principally the Pee Dee Aquifer and coal combustion residuals (CCR) derived water; and 3) provide geochemical and isotopic support of hydrologic site conceptual models.

These objectives are also consistent with the CCR rule options. As provided for in 40 CFR 257.949(e)(2) "The owner or operator may demonstrate that a source other than the CCR unit caused the statistically significant increase over background levels for a constituent or that the statistically significant increase resulted from error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality." The CCR

Rule does not define the scope and extent of the process needed to define the alternative source (EPA, 2015).

While B levels in wells downgradient of the ash pond in both the surficial aquifer (<0.05 to 1.46 mg/L) and upper Pee Dee Aquifer (0.167 to 1.56 mg/L) are significantly above background B concentrations (<0.05 to 0.262 mg/L), B concentrations in lower Pee Dee background wells (0.116 to 4.36 mg/L) are within the range of concentrations (1.83 to 2.55 mg/L) seen in lower Pee Dee downgradient wells. Chemical concentrations alone, therefore, are insufficient to confirm source at this site and stable isotope analyses for B, and other supporting constituents should provide additional specificity. B isotope determinations (δ^{11}B) have a history of application to hydrologic studies because of: 1) the broad range of naturally occurring reported values from approximately -40 to 60‰; 2) chemically conservative groundwater transport with no significant precipitation concerns; 3) absence of redox effects; and 4) narrow ranges of δ^{11}B values for many potential sources such as marine water, oil and gas brines, deep basin brines, saline lakes, wastewater, etc. (Bassett, 1990; Coplen et al., 2002; Foster et al., 2016; Vengosh et al., 1991). Recently, δ^{11}B measurements have extended to CCR applications (Bassett and Muller, 2017; Buszka et al., 2007; Davidson and Bassett, 1993; Ruhl et al., 2014; EPRI, 2012; Spivak-Birndorf, L.J. and B.W. Stewart. 2006). The unique contribution to CCR is that the δ^{11}B analysis is for B which is a key indicator element specifically monitored as an Appendix III constituent of interest. It has now been shown that the δ^{11}B range for CCR is narrow (-19.2 to 5.0‰, EPRI, 2012), and depleted relative to groundwater in general; however, the general range is less significant than is a determination of the specific values at a given location. At this site the currently available relevant δ^{11}B range for CCR is narrower (-4.6 to 1.0‰) than the range of published values; and significantly depleted from other sources. For comparison, a locally measured marine water δ^{11}B value was 38.1‰ and the δ^{11}B range for the surficial and Pee Dee aquifers is from 6.7‰ to 41.2‰. Similarly, the sulfur isotopic analysis (δ^{34}S) expands the interpretation capabilities for sulfate (and H_2S); SO_4 is also an Appendix III monitored constituent, and direct application of δ^{34}S to SO_4 concentrations could be correlative with the δ^{11}B and B results. Furthermore, stable isotopes of hydrogen (δD) and oxygen (δ^{18}O) are commonly used as an indicator for the water transporting monitored constituents; source specific signatures provide additional independent data beyond chemical composition.

Additionally, strontium (^{87}Sr/^{86}Sr) isotopic ratios have historically been widely employed in geologic and hydrologic studies and this analysis is a valuable co-migrating indicator constituent in CCR studies (Brubaker, 2010; Hamel et al., Hurst et al, 1991; Mattigod et al., 1990; 2010; Ruhl, et al., 2014; Spivak-Birndorf, 2012; WDNR, 2013). Determining a representative Sr isotopic value can be complicated by solubility concerns in carbonate aquifers that are releasing Sr by dissolution; however, the ^{87}Sr/^{86}Sr values are often somewhat unique to the stratigraphic age of a specific carbonate mineral source. In this study, all of these isotopic tools are employed to assess the presence of elevated

concentrations of monitored constituents in both the surficial and Pee Dee aquifers and evaluate whether or not an alternative source to CCR should be considered.

Figure 1. Site location map with sample wells and cross section locations (modified from SynTerra, 2016b).
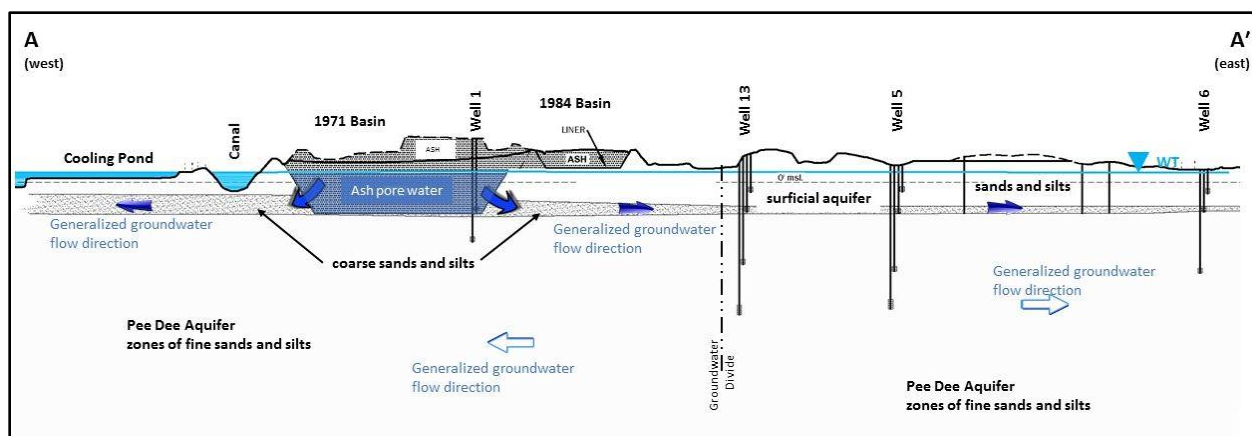
GEOLOGY AND HYDROGEOLOGY

The Site is located within the narrow Coastal Plain (approximately 90 to 150 miles (145 to 241 km)) in width from the Atlantic Ocean westward to the Piedmont province and comprises two subdivisions: a tidewater region and the Inner Coastal Plain. The Site lies within the tidewater region, a coastal area where large streams and their tributaries are affected by ocean tides (Bain, 1970; McSwain et al., 2014, Woods, et al., 2000). At the Site, the sedimentary units include Coastal Plain surficial deposits and the Pee Dee Formation. The surficial deposits extend from the surface to approximately 50 feet (15 m) below ground surface (bgs), with the upper 20 feet (6.1 m) comprised of well-sorted

fine to medium grained sand with poorly sorted medium- to coarse-grained sands with discontinuous layers of sandy gravel in the lower 30 feet (9.1 m). The ash basins and former disposal areas sit atop the surficial deposits north and northwest of the main Plant area (Figure 1).

The Pee Dee Formation lies unconformably below the surficial deposits, consists of fine sands and silts with occasional clay lenses, and becomes finer grained with depth becoming in places a low plastic clayey silt. No underlying crystalline rocks were encountered at the deepest horizon. Both the surficial deposits and Pee Dee Formation are unconsolidated, and no geologic structures are present within the Site area. South of the Site, a confining unit is reported to be present between the surficial zone and Pee Dee Formation, however, this confining unit was not found to be present at the site. The contact between Pee Dee Formation and the surficial aquifer is sharp and with greatly contrasting soil types. It is expected that even the coarsest sediments of the Pee Dee Formation are less permeable than the surficial deposits and will impede vertical groundwater flow, while the flow within the coarse-grained layers of the surficial aquifer will be significantly higher. All site drilling and aquifer characterization data are provided by SynTerra (2015a, 2015b, 2016a, 2016b).

Regional groundwater flow in the surficial aquifer within the peninsula may be either to the west or east towards one of the rivers on either side of the peninsula, or to the south where the rivers converge. At the Site, the hydrogeology has been evaluated by SynTerra Corporation (2015a). The 1971 ash basin was excavated below the water table to approximately 40 feet (12.2 m) below grade. All but the lower two feet of surficial sands were removed during evacuation, therefore there is approximately 80 feet (24.4 m) of ash lying just above the contact between the surficial and Pee Dee Aquifers, half of which is saturated. The water table at the Site is located at depths between 3 to 18 feet (1 to 5.5 m) bgs. The initial zone of saturation is comprised of pore water located within the ash basins and shallow sediment. Infiltration of surface water causes mounding in the ash, and groundwater flows radially from the 1971 ash basins (Figure 2). The surficial aquifer groundwater flow is hydraulically bounded and groundwater elevations controlled to the south by the discharge canal (Figure 1) and on the west and south by the cooling ponds and Cape Fear River (Figure 1). Surficial groundwater east and south of the ash basins flows to the east, southeast and south. A line of sand hills has created a localized recharge area and groundwater divide, extending roughly north to south, northeast of the ash ponds. Surficial groundwater from this divide flows radially, primarily east and west. Groundwater gradients in the surficial aquifer are influenced by this groundwater divide and site geology as well as the presence of man-made features (e.g. plant, cooling pond, ash basin) and onsite and offsite extraction wells. In contrast, water level data indicates the groundwater flow in the Pee Dee Aquifer is flowing radially from a hydrologic high east of the ash basin area; west of the hydrologic high groundwater flow is westwards under the ash basins and cooling ponds and southward out of the complex property. The hydraulic

conductivity of the surficial aquifer is larger than that of the Pee Dee Aquifer, resulting in preferential lateral flow. The lateral flow is influenced by the presence of surface water bodies and the operation of production wells located along the eastern Site boundary (SynTerra, 2015a). There is a downward vertical gradient between the upper and lower surficial aquifer wells in most locations, but because of the lower hydraulic conductivities in the Pee Dee, the flux of water is greater in the shallow formations above the Pee Dee. Groundwater velocity calculations indicate flow rates from the ash basins to surrounding areas are the highest due to the hydraulic gradients from the basins to the surrounding areas.

Figure 2. Generalized site hydrogeology for W-E cross-section (Figure 1 for reference).

METHODS

Sample Collection
A total of 42 water samples were collected for isotopic analysis; a summary of analytical results is provided in Table 1. A sample of open ocean surf zone seawater was collected from Wrightsville Beach, North Carolina. Groundwater samples were collected from monitoring wells, a water supply well, and four samples collected in July 2017 from temporary wells screened in the Surficial aquifer immediately below the bottom of the ash basin (samples TW-46, TW-132, TW-136, and TW-202, Table 1). Samples were collected using professionally accepted procedures, field filtered, collected in plastic bottles, and shipped without preservative to appropriate analytical laboratories. All field sampling was conducted by personnel from SynTerra Corporation.

Analytical Methods
Hydrogen (δD) and oxygen (δ^{18}O) isotopes of water were measured at the University of Arizona Environmental Isotope Laboratory using a gas-source isotope ratio mass spectrometer (Finnigan Delta S). For hydrogen, samples were reacted at 750°C with Cr metal using a Finnigan H/Device coupled to the mass spectrometer. For oxygen,

samples were equilibrated with CO_2 gas at approximately 15°C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials VSMOW and SLAP. Precision is 0.9‰ or better for δD and 0.08‰ or better for $\delta^{18}O$ based on repeated internal standards.

Boron ($\delta^{11}B$) isotopic composition was measured at the Tetra Tech Boron Isotope Laboratory by negative thermal ionization mass spectrometry (NTIMS) on a TIMS VG 336, built by VG Isotopes Limited, Cheshire, England. Sample preparation and analytical procedures are based on the methods described in Hemming and Hanson, 1994. The NBS SRM 951 standard was used for correcting measured ratios to the accepted reporting $\delta^{11}B$ formalization with precision of 1‰ (2σ) or better.

Strontium ($^{87}Sr/^{86}Sr$) was measured by Isotope Tracer Technologies by thermal ionization mass spectrometry (TIMS) using a Triton (Thermo Finnigan, Bremen, Germany) mass spectrometer. Strontium separation is conducted via ion-exchange procedure that utilizes Sr-specific resin method (Horwitz, et al., 1992). All Results are corrected and reported against the International Standard NIST SRM 987 $^{87}Sr/^{86}Sr$ (Actual value = 0.710245). Continuous monitoring of standards in the sample log book provides the first check on the analytical results. The standards (NIST 987) analyses must remain within the working limits of 0.71024 ± 0.00004.

Sulfur ($\delta^{34}S$) was measured by Isotope Tracer Technologies on SO_2 gas by infrared mass spectrometry. Samples are loaded into a Fisons Instruments elemental analyzer to be flash combusted at 1100°C. Released gases are carried by ultrapure helium through the analyzer, then separated by gas chromatography. Clean SO_2 gas is carried into the Mat 253, Thermo Scientific, IRMS for analysis. Data is corrected and normalized using three international standards, IAEA SO6, IAEA SO5, NBS 127, and two calibrated internal standards that bracket the samples Standards are run at the beginning, middle, and end of every run. Repeats of samples are another way of checking the stability and precision of the analytical procedure. Typically, at least one repeat is included for every three (3) samples. The error for sulfate standard material is expected to be +/- 0.5‰ or better.

All documentation, transfers, and data quality have been reviewed and conform to the QA/QC criteria established by the analytical laboratory, and internal quality review protocols

RESULTS

A summary of chemical and isotope analytical results is provided in Tables 1 and 2. All samples were checked for acceptable quality and stability and were deemed to be consistent with any prior analyses from the same locations. Some sample procedures for volumes required, and schedule, were modified from the standard protocol to

accommodate the need for isotopic analyses. B, S, and Sr isotopic analyses are performed on filtered samples only and larger volumes were required to provide enough mass for the measurements.

Parameter			Alk[1]	B	Br	Ca	Cl	Mg	Na	Sr	SO4
Well Location	Sample ID	Collection Date	Analytical Results (mg/L)								
Source											
1	ABMW-01S	6/4/2015	400	3.94	NA	128	83	51	54.5	6.28	83
2	ABMW-02S	6/7/2017	216	0.159	<0.1	58.4	6.2	6.2	10.1	1.42	<0.1
2	AMBW-02D	6/7/2017	119	0.823	<0.5	41.2	48	11.9	42	1.41	96
8	CCR-103B	9/7/2017	150	1.3	NA	43.6	5.8	10.4	8.36	0.1	33
23	TW-46	7/25/2017	352	1.1	NA	97.6	6	34.1	15.2	3.03	100
24	TW-202	7/25/2017	465	1.68	NA	140	11	38.2	26.2	4.98	140
25	TW-132	7/25/2017	438	2.9	NA	93	49	43.9	87.8	3.49	140
26	TW-136	7/25/2017	362	1.22	NA	98.4	39	30.8	42	3.69	74
Upper Pee Dee Aquifer											
3	AW-02D	6/3/2015	180	0.666	NA	13.3	160	7.58	172	0.107	35
4	AW-05D	1/13/2016	136	0.334	NA	12.8	120	5.97	105	0.084	15
5	AW-06RD	6/6/2017	179	0.806	0.69	6.47	160	5.7	188	0.115	20
6	AW-07RD	6/6/2017	229	0.779	0.52	9.47	130	6.07	168	0.081	5.1
7	AW-09D	6/6/2017	194	0.668	0.96	14.7	250	9.43	231	0.131	52
10	MW-05CD	7/6/2017	241	0.111	1.2	16.6	280	11.1	313	0.14	160
10	MW-05D	7/6/2017	367	0.262	2.8	16.6	280	12.9	590	0.208	100
13	MW-23D	6/6/2017	270	0.902	0.7	9.79	170	6.27	223	0.096	15
14	MW-37CD	7/7/2017	104	<0.050	<0.5	12	6.9	0.119	50.9	0.083	6.1
14	MW-37D	7/7/2017	116	0.12	0.17	11.8	48	2.09	64.7	0.047	7.6
15	MW-38D	6/8/2017	346	1.56	2	13.4	470	14	437	0.21	120
16	MW-39D	6/8/2017	140	1.08	<2	4.09	380	9.07	362	0.143	43
17	MW-40D	6/8/2017	289	1.22	1.5	9.36	360	11.2	332	0.15	110
19	PZ-06D	6/7/2017.	171	0.769	0.77	13	180	6.3	173	0.116	42
20	PZ-10D	6/7/2017	151	0.483	0.61	15.4	140	7.38	145	0.116	31
1	ABMW-01D	6/17/2015	140	0.167	NA	31.7	53	9.84	59.5	0.179	1.6
8	CCR-103D	9/7/2017	240	0.763	<0.1	4.93	210	6.1	221	0.1	68
22	SMW-06D	1/14/2016	353	1.03	NA	12.4	190	4.05	280	0.107	<0.5
Lower Pee Dee Aquifer											
4	AW-05E	1/13/2016	375	1.83	NA	4.53	580	11.1	541	0.157	33
5	AW-06RE	6/6/2017	362	2.01	1.8	12.6	440	6.41	457	0.123	80
10	MW-05RE	7/6/2017	81.8	0.116	<0.5	24.6	30	1.07	49.9	0.082	27
11	MW-08E	7/6/2017	528	4.36	7	22.5	1500	22.6	1250	0.55	120
13	MW-23E	6/6/2017	278	2.55	2.1	3.06	530	7.56	483	0.13	120
14	MW-37E	7/7/2017	279	1.5	<2	11.2	410	10	382	0.167	79
18	MW-41E	7/6/2017	584	4.25	5.9	18.7	1300	16.7	1080	0.481	94
Seawater											
	Seawater[2]		145	4.5	67	411	19350	1290	10760	8	2710
Upper surficial aquifer											
4	AW-05B	1/13/2016	<5	<0.05	NA	4.17	2.4	0.178	1.62	0.006	16
9	MW-04A	1/13/2016	<5	0.067	NA	16.9	2.7	5.16	3.16	0.063	83
10	MW-05A	6/8/2017	<5	<0.05	<1	0.169	1.6	0.114	0.948	<0.005	3.9
10	MW-05B	6/8/2017	<5	<0.05	<0.5	0.777	2.7	0.368	1.47	0.008	5.4
13	MW-23B	6/6/2017	31	<0.05	NA	13.4	2	1.03	1.32	0.226	4.9
14	MW-37B	6/8/2017	<5	<0.05	NA	0.385	2.6	0.134	1.55	<0.005	5.2
21	SMW-01B	1/13/2016	14.5	0.175	NA	25.5	17	2.07	12.1	0.075	68
22	SMW-06B	1/14/2016	6.4	0.057	NA	8.28	5.6	0.973	8.52	0.038	40
Lower surficial aquifer											
4	AW-05C	1/13/2016	<5	<0.05	NA	5.45	3.2	0.563	1.93	0.028	16
10	MW-05C	6/8/2017	7.5	<0.05	NA	2.79	11	1.66	10	0.016	12
11	MW-08	6/6/2017	11.9	<0.05	0.11	4.71	15	2.47	10.9	0.035	17
12	MW-12R	6/6/2017	40.3	1.46	NA	56.4	130	10.7	72.8	1.32	140
13	MW-23C	6/6/2017	28.3	0.365	NA	14.4	5	2.74	4.23	0.423	23
14	MW-37C	6/8/2017	44	<0.05	NA	11	3.6	1.94	2.47	0.02	9.3
21	SMW-01C	6/9/2017	<5	0.78	<1	31.8	48	6.2	31.7	0.487	130
22	SMW-06C	1/14/2016	<5	0.298	NA	22.8	34	4.07	18.2	0.178	70

Notes:
1. ALK = Alkalinity as $CaCO_3$
2. Data reported in Table 12-1: The Composition of Seawater in The Geochemistry of Natural Waters (Drever, 1982)
< = Concentration not detected at or above reporting limit
NA = Not analyzed

Table 1. Chemical analyses of wells sampled for isotope analyses.

| | Analysis | B | Sr | SO$_4$ | δD | δ^{18}O | δ^{11}B | δ^{34}S | ^{87}Sr/^{86}Sr |
| | Reporting Units | mg/L | mg/L | mg/L | ‰ | ‰ | ‰ | ‰ | ratio |
Well Location	Sample ID	Collection Date				Analytical Results				
Source										
2	ABMW-02D	5/17/2017	0.831	1.37	99	-7	-1.4	-2.1	10.2	0.71042
2	ABMW-02S	5/17/2017	0.169	1.47	<0.1	-18.9	-4.3	1	NS	0.71042
8	CCR-103B	5/17/2017	1.18	0.1	49	-17.7	-4	0	10.2	0.71031
23	TW-46	7/25/2017	1.1	3.03	100	NS	NS	-4.6	NS	NS
24	TW-202	7/25/2017	1.68	4.98	140	NS	NS	-1.4	NS	NS
25	TW-132	7/25/2017	2.9	3.49	140	NS	NS	-0.9	NS	NS
26	TW-136	7/25/2017	1.22	3.69	74	NS	NS	-3.4	NS	NS
Upper surficial aquifer										
4	AW-05B	5/15/2017	0.019	0.047	19	-28.9	-5.2	13.9	5.7	0.70915
5	AW-06RB	5/15/2017	0.02	0.049	36	-21	-4.2	15.3	6.1	0.71045
9	MW-04A	5/15/2017	0.008	0.007	3.8	-37	-6.1	34	NS	0.71113
10	MW-05A	5/16/2017	0.006	<.005	9.2	-21.6	-4.5	NA	6.3	NS
10	MW-05B	5/17/2017	0.007	0.008	15	-20.5	-4.2	31.7	12	0.71088
13	MW-23B	5/16/2017	0.019	0.259	5.2	-19.2	-3.9	14	2	0.71042
14	MW-37B	5/18/2017	0.01	<.005	7.1	-24.6	-5	33.2	5.2	NS
21	SMW-01B	5/17/2017	0.318	0.191	76	-16.8	-3.1	12.2	6.5	0.7102
22	SMW-06B	5/17/2017	0.07	0.028	38	-21.1	-3.9	16.3	6.8	0.70966
Lower surficial aquifer										
4	AW-05C	5/15/2017	0.016	0.015	15	-24	-4.8	20.4	0.7	0.71031
10	MW-05C	5/17/2017	0.028	0.017	12	-22.4	-4.6	24.2	9.4	0.70845
11	MW-08	5/16/2017	0.038	0.034	15	-23.2	-4.4	NA	3.3	0.70841
12	MW-12R	5/15/2017	0.989	0.923	110	-8.8	-1.3	6.7	9.4	0.7103
13	MW-23C	5/16/2017	0.414	0.474	27	-25.8	-4.6	23.7	10	0.71039
14	MW-37C	5/18/2017	0.016	0.02	9.5	-21.9	-4.6	33.7	6.8	0.709
8	CCR-103C	5/17/2017	3.03	0.1	170	-15	-2.9	9.3	8.9	0.71041
21	SMW-01C	5/17/2017	0.705	0.524	120	-12.3	-2.3	12	8.4	0.71008
22	SMW-06C	5/17/2017	0.259	0.156	65	-17.1	-3.6	2.5	10.6	0.70957
Upper Pee Dee Aquifer										
4	AW-05D	5/15/2017	0.339	0.074	13	-20.6	-4.2	28.2	33.7	0.70899
5	AW-06RD	5/15/2017	0.938	0.086	3.3	-20.4	-3.9	33.6	29.5	0.70886
10	MW-05CD	5/16/2017	1.15	0.155	180	-22.9	-4.2	35.8	3.7	0.70846
10	MW-05D	5/17/2017	2.46	0.21	91	-17.8	-3.8	40.9	13.1	0.70838
13	MW-23D	5/16/2017	0.897	0.092	13	-19.9	-4	23.7	20.6	0.70875
14	MW-37CD	5/15/2017	0.057	0.096	8.2	-25.6	-4.7	18.9	8.2	0.70917
14	MW-37D	5/18/2017	0.13	0.051	7.5	-21.9	-4.6	29.1	38.6	0.70842
8	CCR-103D	5/17/2017	0.828	0.1	72	-19.3	-4.1	36.9	12.4	0.70898
22	SMW-06D	5/17/2017	1.12	0.115	0.7	-17.7	-3.9	31	NS	0.70837
Lower Pee Dee Aquifer										
4	AW-05E	5/15/2017	1.94	0.186	12	-15	-3.4	35.1	40.7	0.7086
5	AW-06RE	5/15/2017	2.5	0.156	110	-19	-3.7	38.9	28.3	0.70847
10	MW-05RE	5/16/2017	2.66	0.475	390	-21.8	-4.2	27.7	-6.3	0.70831
11	MW-08E	5/16/2017	4.73	0.827	160	-16.4	-3.4	35.9	31.5	0.70826
13	MW-23E	5/16/2017	2.55	0.124	98	-16.6	-3.5	41.2	31.1	0.70866
14	MW-37E	5/15/2017	1.49	0.17	59	-17	-3.4	32.4	35.9	0.709
18	MW-41E	5/16/2017	4.54	0.515	99	-16.9	-3.5	38.4	35.1	0.70826
Ocean-Sutton										
OCEAN-SUTTON		5/15/2017	4.6	8.04	2900	6.8	0.9	38.1	20.9	0.70918

Notes:

NA = Not analyzed due to insufficient element mass

NS= Analysis not scheduled as a part of the sampling and analysis plan

Table 2. Results of isotope analyses.

ALTERNATIVE SOURCE OPTIONS

At most sites, consideration should be given to the fact that CCR related releases of leachate may not be the source for some constituents detected in the groundwater above background or may be a fractional component of the sample collected at a monitoring well. To assess this, alternative source definition either onsite or offsite will

be required to adequately explain elevated concentrations or temporal variability of Appendix III constituents. For this Site, Appendix III constituents (B, SO_4, TDS) have been observed at elevated levels in both the surficial and Pee Dee aquifers. Elevated TDS, B, and Cl in the coastal plain aquifers is ostensibly of marine water origin, but other sources are certainly plausible. Criteria considered in this study for alternative sources includes a broad and objective list of source types (Table 3). First consideration should be on whether any specific potential source for these constituents has ever been identified in the proximity of the Site; proximity could be interpreted as up to several miles in distance if migration by surface or groundwater flow supports it. Secondly, whether the hydrogeology is favorable, which includes presence and aerial extent of shallow aquifers with adequate hydraulic properties (e.g., porosity and hydraulic conductivity, and appropriate current or historical flow gradients). Thirdly the possibility of a hydraulic connection to site aquifers of any potential source would be required; and fourthly, the potential sources must have relevant chemical composition. This approach was selected for this study to be objective and comprehensive. All plausible sources identified in Table 3, other than residual marine water and migration of CCR leachate from onsite sources, can be reasonably eliminated. All other listed potential sources such as oil and gas brines, mining and municipal waste water, landfills etc. can be documented generically as being capable of releasing wastewater with chemical compositions that have these elevated constituents, and more (TDS, Cl and B); none, however, are found in the region and thus fail the proximity criteria and are not applicable and cannot be evaluated with respect to hydrology criteria. Naturally occurring geologic material as a source is not justifiable for these constituents at the site because extensive borings and excavations have been completed without unexpected changes in lithology. The last category of "Other Unidentified Sources" (Table 3) is important and will need to be pursued if the population of "Identified" alternative sources fail to adequately describe the observed data.

Potential Alternative Sources	Qualifying Criteria: Proximity	Qualifying Criteria: Hydrogeology	Qualifying Criteria: Hydraulic Connection	Qualifying Criteria: Chemical Composition
Onsite CCR Sources	Yes	Yes	Yes	Yes
Offsite CCR Sources	None Identified	No	No	Yes
Marine Water	Yes	Yes	Yes	Yes
Municipal/Residential Wastewater	None Identified	No	No	Yes
Oil/Gas/Mining Operations	None Identified	No	No	Yes
Commercial/Industrial Disposal	None Identified	No	No	Yes
Private/Municipal Landfills	None Identified	No	No	Yes
Naturally Occurring Geologic Origin	None Identified	No	No	?
Other Unidentified Sources	Pending, dependent on outcome of this study	No	No	Yes

Table 3. Alternative Source Considerations for Appendix III Constituents.

CCR leachate and marine water both can be contributors to the elevated monitored constituents of TDS, Cl, B and Ca; CCR leachate is derived from the plant site, marine water intrusion is well documented for these coastal areas, and the hydrogeology is favorable. Distinguishing among these two options for the surficial and Pee Dee aquifers is accomplished by using both chemical and isotopic composition.

EVALUATION OF A MARINE SOURCE CONTRIBUTION TO THE PEE DEE AQUIFER USING GENERAL CHEMISTRY

Seawater incursions in general do not completely convert groundwater to marine water composition at most sites, but rather mix baseline chemical compositions, and in many locations the Pee Dee Aquifer is in transition. At the Site, samples of background groundwater composition for the Pee Dee Aquifer that are unequivocally unaffected by marine water have not been identified. The upper and lower Pee Dee Aquifers at the site are consistently a Na-HCO_3-Cl water type, whereas the CCR source leachate is a Ca-HCO_3-SO_4 type and the surficial aquifer a Ca- SO_4 type. A star display is used as a means of characterizing the general chemical composition of the surficial aquifer, Pee Dee Aquifer, both upper and lower zones, and the CCR source leachate (Fig. 3). The upper and lower Pee Dee zones are hydraulically connected, but a small compositional difference is evident between the zones. A larger difference can be observed between the Pee Dee Aquifer and either the surficial aquifer (upper and lower) or the CCR leachate samples.

The upper and lower Pee Dee units both contain a Na-HCO_3-Cl type water which is consistent with marine influence, but an order of magnitude more dilute than seawater. It is instructive to compare general seawater composition to the Pee Dee Aquifer to illustrate the differences and similarities. Seawater has a Cl value of ~19,000 mg/L, compared to the highest observed value for the samples collected from MA-08E in the Pee Dee Aquifer of 1,500 mg/L (Table 1). The difference is approximately a factor of 10. By diluting the seawater by a factor of 10 and making the appropriate scaling changes for B, Sr and Mg, the "diluted" seawater is added to the Star Diagram for the Lower Pee Dee (Figure 3). The discrepancies between the diagram for seawater and the Pee Dee are primarily with respect to concentration rather that the compositional shape except for Mg and B. Mg is known to be enriched in seawater and ion exchange with the sediments in the Pee Dee would be a reasonable process for the lower Mg observed in Pee Dee Aquifer water. B in some samples is higher than expected and is probably derived from desorption as discussed below. This seawater plot includes diluted seawater and does not include the effect of mixing with the background groundwater composition.

It has been established already that in some locations the surficial aquifer has been impacted by discharge from CCR landfills and impoundments, but not the Pee Dee Aquifer (SynTerra, 2016a, 2016b). The concentration of Cl can be used to approximate the impact of marine water, but only if the mixed Cl concentration values are high

enough. Cl in seawater is ~19,000 mg/L and even a small percentage by volume should increase Cl by detectable amounts. Regionally the background value for the Pee Dee Aquifer can be estimated as <100 mg/L from the data of McSwain et al. (2014). These authors used 250 mg/L Cl as the lower bounding value for the indication of marine influence in the Pee Dee Aquifer in the region of greater New Hanover County; marine water mixing was suspected for higher Cl concentrations. For the samples used in this study, all but one from the Lower Pee Dee and about a third of the upper Pee Dee samples exceed the 250 mg/L Cl limit (Table 1); nevertheless, even though CCR
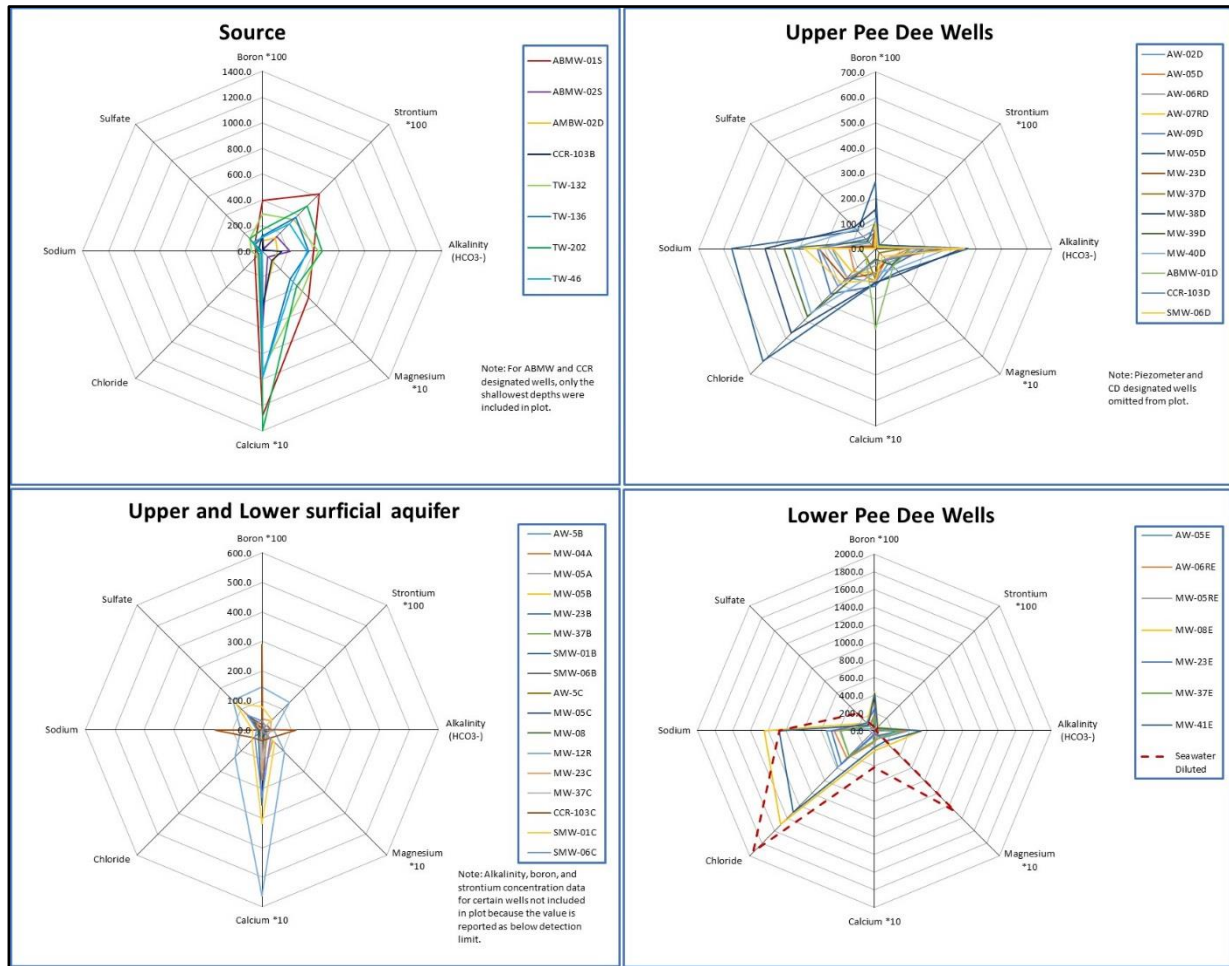
leachate has low Cl content this does not eliminate the potential for CCR influence.

Figure 3. Star Diagrams for the surficial aquifer, Pee Dee Aquifer, and CCR Source.

Using Cl alone for detecting the intrusion of marine water is inconclusive at low mixing percentages: the chemical composition is complex, mixing boundaries are difficult to define, the mixing may involve reactions with the aquifer matrix, and additional local water sources may contribute. The Cl/Br ratio has been used historically to identify the presence of seawater intrusion into freshwater aquifers, and for differentiating oil and gas brines, road salt, animal wastes, etc. from local groundwater (Andresen and Fleck,

1997; Davis et al., 1998; Hudak, 2003; Vengosh et al., 1999; Whittemore, 2007). The marine Cl/Br ratio of ~290 represents a narrow range, is consistent, and is generally different from that of common aquifer systems. The Cl/Br for the Pee Dee Aquifer in the New Hanover region using analytical results of McSwain et al. (2014, Appendix 2) is compared to analytical results from the Site and is shown in Figure 4
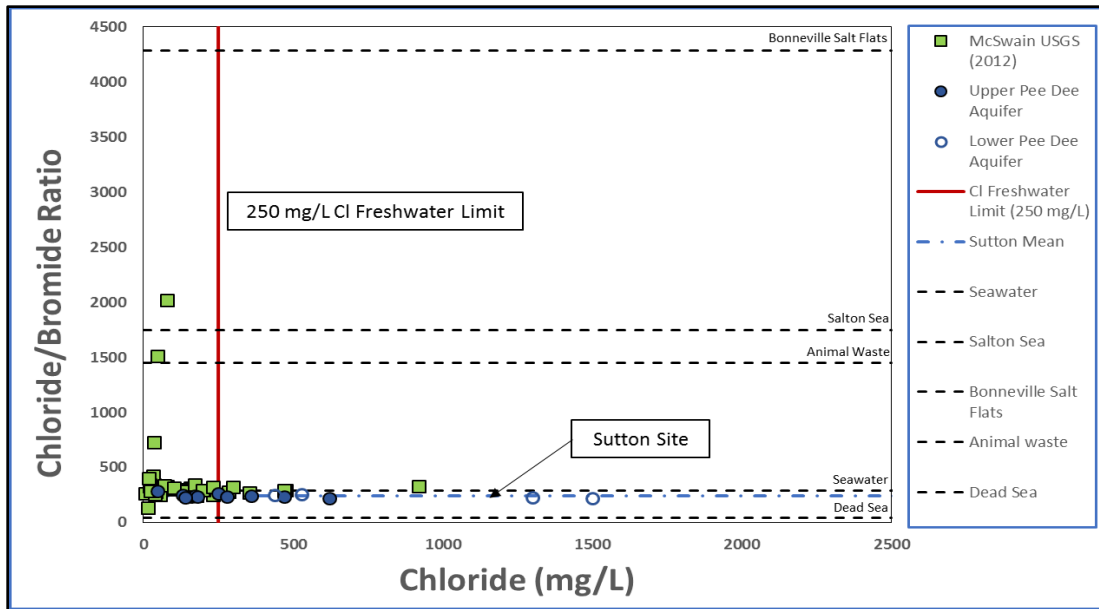

Figure 4. Cl/Br Plot for Comparative Systems.

At higher Cl concentrations (>250 mg/L) the Cl/Br ratios are near to, but not exactly matching, the seawater ratio, and widely deviate (238 to 339 mg/L) from the seawater ratio as chloride concentrations decrease below 250 mg/L Cl (Figure 4). There are too few samples with Cl above 250 mg/L to evaluate a ratio with confidence; however, in comparison to Cl/Br ratios from other referenced sources the seawater comparison is reasonable, but not definitive.

The "native" or background composition for the Pee Dee Aquifer is not known for this site. As an example of the possible mixing circumstance for the local Pee Dee Aquifer, it could be assumed that background native Pee Dee Aquifer composition is similar to wells such as the analysis for well NH-864 as reported in McSwain et al. (2014, Appendix 2, Table 4.2). This analysis from the Pee Dee Aquifer, is similar to other background candidates, has low Cl (18.6 mg/L) and is located reasonably far (~10 miles (10 Km)) from the shore line. If this water were assumed representative of native groundwater, then a mixture of 8% seawater and 92% background groundwater would be comparable to that observed in the MW-08E in the lower Pee Dee Aquifer at the Site. This approximation is significant because it supports the supposition that the Pee Dee Aquifer should be recognized as a mixture predominantly background groundwater and a very minor, but influential percentage of seawater. Of note is the fact that the concentration of B is, in some samples

of the Pee Dee Aquifer, higher than would be expected from mixing alone. There may be another source of B that elevates the boron concentration in the Pee Dee Aquifer. This circumstance is not a support for the inclusion of B that originates from CCR waste because the entire chemical signature would also change if that were true. All the above circumstances support a seawater origin as a component of the Pee Dee Aquifer, so the additional B must be intrinsic. The excess B could be a consequence of desorption of boron alone from marine clay material especially as the pH changes.

SOURCE DISTINCTION USING ISOTOPIC COMOSITIONS

Boron
Groundwater at a specific location generally derives its naturally occurring B concentrations and consequently the isotopic signatures from: 1) the dissolution of weathered rocks in the recharge area, 2) dissolution of soluble minerals in the aquifer matrix, and 3) from mixing with water from other sources which in this case is assumed to include marine water or CCR leachate. Dissolved B is chemically conservative, does not change oxidation state, and in groundwater environments is mobile as most borate minerals are highly soluble. Thus, dissolved B with its attendant $\delta^{11}B$ should migrate and mix as a relatively unreactive constituent maintaining the source signatures; consequently, it is a key indicator at the site.

The first consideration is whether the absolute values for the $\delta^{11}B$ are distinctively different between sources (Table 2, Figure 5). The CCR leachate is significantly depleted with values clustering between $\delta^{11}B$ of -4.6‰ and 1.0‰; whereas all Pee Dee samples are enriched, with $\delta^{11}B$ of 23.7‰ and greater (Figure 5). The observed range for the CCR leachate is commonly depleted and is consistent with other sites (Davidson and Bassett, 1993; EPRI, 2012; Ruhl et al., 2014); from a compilation of published values the range of $\delta^{11}B$ in seawater is from 37.7 to 40.4‰, with a mean of 39.5‰ (Foster, et al. 2010), the measured seawater value from this project was $\delta^{11}B$ of 38.1‰ (Table 2).

If the elevated boron concentrations in the Pee Dee Aquifer are derived from CCR waste leachate, then mixing between the leachate and Pee Dee compositions should be observable. Mixing of stable isotope values between endmember components can be demonstrated by plotting the inverse of the concentration of the element and the isotopic value for each sample. If mixing between these sources is occurring the data representing mixed samples are linearized between endmembers and this is not observed for the Pee Dee Aquifer (Figure 5a). In this comparison, the data are separate populations with no evidence of mixing between CCR source material and the water in the Pee Dee Aquifer. In contrast, for the surficial aquifer which has known mixing between CCR material and the shallow aquifer at some locations, mixing indications using this plot are observed as mixing Zone I (Figure 5b). There is also what appears to

be mixing between the native surficial aquifer and some marine water influence as δ^{11}B values range linearly between ~12‰ and ~35‰ (Figure 5b; Zone II).

Several Pee Dee samples (Table 3) have δ^{11}B values exceeding the measured seawater values of 38.1‰. Within analytical error, however, these values fall within the range of published values for seawater.
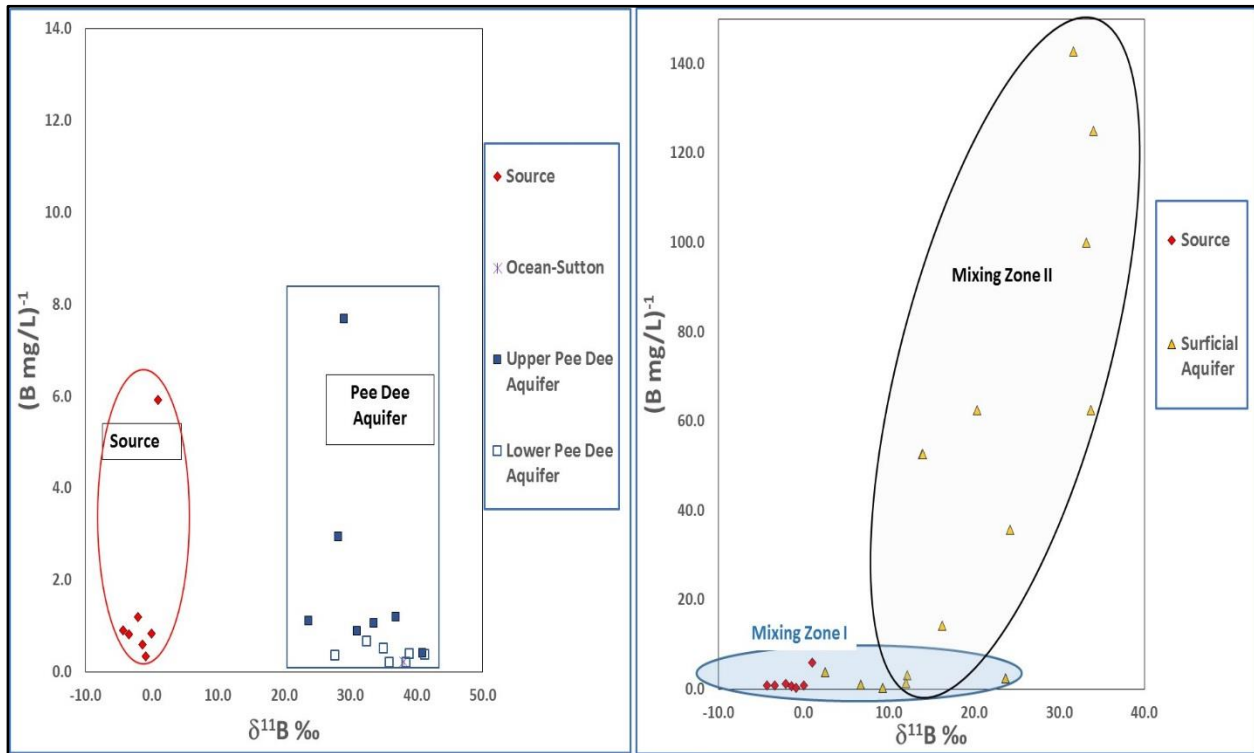
Figure 5. The δ^{11}B differentiation for (a) the Pee Dee and (b) surficial aquifers.

The cross-section shown in Figure 6 identifies the zones in which B concentration is elevated; initial interpretation considered the possibility that the elevated B in the Pee Dee was part of a plume derived from leakage from the 1971 surface impoundment and thus flow lines for the site conceptual model would connect surface impoundments with the Pee Dee Aquifer. The δ^{11}B, however, clearly distinguishes the regions of elevated B from each other in which the landfill and adjacent surficial aquifer zones may be mixing; however, the elevated B in the Pee Dee is clearly not indicated as originating from the CCR sources. Furthermore, the δ^{11}B, the Cl/Br ratio, and the Cl mixing consistence all support the presence of marine water in the Pee Dee Aquifer rather than that of CCR leachate (Figure 6).
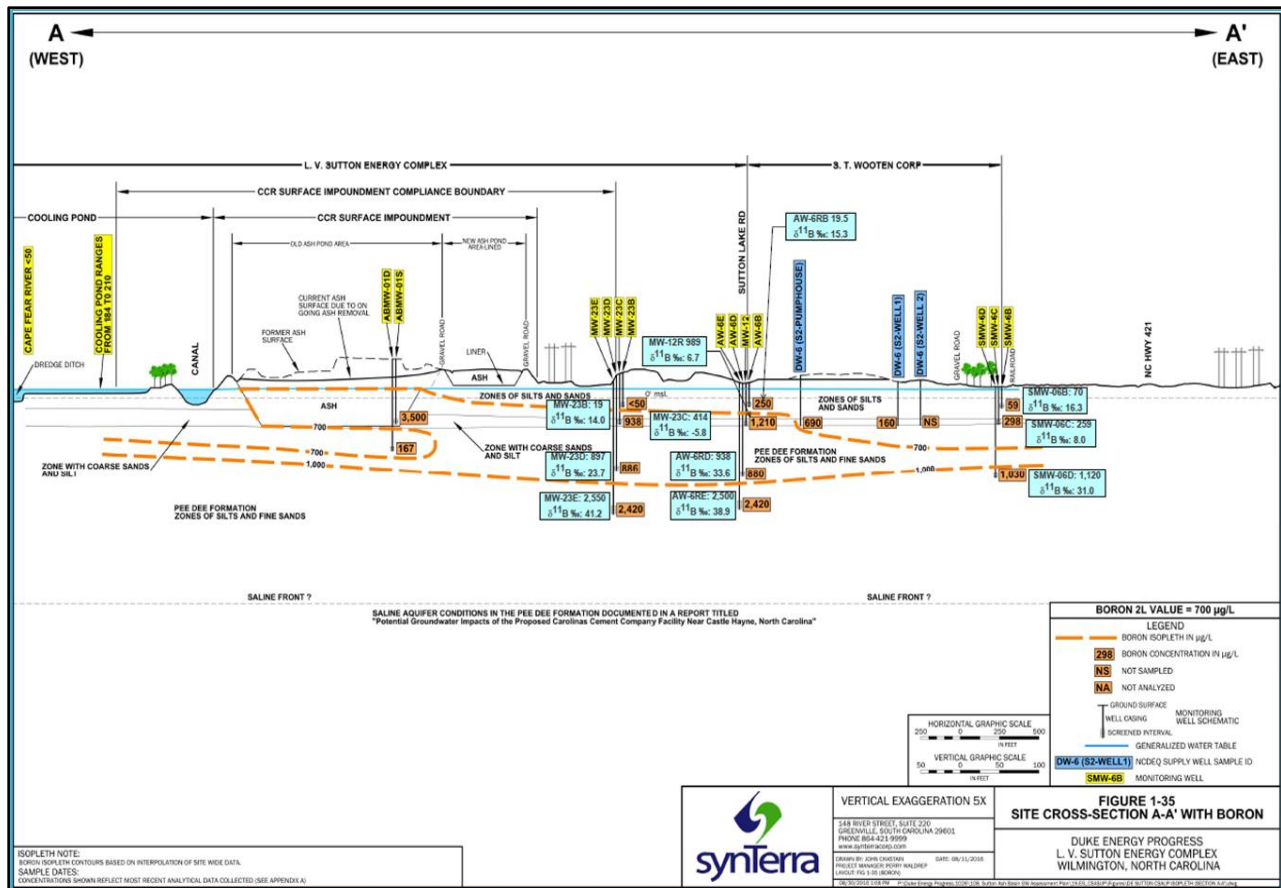
Figure 6. Cross-Section with example B versus d[11]B indicators

Strontium

The $^{87}Sr/^{86}Sr$ data support the same conclusion; a cross-plot of $\delta^{11}B$ with $^{87}Sr/^{86}Sr$ provides additional definition (Figure 7). The plot includes the results for seawater analysis. The data for the Pee Dee are clustered in the seawater field which is consistent with the observation that the Pee Dee Aquifer in this region has a strong marine influence. Differentiation from native groundwater mixed with marine water from CCR sources is reasonably effective using this cross-plot because seawater has a well-defined and narrow range for both $\delta^{11}B$ and $^{87}Sr/^{86}Sr$. The CCR leachate has been shown to be significantly depleted in its $\delta^{11}B$ signature which is the observation made for this site as well.

The maximum $^{87}Sr/^{86}Sr$ ratio measured for the Pee Dee Aquifer is 0.709171 (Table 2) which is below the value for modern seawater ratio of ~0.7092 (measured value for Ocean Sutton is 0.709180, Table 2). All other $^{87}Sr/^{86}Sr$ results for the Pee Dee samples being lower values (Table 2; Figure 7). Denison et al. (1993) reported $^{87}Sr/^{86}Sr$ values between 0.7076 and 0.7080 for carbonate rocks in the Pee Dee Formation in North Carolina, which would support the range of values observed at this Site. It can be

speculated at this point that some of the carbonate in the Pee Dee Formation matrix have reacted with the groundwater, releasing strontium with a lower $^{87}Sr/^{86}Sr$ ratio, and that source is mixing with the seawater derived strontium, yielding the population of lower values observed in the samples collected in this study. The measured CCR leachate has $^{87}Sr/^{86}Sr$ values 0.710309 or greater, with distinct separation from the Pee Dee results (Figure 4.7). The specific origin of the observed $^{87}Sr/^{86}Sr$ ratios within CCR is a mixture of sources especially if flue gas desulfurization gypsum part of the source material as discussed by Ruhl et al., (2014). For this site the integrated leachate isotopic value is the most definitive measurement for the purposes of this study.
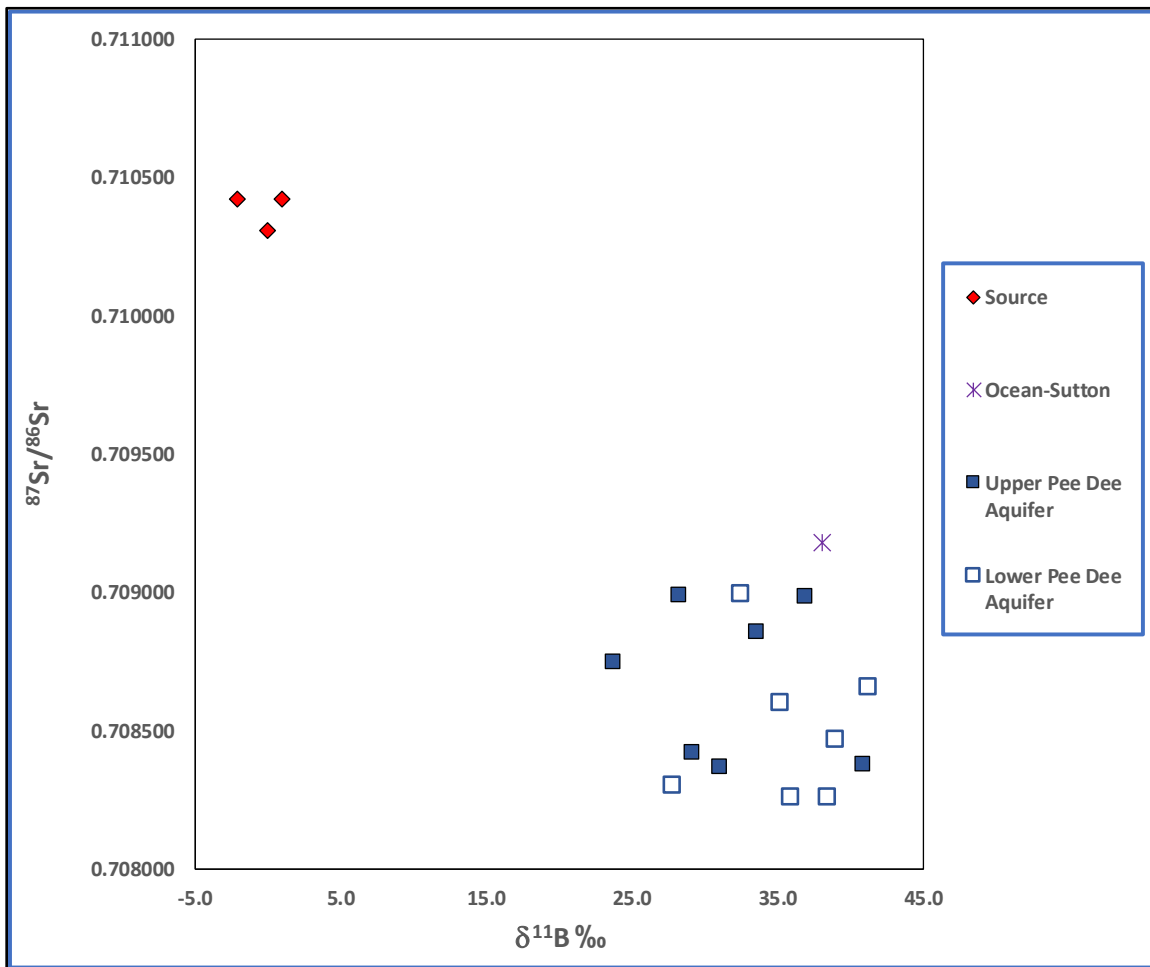

Figure 7. Cross-Plot of $\delta^{11}B$ and $^{87}Sr/^{86}Sr$

Sulfur
A large range is observed of more than 40 per mil from $\delta^{34}S$ of -6.3‰ to 38‰, which should be sufficient to provide significant discrimination among sources if the endmembers are unique. A cross plot by aquifer type for the $\delta^{34}S$ versus the $\delta^{11}B$ signature does not provide distinguishing characteristics for the individual samples but

does illustrate the effect of CCR signature on the surficial aquifer. Note that the Pee Dee Aquifer is clearly not defined with respect to δ^{34}S which ranges over the entire breadth of reported results. It would have been reasonable to expect that the δ^{34}S might be dominated by the influence of seawater which has a δ^{34}S of 20.0‰ (Coplen et al., 2002); a value consistent with the ocean water sample analyzed for this project of 20.9‰ (Table 2). Measured values from the Pee Dee Aquifer for δ^{34}S are widely variable ranging ± 20 ‰ from that of seawater; this range is larger than would be expected for a seawater influenced aquifer. There should not be any sources of such enriched δ^{34}S from sulfate in minerals at the site, and few minerals other than pyrite or CCR landfill materials like gypsum would be alternative sources for sulfur. The explanation could be that sulfate reduction is partially responsible for the range. During sulfate reduction, bacteria progressively reduce the sulfur (+6) in sulfate to sulfur (-2) and the reduced form of S as H_2S is fractionated to much more depleted values, often by large per mil shifts of 30 per mil or more. If the initial sulfate had a δ^{34}S near that of seawater, then as H_2S is generated the H_2S becomes depleted and the residual sulfate is progressively enriched to values significantly greater than sea water and could easily reach the range observed in these samples. This process would require that some areas on the aquifer become anaerobic which is probable since drilling in the Pee Dee Aquifer is known to yield an odor of reduced sulfur gasses (Z. Hall, oral communication, 2017).
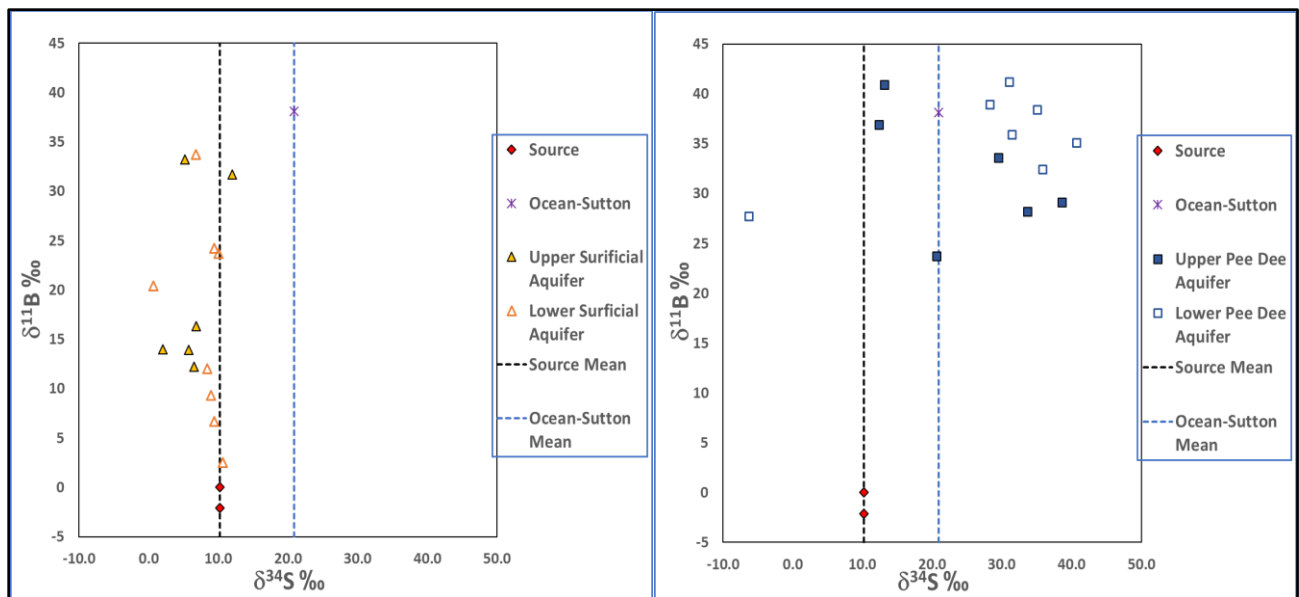
Figure 8. The δ^{34}S values for CCR Source Material, surficial, and the Pee Dee Aquifers.

The more narrowly constrained values of δ^{34}S for CCR material and mixed surficial water samples are consistent with iron sulfide phases associated with CCR or pyrite in the aquifer which when oxidized by the oxygenated aquifer conditions converts to

dissolved iron and sulfate. The iron should rapidly precipitate as iron hydroxide, and the dissolved sulfate would be mobile and would generally be expected to maintain a $\delta^{34}S$ value like that of the original sulfide phase. This is consistent with aquifer mineralogy, redox conditions in the aquifer, and observed $\delta^{34}S$ related to CCR and the surficial aquifer. In a general way, the $\delta^{34}S$ values further indicate that the surficial and Pee Dee Aquifers are isolated from one another because the sulfur isotope values are characteristically different (Figure 8).

Hydrogen and Oxygen
The environmental isotopes of δD and $\delta^{18}O$ are analyzed for many applications in hydrology, among them are to obtain: 1) information regarding the origin of the groundwater at a specific locale, and 2) evidence that physical processes such as evaporation might have occurred which would provide additional methods of discrimination among aquifers. First, because the Sutton Site is underlain by two aquifers with different recharge and mixing histories, it is reasonable to suspect that the water itself can be distinguished by using the δD and $\delta^{18}O$ analysis. These analyses for all wells sampled during this project are shown in Figure 9; the data align primarily along the Global Meteoric Water Line (GMWL) except for a few analyses that may have been affected by CCR source water. The range of values is from the most depleted results for δD and $\delta^{18}O$ of -37.0‰ and -6.2‰ to the most enriched results of -7.0‰ and -1.4‰, respectively. These data indicate that both aquifers are comprised of water that has not been modified significantly from the initial meteoric water signature. It is common for meteoric water results for a specific location to vary in absolute value along the GMWL because of seasonal changes in precipitation type and temperature and with different storm tracks.

Several surficial aquifer samples collected at the Sutton site align to the right of the GMWL (Figure 9). Note that these five samples are all shallow, are either directly associated with landfill ash or are downgradient of the ash basins and have $\delta^{11}B$ values (-2.1 to 12.2‰) that indicate a mixing with boron derived from CCR. The most frequent causes for shift away from the GMWL are chemical reactions and evaporation. In this case, the likelihood for evaporation occurring in the ash landfills is high, and the correlation with $\delta^{11}B$ derived from ash sources strongly suggests this is the process responsible for the deviation from the GMWL. The process of evaporation yields a trajectory for the residual water that deviates from the GMWL. This lower slope is due to temperature and water vapor content which is indicated by the alignment of the data, although only a few measurements are available (Figure 9).

It is also noteworthy that the spread of analyses for the surficial aquifer along the GMWL is broader as compared to the much tighter cluster of data for the Pee Dee Aquifer (Figure 9). The surficial aquifer is more directly influenced throughout the year by infiltration of meteoric water, e.g. seepage from ponded areas or recharge from overland flow in low areas. This contrasts with a deeper aquifer such as the Pee Dee

that is more homogeneous, somewhat isolated from seasonal recharge, and has values averaged over a longer time. These data are also still consistent with the conceptual model of mixing of a native aquifer composition with encroaching sea water, because the sea water contribution would be less than 10% by volume and thus would not noticeably impact this isotopic signature toward a marine value.
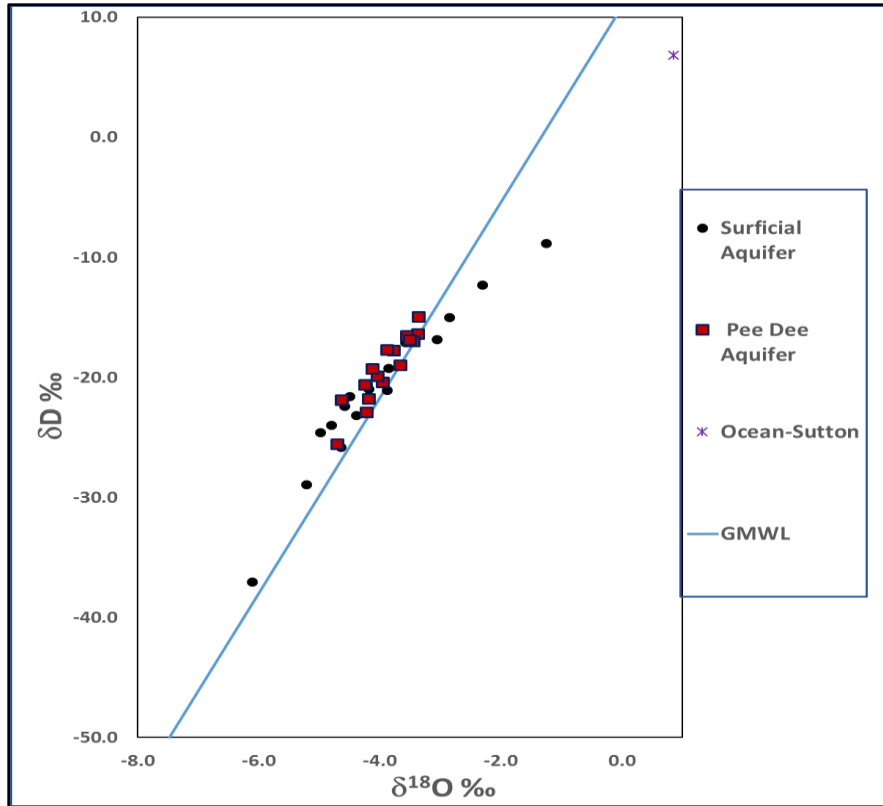
Figure 9. The δD and δ^{18}O of the surficial and Pee Dee Aquifers.

SUMMARY AND CONCLUSIONS

Evaluation of the surficial aquifer characteristics is outside the scope of this report; however, a comparison to the Pee Dee Aquifer in terms of general water chemistry demonstrates that each have a significantly different chemical composition. The surficial aquifer is a Ca-SO$_4$ water type, and the Pee Dee Aquifer is a Na-HCO$_3$-Cl water type; both have elevated concentrations of B which is a monitored CCR Appendix III constituent.

- The Pee Dee Aquifer exhibits characteristics of native groundwater with some small component of seawater. This seawater component would explain the elevated boron concentrations in the Pee Dee Aquifer. Seawater influence on the

chemical composition of the Pee Dee Aquifer would explain the general chemical composition as well as the elevated Cl concentrations which is consistent with locations in the region with identified seawater intrusion. Similarly, the Cl/Br ratio for the Pee Dee Aquifer at the Sutton Site is also consistent with marine influence and is more definitive as the Cl concentration increases above the 250 mg/L Cl reference line used in local investigations.

- Several of the Pee Dee samples collected for this project have Cl concentrations significantly above 250 mg/L. A comparison of a seawater sample diluted by a factor of 10 yields a water type like that of the Pee Dee Aquifer. A mixture of approximately 8% native groundwater from the area and 92% seawater will yield a mixed water sample that matches the Cl of the most concentrated Pee Dee sample and yields a water type consistent with the Pee Dee Aquifer.

- The boron concentrations in CCR samples collected in this study related to the ash landfills range from 0.2 to 3.0 mg/L B, and a few samples from the surficial aquifer have B concentrations from 1.1 to 2.9 mg/L B; whereas the bulk of the remaining surficial aquifer samples have B concentrations less than 0.1 mg/L. The underlying Pee Dee Aquifer also has elevated B concentrations, of the 15 samples, all but 3 have concentrations of approximately 0.9 to 4.5 mg/L. The implication from the boron data is the CCR leachate may have mixed with the Pee Dee Aquifer. The overall chemical composition and isotope data, however, does not support this interpretation.

- The $\delta^{11}B$ composition for the seven CCR related landfill ash pore water and leachate samples are distinctively depleted, with values of $\delta^{11}B$ from -4.6 to 1.0‰. This depleted characteristic is commonly observed and provides a distinct signature for CCR material. The $\delta^{11}B$ for both the upper and lower Pee Dee Aquifer is in all cases greater than a $\delta^{11}B$ of 20‰, with values of near that of seawater for as many as six samples. These results indicate that the $\delta^{11}B$ provide no evidence for CCR waste leachate being detected in the Pee Dee Aquifer, and additionally further support the presence of some measurable component of seawater.

- The $^{87}Sr/^{86}Sr$ results are similarly supportive of the absence of CCR leachate and the presence of seawater in the Pee Dee Aquifer. The cross-plot of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ is a clear depiction of the separation of the results of these two water types.

- The stable isotope results for B and Sr are particularly useful in identifying mixing between water sources when plotted with the inverse of the respective concentrations. The mixing of two sources will follow a straight line connecting the two endmembers consistent with proportional mixing if it is occurring. This mixing process was not observed with respect to either the $\delta^{11}B$ or the $^{87}Sr/^{86}Sr$ data. Without indication of mixing the assumption that CCR leachate has not mixed with groundwater in the Pee Dee Aquifer is plausible.

- The environmental isotopes of δD and δ^{18}O indicate that groundwater in both the surficial and Pee Dee aquifers still retain a meteoric water signature except for the few samples associated with ash landfill areas. The range of values for the surficial aquifer is broad and consistent with a shallow aquifer influenced seasonally by infiltration and seepage. The Pee Dee Aquifer has a much narrower range of values consistent with limited seasonal variation and is indicative of a greater homogeneity in the aquifer, also consistent with aquifer separation or minimal interaction.

- The δ^{34}S values are non-distinct for the Pee Dee Aquifer ranging from -6.3 to 41.2‰, over more than ±20‰ from the seawater value. The mechanism for the large range and significant enrichment is not identified; however, the process of sulfate reduction can leave a residual δ^{34}S enriched to that extent. The CCR related values are narrowly defined around a mean value of δ^{34}S of 10‰ for leachate and essentially the same mean value for all surficial aquifer samples. The distinction in the two aquifers is again indicated; however, the data populations do overlap in the ~10‰ area at which point the values are the same, but it is incidental and not indicative of any specific connection between the two aquifer systems.

In summary, all five isotopic systems support a site conceptual model that separates the Pee Dee Aquifer from direct and rapid infiltration from the surficial aquifer or from CCR facilities; and infer that the chemical composition and isotopic analyses are consistent with the intrusion of marine water into the Pee Dee Aquifer creating an alternative source for the elevated Appendix III constituents, in particular B, SO_4, and TDS.

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