ASSESSMENT OF CORRECTIVE MEASURES REPORT
Central Carolina Tire Monofill Landfill Phases I/II
Harnett County, North Carolina
Permit # 43-04

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1.0 INTRODUCTION

This report presents an Assessment of Corrective Measures (ACM) to address groundwater impacts resulting from periodic, low volume, incidental releases of tetrachloroethene (PCE) at the closed Central Carolina Tire Phase I/II Monofill landfill facility in Harnett County, North Carolina (**Figure 1**). The purpose of the ACM is to identify and evaluate the applicability and effectiveness of potential corrective measures to mitigate the environmental impacts associated with the PCE release.

1.1 Site Description and Background

The Central Carolina Tire facility is located approximately 10 miles southeast of Cameron, North Carolina, on McKoy Town Road (NC Highway 1105), approximately 8,500 feet south of the intersection with NC Highway 24/27 (**Figure 1**). The topography at the area of investigation varies in elevation from approximately 340 feet msl in the southern area to approximately 355 msl feet in the western and northern areas (**Figure 2**). On-site surface drainage is primarily to the east-southeast and is conveyed by an east-southeast trending drainage feature to the north of the access road on the northern perimeter of the Phase I/II landfill to an unnamed creek surrounded by wetlands to the west and south of the landfill. The unnamed creek drains to an unnamed stream which borders the site approximately ¾-mile to the east and flows south. Site drainage ultimately discharges to the Cape Fear River.

Phase I/II of the Central Carolina Tire Monofill landfill is operated in accordance with Solid Waste Permit #43-04. The Phase I Area of the Central Carolina Tire Monofill landfill began operation in 1992 and the Phase II Area began operation in 1997. The combined footprint of the Phase I/II Monofill is approximately 37-acres. The Phase I/II landfill reached capacity in the fall of 2008 and is now closed.

PCE has been detected in groundwater samples collected from monitoring well MW-8 at the Phase I/II landfill during semi-annual sampling conducted over the last eight years (**Figure 2**). The concentrations of PCE have been in excess of the North Carolina 15A NCAC 2L .0202 groundwater quality standard for the last six years.

The results of assessment activities conducted at the site indicate that a bow-shaped plume of dissolved chlorinated ethenes (including PCE, trichloroethene (TCE) and cis-1,2-dichloroethene (cis-1,2-DCE)) originates within the shallow surficial aquifer in the vicinity of monitoring well GW-10, east of the maintenance shelter, and extends along two distinct axes: 1) to the south in the general direction of monitoring well GW-7S and

the Phase I/II landfill; and 2) to the east and southeast beyond the location of monitoring well GW-10. These results further indicate that the source area of the plume appears to be located in the vicinity of monitoring well GW-10.

The maintenance shelter and surrounding area were previously used to maintain and repair equipment for the landfill. The maintenance shelter is an open-air structure with a soil floor. The surrounding area is unpaved. Equipment maintenance and repair included routine use of a parts cleaning solution that contains PCE. Periodic, low volume, incidental spills of parts cleaning solution onto the ground surface over time are considered the source of PCE in groundwater at the site. It is noted that equipment maintenance is no longer conducted at the maintenance shelter and is currently conducted inside an enclosed garage building with paved floors.

The dissolved chlorinated ethenes plume is confined to the shallow surficial aquifer and is not present in the deeper zone of groundwater occurrence monitored by deep monitoring wells. Further, the chlorinated ethenes plume has been adequately delineated by the network of assessment monitoring wells installed during Phases 1 through 4 of the Hydrogeologic and Groundwater Quality Assessment.

The results of the previous assessments are presented in the January 2011 *Preliminary Site Assessment Report*, the June 2012 *Phase 2 Hydrogeologic and Groundwater Quality Assessment Report*, the May 2013 *Phase 3 Hydrogeologic and Groundwater Quality Assessment Report*, and the October 2014 *Phase 4 Hydrogeologic and Groundwater Quality Assessment Report* previously submitted to the North Carolina Department of Environment and Natural Resources (NCDENR), Division of Waste Management (DWM), Solid Waste Section.

2.0 REGIONAL GEOLOGY AND HYDROGEOLOGY

The Central Carolina Tire landfill facility is located in the Atlantic Coastal Plain physiographic province in North Carolina (**Figure 3**). The area of the site is underlain by sediments of the Late Createaceous age Middendorf Formation, which are predominantly fluvial-deltaic intercalated, lensing, thick-bedded micaceous quartz sands and clays with local concentrations of clay clast conglomerates.[1] The sediments of the Middendorf Formation are typical of those deposited in a deltaic environment and commonly include cross-bedding, lenses, pinch-outs and facies changes. The Middendorf Formation deposits unconformably overlie sands and clays of the Late Cretaceous age Cape Fear Formation, which outcrop in primary stream valleys in Harnett County. The Cape Fear Formation sediments unconformably overlie crystalline basement rocks, the surface of which occurs at a depth of approximately 200 to 250 feet below grade near the site. Thin, discontinuous Neogene and Quaternary age sediments overlie the Cretaceous age deposits at some locations. Subsurface materials encountered during the preliminary environmental assessment and drilling conducted as part of the Phase 2, 3 and 4 assessments are consistent with descriptions of Middendorf Formation sediments mapped in the area of the site.

Groundwater within the surficial aquifer at the site occurs under unconfined conditions within sandier zones of appreciable thickness of the Middendorf Formation sediments. Laterally extensive and thick clay beds within the Middendorf Formation form confining to semi-confining layers separating the surficial aquifer from deeper occurrences of groundwater. The surficial aquifer, which extends over a large part of the Coastal Plain, discharges water laterally to streams and rivers and provides the bulk of recharge to deeper aquifers. Recharge to the surficial aquifer occurs via rainfall. Shallow groundwater flow at the site is generally to the southeast toward unnamed streams and associated wetlands that surround the eastern and southern boundaries of the closed Phase I/II landfill.

[1] Sohl, Norman F. and James P. Owens, 1991; Cretaceous stratigraphy of the Carolina coastal plain, in *The Geology of the Carolinas*, J. W. Horton, Jr. and V. A. Zullo, eds., The University of Tennessee Press, pp. 191-220.

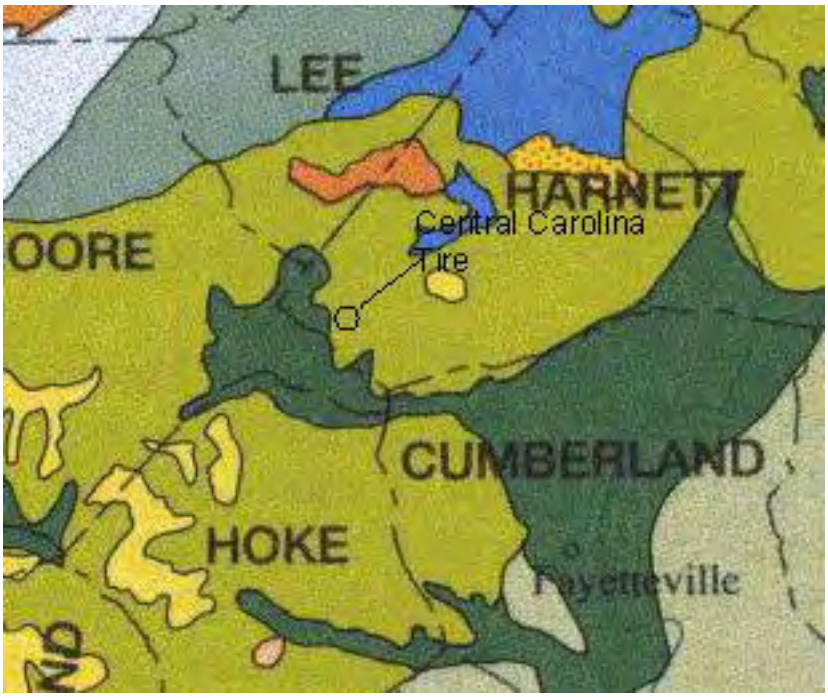

Figure 3. Excerpt from Generalized Geologic Map of North Carolina (1985)

3.0 RESULTS OF HYDROGEOLOGIC INVESTIGATIONS

3.1 Site Reconnaissance

3.1.1 Topographic Setting and Drainage

Land surface elevations in the vicinity of the assessment area range from approximately 340 feet msl in the southern area to approximately 355 feet msl in the western and northern areas (**Figure 2**). Surface drainage in the area follows the land surface contours. The main topographic features controlling the bulk of surface drainage in the assessment area are the topographically high ground in the immediate vicinity of the maintenance shelter and to the west along the main access road, and an east-southeastward sloping drainage feature that separates the assessment area to the north from the Phase I/II landfill to the south. The majority of surface drainage in the assessment area flows southeastward from the topographic upland area near the maintenance shelter to the southeast toward the east-southeast trending drainage feature. Surface drainage in the drainage feature is conveyed to an unnamed creek surrounded by wetlands to the east and south of the landfill. The unnamed creek drains to an unnamed stream which borders the site approximately ¾-mile to the east and flows south. Site drainage ultimately discharges to the Cape Fear River.

3.1.2 Groundwater Discharge Features

The primary groundwater discharge features in the Coastal Plain are dendritic streams that dissect the terrain and the associated wetlands within the floodplains of the streams. Other groundwater discharge occurs through evapotranspiration in areas where the water table is located in close proximity to the land surface and in topographically low features such as ponds, lakes, and wetlands. Additionally, groundwater may discharge through springs or seeps that occur in upland areas resulting from the presence of low permeability strata that divert groundwater flow laterally to areas where the strata intersect the land surface.

Ponds, lakes, springs, and seeps were not observed in the broader area of assessment. An unnamed creek surrounded by wetlands is present to the east and south of the Phase I/II landfill. The unnamed creek drains to an unnamed stream with associated wetlands which borders the landfill property approximately ¾-mile to the east and flows south. Groundwater discharge likely provides base flow to the unnamed creek and stream. In addition, groundwater discharge via evapotranspiration likely occurs in the immediate vicinity of the wetlands.

3.2 Monitoring Well Boring and Geotechnical Laboratory Data

3.2.1 Monitoring Well Boring Data

Summaries of the test boring data, including completion depth, monitoring well construction specifications, ground surface elevations, top of casing elevations, and top and bottom of well screen elevations are presented in **Table 1**. Standard penetration tests were performed at designated intervals in the well borings in accordance with ASTM D 1586 to provide an index for estimating soil strength and relative density.

3.2.2 Geotechnical Laboratory Data

Grain size analyses of soil samples collected from the saturated zone of the well borings for monitoring wells GW-1S/D through GW-7S/D and GW-8 were conducted as part of the Phase 2 assessment. The results of the grain size analyses were used to estimate specific yield of the unconsolidated sediments in the surficial aquifer. The results of the grain size analyses conducted as part of the Phase 2 assessment are summarized in **Table 2**.

3.3 Site Geology and Hydrogeology

The evaluation of subsurface geology and hydrogeology presented below is based on published information regarding the regional geological and hydrogeological framework (discussed in **Section 2.0**) in conjunction with the descriptions of subsurface materials recorded in the drilling logs for the site monitoring wells and the results of rising-head permeability (“slug”) tests.

3.3.1 Site Geology

Natural subsurface materials encountered during drilling of the site monitoring wells are consistent with descriptions of the regional geology presented in the published literature (see **Section 2.0**) and descriptions of soils encountered during previous drilling conducted at the site. The locations of the site monitoring wells are shown in **Figure 2**. A geologic cross section location map is presented as **Figure 4**, and geologic cross sections through the site are presented as **Figures 5** through **7**. In general, based on the drilling logs, the shallow subsurface lithology is composed of an upper complex of interbedded layers of sandy clay and clayey sand (Unit 1a) in the western half of the area of investigation. In the eastern half of the area of investigation, the upper unit (Unit 1b) is generally composed of silty sand interbedded with clayey sand and occasional very fine to fine grained sand and sandy silt. Units 1a and 1b overly micaceous variably sandy clay and very stiff to hard clay (Unit 2), which in turn overlies medium dense to very dense clayey sand (Unit 3).

Units 1a, 1b and the sandy clay of Unit 2 comprise the surficial aquifer at the site, and contain frequent lenses and pinch-outs and thin lenses of silty clay and relatively clean sand, typical of a deltaic environment. The basal clay of Unit 2 frequently contains abundant mica, and is generally mottled in some combination of gray-red-purple-orange brown-tan. The basal clay of Unit 2 appears to form a semi-confining to confining layer separating the surficial unconfined aquifer from deeper occurrences of groundwater and appears to be continuous under the entire area of assessment. Underlying the basal clay of Unit 2 is generally dense clayey sand that frequently contains abundant weathered white feldspar and other weathered mineral grains. This unit comprises a deeper groundwater-bearing unit at the site, although groundwater yield from the unit is very low. The lower unit was not fully penetrated during drilling so the thickness of the unit is not known based on available site data.

3.3.2 Site Hydrogeology

Measured depths to groundwater in the shallow Type II monitoring wells at the site in August 2014 ranged from 6.79 feet (MW-8) to 18.05 feet (GW-4S) below grade. The depths to groundwater measured in the deep Type III wells ranged from 17.30 feet (GW-5D) to 23.16 feet (GW-6D) below grade. Depths to groundwater measured in the site monitoring wells in August 2014 are presented in **Table 5**.

Groundwater within the surficial unconfined aquifer at the site occurs under water-table (unconfined) conditions within the interstitial pore spaces of the sediments in Units 1a, 1b and the sandy clay of Unit 2. A water-table elevation contour map based on the August 2014 groundwater gauging data for the shallow monitoring wells is presented as **Figure 8**. The geometric configuration of the water-table elevation contours presented in **Figure 8** indicate that shallow groundwater flow at the site is generally to the south and southeast, which is consistent with the overall topography in the assessment area. The hydraulic gradient of the water table ranges from approximately 0.010 ft/ft in the northern part of the assessment area to approximately 0.068 ft/ft in the southeast part of the assessment area based on the water-table elevations measured at the shallow monitoring wells in August 2014 (see **Table 5**).

Deeper groundwater at the site is present in the clayey sand unit (Unit 3) underlying the clay semi-confining to confining layer of Unit 2. A groundwater elevation contour map based on the August 2014 groundwater gauging data for the deep monitoring wells is presented as **Figure 9**. The geometric configuration of the water-table elevation contours presented in **Figure 9** indicate that groundwater flow in the deep water-bearing

unit at the site is generally to the southeast, consistent with the flow direction in the shallow aquifer. The hydraulic gradient of the potentiometric surface of the deeper water-bearing zone varies from approximately 0.026 ft/ft in the northern portion of the assessment area to approximately 0.066 ft/ft in the southwest portion of the assessment area based on the groundwater elevations measured at the deep monitoring wells in August 2014 (see **Table 5**). With respect to vertical potentiometric gradients, downward gradients are observed at all shallow and deep well pairs based on the August 2014 groundwater elevation data, with pronounced gradients at all well pairs except GW-1S/D and GW-4S/D.

Estimates of the hydraulic conductivity (K) of the shallow aquifer at the locations of the shallow monitoring wells were made based on analyses of the water level versus time data collected during the slug tests conducted in April 2012, April 2013 and August 2014. The data analysis was conducted by the Bouwer and Rice (1976) solution method using AQTESOLV™ for Windows, an aquifer test data analysis program developed by HydroSOLVE, Inc. of Reston, Virginia. Calculated values of K based on the slug test data for all shallow site assessment monitoring wells (GW-1S through GW-7S and GW-9 through GW-16) and detection monitoring well MW-8 are presented in **Table 3**. The calculated values of K for the shallow surficial aquifer ranged from 0.88 ft/day (GW-10) to 42.3 ft/day (GW-5S). The geometric mean value of K for the shallow surficial aquifer is 6.93 ft/day.

It is noted that the yield of groundwater to the deep monitoring wells (GW-1D through GW-8D) was observed to be extremely slow. Recovery of water levels to greater than 80% of static conditions required several days to achieve. Consequently, slug tests were not completed in the deep monitoring wells in April 2012 due to the slow rate of recovery and apparent very low permeability of the deep aquifer sediments. Based on the observed rate of recovery, it is estimated that the hydraulic conductivity of the deep aquifer sediments is less than 10^{-6} cm/sec.

The average interstitial groundwater flow velocity (v_w) can be expressed according the relation $v_w = Ki/\eta$, where K is the hydraulic conductivity, i is the hydraulic gradient, and η is the effective porosity of the aquifer material. Estimates of the effective porosity (specific yield) of the surficial aquifer sediments were made based on the results of the grain size analyses conducted for the Phase 2 assessment using the method of Johnson (1967).[2] Calculations of the horizontal groundwater flow velocity are presented

[2] Johnson, A. I., 1967. Specific Yields for Geologic Materials. USGS Water Supply Paper 1662-D.

in **Table 4**. Based on the calculations presented in **Table 4**, the average interstitial groundwater flow velocity in the shallow aquifer is estimated to range from 0.03 ft/day (10.96 ft/yr) to 7.51 ft/day (2,743 ft/yr), with a geometric mean of 0.30 ft/day (109.58 ft/yr).

4.0 RESULTS OF GROUNDWATER QUALITY ASSESSMENTS

Four phases of environmental and groundwater quality assessment were conducted at the site during the period of November 2010 to August 2014 related to the release of PCE in the vicinity of the maintenance shelter. Twenty three groundwater monitoring wells were installed at the site as part of the assessments. During purging of groundwater from the monitoring wells and prior to sampling, measurements were made in the field of the pH, temperature, specific conductance, turbidity, oxidation-reduction potential (ORP), and dissolved oxygen (DO) concentrations. The results of the field analyses of these parameters measured in August 2014 are presented in **Table 5**.

The results of the field-measured water-quality parameters indicate that the values measured in groundwater collected from the site monitoring wells were generally within applicable stabilization criteria (see Groundwater Sample Collection Forms). Shallow groundwater at the site is acidic to slightly acidic based on the pH values measured in the field (1.54 to 6.26), and groundwater within the deeper water-bearing unit is acidic to neutral (4.36 to 7.70). Specific conductance values ranged from 28 (GW-4S) to 299 (GW-12) μS/cm in groundwater at the monitoring wells. Turbidity values ranged from 4.01 (GW-9) to 194 (GW-13) NTUs. ORP values ranged from -47.4 (GW-12) to 217.8 mV (GW-3S), with higher values generally observed in the shallow groundwater. DO concentrations ranged from 0.38 (GW-12) to 6.22 (GW-15) mg/L, with all values except at GW-12 exceeding 2.0 mg/L, indicating relatively oxidizing conditions in groundwater at the site.

Summarized results of laboratory analyses of the groundwater samples collected from the site monitoring wells during August 2014 are presented in **Table 6**. Benzene was detected at a concentration of 0.97 µg/L in the groundwater sample collected from monitoring well GW-12, which is marginally below the 15A NCAC 2L groundwater quality standard of 1.0 µg/L. Benzene was not detected in any other groundwater samples collected. Chloroethane was detected at a concentration of 0.55 µg/L in the groundwater sample collected from monitoring well GW-12, which is well below the NCAC 2L groundwater quality standard of 3,000 µg/L. Chloroethane was not detected in any other groundwater samples collected. 4-Isopropyltoluene was detected in the groundwater sample collected from GW-12 at a concentration of 0.91 µg/L. No 15A NCAC 2L .0202 groundwater quality standard or EPA Maximum Contaminant Level (MCL) has been established for 4-Isopropyltoluene. Methyl tertiary-butyl ether (MTBE) was detected in the groundwater samples collected from GW-3S and GW-7S at

concentrations of 1.2 µg/L and 1.5 µg/L, respectively, both of which are well below the 15A NCAC 2L .0202 groundwater quality standard of 20 µg/L.

Several trihalomethanes (THMs) were detected at low concentrations in five of the 24 groundwater samples collected from the site during August 2014, three of which were collected from the newly installed monitoring wells. The THMs detected include bromodichloromethane, bromoform, chloroform, and dibromochloromethane. THMs are a common byproduct of disinfection of potable water in municipal water treatment plants. Potable water is provided to the Central Carolina facility by the Harnett County Water System. Potable water from the site was used to mix grout to secure the well casings and to provide hydraulic ballast during hollow stem auger drilling during installation of the shallow monitoring wells to prevent the influx of sand into the auger flight. Moreover, the total concentrations of THMs detected in the groundwater samples collected from the site fall well within the range to total THM concentrations reported in the 2011 Harnett County Water Quality Report (individual concentrations of THMs were not reported). Consequently, the presence of THMs in the groundwater samples collected from the site during August 2014 is attributed to the use of potable water from the site during drilling.

The groundwater analytical data indicate that PCE was detected in the groundwater sample collected from background shallow monitoring well GW-1S at a concentration of 2.1 µg/L, which marginally exceeds the 15A NCAC 2L groundwater quality standard of 0.7 µg/L. No other VOCs were detected in the groundwater sample from GW-1S. With the exception of a trace concentration of chloroform (0.58 µg/L), no other VOCs were detected in the groundwater sample collected from background deep monitoring well GW-1D. It is noted that the presence of chloroform is attributed to the use of municipal water during drilling, indicating that the Unit 2 clay layer is acting as an effective confining unit between the shallow aquifer and deeper zones of groundwater occurrence.

The groundwater laboratory analytical results further indicate that PCE, TCE, cis 1,2-DCE were detected in shallow groundwater samples collected from the site. The latter two compounds are environmental transformation products of the sequential anaerobic reductive biotransformation of PCE. Of these compounds, PCE was detected at the most well locations (10) and is the most widespread chlorinated ethene at the site. The concentrations of PCE detected in shallow groundwater ranged from 0.54 µg/L (GW-4S) to 58 µg/L (GW-10). PCE was reported in concentrations exceeding the 15A NCAC 2L groundwater quality standard (0.7µg/L) at eight of the 10 monitoring well locations at

which it was detected. The concentrations of cis-1,2-DCE and TCE detected in shallow groundwater were all well below the corresponding NCAC 2L groundwater quality standards (60 µg/L and 3 µg/L, respectively).

Isoconcentration contour maps of PCE and total chlorinated ethenes (i.e., total concentrations of PCE, TCE and cis-1,2-DCE) in shallow groundwater, based on the August 2014 groundwater analytical data, are presented as **Figures 10** and **11**. The configuration of the isoconcentration contours indicate that the dissolved chlorinated ethenes plume appears to emanate from the general area immediately east of the maintenance shelter in the vicinity of monitoring well GW-10 and extends along two distinct axes: 1) to the south in the general direction of monitoring well GW-7S and the Phase I/II landfill; and 2) to the east beyond the location of monitoring well GW-10. The general configuration of the plume appears to form a bow shape, extending around the margins of the general area encompassing monitoring wells GW-8D, GW-11 and GW-12, where a considerable thickness of dense clay (Unit 2) is present beginning at approximately 6 to 8 feet below grade, thereby providing an impediment to shallow groundwater flow. Based on the results of the four phases of assessment completed at the site, the horizontal and vertical extent of the dissolved PCE plume in the shallow surficial aquifer is adequately delineated by the network of assessment monitoring wells. Moreover, the source area of the plume appears to be located in the vicinity of monitoring well GW-10, east of the maintenance shelter.

5.0 CONTAMINANT CHARACTERIZATION

5.1 Contaminants of Concern

Based on the results of the four phases of assessment completed at the site, PCE is the most widespread of the groundwater contaminants detected. Moreover, with the exception of THMs, the presence of which is attributed to the use of municipal water during drilling and installation of monitoring wells (see **Section 4.0**), PCE was the only groundwater contaminant detected at concentrations exceeding the corresponding 15A NCAC 2L .0202 groundwater quality standard (0.7 µg/L) in August 2014 (8 of 10 locations detected). TCE was detected at a concentration that slightly exceeds the 15A NCAC 2L .0202 groundwater quality standard (3.0 µg/L) at monitoring well GW-2S (4.0 µg/L) in April 2013 and at a concentration slightly less than the 15A NCAC 2L groundwater quality standard at monitoring well GW-5S (2.7 µg/L) in August 2014. Based on these observations, PCE and TCE are considered the contaminants of concern (COCs) at the site.

5.2 Contaminant Source Confirmation

The maintenance shelter and surrounding area were previously used to maintain and repair equipment for the landfill (**Figure 2**). The maintenance shelter is an open-air structure with a soil floor. The surrounding area is unpaved. Equipment maintenance and repair included routine use of a parts cleaning solution that contains PCE. Based on the results of the four phases of assessment completed at the site, periodic, low volume, incidental spills of parts cleaning solution onto the ground surface over time are considered the source of PCE and its environmental degradation products in groundwater at the site.

5.3 Source Control Measures

Identification of periodic, low volume, incidental spills of parts cleaning solution containing PCE as the source of groundwater impact in the general area of the maintenance shelter was made early in the environmental assessment process at the site. Consequently, Central Carolina Tire discontinued all equipment maintenance at the shelter immediately thereafter and relocated equipment maintenance to an enclosed garage building with paved floors located in another area of the site. This action has prevented further low volume releases of parts cleaner in the area of the maintenance shelter and, thereby, addition of contaminant mass to the source area.

5.4 Groundwater End Use

The Central Carolina Tire facility is located in a rural area of Harnett County and encompasses approximately 344 acres. The facility is bordered by residential properties to the north and agricultural properties to the west, south and east. The maintenance shelter and area of groundwater impact are located in the west-central area of the property near agricultural property to the west and the closed Phase I/II landfill to the south.

The maintenance shelter and known areas of dissolved COCs at the site are located between the Phase I/II and Phase III landfills. Based on groundwater elevation data, the direction of shallow groundwater flow in the area of the maintenance shelter is to the south and southeast toward unnamed streams and associated wetlands that surround the eastern and southern boundaries of the Phase I/II landfill. Consequently, the spectrum of receptors that could potentially be impacted by dissolved COCs in groundwater is limited in scope. Based on the known site conditions, a receptor survey was conducted during the Phase 2 assessment to identify water supply wells located within 1,500 feet of the maintenance shelter.

Potable water is provided to the Central Carolina Tire facility and surrounding area by the Harnett County Water System. No potable water supply wells are located on the facility property. In addition, no potable water supply wells are located within a 1,500 foot radius of the maintenance shelter. It is noted that well houses were observed at several residential properties to the north of the facility. However, these properties are located well outside a 1,500 foot radius surrounding the maintenance shelter and are also hydraulically up gradient of the area of groundwater impact. Consequently, the wells observed at the residential properties are not considered to be at risk of impact from the dissolved contaminant plume at the site.

All properties immediately surrounding the facility are owned by Thomas A. Womble (President of Central Carolina Tire) and/or his wife, Diane T. Womble, except for the property located immediately northeast of the facility, which is owned by S. T. Wooten Corporation. The S. T. Wooten Corporation property is located hydraulically up gradient of the maintenance shelter and the area encompassed by the dissolved contaminant plume and is not considered to be at risk of impact by the plume.

5.5 Media of Concern

The four phases of environmental assessment completed at the site included sampling and laboratory analysis of soil and groundwater for volatile organic compounds by SW-846 Method 8260B. In addition, routine semiannual water quality monitoring for the Phase I/II landfill includes sampling and analysis of surface water at two locations (designated SW-1 and SW-2) for volatile organic compounds by SW-846 Method 8260B.

Soil sampling was conducted in soil and monitoring wells borings drilled within and surrounding the maintenance shelter during phases 1 and 2, respectively, of the environmental assessment conducted at the site. A total of 13 soil samples collected from the vadose (unsaturated) zone were retained and submitted for laboratory analysis. The results of the laboratory analyses indicate that PCE and its environmental breakdown products were not detected in any of the soil samples analyzed. These results support a release scenario of periodic, low volume incidental spills as the source of groundwater impact at the site in various locations within the general area of the maintenance shelter and monitoring well GW-10. Consequently, no area of significant accumulated contaminant mass in soil was identified within the broader source area. Therefore, impacted soil is not considered a medium of concern at the site.

The results of the four phases of environmental assessment conducted at the site indicate that groundwater in the shallow surficial aquifer is impacted by the site COCs. PCE is the most widespread groundwater contaminant in the shallow surficial aquifer and was reported at concentrations exceeding the 15A NCAC 2L groundwater quality standard at 8 of the 10 shallow monitoring wells where it was detected in August 2014. Consequently, shallow groundwater is considered a medium of concern at the site.

Shallow groundwater flow at the site is generally to the south and southeast in the general direction of the Phase I/II landfill, which is consistent with the overall topography in the assessment area. An unnamed creek surrounded by wetlands is present to the east and south of the Phase I/II landfill. The unnamed creek drains to an unnamed stream with associated wetlands which borders the landfill property approximately ¾-mile to the east and flows south. Groundwater discharge provides base flow to the unnamed creek and stream. Surface water sampling location SW-1 is located approximately 140-feet south-southeast of the south-central sedimentation pond and within the drainage feature that parallels the southern limits of scrap tire disposal within

the Phase I/II landfill. Surface water sampling location SW-2 is located approximately 250-feet south-southeast of the southeastern sedimentation pond and within the primary drainage feature that parallels the eastern limits of the Phase I/II landfill. These sampling locations are considered appropriately positioned to effectively monitor any potential discharges of impacted groundwater originating from the area of the maintenance shelter to surface water south and east of the Phase I/II landfill. The historical results of surface water monitoring at SW-1 and SW-2 extending back to at least 2002 indicate that PCE and its environmental breakdown products have not been detected at sampling locations SW-1 and SW-2. Consequently, surface water is not considered a medium of concern at the site.

5.6 Potential Receptors and Exposure Pathways

Based on an analysis of site conditions, shallow groundwater is the only medium of concern identified at the site (**Section 5.5**). The direction of shallow groundwater flow in the area of groundwater impact is to the south and southeast toward unnamed streams and associated wetlands that surround the eastern and southern boundaries of the closed Phase I/II landfill. Shallow groundwater (and the associated dissolved chlorinated ethenes plume) flows from the area of impact in the vicinity of the maintenance shelter and discharges to the unnamed streams and fringing wetlands bordering the closed Phase I/II landfill. Consequently, the area of impacted groundwater and areas of potential contaminant plume migration are located entirely within the property boundaries of the Central Carolina Tire landfill facility.

Potential receptors include human and ecological populations (e.g., birds, fish, and other wildlife) that may be exposed to contaminants in the environment. As discussed in **Section 5.5**, contaminated shallow groundwater is the medium of concern for potential exposure of receptors. It is noted that groundwater is not used as a source of potable or non-potable water at the site. Access to the Central Carolina Tire site is restricted to company employees and non-employee support personnel. Although access to the site by unauthorized people is possible, it is not considered to be a common occurrence since direct access to the site is through a main gate at the facility entrance. Therefore, company employees and non-employee support personnel working in the general area of the maintenance shelter are considered the only human population potentially at risk of exposure to the site contaminants. Such potential exposure would only be possible in the event that company employees and/or non-employee support personnel conducted excavation activities in which shallow groundwater is encountered. In the area of impact at the site, the depth to groundwater averages greater than 10 feet below the ground surface. With regard to ecological

receptors, potential risk of exposure is considered to be minimal because of the depth to groundwater at the site and no evidence of surface water impact from discharge of contaminated groundwater is evident from historical surface water monitoring data as discussed in **Section 5.5**.

The Agency for Toxic Substances & Disease Registry (ATSDR) recognizes five elements of an exposure pathway.[3] These include:

1. Contaminant Source – surface spills, leaking underground tanks, drums, landfills, etc.
2. Media – the media through which the contaminants move away from the source (soil, surface water, groundwater, air).
3. Exposure Point - the specific location(s) where people or ecological receptors might come into contact with a contaminated medium.
4. Exposure Route - the means by which receptors physically contact environmental contamination at the exposure point (e.g., by inhalation, ingestion, or dermal contact).
5. Receptor Population – potentially exposed human and/or ecological populations.

The extent to which exposures may have occurred, may be occurring, or may occur in the future at and around a release site are largely determined by these five elements. Moreover, all five elements of an exposure pathway must be present to consider that pathway "complete." It is noted, however, that even if a complete exposure pathway exists, a public health hazard may not exist as a result. The specific conditions of exposure, such as the route of exposure and the magnitude, frequency, and duration of exposures need to be examined more closely to evaluate possible health implications of the exposures.

At the Central Carolina Tire site, elements 1, 2 and 5 of an exposure pathway exist with respect to contaminated groundwater. However, under current site conditions, elements 3 and 4 do not exist because: 1) the contaminants are confined to groundwater that is located on average greater than 10 feet below grade and is not readily accessible to potential receptors; and 2) the results of long-term periodic sampling and laboratory analysis of surface water from the unnamed streams bordering the closed Phase I/II landfill where shallow groundwater originating in the area of impact ultimately discharges indicate that PCE and its environmental breakdown products have not been

[3] Public Health Assessment Guidance Manual; January 2005; U. S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry; 357 pp.

detected. Consequently, the current site conditions indicate an incomplete exposure pathway with respect to potential exposure to contaminated groundwater and, therefore, minimal risk with respect to human health impacts. Moreover, imposing restrictions on excavation activities in the area of groundwater impact until such time that the concentrations of groundwater contaminants return to levels below the applicable groundwater protection standards will eliminate the possibility of producing a complete exposure pathway.

6.0 POTENTIAL CORRECTIVE MEASURES

6.1 Overview

Numerous approaches and technologies are available for remediation of groundwater impacted by chlorinated aliphatic hydrocarbons (CAHs) such as the COCs at the Central Carolina Tire site. Identification of potentially applicable remedial approaches and technologies for corrective measures at a contaminant release site requires development and selection of the following[4]:

- **Conceptual Site Model (CSM)** - includes background information, geologic and hydrogeologic data, contaminant source, distribution and fate and transport data, and risk assessment information for a given site. The elements of the CSM for the Central Carolina Tire site are presented in **Sections 1.0 through 5.0** herein and in the January 2011 *Preliminary Site Assessment Report*, the June 2012 *Phase 2 Hydrogeologic and Groundwater Quality Assessment Report*, the May 2013 *Phase 3 Hydrogeologic and Groundwater Quality Assessment Report*, and the October 2014 *Phase 4 Hydrogeologic and Groundwater Quality Assessment Report* previously submitted to the NCDENR Division of Waste Management.
- **Remedial Action Objectives (RAOs)** – RAOs are medium-specific (e.g., soil or groundwater specific) goals for protecting human health and the environment and are based on the following elements identified in the CSM: 1) the COCs; 2) the impacted media; 3) fate and transport of COCs; 4) exposure routes; and 5) potential receptors. The RAOs should provide a clear and concise description of what the remedial action should accomplish at a given site. For example, a RAO for contaminated groundwater might be to prevent COCs in groundwater from reaching points of compliance (POCs) at concentrations above the site clean-up goals.
- **Final Remedial Goals (FRGs)** - Once the RAOs have been established, the FRGs are selected to meet the identified objectives. FRGs may be established based on regulatory standards, such as MCLs for groundwater consumption, or site-specific risk-based values that have been determined to be protective of human health and the environment.
- **Target Treatment Zone (TTZ)** - A TTZ is the volume or area of a targeted medium at which the application of remedial action is considered to be the most effective. The TTZ is selected considering risk reduction, exposure routes, and the nature and extent of contamination as defined by the CSM and RAOs. The

[4] Guidance for Optimizing Remedy Evaluation, Selection, and Design; 2010; Battelle Memorial Institute for Naval Facilities Engineering Command Engineering Service Center; 84 pp.

TTZ for contaminated soil or sediment may be limited to hot spots with elevated contaminant concentrations or may extend over the entire impacted area. The TTZ for contaminated groundwater may encompass the source zone, the dissolved plume, localized areas with elevated concentrations within the plume, and/or the down gradient boundary of the dissolved plume.

Development and selection of the CSM, RAOs, FRGs, and the TTZ constrain the remedial approaches and technologies potentially applicable to a release site. The remainder of this section presents the RAOs, FRGs, and the TTZ applicable to the Central Carolina Tire site with respect to the PCE release, as well as analyses of potentially applicable remedial approaches and technologies that could be applied to the PCE release for corrective measures.

6.2 Remedial Action Objectives

Based on the CSM derived from the four phases of environmental and groundwater quality assessment, as well as the analysis of potential receptors and exposure pathways, three RAOs are applicable to the site.

1. Protect site workers from unacceptable risks associated with inhalation, dermal contact and ingestion of CAHs in groundwater.
2. Prevent migration of COCs to the streams and fringing wetlands bordering the closed Phase I/II landfill at concentrations that would cause surface water quality standards to be exceeded.
3. Reduce contaminant mass in the source area to the degree necessary to prevent further degradation of the groundwater above groundwater clean-up standards and minimize the aquifer clean-up time.

The RAOs guide the selection of FRGs for the site.

6.3 Final Remedial Goals

Based on the RAOs for the site, the goal of the corrective measures will be to restore groundwater quality on the Central Carolina Tire property to the levels of the standards in 15A NCAC 2L .0202 for COCs exceeding the standards as identified in the CSM. Screening of potential corrective measures will be based on the ability of the evaluated technologies and approaches to meet the site RAOs and FRG.

6.4 Target Treatment Zone

The dissolved CAHs plume at the Central Carolina Tire site can be generally characterized as diffuse and principally composed of relatively low levels of contaminants outside of the comparatively localized contaminant source area. The contaminant source area (i.e., collective locations of small volume incidental spills) is confined to a relatively small area in the vicinity of monitoring well MW-10 and the maintenance shelter and contains higher concentrations (albeit relatively low) of dissolved CAHs. Based on the CSM, the bulk of the contaminant mass is confined to the source area with the remainder of the contaminant mass existing within a diffuse low concentration plume hydraulically down gradient of the source area.

The historical results of surface water monitoring at the site extending back to at least 2002 indicate that PCE and its environmental breakdown products have not been detected in surface water (**Section 5.5**). Moreover, the results of the evaluation of potential receptors and exposure pathways (**Section 5.6**) indicate that no complete exposure pathways currently exist at the site with respect to the COCs and no potential receptors are at immediate or imminent risk of exposure to the dissolved CAHs in groundwater.

Based on the current site conditions as summarized above and encompassed by the CSM, it is not practical from the perspective of ease of implementation or cost-effectiveness to restore the concentrations of dissolved CAHs to the levels of the cleanup standards throughout the entire extent of the contaminant plume via aggressive and potentially somewhat costly remediation methods. Further, aggressive treatment of the entire plume is not necessitated from the perspective of reduction of risks to human health because no complete exposure pathways exist at the site. Consequently, the TTZ for more aggressive corrective measures (TTZ-1) at the site will be confined to the source area in the vicinity of monitoring well MW-10 and the maintenance shelter. Further, the TTZ for less aggressive corrective measures (TTZ-2) encompasses the remainder of the dissolved CAHs plume with PCE concentrations exceeding the corresponding 15A NCAC 2L groundwater quality standard (0.7 μg/L). A graphical depiction of the TTZs superimposed on the dissolved CAHs plume as delineated in August 2014 is presented in **Figure 12**.

6.5 Screening of Potential Corrective Measures

As required by 15A NCAC 2B .1635, the effectiveness of the potential corrective measures presented below will be screened and evaluated in accordance with the following criteria.

1. The performance, reliability, ease of implementation, and potential impacts of potential remedies, including safety impacts, cross-media impacts, and control of exposure to any residual contamination;
2. The time required to begin and complete the remedy;
3. The costs of remedy implementation; and
4. The institutional requirements such as State and Local permit requirements or other environmental or public health requirements that may affect implementation of the remedy(s).

Based on the analysis of potential receptors and exposure pathways, the most plausible risk of human exposure to the site contaminants would result from company employees and non-employee support personnel conducting excavation activities in the general area of the maintenance shelter in which shallow groundwater is encountered (see **Section 5.6**). To minimize the risk of exposure to site contaminants during implementation of corrective measures, reduce the potential for cross-media transfer of contaminants that is commonly associated with *ex situ* treatments, as well as other risks associated with the handling of contaminated groundwater, *in situ* remediation technologies are considered the most appropriate for addressing the groundwater contamination at the site.

In situ groundwater remediation processes treat contaminated groundwater in place (i.e., without removal). This approach has the potential advantages of reducing the costs of materials handling and some environmental impacts. *In situ* treatment of groundwater involves the application of chemical or biological mechanisms for reducing the concentrations of groundwater contaminants. *In situ* treatment technologies include: 1) natural attenuation, in which natural biotic and abiotic processes are relied upon to reduce the mass of site contaminants; 2) enhanced bioremediation, in which substances are added to the subsurface to promote natural biological degradation processes (e.g., carbon substrates that promote microbial degradation of organic constituents); and 3) chemical treatment, in which substances are added to the subsurface that promote the destruction or sequestration of the groundwater contaminants by chemical means (e.g., chemical oxidation or chemical reduction). Although *in situ* processes may be limited in terms of the ability to control or manipulate

the physical and/or geochemical environment in place, the site conditions at the Central Carolina facility as encompassed by the CSM appear to be amenable to *in situ* treatment technologies.

Based on the CSM, RAOs, FRGs and TTZ discussed above, five *in situ* groundwater corrective measures were selected for screening.

- Monitored Natural Attenuation (MNA)
- Enhanced In Situ Bioremediation
- In Situ Chemical Oxidation (ISCO)
- In Situ Chemical Reduction (ISCR)
- Nano-Scale Zero Valent Iron

Potential institutional controls and corrective measures technologies for addressing groundwater contamination associated with the PCE release at the Central Carolina Tire site are discussed, evaluated and screened in the following section.

7.0 EVALUATION AND SCREENING OF POTENTIAL CORRECTIVE ACTION MEASURES

7.1 Institutional Controls

EPA defines institutional controls (ICs) as "non-engineered instruments, such as administrative and legal controls, that help to minimize the potential for human exposure to contamination and/or protect the integrity of a response action. ICs are typically designed to work by limiting land or resource use or by providing information that helps modify or guide human behavior at a site. Some common examples of ICs include zoning restrictions, building or excavation permits, well drilling prohibitions, easements, and covenants."[5] As used herein, ICs also include engineering and physical barriers, such as fences and security guards. ICs are used when contamination is first discovered, when remedies are ongoing, and when residual contamination remains onsite at a level that does not allow for unlimited use and unrestricted exposure after cleanup.

Inasmuch as minimizing the risk of exposure to the groundwater contaminants by company employees and non-employee support personnel is one of the primary RAOs for the site, a restriction on activities in the area of groundwater impact that would result in contact of workers with contaminated groundwater is considered an appropriate institutional control. The restriction should remain in force until the concentrations of the site COCs in groundwater are reduced to levels that would allow unrestricted land use throughout the area of impact. As a conservative measure, the restriction should encompass all activities involving excavation of soil beyond surficial land disturbance.

7.2 Monitored Natural Attenuation

7.2.1 Technology Description

The EPA defines monitored natural attenuation (MNA) as: "the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include

[5] Institutional Controls: A Guide to Planning, Implementing, Maintaining, and Enforcing Institutional Controls at Contaminated Sites, Interim Final; November 2010; EPA-540-R-09-001; 37 pp.

biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants." [6]

Natural attenuation processes that degrade or destroy contaminants are generally preferred for site remediation (generally biologically mediated processes, but can include abiotic processes). Moreover, MNA will generally only be appropriate for sites that have a low potential for continued contaminant migration. Further, MNA can be used in conjunction with more aggressive active remediation technologies applied to the contaminant source area, thereby providing a multicomponent corrective measures approach to address the full extent of contaminant impact to groundwater.

Based on EPA guidance[6], a three-tiered approach is recommended to evaluate site specific data in estimating with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve RAOs. This approach involves analysis of successively more detailed site information, as deemed necessary, to provide increasing levels of confidence with regard to estimates of attenuation rates and remediation timeframe. The three tiers include:

1. Historical groundwater quality data that demonstrate a stable or decreasing trend of contaminant concentration and/or mass at appropriate monitoring points.
2. Hydrogeologic and geochemical data that indirectly demonstration the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to the FRGs.
3. Data from field or microcosm studies which **directly** demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the COCs.

The three-tiered approach is a hierarchical process in which the results of each tier of analysis are judged as to whether the data are of sufficient quality to support a decision to use MNA. If the results of analysis of a tier are deemed insufficient to definitively support the decision to use MNA, the next tier of analysis should be conducted.

The most important factors to consider regarding the suitability of MNA as the sole remedy or a remedy component for site contamination are: 1) whether the COCs are amenable to natural attenuation processes; 2) whether the groundwater contaminant

[6] U.S. EPA, 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17P. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC.

plume has stabilized or is shrinking; and 3) the potential for unacceptable risks to human health or environmental resources by the site contamination.[6] Sites where the contaminant plumes are no longer increasing in extent, or are shrinking, are the most appropriate candidates for MNA remedies. Source control measures should be implemented as part of the site wherever possible, particularly where MNA is under consideration as the sole remedy or as a remedy component. Source control measures include removal, treatment, or containment, or a combination of these approaches.

7.2.2 Potential Site Applicability

The June 2008 NCDENR-DWM, Solid Waste Section, MNA Guidance Document lists site-specific conditions that limit the effectiveness of MNA, and preclude the use of MNA as a ***sole*** remedy, if present. These include:

- An advancing groundwater plume indicates that the natural attenuation capacity of the system is unable to control the migration of contaminants.
- The contaminated media is difficult to assess as in some bedrock aquifers.
- Contaminant concentrations exceed groundwater standards established in 15A NCAC 02L .0202 beyond the relevant point of compliance.
- Points of exposure other than the property boundary are currently impacted.
- Mobile free product is present at the site, and no remedial method addressing the free product removal has been proposed.
- One or more of the other four exposure pathways (Subsurface Soil Leachate to Groundwater, Surficial Soil, Groundwater to Indoor Air Inhalation and Soil Vapor to Indoor Air Inhalation) exists at the site, and no active remediation method has been proposed to eliminate them.
- Contaminants are present which do not readily biodegrade.
- Fractured bedrock contamination.
- Contamination that has impacted receptors or creates an imminent threat to receptors (e.g., drinking water wells, surface water, other environmental receptors)
- Source water protection areas.
- Well head protection areas.

Based on the CSM, the site meets most of the site-specific criteria listed in the MNA Guidance Document to allow use of MNA as the sole technology to address groundwater contamination associated with the PCE release. However, site data indicates that the dissolved CAHs plume exhibits some evidence of continuing advancement. Monitoring well MW-8 is a permit compliance well for monitoring

groundwater quality associated with the closed Phase I/II landfill. This well was also used for the assessment of groundwater impacts associated with the PCE release at the site and is the only well with a groundwater quality database covering a sufficient duration of time to assess the degree of stability of the dissolved CAHs plume. **Figure 13** presents a graph of PCE concentrations in groundwater versus time for samples collected from MW-8 during the period of October 2006 to April 2015. The graph shows a clear increase in PCE concentrations during the monitoring period, indicating that the dissolved CAHs plume is continuing to advance in the vicinity of MW-8. This finding precludes the use of MNA as a sole remedy for addressing groundwater contamination.

Natural biodegradation of PCE occurs by way of both co-metabolism and direct reductive transformation under anaerobic conditions. Biotransformation of PCE under aerobic conditions has not been documented. Under suitable oxidation-reduction conditions, anaerobic transformation of PCE via reductive dechlorination can proceed at least through the formation of ethene. The general transformation sequence is: PCE $\rightarrow$ TCE + Cl^- $\rightarrow$ DCE (1,1-DCE and 1,2-DCE isomers) + Cl^- $\rightarrow$ VC + Cl^- $\rightarrow$ ethene + Cl^-. Anaerobic transformation of PCE through DCE can occur under mildly reducing conditions, however, complete transformation through the production of ethene generally requires more strongly reducing conditions, such as those suitable for methane fermentation (methanogenesis). Consequently, the presence of VC in a PCE-contaminated aquifer is an indicator of methanogenic conditions.

The biochemical energy associated with the various microbial metabolic pathways can be expressed by the oxidation-reduction potential of the alternative electron acceptors, with the more positive oxidation-reduction potentials representing the more thermodynamically favorable reactions.[7] The following table shows the relative oxidation-reduction potential and reaction preference for the alternative electron acceptors (adapted from Newell *et. al.*, 1995).

[7] Newell, C. J., J. A. Winters, R. N. Miller, J. Gonzales, H. S. Rifai, and T. H. Wiedemeier, 1995. Modeling intrinsic remediation with multiple electron acceptors: Results from seven sites, in *The Proceedings of the 1995 Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference and Exhibition*, Houston, Texas, November 1995, pp. 33-47.

Electron Acceptor	Type of Reaction	Metabolic By-Product	Oxidation-reduction Potential (pH=7; mV)	Reaction Preference
Oxygen	Aerobic	CO_2	+ 820	Most Preferred
Nitrate	Anaerobic	N_2, CO_2	+ 740	⇓
Ferric Iron (solid)	Anaerobic	Ferrous Iron (dissolved)	- 50	⇓
Sulfate	Anaerobic	H_2S	-220	⇓
Carbon Dioxide	Anaerobic	CH_4	-240	Least Preferred

In addition to the biochemical energy of the metabolic pathways, another principal factor influencing the preferential utilization of the various electron acceptors at a particular site is the availability of the specific electron acceptors. The distribution of electron acceptors is a function of site-specific hydrogeochemical processes and can vary significantly among sites.

To assess the potential for alternative biodegradation reactions in groundwater, and the potential for biologically mediated contaminant mass removal (i.e., biodegradation capacity) of the aquifer, the depletion of electron acceptors and accumulation of metabolic by-products in groundwater can be monitored in the field. This is most readily accomplished by measuring the concentrations of the dissolved electron acceptors oxygen, nitrate, and sulfate, and the concentrations of the metabolic by-products dissolved iron and methane in groundwater at background locations and within the area of the dissolved contaminant plume. Qualitatively, a pattern in which depletion of electron acceptor concentrations or accumulation of metabolic by-product concentrations is observed within a contaminant plume relative to background locations is a positive indicator of active microbial metabolism of the dissolved organic contaminants. In addition, the accumulation of dissolved ethene, ethane and chloride (Cl^-) within a dissolved chlorinated ethenes plume relative to background locations is a positive indicator of suitable aquifer conditions for the complete reductive dechlorination of the parent chlorinated ethene.

The natural attenuation potential of the shallow surficial aquifer with respect to dissolved CAHs in groundwater was evaluated as part of the June 2012 Phase 2 Hydrogeologic and Groundwater Quality Assessment report. The results of the evaluation indicate: 1) TCE and cis-1,2-DCE, which are daughter products of biodegradation of PCE, have been detected in the area of groundwater impact; 2) oxidation-reduction conditions

within the shallow surficial aquifer are dominated by mild, nitrate reduction, even though DO concentrations typically exceed 2.0 mg/L based on field measurements; 3) naturally occurring microbes are likely utilizing dissolved organic carbon (DOC) as a primary carbon source at least within the main body of the dissolved PCE plume and are partially using dissolved chlorinated ethenes as terminal electron acceptors leading to anaerobic reductive dechlorination at least through the production of DCE; and 4) concentrations of chloride detected at all monitoring wells located hydraulically down gradient of the maintenance shelter are approximately 1.85 to 5.3 times higher than the concentration measured at the background shallow monitoring well, indicating active anaerobic reductive dechlorination of dissolved chlorinated ethenes in the shallow surficial aquifer.

These observations indicate that natural attenuation of the dissolved CAHs via biologically mediated reductive dechlorination in groundwater is occurring at the Central Carolina Tire site. The reductive biotransformation of PCE appears to be incomplete. However, VC has been shown to be amenable to direct and co-metabolic biodegradation under aerobic conditions.[8] The less chlorinated compounds tend to be more readily transformed under aerobic conditions. Oxidation of VC results in the production of labile, and generally innocuous, end products. Aerobic biodegradation of chlorinated ethenes can only occur if sufficient DO (direct and co-metabolic) and suitable primary organic substrate (co-metabolic) are present. At the Central Carolina Tire site DO concentrations in excess of 2.0 mg/L predominate in the shallow aquifer. Moreover, sufficient DOC appears to be present to act as a primary organic substrate for microbial co-metabolism of amenable chlorinated ethenes. Consequently, the lack of detection of VC in groundwater within the surficial aquifer may be indicative of direct aerobic or aerobic co-metabolic degradation rather than incomplete biotransformation of PCE.

Based on the analysis of available site data presented above, MNA may be suitable as one component of a multicomponent corrective measures strategy to address groundwater contamination associated with the PCE release. In particular, MNA may be appropriate as a corrective measures technology to address residual groundwater contamination in TTZ-2. However, MNA is not suitable as a sole remedy for addressing groundwater contamination over the entire area of groundwater impact.

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[8] McCarty, P.L., 1996. Biotic and abiotic transformations of chlorinated solvents in groundwater; in *Symposium on Natural Attenuation of Chlorinated Organics in Groundwater*, U. S. EPA Document EPA/504/R-96/509, pp. 5-8.

7.2.3 Performance and Reliability

During the past 25 years, the use of MNA for remediation of CAHs in groundwater has advanced rapidly as scientific understanding of the governing processes evolved considerably along with the protocols for determining the appropriateness of applying the approach at specific sites and measuring the progress toward meeting remediation goals. MNA was a component of more than 18% of National Priority List (NPL) sites where groundwater is contaminated during the period 2005 through 2008.[9] The Interstate Technology Regulatory Council (ITRC) reported on 24 sites located in 12 states where MNA was selected as a component of the final site remedy for addressing CAHs in groundwater.[10] Based on these and numerous other case studies in the literature, MNA has proven to be a generally effective and reliable component of site remedies for treatment of groundwater impacted by CAHs. It is noted, however, in general, MNA has been used as one component of a multicomponent corrective action strategy at most sites and not as a sole remedy.

7.2.4 Implementation

Implementation of MNA requires a comprehensive groundwater monitoring program that includes a monitoring well network designed to assess the progress and effectiveness of MNA with regard to plume attenuation, as well as the nature and extent of the contaminant plume over time (i.e., plume stability). A proposed monitoring well network is an integral component of any corrective action plan (CAP) in which MNA is proposed as a component of the site remedy, and requires regulatory approval. In accordance with the June 2008 NCDENR-DWM, Solid Waste Section, MNA Guidance Document, groundwater is to be sampled from wells in the monitoring network and analyzed for a suite of specific MNA performance parameters on a semiannual basis for at least two calendar years (four semiannual sampling events) to establish baseline trends. The MNA performance parameters are designed to provide data with respect to the microbial and biogeochemical reactions and processes that are occurring within the subsurface. Also in accordance with the 2008 MNA Guidance Document, an EPA approved MNA screening model is required to be run based on the results of each semiannual baseline event and submitted with the semiannual groundwater monitoring reports for the site. The screening model must include the ability to measure mass flux.

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[9] Wilson, John T., 2011. An approach for evaluating the progress of natural attenuation in groundwater; U.S. Environmental Protection Agency; EPA 600/R-11/204; 84 pp.

[10] ITRC (Interstate Technology & Regulatory Council). 2008. *Enhanced Attenuation: Chlorinated Organics*. EACO-1. Washington, D.C.: Interstate Technology & Regulatory Council, Enhanced Attenuation: Chlorinated Organics Team. 109 pp.

After completion of the baseline groundwater sampling events, the MNA performance parameters may be re-evaluated to determine if the frequency of sampling may be reduced for one or more performance parameters or if one or more performance parameters may be removed from the corrective action sampling program based upon its technical relevance. In any case, groundwater sampling and analysis in support of MNA will be conducted on a semiannual basis until the RAOs are met and the FRGs are achieved and maintained for three consecutive years.

According to EPA guidance[6], the following technical and scientific demonstrations are necessary to provide evidence in support of the effectiveness of MNA:

1. The reduction of the contaminant concentrations is caused by chemical or biological attenuation of the contaminant;
2. The sampling analytical results show that the plume has stabilized horizontally and vertically in size and is not migrating; and
3. A statistical reduction in the contaminant concentrations along specific flow paths can be shown.

After the baseline sampling events have been completed, an EPA approved MNA screening model is required to be run at least annually to simulate the groundwater remediation at the facility and determine the mass flux and mass balance. The results of the model runs are to be included in one of the two required semiannual monitoring reports. In addition, the 2008 MNA Guidance Document requires that the MNA performance parameter data and the technical evaluation of MNA as a remedy at the facility be presented in a comprehensive MNA Corrective Action Evaluation Report at least once every five calendar years. The MNA Corrective Action Evaluation Report must include interpretations of the three technical and scientific demonstrations above. In addition, land use restrictions are to be imposed during the duration of MNA.

Finally, the 2008 MNA Guidance Document requires that any approved MNA program include a contingency plan with a list of triggering events and established corrective action responses to those triggering events. If MNA is not performing in accordance with the objectives set forth in the approved CAP after the first five consecutive calendar years, the contingency plan is required to be implemented immediately.

7.2.5 Potential Impacts

In general, MNA does not cause negative impacts with respect to human health or the environment, because it does not result in the generation of significant volumes of

wastes from remediation processes. In addition, MNA does not involve disturbance of the contaminant source material or the introduction of biological/chemical treatment substances into the subsurface. At the Central Carolina Tire site no potential receptors are at imminent risk of exposure to the COCs and implementation of MNA as a component of any contemplated site remedy would not alter the risk scenario. In addition, the maximum concentration of the PCE detected in groundwater is low (approximately 0.04% of the solubility concentration) so that the risks of cross-media impacts and significant vapor generation are likewise low.

7.2.6 Remediation Time Frame

The site data indicates that the dissolved CAHs plume exhibits some evidence of continuing advancement, specifically in the vicinity of monitoring well MW-8, which by extension indicates that the contaminant source area remains an active source of contaminant mass flux in groundwater. Moreover, this observation indicates that the natural attenuation capacity of the shallow surficial aquifer is insufficient to effectively assimilate the contaminant mass from the source area within the volume of aquifer material that is currently impacted. Consequently, the use of MNA as the sole remedy for addressing groundwater contamination is not appropriate and source control measures are required if MNA is contemplated as a component of an overall site remedy.

Inasmuch as the source area remains an active source of contaminant mass flux in groundwater, estimating the time frame for remediation under a MNA program is challenging. However, gross estimates of the time to reach remediation goals can be made if it is assumed that source area treatment will be combined with MNA and some simplifying assumptions are applied. Typical first-order rate constants for the attenuation of various contaminants (including PCE) over time in groundwater are presented in Wilson (2011).[9] The rate constants are based on the results of analyses of groundwater samples collected from monitoring wells over time and were compiled and derived from multiple published sources for multiple sites across the United States. The time to reach a remediation goal at a monitoring point within a dissolved contaminant plume can be estimated based on the following relation[11]:

$$t = -Ln[C_{goal}/C_{start}]/k_{point},$$

[11] Newell, Charles J., Hanadi S. Rifai, John T. Wilson, John A. Connor, Julia A. Aziz, and Monica P. Suarez, 2002; Calculation and use of first-order rate constants for monitored natural attenuation studies; U. S. Environmental Protection Agency, EPA/540/S-02/500; 28 pp.

where t is the time to reach the remediation goal, C_{goal} is the remediation goal in terms of concentration (µg/L), C_{start} is the starting contaminant concentration (µg/L), and k_{point} is the point decay first-order rate constant (time per year). The first-order rate constants represent an integrated average of all of the physical, chemical and biological processes of natural attenuation operating at a site.

The following presents estimated times to reach the 15A NCAC 2L .0202 groundwater quality standard of 0.7 µg/L for PCE (C_{goal}) at monitoring wells GW-2S, GW-3S, GW-5S, GW-7S, MW-8 and GW-10S using the highest concentration of PCE detected in groundwater to date at each well for C_{start} and a k_{point} value of 0.23 per year based on the data provided in Wilson (2011). [9]

Monitoring Well ID	C_{start} (µg/L)	Time to reach C_{goal} (yr)
GW-2S	22	14.99
GW-3S	8.0	10.59
GW-5S	12	12.35
GW-7S	13	12.70
MW-8	9.2	11.20
GW-10S	58	19.20
	Average:	13.50

The results of the analysis of potential remediation timeframes under a scenario of source area treatment and MNA indicates estimated times to reach the remedial goals ranging from approximately 11 to 19 years. Although these timeframes are gross estimates based on limited site-specific data, they illustrate that the time to reach remediation goals using MNA in TTZ-2 (i.e.; outside the source area) are reasonable and comparable to what would be expected using more aggressive remediation approaches.

7.2.7 Estimated Cost

Costs associated with MNA monitoring and reporting are expected to range from approximately $20,000 to $25,000 per year. Assuming a maximum estimated time to achieve the FRGs (see **Section 7.2.6**) of approximately 19 years, the total cost to implement and complete MNA in TTZ-2 at the site is estimated to range from $375,000 to $480,000.

7.3 Enhanced In Situ Bioremediation

7.3.1 Technology Description

Enhanced in situ anaerobic bioremediation involves distribution of a reduced organic substrate (carbon source) into groundwater to stimulate microbial growth and development, create and sustain anaerobic conditions within the groundwater treatment zone, and generate hydrogen and fatty acids through fermentation reactions.[12,13] The hydrogen and low-molecular weight fatty acids generated through fermentation provide a source of carbon and energy to the microorganisms. The reducing conditions established following introduction of a carbon substrate to the subsurface are favorable for enhancing the rates and completeness of anaerobic biodegradation (direct and cometabolic reductive dechlorination) of chlorinated solvents dissolved in groundwater. In some cases, the addition of selected microorganisms (bioaugmentation) may be required, but only if the natural microbial population is incapable of performing the required transformations.[12]

Enhanced in situ anaerobic bioremediation can be an effective method of degrading various chlorinated solvents dissolved in groundwater, including chloroethenes, chloroethanes, and chloromethanes (collectively referred to as chlorinated aliphatic hydrocarbons (CAHs)).[12] The following factors are required for enhanced in situ anaerobic bioremediation of CAHs to be effective.[12]

- The contaminant(s) is anaerobically biodegradable.
- Strongly reducing conditions can be generated and conditions for microbial growth are met.
- A microbial community capable of degrading the contaminant(s) is present or can be introduced to the subsurface; and
- A readily digestible carbon source can be adequately distributed throughout the subsurface treatment zone.

CAHs such as PCE and its daughter products from biotransformation (i.e., TCE, 1,2-DCE, and VC) exist in an oxidized state, and therefore are generally much less susceptible to aerobic oxidation processes. However, they are susceptible to reduction under anaerobic conditions by either biotic (biological) or abiotic (chemical) processes.

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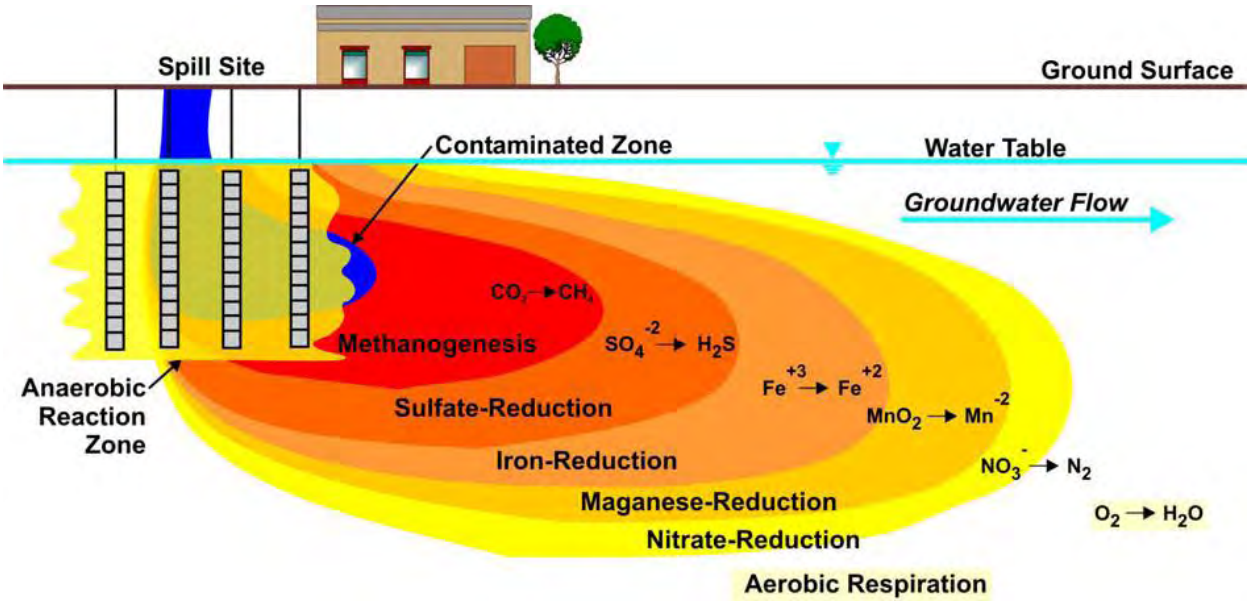
[12] Air Force Center for Energy and the Environment (AFCEE). 2004. Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents; 457 pp.

[13] U.S. EPA, 2013. Introduction to In Situ Bioremediation of Groundwater;EPA-542-R-13-018; U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response; 86 pp.

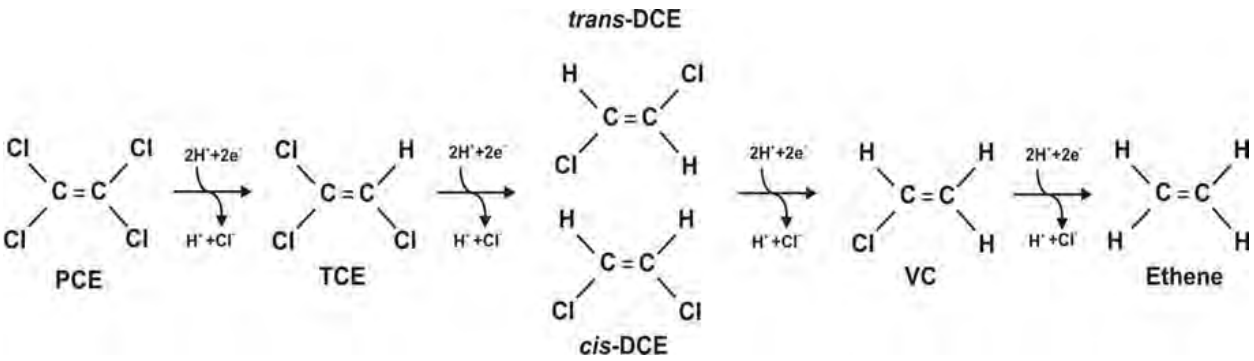
Enhanced in situ anaerobic bioremediation primarily exploits biotic anaerobic processes to degrade CAHs in groundwater (direct and cometabolic reductive dechlorination).

During biodegradation of an organic substrate, microorganisms sequentially consume native electron acceptors beginning with the most oxidized and transitioning to the least oxidized. Depletion of the electron acceptors lowers the oxidation-reduction potential (ORP) of groundwater, thereby producing conditions favorable to anaerobic degradation processes. After DO is consumed, anaerobic microorganisms typically consume native electron acceptors (as available) in the following order of thermodynamic preference: nitrate, manganese and ferric iron oxyhydroxides, sulfate, and finally carbon dioxide.

The following figure illustrates a CAH plume where a readily digestible organic carbon substrate has been injected into the source area (adapted from AFCEE, 2004).[12] Biodegradation of the organic carbon substrate generates an anaerobic treatment area composed of nested zones that are progressively less anaerobic further from the source of organic carbon as electron acceptors are depleted. Biotic anaerobic dechlorination of CAHs can occur under nitrate, iron, and sulfate reducing conditions, but methanogenic conditions produce the most rapid biodegradation rates and affect the widest range of CAHs.[12]



In general, anaerobic degradation of CAHs proceeds via reductive dechlorination through sequential removal of chloride ions. Sequential anaerobic transformation of PCE to ethene is illustrated below (adapted from AFCEE, 2004).[12]



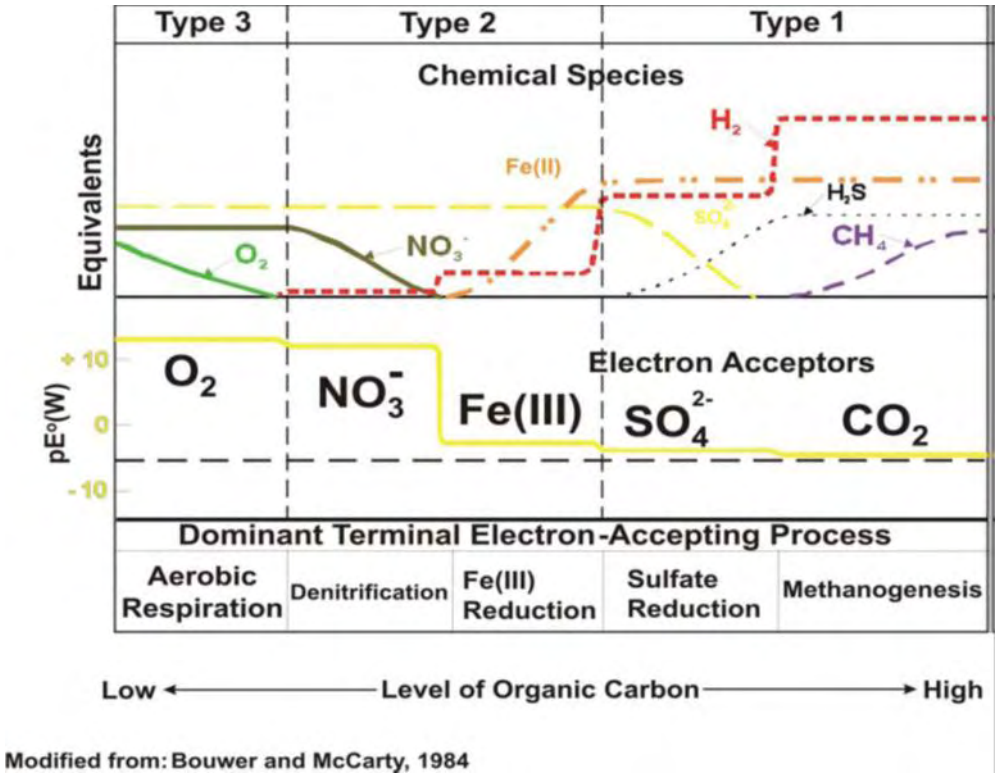
In this reaction, hydrogen is the electron donor (reducing agent), and the chlorinated ethene molecule is the electron acceptor (oxidizing agent). Hydrogen is generally the most important electron donor for anaerobic dechlorination of CAHs; however, other fermentation products (e.g., acetate) may serve as an electron donor.[12]

Anaerobic reductive dechlorination of more highly chlorinated (more oxidized) CAHs, such as PCE and TCE, is more thermodynamically favorable and thus occurs more readily than dechlorination of somewhat more reduced (les oxidized) CAHs, such as 1,2-DCE and VC.[12] Consequently, 1,2-DCE and VC may accumulate in an aquifer system in which the rate at which they generated is greater than the rate at which they are degraded or if the natural microbial population is incapable of performing the required transformations to ethene. For the latter case, the addition of selected microorganisms (bioaugmentation) may be required. However, there are other degradation pathways that can often mitigate the formation and persistence of large plumes of 1,2-DCE and VC.[12]

Many organic substrates can be naturally degraded and fermented in the subsurface resulting in the generation of hydrogen for use in anaerobic reductive dechlorination. However, the organic substrate(s) selected should be appropriate for the biogeochemistry and hydrodynamics of the impacted aquifer.[12] Commonly used substrate types include soluble substrates (lactate, molasses), slow-release substrates (vegetable oil, emulsified vegetable oil (EVO), Hydrogen Release Compound [HRC®]), and solid substrates such as mulch and compost.[12]

Chlorinated solvent plumes can exhibit various types of biogeochemical behavior, principally depending on the amount of biologically available organic carbon (electron donor) in the aquifer and the type and distribution of electron acceptors being used by native microbes.[12] Further, the prevailing redox conditions influence the rate and extent of anaerobic dechlorination of CAHs. Consequently chlorinated solvent plumes can be classified according to the prevailing redox conditions and resulting potential for dechlorination to occur.[12]

A classification scheme that depends on the relative amount of organic substrate available (natural or introduced) to produce the hydrogen that drives anaerobic dechlorination and the redox conditions that predominate within an aquifer system is presented in AFCEE (2004). The relative amount of organic substrate is emphasized because enhanced anaerobic bioremediation modifies this parameter to achieve redox conditions that are optimal for anaerobic dechlorination to occur. The three different types of plume behavior summarized below can be used to delineate zones of differing anaerobic biodegradation potential within a chlorinated solvent plume. The following figure, from AFCEE (2004), illustrates the geochemical characteristics of the three types of environments.[12]



Type 1 environments are characterized by highly anaerobic conditions due to high organic carbon levels which exert a substantial electron acceptor demand on the aquifer.[12] Further, Type 1 environments exhibit very low concentrations of DO (<0.5 mg/L), nitrate and sulfate, as well as well as elevated concentrations of ferrous iron and methane.[12] Natural aquifer systems rarely contain sufficient natural organic carbon to generate and sustain the highly reducing conditions associated with predominant sulfate reduction and methanogenesis.[12] Geochemical conditions in a Type 1 environment are favorable for extensive dechlorination of more highly chlorinated CAHs such as PCE and TCE. Consequently, the goal of enhanced anaerobic bioremediation is to establish Type 1 conditions within the TTZ in which CAHs are completely dechlorinated.

Type 2 environments are characterized by mildly anaerobic conditions due to moderate organic carbon levels. Redox reactions are predominantly nitrate, manganese and iron reduction. Many natural aquifer systems are characteristically Type 2.[12] Geochemical conditions in a Type 2 environment promote slower rates of dechlorination of more highly chlorinated CAHs and incomplete dechlorination of less chlorinated CAHs (e.g., 1,2-DCE) as compared with a Type 1 environment.[12] Consequently, products of dechlorination of the more highly chlorinated CAHs can accumulate in Type 2 environments. However, addition of organic substrate can transform a Type 2 environment to a Type 1 environment capable of complete degradation of dechlorination products.[12]

Type 3 environments are characterized by aerobic systems with low levels of organic carbon. DO concentrations are typically greater than 1.0 mg/L, anaerobic dechlorination of CAHs will not occur, and extensive dissolved-phase plumes can result.[12] It is noted, however, that less chlorinated CAHs such as VC and 1,2-DCE can be rapidly oxidized under Type 3 conditions.[12] Type 1 conditions can be induced at many Type 3 sites due to microbial heterogeneity and the presence of anaerobic micro-environments in the aquifer system. However, generating Type 1 conditions can take a longer to establish at Type 3 sites than for Type 2 sites due to the lag time required for acclimation and growth of anaerobic dechlorinating microbial populations.[12]

A dissolved-phase plume of CAHs can exhibit all three types of environments in different parts of the plume. Under such circumstances, Type 1 conditions are often observed in the source area and Type 2 and 3 conditions are observed down gradient from the source. Under this scenario, dechlorination of PCE, TCE, and 1,2-DCE, with accumulation of VC occurs near the source or treatment area (Type 1 behavior) and oxidation of VC, and possibly 1,2-DCE, (Type 3 behavior) occurs either aerobically or

via iron reduction down gradient from the source area.[12] Enhanced anaerobic bioremediation systems can be designed to take advantage of mixed reaction zones by employing a strategy using sequential anaerobic/aerobic degradation where more highly chlorinated compounds (e.g., PCE and TCE) are dechlorinated in an anaerobic reaction zone in the source area, and less chlorinated compounds (e.g., DCE and VC) are degraded by oxidation processes in an aerobic redox recovery zone (natural or engineered) down gradient from the source area.[12]

7.3.2 Potential Site Applicability

The applicability of enhanced anaerobic bioremediation for treatment of a dissolved-phase plume of CAHs requires consideration of numerous technical factors related to contaminant type and distribution, microbiology, hydrogeology, and groundwater geochemistry.[12] The goal of organic substrate addition in enhanced aerobic bioremediation is to create Type 1 conditions in the treated aquifer. In evaluating the potentially applicability of enhanced anaerobic bioremediation, it is important to consider the predominant type of environment and groundwater geochemistry in the aquifer to be treated.[12] Generally, enhanced anaerobic bioremediation is capable of more easily and rapidly treating aerobic or borderline aerobic/anaerobic aquifers that have insufficient dissolved organic matter to sustain highly anaerobic conditions and complete dechlorination of CAHs. Some dechlorination products (e.g., 1.2-DCE, VC) are characteristically present at these types of sites. However, the lack of sufficient organic substrate and highly anaerobic conditions inhibits the rate and extent of dechlorination of CAHs. Aquifers exhibiting Type 3 environments are often also amenable to enhanced anaerobic bioremediation. However, creating Type 1 conditions in a Type 3 environment generally requires the addition of more organic substrate and a longer time to establish than in a Type 2 environment due to the lag time required for acclimation and growth of anaerobic dechlorinating microbial populations.[12]

Typical criteria used to determine the suitability of applying enhanced anaerobic bioremediation at a site are presented in the following table. Although not exhaustive, the criteria listed in the table are useful for a preliminary evaluation of the applicability of enhanced anaerobic bioremediation. Criteria that are met by the conditions at the Central Carolina Tire site are highlighted in green; conditions not meeting the criteria are highlighted in red; and conditions for which there is insufficient site data the criteria are highlighted in yellow.

Suitability of Site Characteristics for Enhanced Anaerobic Bioremediation

Site Characteristic	Suitable for Enhanced Bioremediation	Suitability Uncertain	Suitability Unclear - Possible Red Flag - Requires Further Evaluation
DNAPL Presence	Residual DNAPL or sorbed sources.	Poorly defined sources may require additional characterization.	May not be appropriate for aggressive treatment of pools of DNAPL.
Plume Size	Small, a few acres or less.	Medium to large, a few acres plus. May require concurrent technology.	Large plumes of many acres. May require concurrent technology.
On or Near Site Infrastructure	The risk of vapor intrusion from contaminants or biogenic gases is deemed acceptable.	Target treatment zone in close proximity to sensitive infrastructure.	Target treatment zone in an area where known vapor intrusion or high methane problems exist.
Evidence of Anaerobic Dechlorination	Slow or stalled dechlorination	Limited evidence of anaerobic dechlorination.	No evidence of any degradation.
Depth	<50 feet to water	>100 feet to groundwater	Deep groundwater and deep contamination.
Hydraulic Conductivity	> 1 ft/day (>3 x 10^{-4} cm/sec)	0.01 to 1 ft/day (3 x 10^{-6} to 3 x 10^{-4} cm/sec)	<0.01 ft/day (<3 x 10^{-6} cm/sec)
Groundwater Velocity	30 ft/yr to 5 ft/day	10 ft/yr to 30 ft/yr, 5 ft/day to 10 ft/day	< 10 ft/yr, > 10 ft/day
pH	6.0 – 8.0	5.0 to 6.0, 8.0 to 9.0	< 5.0, > 9.0
Sulfate Concentration	< 500 ppm Unknown	500 to 5,000 ppm (with caution)	>5,000 ppm or presence of mineral gypsum may not be suitable

Adapted from AFCEE (2004)[12]

As indicated in the table above, the conditions at the Central Carolina Tire PCE release location meet seven of the nine criteria listed for assessing the suitability of a site for enhanced anaerobic bioremediation. The criterion regarding sulfate concentration could not be evaluated due to a lack of site-specific data. The only criterion that the site did not meet was for pH. The typical pH of groundwater in the PCE release location is less than 5.0. However, it is noted that evidence of anaerobic reductive dechlorination in the form of accumulation of TCE, 1,2-DCE, and VC is present at the site indicating that the groundwater pH is not inhibiting growth of anaerobic dechlorinating bacteria. Based on the analysis presented above, enhanced anaerobic bioremediation is suitable to address groundwater contamination associated with the PCE release.

7.3.3 Performance and Reliability

Enhanced anaerobic bioremediation of chlorinated solvents in groundwater (commonly referred to as enhanced reductive dechlorination or ERD) has been successfully applied to many sites, both public and private, over the past twenty years. The state of the technology in terms of understanding the underlying principals and options for organic substrates and delivering the substrates to the subsurface continues to grow at a rapid pace. Multiple case studies of successful applications of enhanced anaerobic bioremediation of chlorinated solvents in groundwater can be found on the websites of the U. S. Department of Defense, Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program, the Federal Remediation Technologies Roundtable (FRTC), and the Interstate Technology Research Council (ITRC), as well as the U. S. Environmental Protection Agency Contaminated Site Clean-up Information (CLU-in) website. Based on the numerous case studies in the literature, enhanced anaerobic bioremediation has proven to be an effective and reliable component of site remedies for treatment of groundwater impacted by CAHs, and can be used as a sole remedy under the proper circumstances.

7.3.4 Implementation

Implementation of enhanced anaerobic reductive bioremediation of groundwater impacted by CAHs requires selection of an appropriate organic substrate, calculation of the quantity of organic substrate sufficient to treat the mass of contaminants, and a delivery system for the substrate into the impacted aquifer. As discussed in **Section 7.3.1**, many organic substrates are available to drive in situ enhanced anaerobic reductive bioremediation of CAHs. Selection of the appropriate substrate depends on the nature and extent of the contaminant(s) to be treated, as well as the hydrogeologic and geochemical properties of the impacted aquifer. Calculation of the required quantity of organic substrate to treat the mass of contaminants at the site can be done empirically (based on experience and field process monitoring) or based on site-specific data (based on stoichiometric reactions). Generally, a combination of both methods is used. Selection of the appropriate delivery system for the organic substrate largely depends on the geologic and hydrogeologic nature (e.g., aquifer heterogeneity) of the impacted aquifer. The potential for successful application of the technology is greatly increased by generating the most uniform distribution of the organic substrate through the zone of treatment as possible. The organic substrate delivery systems used most commonly for treatment of groundwater impacted with CAHs include direct-push methods, recirculation systems or permeable reactive barrier construction. Details of the selected organic substrate, quantities of substrate for subsurface emplacement, and

the substrate delivery system are presented in a Corrective Action Plan (CAP) for the site.

Placement of organic substrate in the subsurface may require acquisition of an Underground Injection Control (UIC) permit from the NCDENR, Division of Water Resources (DWR). In addition, if recirculation wells are used well permits for construction of the groundwater withdrawal and injection wells will also be required from the NCDENR-DWR.

7.3.5 Potential Impacts

Enhanced anaerobic bioremediation can cause substantial changes in the geochemistry and distribution of contaminants in aquifers where it is implemented. However, implementation of system design alternatives based on an understanding of the biogeochemistry and hydrogeology of the impacted aquifer can mitigate these effects in most cases. The two major potential impacts of enhanced anaerobic bioremediation involve changes in groundwater quality and generation of volatile byproducts and noxious gases.[12]

Changes in groundwater quality occur principally within the anaerobic treatment zone. Such changes are typically of greatest concern in situations where drinking water standards are the FRGs. Groundwater quality changes in aquifers impacted by CAHs primarily involve mobilization of CAH mass (displacement of the dissolved-phase plume or free-phase DNAPL during substrate injection) or reducible metals (e.g., arsenic) and/or production of reductive dechlorination byproducts (e.g., 1,2-DCE, VC).[12] In addition, groundwater quality can be degraded by non-CAH byproducts of anaerobic bioremediation such as elevated BOD, COD, TDS and sulfides, as well as taste and odor issues.[12] Degradation of groundwater quality is typically ephemeral and will decrease with continued treatment, and can also be accounted for in the treatment design.

Inducing enhanced anaerobic biodegradation in an aquifer system can enhance production of volatile byproducts and noxious gases (e.g., VC, methane and hydrogen sulfide) that can degrade groundwater quality and/or accumulate in the vadose zone or subsurface structures.[12] Excessive production of volatile byproducts and noxious gases are of most concern at sites with substantial contaminant mass or high levels of natural organic carbon. Passive venting of volatile byproducts and gases through the vadose zone to the atmosphere, as well as in situ degradation during transport are often sufficient to mitigate safety concerns.[12] In addition, the potential production of volatile

byproducts and noxious gases can be performed based on site-specific data and accounted for in the final treatment system design.

7.3.6 Remediation Time Frame

The timeframe for enhanced anaerobic bioremediation to achieve remediation goals varies widely depending on numerous factors, including:

- Presence of microbiological population capable of complete degradation of CAHs under the proper anaerobic conditions.
- Presence of contaminants amenable to anaerobic biodegradation.
- The magnitude and extent of CAHs in the impacted aquifer.
- The size of the contaminant source area and the presence of adsorbed and/or free-phase DNAPL.
- The hydrogeology and biogeochemistry of the impacted aquifer.
- The ability to create and sustain highly anaerobic conditions within the TTZ to drive the dechlorination of CAHs to completion.
- The ability to efficiently and effectively distribute organic substrate throughout the TTZ.

Remediation time frames can vary from less than 1 year to greater than 10 years depending on these site-specific factors.

At the Central Carolina Tire facility, site data indicate that the dissolved concentrations of CAHs in groundwater within the source area are relatively low (<75 μg/L), which further indicates a relatively weak contaminant source. These observations are consistent with a release scenario of periodic, low-volume releases of parts cleaning solution containing PCE to the ground surface in the source area. Moreover, the site data indicate a viable microbial population that is capable of anaerobic reductive dechlorination of the CAHs at the site. Based on the available site data, the time required to achieve the site FRGs via enhanced anaerobic bioremediation within a selected TTZ is anticipated to be in the range of approximately 3 to 5 years.

7.3.7 Estimated Cost

Costs associated with enhanced anaerobic bioremediation include system design, permits, organic substrate, substrate emplacement, monitoring, and reporting. Although enhanced anaerobic bioremediation can be applied to treat the entire area of impact of the site aquifer, it is considered impractical to do so from the perspective of cost and logistics. Consequently, the costs presented here only apply to treatment of TTZ-1 and

it is assumed that TTZ-2 will be treated using an alternative technology. It is acknowledged, however, that enhanced anaerobic biodegradation may be cost-effectively implemented as a permeable reactive barrier or treatment wall along the down gradient margin of the contaminant plume to treat groundwater leaving TTZ-2. Total costs for implementation of enhanced anaerobic bioremediation in TTZ-1 are expected to range from approximately $400,000 to $500,000, assuming the volume of aquifer to be treated is approximately 10,500 yd^3, the cost per yd^3 for treatment ranges from $38 to $48, and a maximum estimated time to achieve the FRGs of approximately 5 years.

7.4 In Situ Chemical Oxidation

7.4.1 Technology Description

The remediation of groundwater impacted with organic contaminants using in situ chemical oxidation (ISCO) involves injecting chemical oxidants, and possibly co-amendments, into the contaminant source zone and, depending on site conditions, hydraulically down gradient of the source zone. Reactions of the oxidant chemicals with the contaminants produce innocuous substances such as carbon dioxide, water, and, in the case of chlorinated compounds, inorganic chloride. When an adequate oxidant dose is applied, the reactions proceed to completion, and the end products are reached quickly. Contaminants amenable to treatment by ISCO include the following[14]:

- benzene, toluene, ethylbenzene, and xylenes (BTEX);
- methyl-tertiary-butyl ether (MTBE);
- total petroleum hydrocarbons (TPH);
- chlorinated aliphatic hydrocarbons (CAHs);
- polycyclic aromatic hydrocarbons (PAHs);
- polychlorinated biphenyls (PCBs);
- chlorinated benzenes (CBs);
- phenols;
- organic pesticides (insecticides and herbicides); and
- munitions constituents (RDX, TNT, HMX, etc.).

[14] ITRC (Interstate Technology & Regulatory Council). 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd ed. ISCO-2. Washington, D.C.: Interstate Technology & Regulatory Council, In Situ Chemical Oxidation Team. 172 pp.

It is interesting to note that ISCO has most commonly been used to treat source zones where the COCs are chlorinated ethenes.

The two main advantages of using ISCO over other conventional treatment technologies are that it does not generate large volumes of waste, and treatment usually requires much shorter time frames.[14] Savings on material, monitoring, and maintenance often result from these advantages.

The four major oxidants used for soil and groundwater remediation are permanganate, persulfate, peroxide, and ozone. Oxidants are usually injected into the subsurface as a liquid or gas. A particular oxidant and set of conditions can yield one or more reactive species which differ in oxidative strength.[15] Standard electrode potentials (oxidative potentials) are a useful general reference of the strength of an oxidant. Electrode potentials of reactive oxidant species commonly produced during ISCO (depending on the primary oxidant material used) are listed below.

Reactive Species	Formula	Electrode Potential (Eh), volts (V)
Hydroxyl radical	$OH\bullet$	+2.8 V
Sulfate radical	$SO_4\bullet^-$	+2.6 V
Ozone	O_3	+2.1 V
Persulfate anion	SO_4^{2-}	+2.1 V
Hydrogen peroxide	H_2O_2	+1.77 V
Permanganate anion	MnO_4^-	+1.7 V
Perhydroxyl radical	$HO_2\bullet$	+1.7V
Oxygen	O_2	+1.23 V
Hydroperoxide anion	HO_2^-	-0.88 V
Superoxide radical	$O_2\bullet^-$	-2.4 V

Adapted from Siegrist et al. (2011)[15]

Four major factors govern whether a chemical oxidant will react with a certain contaminant in the field[14]:

- Kinetics
- Stoichiometry

[15] Siegrist RL, M Crimi, TJ Simpkin (eds). 2011. In Situ Chemical Oxidation for Groundwater Remediation. Springer Science+Business Media, LLC, New York, New York. A volume in SERDP/ESTCP Remediation Technology Monograph Series, C.H. Ward (Series ed).

- Thermodynamics
- Contact between the oxidant and contaminant

Kinetics of reaction (or reaction rate) is an extremely important factor in determining whether ISCO can be successfully applied in the field. Oxidation reaction rates in the field are dependent on many variables that must be considered simultaneously, including pH, temperature, reactant concentrations, catalysts, reaction by-products, and system impurities (e.g., natural organic matter (NOM), oxidant scavengers, etc.).[14]

Stoichiometry is the calculation of the quantities of chemical elements or compounds involved in chemical reactions. For ISCO to be successful, the various chemical reactions that the oxidant species can be involved with in the field (particularly those that involve non-target compounds such as NOM or other oxidant scavengers) must be considered to ensure that sufficient oxidant is delivered to the TTZ to treat the target contaminants.

Thermodynamics is the study of energy changes accompanying physical and chemical changes. Chemical reactions that are thermodynamically favorable are generally those that result in a reduction in the overall energy state of the reaction product. However, with regard to ISCO, reactions that would be considered thermodynamically favorable based on oxidation potential values alone may be impractical under field conditions where multiple competing reactions may occur.

Successful application of ISCO requires having a sufficient quantity of the correct oxidant in contact with the COCs for a long enough period of time to react effectively. Under ideal conditions, the oxidant delivery technique would ensure that the oxidant is evenly dispersed throughout the TTZ. Stronger oxidants are required to oxidize some of the more stable contaminants. However, stronger oxidants undergo rapid consumption in the subsurface, which limits the distance the oxidant can travel.[14] Conversely, less reactive oxidants are more stable and can be transported greater distances in the subsurface before being consumed.[14] Consequently, it is important to consider the volume of aquifer to be treated when choosing an oxidant for ISCO.

An important consideration for all ISCO designs is the amount of contaminated water displaced during oxidant injection, especially in source areas.[14] The volume of oxidant solution injected into the saturated zone displaces the same volume of groundwater. Mixing between the oxidant solution and groundwater occurs at the interfaces. Groundwater displacement should be minimized and controlled to ensure that adequate

contact between the oxidant and contaminants is achieved, particularly in source areas where groundwater contamination is grossly elevated.[14] The spatial distribution of both the contaminants and the injected oxidant is also greatly influenced by heterogeneous subsurface geology and the groundwater flow rate and direction.

ISCO can enhance biological activity at many sites with varying lithologies and a wide range of contaminants in both oxidizing and reducing environments.[14] Biological degradation is enhanced via reduction of toxic levels of source area contamination and the addition of chemical reagents beneficial to biological degradation of most organic contaminants.[14] Studies have shown that in areas where ISCO treatment involving either chlorinated or non-chlorinated organic contaminants is applied, microorganisms are initially dormant before treatment due to the toxic contaminant concentrations within the source area.[14] When contaminant concentrations are reduced by ISCO to less toxic levels, the environment becomes more acceptable for bacterial growth.[14] Although ISCO aggressively oxidizes organic matter in a treated aquifer, it does not, in general, render the treatment area biologically inactive. Due to lithologic heterogeneities that are present in almost all aquifer systems, injected oxidant does not distribute evenly throughout a TTZ. Moreover, aquifer microbial populations are often present as biofilms and encapsulated in exopolysaccharides, glycoprotein and glycolipids and are therefore protected from impact by injected oxidants. Consequently, microbial recolonization in aquifers following application of ISCO is common as subsurface conditions favorable to microbial growth are reestablished. Even in areas where ISCO substantially depletes the native microbial population, groundwater from outside the treatment area containing microbes will flow back in to the oxidized zone. Post-treatment populations have been demonstrated to grow rapidly within short periods after even the most aggressive ISCO treatments.[14] Therefore, natural attenuation in aquifers previously treated via ISCO is a viable mechanism for further reduction of residual concentrations of contaminants.

ISCO also can provide specific benefits to dechlorinating bacteria. Microbial cycling through abiotic transformation (oxidation) of expired biomass within soil pores improves aquifer hydraulic conductivity.[11] Trapped nutrients are released in this process for use by viable dechlorinating microbes for CAH destruction.[11] In addition, oxidation of a portion of viable biomass releases nutrients for the subsequent support of other microbes. ISCO also partially oxidizes natural organic matter that increases substrate surface area for dechlorinating bacteria.

7.4.2 Potential Site Applicability

As discussed in **Section 7.4.1**, ISCO is effective for oxidizing numerous organic contaminants over a wide range of concentrations, including the COCs at the Central Carolina Tire site. However, ISCO may not be a cost-effective approach for reducing low groundwater contaminant concentrations, as observed at Central Carolina Tire.[14] The two most critical success factors in all ISCO projects are effective distribution of the reagents in the treatment zone and reactivity of a particular oxidant with the contamination present. At the Central Carolina Tire Site, although the shallow surficial aquifer exhibits considerable heterogeneity, the average hydraulic conductivity of the aquifer ($\approx 10^{-3}$ cm/sec, based on site testing) indicates favorable conditions for adequate distribution of injected oxidants. In addition, the site COCs (PCE and TCE) are amenable to oxidative degradation by all four of the most common chemical oxidants used for ISCO. Therefore, ISCO is considered a potentially applicable technology for groundwater remediation at the Central Carolina Tire site.

7.4.3 Performance and Reliability

ISCO has been successfully applied at many sites, both public and private, for remediation of chlorinated solvents in groundwater over the past twenty years. A particular idiosyncrasy of the technique, however, is that rebound of contaminant concentrations is commonly observed following the initial oxidant application. As such, multiple injections of oxidant are often required to meet remediation goals. The state of the technology in terms of understanding the underlying principals and options for oxidant delivery to the subsurface continues to grow at a rapid pace. Multiple case studies of successful applications of ISCO for remediation of chlorinated solvents in groundwater can be found on the websites of the U. S. Department of Defense, Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program, the Federal Remediation Technologies Roundtable (FRTC), and the Interstate Technology Research Council (ITRC), as well as the U. S. Environmental Protection Agency Contaminated Site Clean-up Information (CLU-in) website. Based on the numerous case studies in the literature, ISCO has proven to be an effective and reliable component of site remedies for treatment of groundwater impacted by CAHs, and can be used as a sole remedy under the proper circumstances.

7.4.4 Implementation

Implementation of ISCO for remediation of groundwater impacted by CAHs requires selection of an appropriate oxidant, calculation of the quantity of oxidant sufficient to treat the mass of contaminants in the TTZ, and a delivery system for the oxidant into the

impacted aquifer. As discussed in **Section 7.4.1**, several oxidants are commonly used for ISCO of CAHs. Selection of the appropriate oxidant depends on the nature and extent of the contaminant(s) to be treated, as well as the hydrogeologic and geochemical properties of the impacted aquifer. Calculation of the required quantity of oxidant to treat the mass of contaminants at the site is generally done both empirically (based on experience and field process monitoring) and based on site-specific data (based on stoichiometric reactions). Determination of the appropriate oxidant quantity must take into consideration system impurities (e.g., natural organic matter (NOM), oxidant scavengers, etc.) that result in non-beneficial consumption of the oxidant. Selection of the appropriate delivery system for the oxidant largely depends on the geologic and hydrogeologic nature (e.g., aquifer heterogeneity) of the impacted aquifer. The potential for successful application of the technology is greatly increased by generating the most uniform distribution of the oxidant through the zone of treatment as possible. Oxidant delivery systems commonly used for treatment of groundwater impacted with CAHs include direct-push methods, injection wells, recirculation systems and permeable reactive barrier construction. Details of the selected oxidant, quantities of oxidant for contaminant treatment, and the oxidant delivery system are presented in a Corrective Action Plan (CAP) for the site.

Placement of oxidant in the subsurface may require acquisition of an Underground Injection Control (UIC) permit from the NCDENR, Division of Water Resources (DWR). In addition, if injection or recirculation wells are used, well permits for construction of the groundwater withdrawal and injection wells will also be required from the NCDENR-DWR.

7.4.5 Potential Impacts

ISCO can cause substantial changes in the geochemistry and distribution of contaminants in aquifers where it is implemented. Potential impacts from application of ISCO for remediation of groundwater contaminants include:

- Displacement of the dissolved contaminant plume during oxidant injection.
- Nonproductive oxidant consumption by non-target system impurities.
- Production of MnO_2 films around residual DNAPL when using permanganate oxidants.
- Mobilization of redox-sensitive metals.
- Reduced aquifer permeability through precipitation of minerals (e.g., MnO_2) or accumulation of gas bubbles.
- Contaminant concentration rebound following initial ISCO treatment.

These effects can be mitigated in most cases by implementation of system design alternatives based on an understanding of the geochemistry and hydrogeology of the impacted aquifer.

7.4.6 Remediation Time Frame

ISCO results in rapid treatment of groundwater contaminants, generally on the order of days to months. The rate of treatment depends on a number of factors, including contaminant concentration, oxidant concentration, the concentration of non-target oxidizable system impurities, pH, temperature, and reaction byproducts. It should be noted, however, that due to logistical and cost considerations, ISCO is not generally selected as a sole corrective measures technology. ISCO is typically applied to contaminant source areas and alternative treatment technologies are selected for treatment of lower concentrations of contaminants in plumes down gradient from the source. Further, as discussed in **Section 7.4.3**, rebound of contaminant concentrations is commonly observed following the initial oxidant application, and as such, multiple injections of oxidant are often required to meet remediation goals. The manifestation of contaminant concentration rebound can take several months to be observed in the field. Therefore, although ISCO provides for rapid treatment of contaminants, the very likely requirement for multiple oxidant injections to achieve remediation goals extends the remediation time frame.

At the Central Carolina Tire facility, site data indicate that the dissolved concentrations of CAHs in groundwater within the source area are relatively low (<75 µg/L), indicating a relatively weak contaminant source and likely low volume of residual DNAPL. Based on the available site data, the time required to achieve the site FRGs via ISCO within a selected TTZ is anticipated to be in the range of approximately 2 to 3 years. It is reiterated, however, that ISCO is not likely a viable candidate for groundwater remediation in TTZ-2 due to logistical and cost considerations.

7.4.7 Estimated Cost

Costs associated with ISCO include system design, permits, oxidant, injection of oxidant, monitoring, and reporting. Although ISCO can be applied to treat the entire area of impact of the site aquifer, it is considered impractical to do so from the perspective of cost and logistics. Consequently, the costs presented here only apply to treatment of TTZ-1 and it is assumed that TTZ-2 will be treated using an alternative technology. Total costs for implementation of ISCO in TTZ-1 are expected to range from approximately $680,000 to $1,250,000, assuming the volume of aquifer to be

treated is approximately 10,500 yd^3, the cost per yd^3 for treatment ranges from $65 to $120, and a maximum estimated time to achieve the FRGs of approximately 3 years.

7.5 ZERO VALENT IRON

7.5.1 Technology Description

Zero valent iron (ZVI) (or elemental iron) is a strong reducing agent that has been successfully applied over the past 20 years to treat CAHs and other organic and inorganic contaminants in groundwater. Granular (coarse sand-sized) ZVI has been successfully used for passive treatment in permeable reactive barrier (PRB) applications. Injection of fluidized nanoscale zero-valent iron (NZVI) particles has been successfully used for treatment of dense, nonaqueous-phase liquid (DNAPL) source zones. NZVI particles (typically between 1,000 to 3,000 nanometers in diameter) have surface areas that are up to several times greater than larger-sized powders or granular iron, which makes them much more reactive in oxidation-reduction (redox) processes. Microscale ZVI is a variant that consists of micron-scale particles (typically between 50 to 300 nanometers in diameter) that are coarser than NZVI particles but finer than granular iron. Consequently, microscale ZVI particles are generally less reactive than NZVI particles, but more reactive than granular iron particles.

ZVI particles are effective reductants and catalysts for treatment of a wide variety of common environmental contaminants. Environmental contaminants that have been shown to be amenable to treatment by ZVI particles include[16]:

Chlorinated methanes
Carbon tetrachloride (CCl_4)
Chloroform ($CHCl_3$)
Dichloromethane ($CH_2\ Cl_2$)
Chloromethane (CH_3Cl)

Chlorinated benzenes
Hexachlorobenzene ($C_6\ Cl_6$)
Pentachlorobenzene (C_6HCl_5)
Tetrachlorobenzenes (C_6H2Cl_4)
Trichlorobenzenes ($C_6H_3\ Cl_3$)
Dichlorobenzenes ($C_6H_4\ Cl_2$)
Chlorobenzene (C_6H_5Cl)

Pesticides
DDT ($C_{14}H_9Cl_5$)
Lindane ($C_6H_6\ Cl_6$)

Trihalomethanes
Bromoform ($CHBr_3$)
Dibromochloromethane ($CHBr_2Cl$)
Dichlorobromomethane ($CHBrCl_2$)

Chlorinated ethenes
Tetrachloroethene (C_2Cl_4)
Trichloroethene (C_2HCl_3)
cis-Dichloroethene ($C_2\ H_2Cl_2$)
trans-Dichloroethene ($C_2\ H_2Cl_2$)
1,1-Dichloroethene ($C_2H_2\ Cl_2$)
Vinyl chloride ($C_2\ H_3Cl$)

Other polychlorinated hydrocarbons
PCBs
Dioxins
Pentachlorophenol (C_6HCl_5O)

[16] Zhang, Wei-xian, 2003. Nanaoscale iron particles for environmental remediation:An overview; Journal of Nanoparticle Research 5:323-332.

Organic dyes
Orange II ($C_{16}H_{11}N_2NaO_4S$)
Chrysoidine ($C_{12}H_{13}ClN_4$)
Tropaeolin O ($C_{12}H_9N_2NaO_5S$)
Acid Orange
Acid Red

Heavy metal ions
Mercury (Hg^{2+})
Nickel (Ni^{2+})
Silver (Ag^{+})
Cadmium (Cd^{2+})

Other organic contaminants
N-nitrosodimethylamine (NDMA) ($C_4H_{10}N_2O$)
TNT ($C_7H_5N_3O_6$)

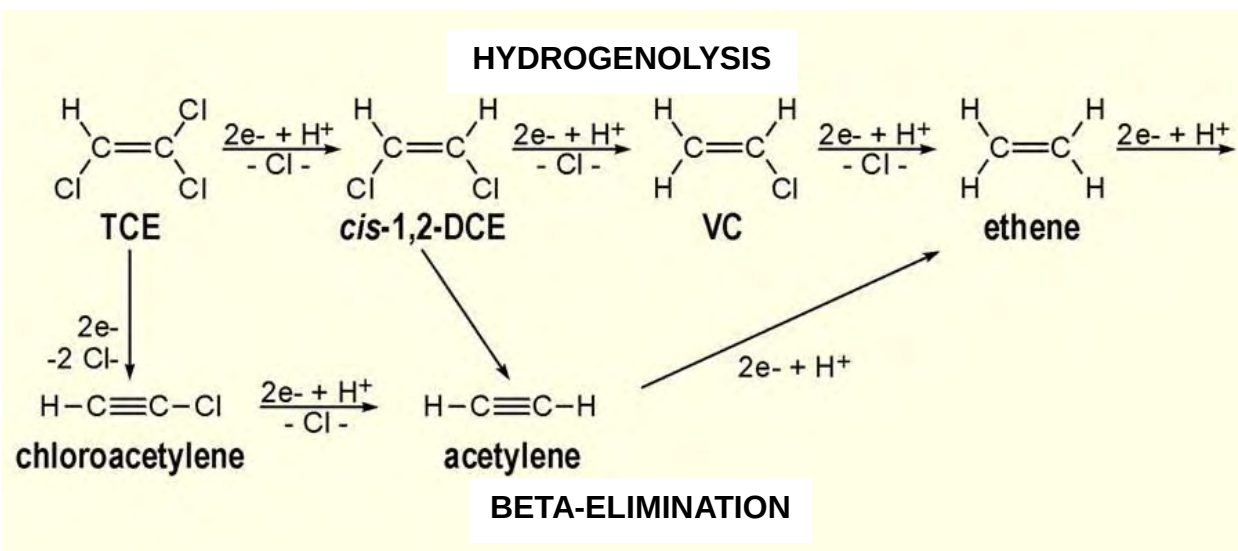
Inorganic anions
Dichromate ($Cr_2O_2^{-7}$)
Arsenic (AsO_3^{-4})
Perchlorate (ClO^{-4})
Nitrate (NO^{-3})

ZVI (Fe^0) is a moderate to strong reducing reagent, which can react with DO and to some extent with water[16]:

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \quad (1)$$

$$Fe^0_{(s)} + 2H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H^2_{(g)} + 2OH^-_{(aq)} \quad (2)$$

CAHs, such as TCE, are dechlorinated by the two reactions shown below in which electrons and hydrogen are provided by oxidation of ZVI (see equations 1 and 2).[17]



The majority of TCE is converted to ethene and chloride via the beta-elimination reaction (70%-90%), which is an abiotic reaction series that proceeds with the formation

[17] Gavaskar, Arun, Lauren Tatar, and Wendy Condit, 2005. Cost and Performance Report, Nanoscale Zero Valent Iron Technologies For Source Remediation; Naval Facilities Engineering Command, Contract Report CR-05-007-ENV; 54 pp.

of short-lived intermediates, such as acetylene. A smaller fraction of TCE decomposes by hydrogenolysis, a sequential reduction pathway that results in the formation of longer-lived intermediates, such as 1,2-DCE and VC.

Hydrogenolysis of chlorinated compounds, such as PCE and TCE, involves replacement of a chlorine atom by a hydrogen atom and requires an electron donor as well as a proton donor (hydrogen).[18] In beta-elimination, chlorine atoms are released by the chlorinated compound without addition of hydrogen. Beta-elimination releases chlorine atoms, resulting in the decrease in the degree of saturation of the carbon–carbon bond (i.e., production of double or triple bonds).[18]

Of particular concern for any technology applied to remediation of CAHs in groundwater is the formation of daughter products that are more toxic than the parent compounds. For example, accumulation of VC can result from hydrogenolysis of PCE, TCE and 1,2-DCE. Conversely, VC is not formed in the beta-elimination of PCE or TCE. Although PCE and TCE may be degraded by ZVI through both reaction pathways, reductive dehalogenation of PCE and TCE using ZVI typically results in production of ethene and ethane with VC typically comprising less than 10% of the daughter products produced.[18] This may be an indication that beta-elimination is the major pathway, and/or that any VC formed is rapidly degraded in the presence of ZVI.[18] Beta-elimination has also been shown to be much more common with chlorinated ethenes such as TCE and PCE.[19]

Biodegradation of PCE and TCE can also occur via hydrogenolysis. However, biodegradation of chlorinated ethenes can lead to production of substantial concentrations of VC. In studies of reductive degradation of TCE and PCE by ZVI, VC is consistently found only in trace amounts or not detected, much lower than from biodegradation, likely due to the dominance of the beta-elimination pathway with ZVI.[18] With ZVI injection the redox potential may be decreased substantially, leading to a potential increase in anaerobic microbial activity and biodegradation.[18] In addition, microbes that dehalogenate chlorinated ethenes may use the H2 produced from ZVI reaction with water.[18]

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[18] O.Carroll, Denis, Brent Sleep, Magdalena Krol, Hardiljeet Boparai, and Christopher Kocur, 2013. Nanaoscale zero valent iron and bimetallic particles for contaminated site remediation. Advances in Water Resources 51:104-122.

[19] Arnold WA, Roberts AL., 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. Environ Sci Technol.; 34:1794–1805.

7.5.2 Potential Site Applicability

As discussed in **Section 7.4.1**, ZVI particles are effective reductants and catalysts for treatment of a wide variety of common environmental contaminants over a wide range of concentrations, including the COCs at the Central Carolina Tire site. Inasmuch as there is a tradeoff between finer particle size of ZVI and persistence in the aquifer, care needs to be taken to balance the selected particle size of ZVI with the required stoichiometric mass ratio between ZVI the COCs for complete degradation, while taking into consideration reductions in ZVI mass and reactivity by non-beneficial processes. Two of the most critical success factors in all ZVI projects are effective distribution of the ZVI in the treatment zone and reactivity of ZVI with the contamination present. At the Central Carolina Tire Site, although the shallow surficial aquifer exhibits considerable heterogeneity, the average hydraulic conductivity of the aquifer ($\approx 10^{-3}$ cm/sec, based on site testing) indicates favorable conditions for adequate distribution of injected ZVI. In addition, the site COCs (PCE and TCE) are amenable to abiotic reductive dechlorination by ZVI. Therefore, ZVI is considered a potentially applicable technology for groundwater remediation at the Central Carolina Tire site.

7.5.3 Performance and Reliability

ZVI has been successfully applied at many sites, both public and private, for remediation of chlorinated solvents in groundwater over the past twenty years. A particular idiosyncrasy of the technique, however, is that rebound of contaminant concentrations is sometimes observed following the initial ZVI application. As such, multiple injections of ZVI are sometimes required to meet remediation goals. The state of the technology in terms of understanding the underlying principals and options for ZVI emplacement in the subsurface continues to grow at a rapid pace. Multiple case studies of successful applications of ZVI for remediation of chlorinated solvents in groundwater can be found on the websites of the U. S. Department of Defense, Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program, the Federal Remediation Technologies Roundtable (FRTC), and the Interstate Technology Research Council (ITRC), as well as the U. S. Environmental Protection Agency Contaminated Site Clean-up Information (CLU-in) website. Based on the numerous case studies in the literature, ZVI has proven to be an effective and reliable component of site remedies for treatment of groundwater impacted by CAHs, and can be used as a sole remedy under the proper circumstances.

7.5.4 Implementation

Implementation of ZVI for remediation of groundwater impacted by CAHs requires selection of the appropriate ZVI particle size for the application, calculation of the quantity of ZVI sufficient to treat the mass of contaminants in the TTZ (taking in consideration stoichiometric requirements and reductions in ZVI mass and reactivity by non-beneficial processes), and an emplacement method for the ZVI into the impacted aquifer. Selection of the appropriate particle size of ZVI is predominantly based on the particular application of the technology chosen for site remediation. For example, coarse-grained ZVI is often the size of choice for PRBs where maintaining hydraulic properties is important to allow the leading edge of the dissolved contaminant plume to pass through the treatment zone, whereas NZVI is often the size of choice for source area treatment where DNAPL is often present and maximizing the reactive surface area of the ZVI is important to effect maximum contaminant treatment. Calculation of the required quantity of ZVI to treat the mass of contaminants at the site is generally done both empirically (based on experience and field process monitoring) and based on site-specific data (based on stoichiometric reactions). Determination of the appropriate ZVI quantity must take into consideration system impurities (e.g., natural organic matter (NOM), nitrate, sulfate) and oxidation (e.g., via DO) of the ZVI (higher with smaller particle size and, hence, larger surface area) that result in non-beneficial consumption of the ZVI. Selection of the appropriate emplacement method for the ZVI largely depends on the geologic and hydrogeologic nature (e.g., aquifer heterogeneity) of the impacted aquifer. The potential for successful application of the technology is greatly increased by generating the most uniform distribution of the ZVI through the zone of treatment as possible. ZVI emplacement methods commonly used for treatment of groundwater impacted with CAHs include direct-injection, pressure pulse injection, pneumatic injection, injection wells, recirculation systems and permeable reactive barrier construction (e.g., excavation, trenching, direct-push). Details of the selected ZVI particle size, quantities of ZVI for contaminant treatment, and the ZVI emplacement method are presented in a Corrective Action Plan (CAP) for the site.

Placement of ZVI in the subsurface may require acquisition of an Underground Injection Control (UIC) permit from the NCDENR, Division of Water Resources (DWR). In addition, if injection or recirculation wells are used, well permits for construction of the groundwater withdrawal and injection wells will also be required from the NCDENR-DWR.

7.5.5 Potential Impacts

ZVI can cause substantial changes in the geochemistry in aquifers where it is implemented. Potential impacts from application of ZVI for remediation of groundwater contaminants include:

- Displacement of the dissolved contaminant plume during ZVI injection.
- Potential daylighting of ZVI to the ground surface and migration outside the target zone due to aquifer heterogeneities and preferential flow pathways.
- Nonproductive ZVI consumption by non-target system impurities and oxidation reactions (substantially dependent on ZVI particle size).
- Mobilization of redox-sensitive metals.
- Reduced aquifer permeability through precipitation of minerals or accumulation of gas bubbles.
- Contaminant concentration rebound following initial ZVI treatment.

These effects can be mitigated in most cases by implementation of system design alternatives based on an understanding of the geochemistry and hydrogeology of the impacted aquifer.

7.5.6 Remediation Time Frame

ZVI can produce relatively rapid treatment of groundwater contaminants, on the order of several months, under ideal field conditions. Typically, however, treatment via ZVI requires longer periods on the order of 2 to 7 years (and perhaps longer) under most field conditions. The rate of treatment depends on a number of factors, including contaminant concentration, injected ZVI mass, the concentration of non-target system impurities (e.g., NOM, nitrate, sulfate, etc.), pH, temperature, and reaction byproducts. ZVI can be applied to contaminant source areas as well as for treatment of lower concentrations of contaminants in plumes down gradient from the source (e.g.in a PRB). However, as discussed in **Section 7.5.3**, rebound of contaminant concentrations is sometimes observed following the initial ZVI application, and as such, multiple injections of ZVI may be required to meet remediation goals. The manifestation of contaminant concentration rebound can take several months to be observed in the field. Therefore, although ZVI provides for relatively rapid treatment of contaminants, the possible requirement for multiple ZVI injections to achieve remediation goals can extend the remediation time frame.

At the Central Carolina Tire facility, site data indicate that the dissolved concentrations of CAHs in groundwater within the source area are relatively low (<75 µg/L), indicating a

relatively weak contaminant source and likely low volume of residual DNAPL. Based on the available site data, the time required to achieve the site FRGs via ZVI within a selected TTZ is anticipated to be in the range of approximately 2 to 4 years. Further, ZVI appears to be a viable candidate for groundwater remediation in TTZ-1, but is not likely a viable candidate for groundwater remediation in TTZ-2 due to logistical and cost considerations. However, ZVI could be considered for use in a PRB constructed within the flow path of the dissolved chlorinated solvent plume at the site (i.e., within TTZ-2).

7.5.7 Estimated Cost

Costs associated with ZVI treatment include system design, permits, ZVI, injection of ZVI, monitoring, and reporting. Although ZVI can be applied to treat the entire area of impact of the site aquifer, it is considered impractical to do so from the perspective of cost and logistics, particularly in the absence of at-risk potential receptors at the site. Consequently, the costs presented here only apply to treatment of TTZ-1 and it is assumed that TTZ-2 will be treated using an alternative technology. Total costs for implementation of ZVI in TTZ-1 are expected to range from approximately $525,000 to $1,050,000, assuming the volume of aquifer to be treated is approximately 10,500 yd^3, the cost per yd^3 for treatment ranges from $50 to $100, and a maximum estimated time to achieve the FRGs of approximately 4 years.

8.0 SELECTED REMEDIAL TECHNOLOGIES

Four potentially applicable remedial technologies were evaluated and screened for application as corrective measures to address dissolved CAHs in groundwater at the Central Carolina Tire site (see **Section 7.0**). All four technologies were deemed potentially applicable site remedies, with each technology having advantages and limitations. In the table below, the remedial technologies are assigned numerical values ranging from 1 (poor) to 5 (excellent) for each of the six evaluation criteria that were used to assess their potential applicability as site remedies. Technologies having the highest total numerical value are considered the most applicable remedial technologies for corrective measures at the site.

Evaluation Criterion	***Monitored Natural Attenuation***	***Enhanced In Situ Bioremediation***	***In Situ Chemical Oxidation***	***Zero Valent Iron***
Potential Site Applicability	3	4	3	4
Performance and Reliability	3	4	3	4
Implementation	5	4	3	4
Potential Impacts	4	3	3	3
Remediation Time Frame	2	5	5	4
Cost	5	4	2	3
TOTAL	22	24	19	22

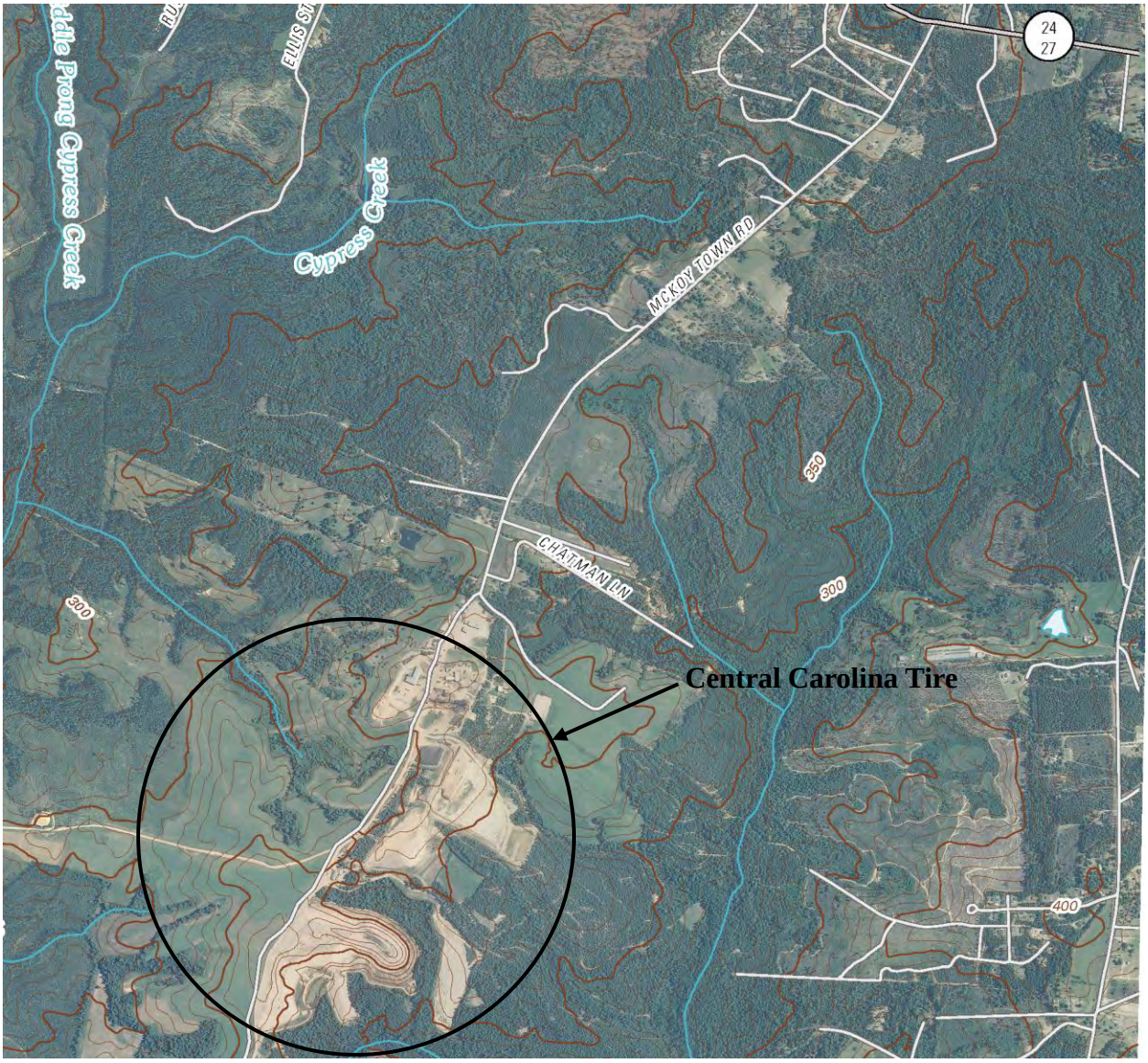
1 = Poor; 5 = Excellent

Based on the results presented in the screening matrix, enhanced in situ bioremediation is the most applicable remediation technology for corrective measures at the site, followed closely by MNA and ZVI.

The results of the four phases of assessment conducted at the site indicate that the dissolved CAH plume is diffuse, containing relatively low concentrations of COCs throughout most of the extent of the plume. Moreover, site data indicate that the dissolved concentrations of CAHs in groundwater within the source area are relatively low (<75 µg/L), indicating a relatively weak contaminant source and likely low volume of residual DNAPL. Consequently, a corrective measures strategy combining a more

aggressive remedial approach restricted to the source area with a lower energy alternative for the remainder of the plume is appropriate for the site. Based on these considerations, the corrective measures strategy selected for the site will combine enhanced in situ anaerobic bioremediation in the contaminant source area with MNA to address the remainder of the plume outside of the source area. Following approval of the selected remedy by the NCDENR-SWS, details of the proposed corrective measures will be presented in a Corrective Action Plan for the facility.

FIGURES AND TABLES



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Source: USGS 7.5' Topographic Quadrangle Series
Murchisontown, NC 2010

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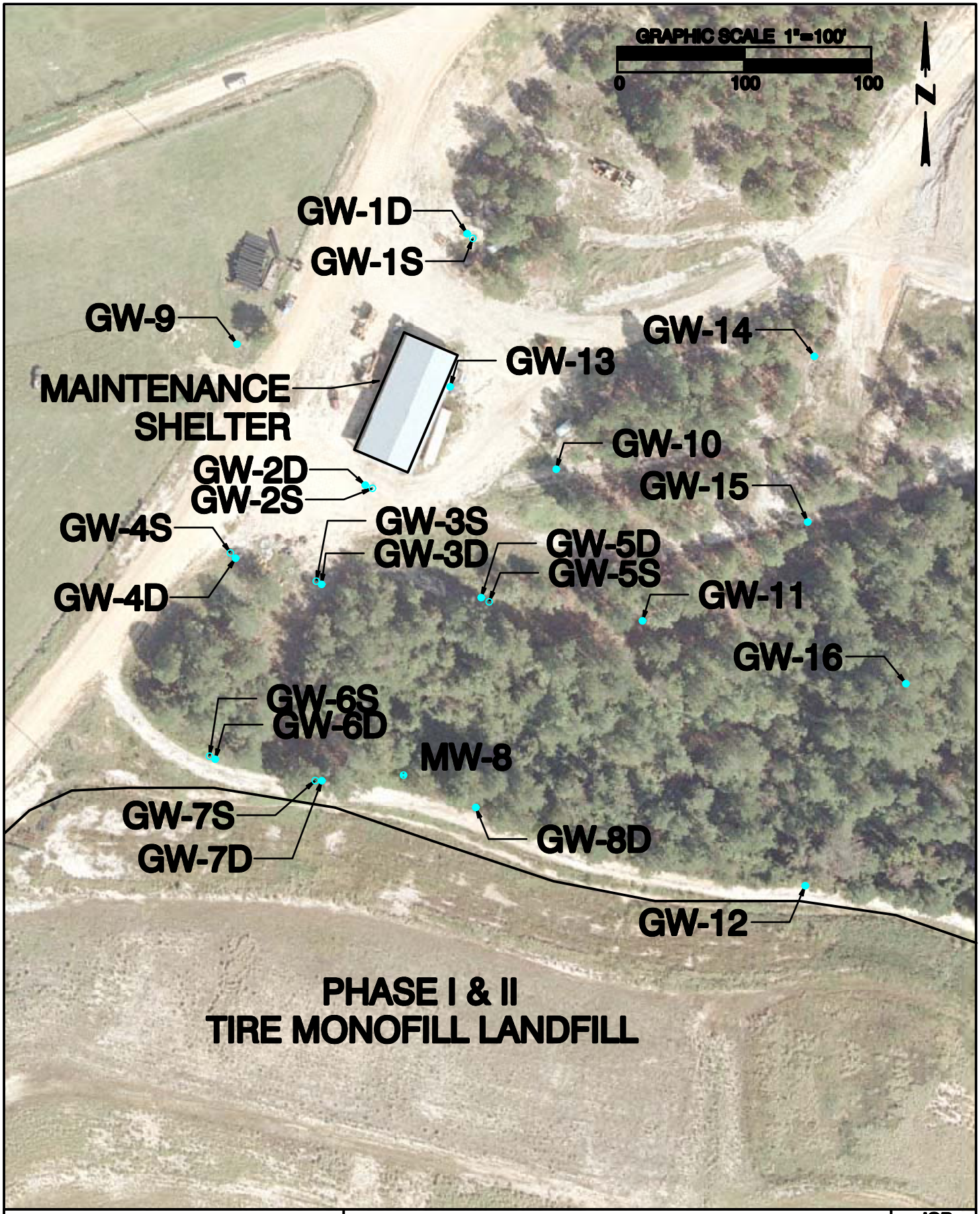
11112 Branding Iron Place
Wendell, NC 27591
Office: (919) 366-3663
Cell: (919) 995-0363

SITE LOCATION MAP

Central Carolina Tire Monofill Landfill
Harnett County, North Carolina

Drawn by:	Reviewed by:	Project #:	Drawing #:	Figure No.
USGS		Scale: 1:24,000	Drawing Date: 05/31/2012	1



Nautilus Geologic Consulting, PLLC

SITE MAP

Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

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FIG
2

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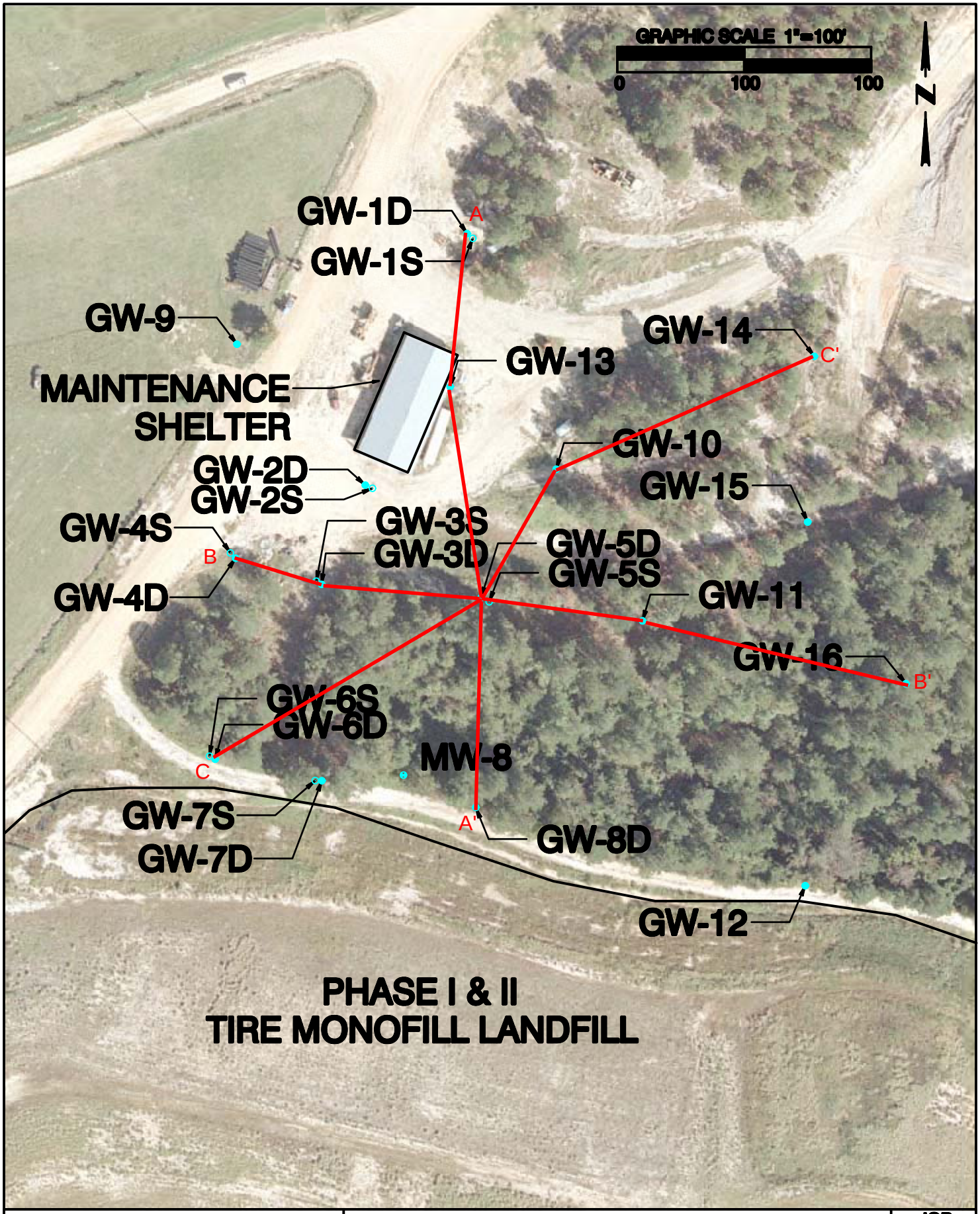

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Lines of Geologic Cross Sections

Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

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FIG
4

V:\Liberty Tire Projects\Central Carolina Tire\Projects\Solid Waste\Groundwater Monitoring\PCE Assessment Monitoring\Phase 4 PCE Assessment\PH I-II GW ASSESSMENT
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Figure 5
Cross-Section A-A'

Nautilus Geologic Consulting, PLLC

Water-table elevation in shallow aquifer as measured in August 2014.

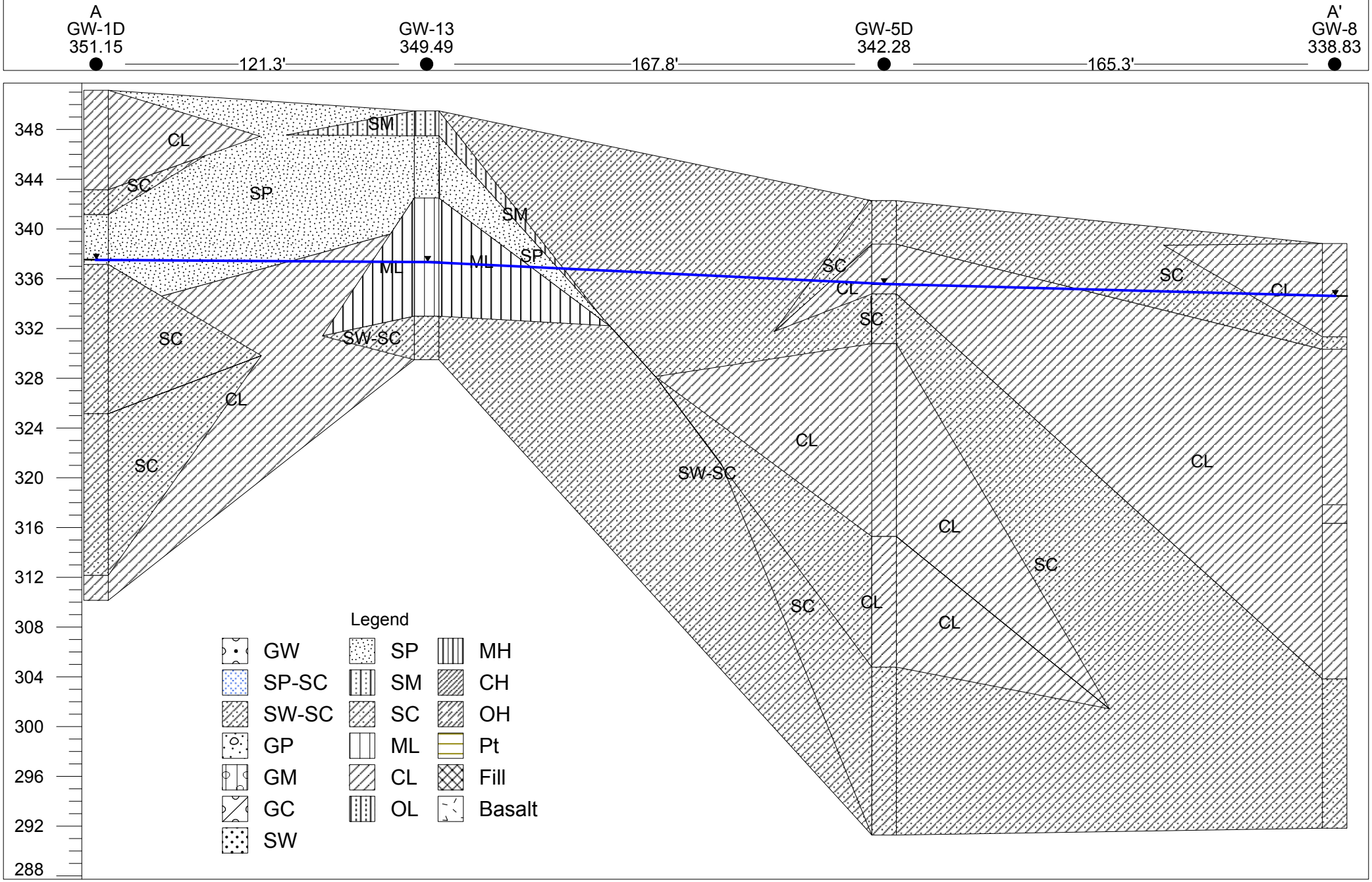


Figure 6
Cross-Section B-B'

Water-table elevation in shallow aquifer as measured in August 2014.

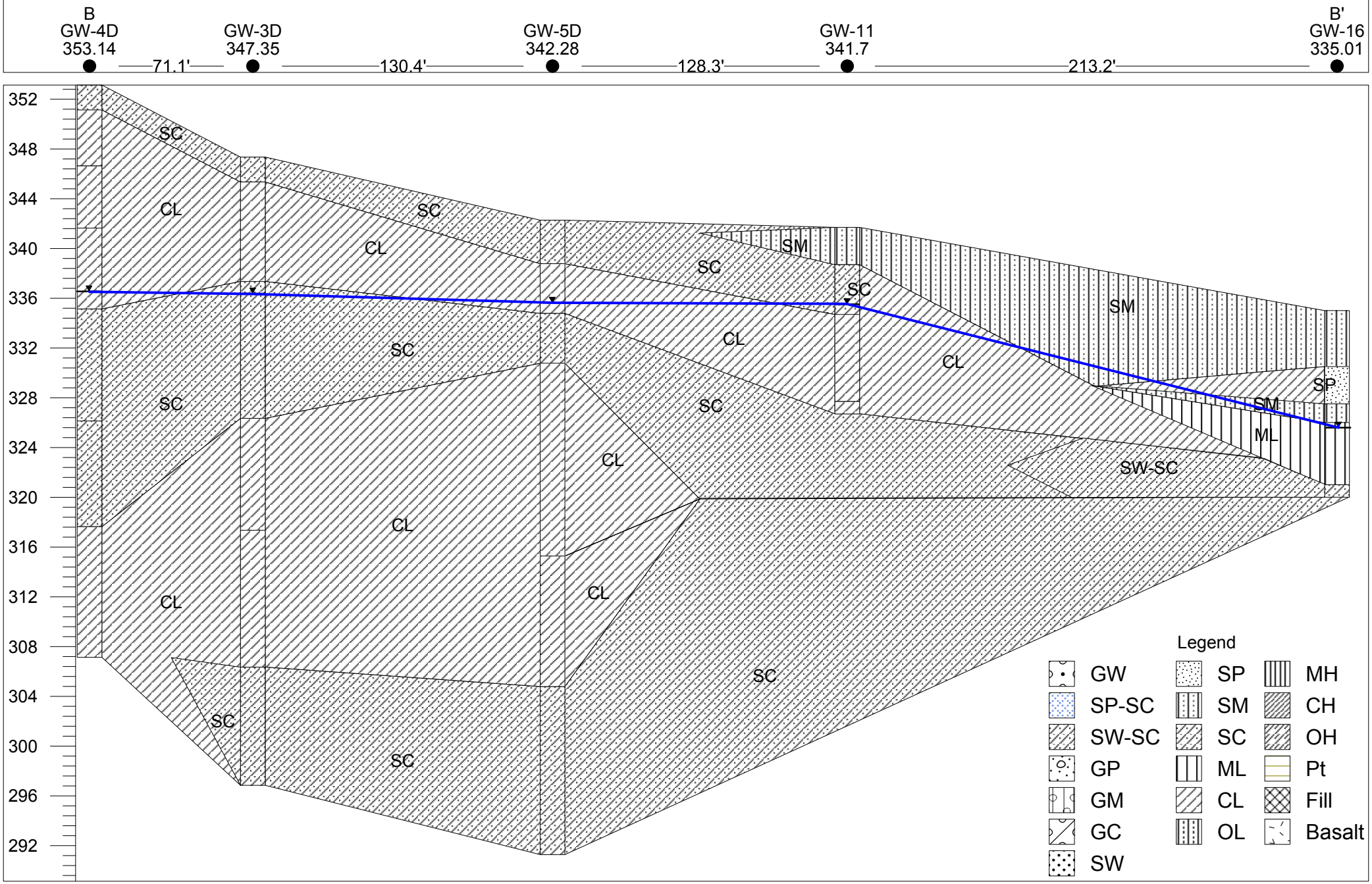
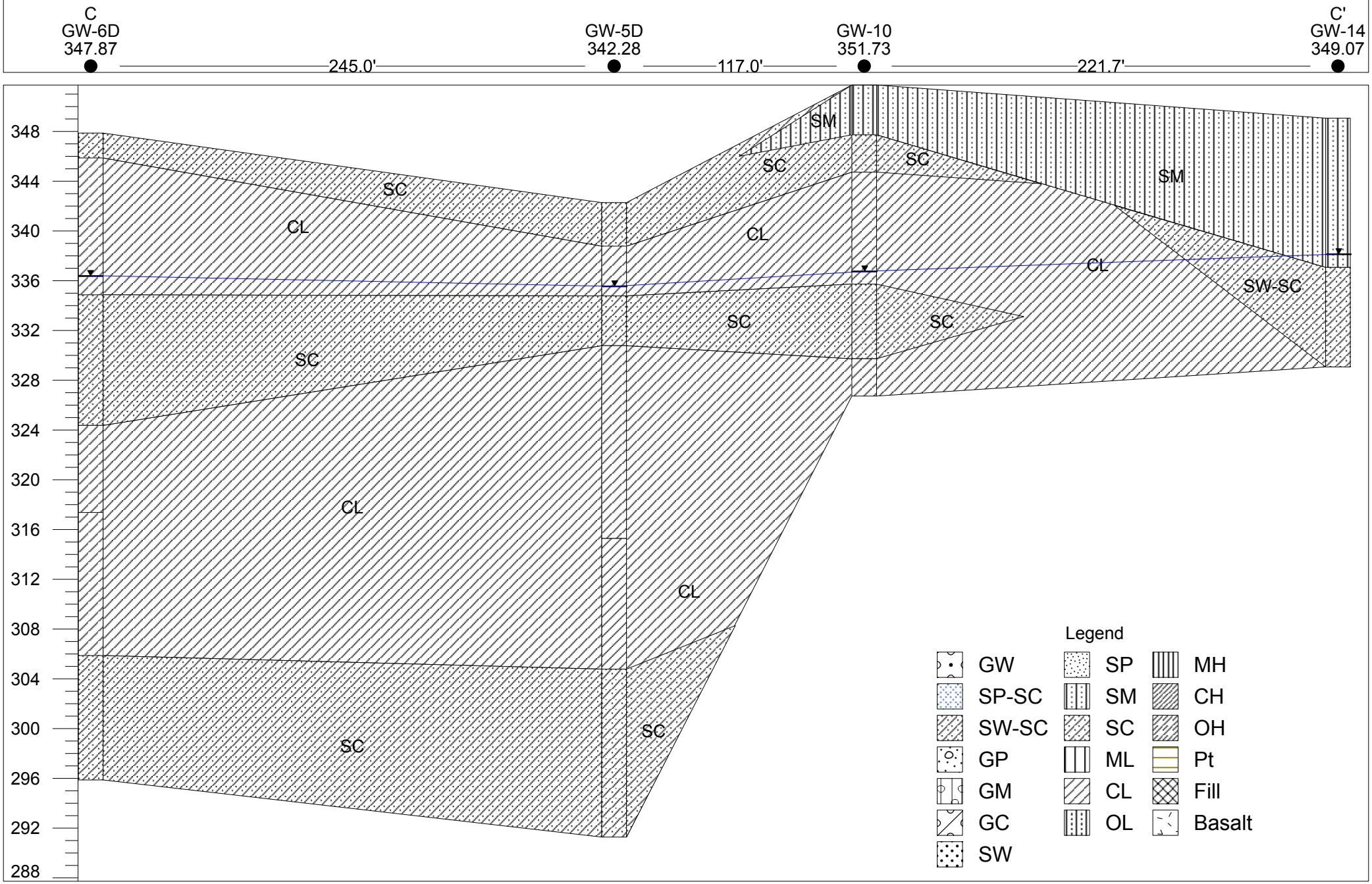
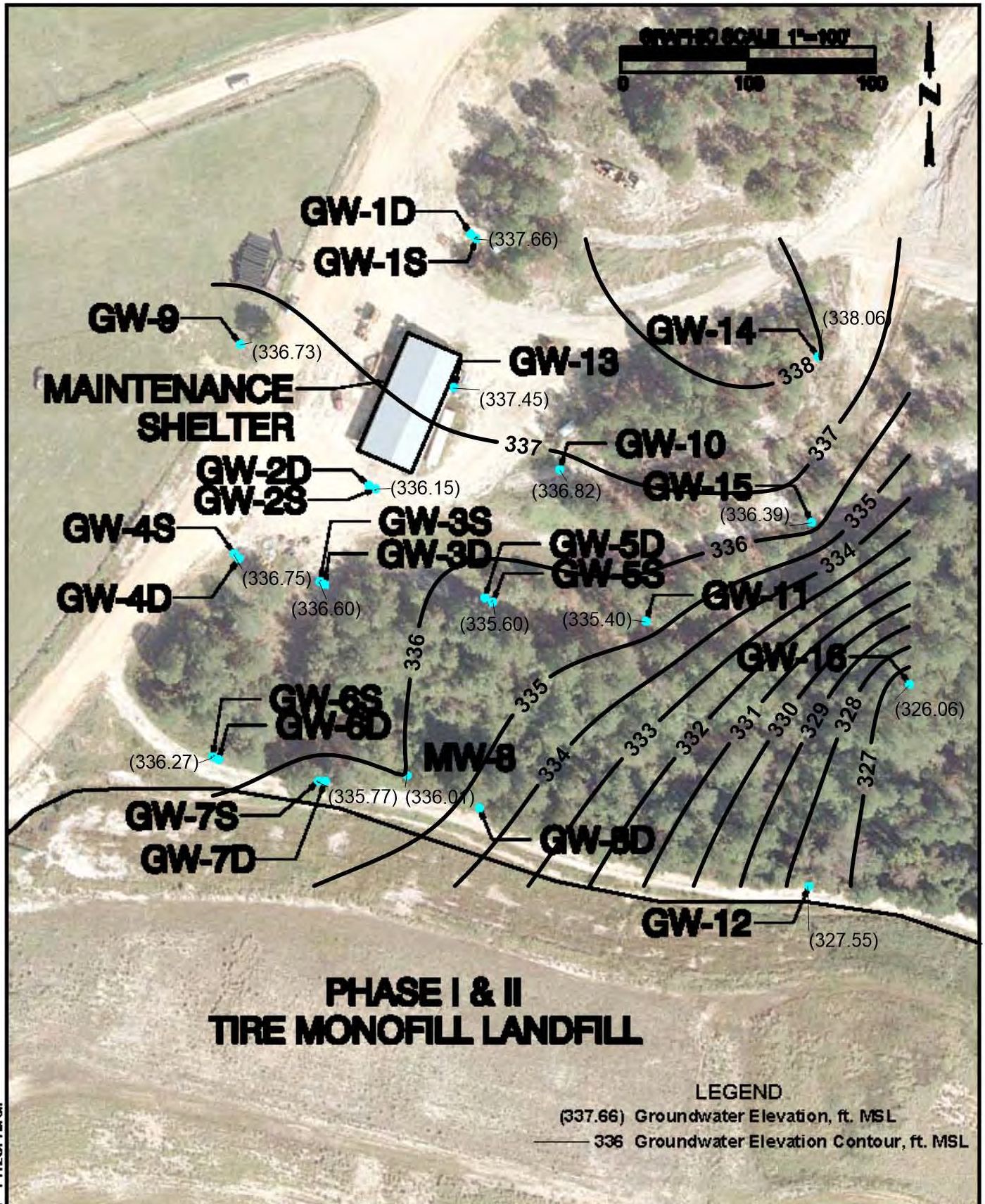


Figure 7
Cross-Section C-C'

Water-table elevation in shallow aquifer as measured in August 2014.





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Groundwater Elevation Contour Map:
Shallow Surficial Aquifer August 2014
Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

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FIG 8

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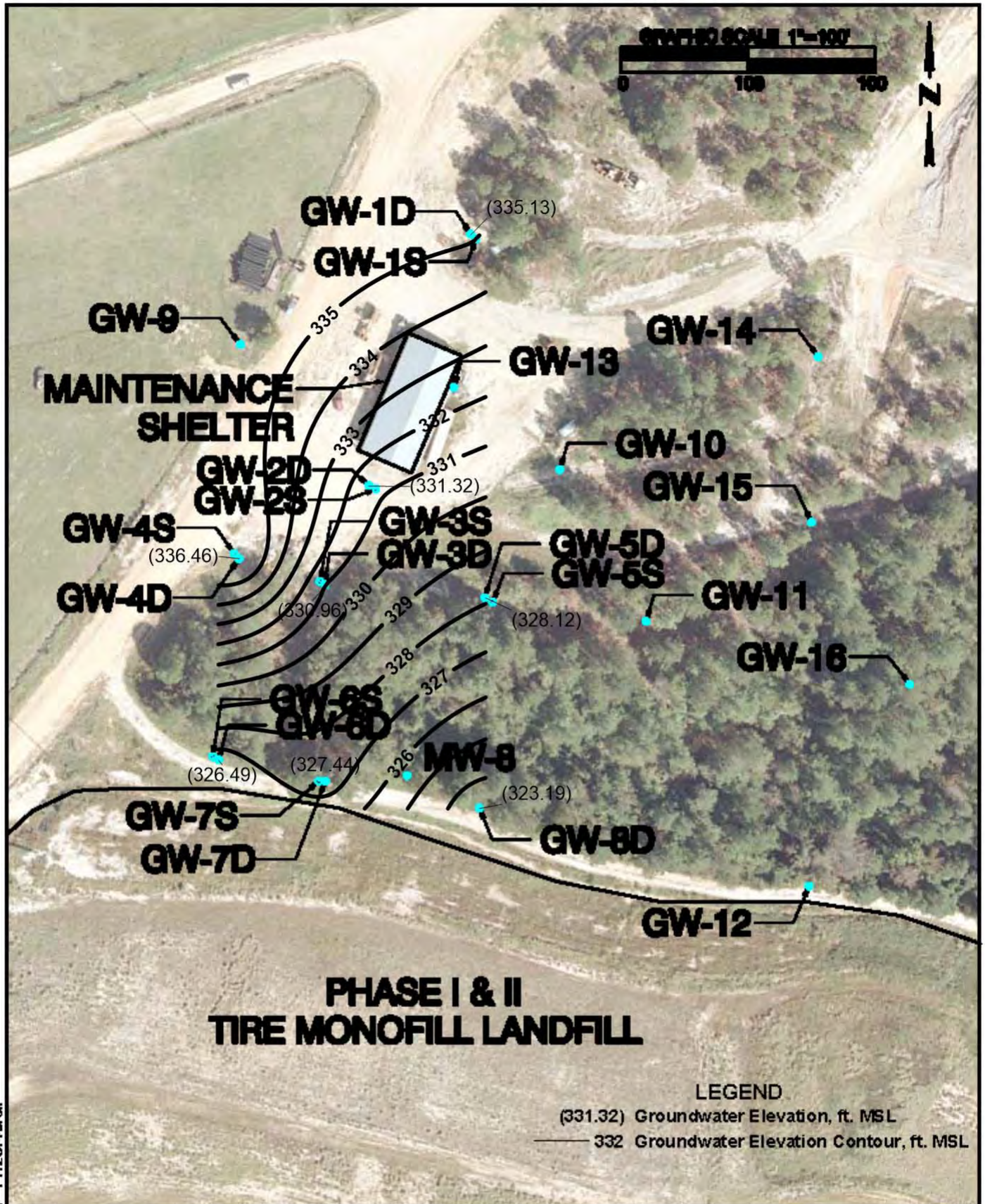

Nautilus Geologic Consulting, PLLC

Groundwater Elevation Contour Map:
Deep Aquifer August 2014
Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

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FIG 9

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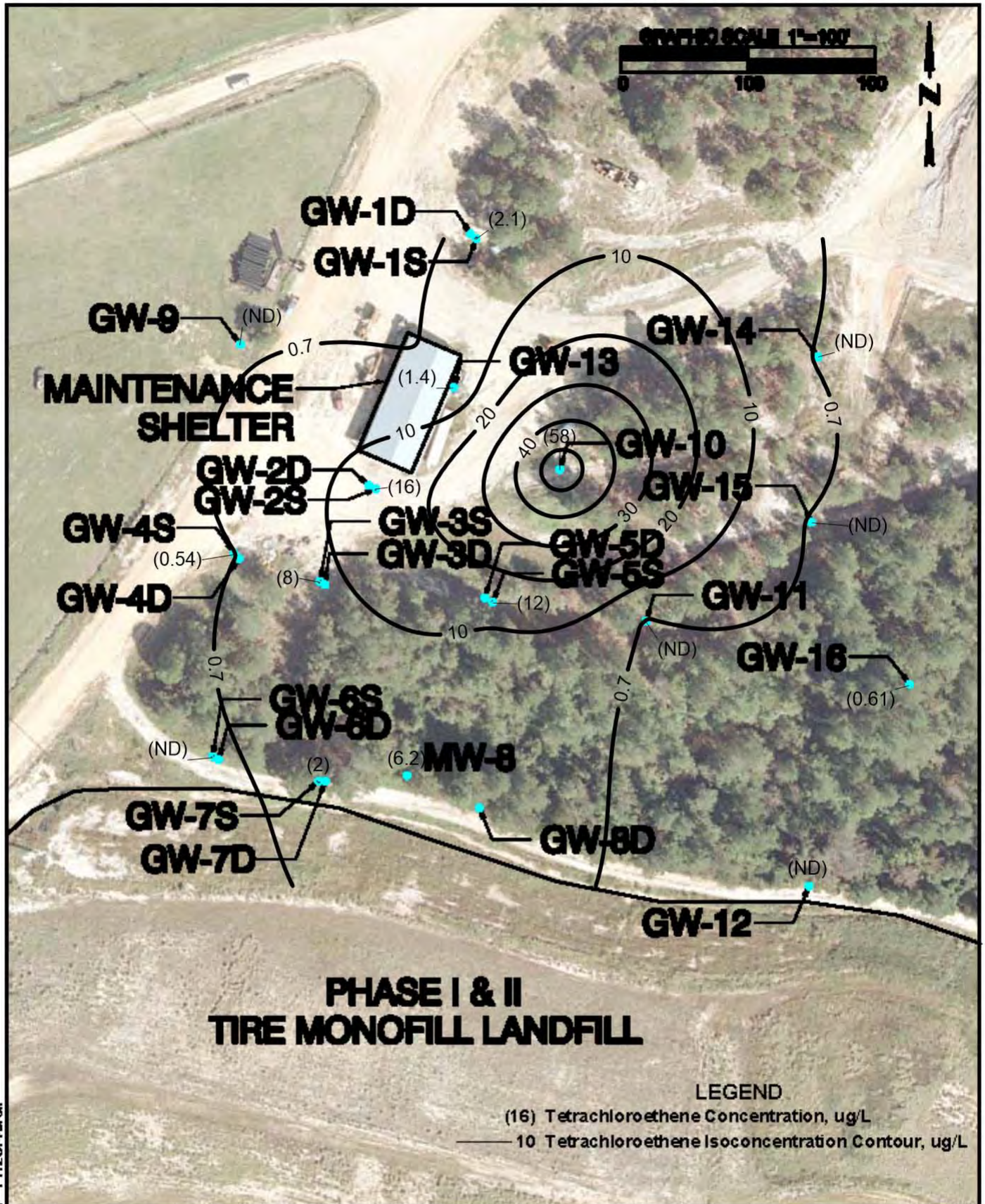


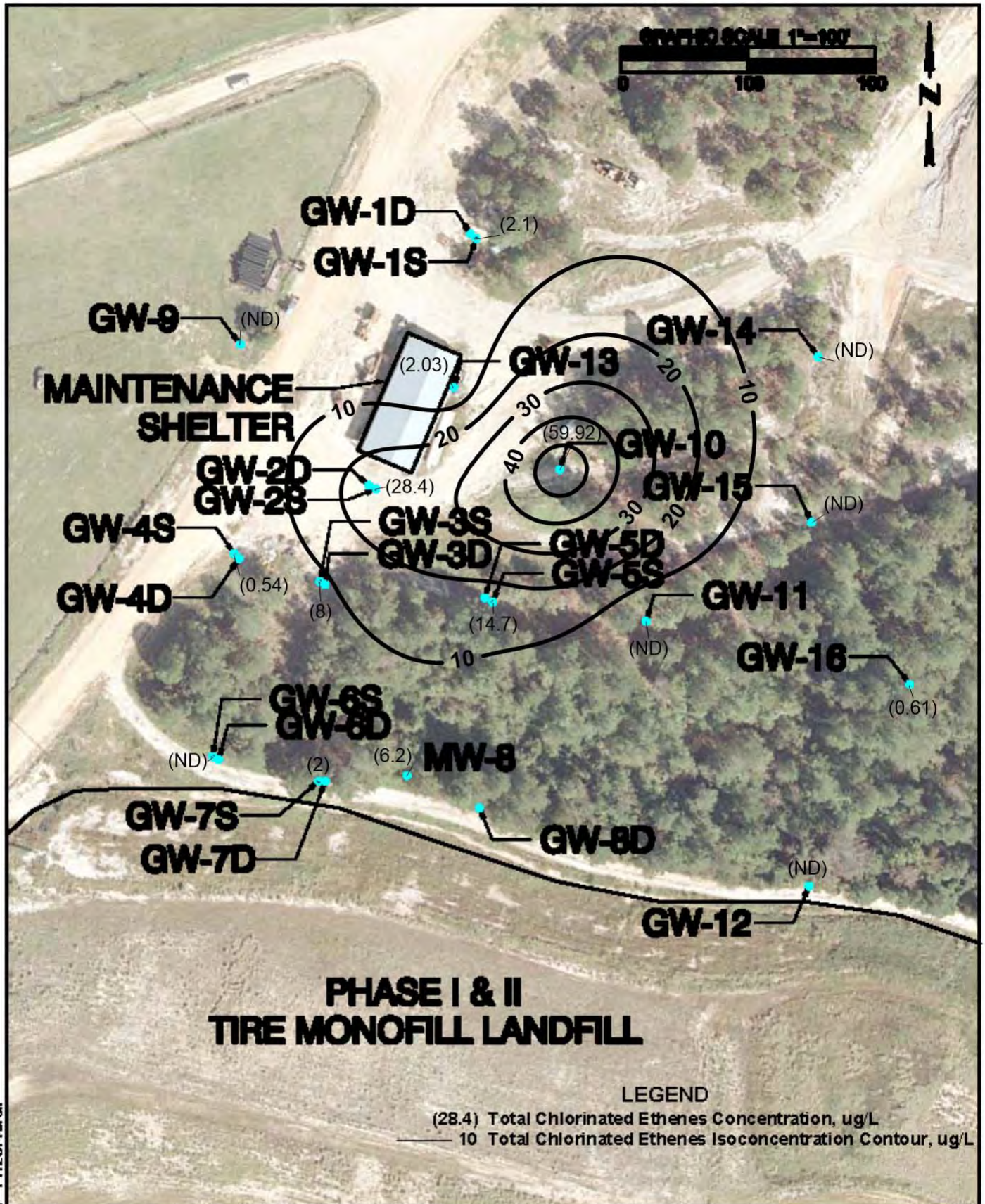
Nautilus Geologic Consulting, PLLC

Tetrachloroethene Isoconcentration Contour Map:
Shallow Surficial Aquifer August 2014
Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

JOB

FIG 10

V:\Liberty Tire Projects\Central Carolina Tire\Projects\Solid Waste\Groundwater Monitoring\PCE Assessment Monitoring\Phase 4 PCE Assessment\PH I-II GW ASSESSMENT
Mon Oct 6, 2014 11:28:46AM



Nautilus Geologic Consulting, PLLC

Total Chlorinated Ethenes Isoconcentration Contour Map:
Shallow Surficial Aquifer August 2014
Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

JOB

FIG 11

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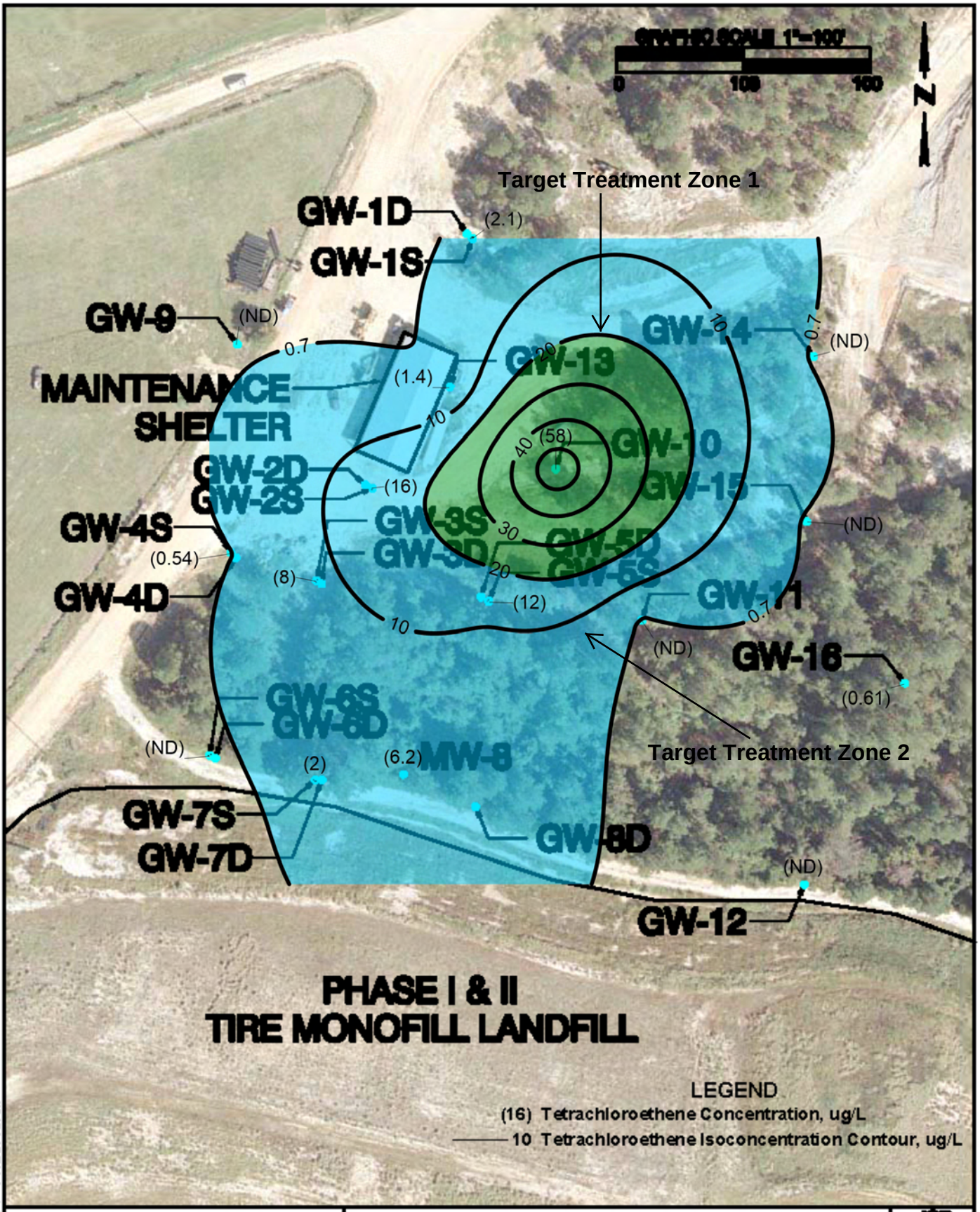

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Nautilus Geologic Consulting, PLLC

Target Treatment Zones

Central Carolina Tire Monofill Landfill
Phase I/II LF Groundwater Assessment

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FIG
12

FIGURE 13

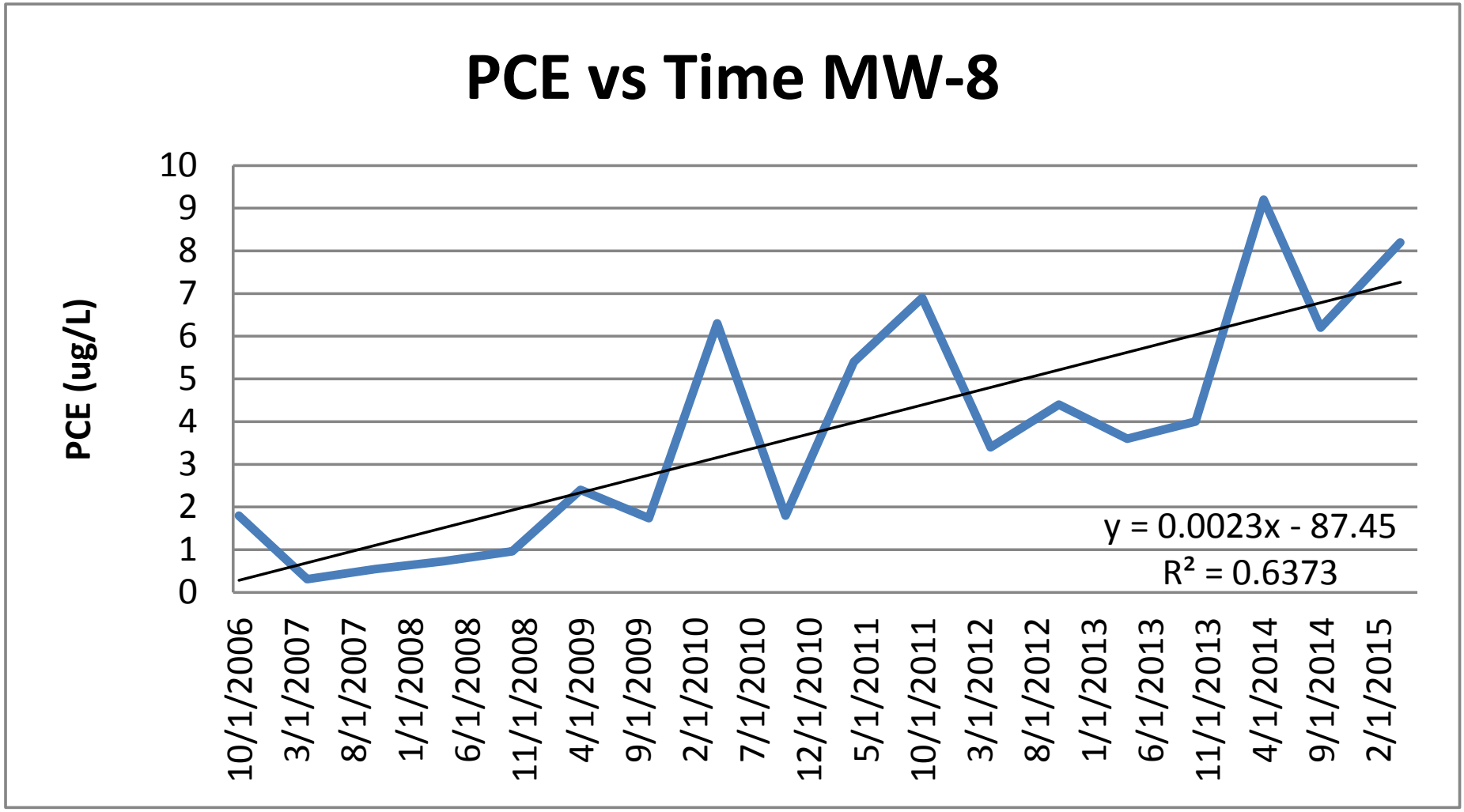
PCE vs Time MW-8
PCE (ug/L)
10
9
8
7
6
5
4
3
2
1
0
y = 0.0023x - 87.45
R² = 0.6373
10/1/2006
3/1/2007
8/1/2007
1/1/2008
6/1/2008
11/1/2008
4/1/2009
9/1/2009
2/1/2010
7/1/2010
12/1/2010
5/1/2011
10/1/2011
3/1/2012
8/1/2012
1/1/2013
6/1/2013
11/1/2013
4/1/2014
9/1/2014
2/1/2015

Table 1
Monitoring Well Data
Phase 4 Hydrogeologic and Groundwater Quality Assessment
Central Carolina Tire Monofill Landfill
Harnett County, North Carolina
Permit # 43-04

		Elevation Data			Test Boring Data		Monitoring Well Construction Data				Hydrogeologic Unit
Boring Number	Boring Date	PVC Pipe Elev.	Ground Elev.	Stickup feet	Total Depth, ft.	Bottom Elevation	Top of Well Screen Depth, ft.	Top of Well Screen Elev.	Bottom of Well Screen Depth, ft.	Bottom of Well Screen Elev.	
GW-1S	4/10/2012	352.95	351.15	1.80	22.0	329.15	12.0	339.15	22.0	329.15	1a
GW-1D	4/13/2012	353.30	351.15	2.15	40.0	311.15	30.0	321.15	40.0	311.15	3
GW-2S	4/10/2012	350.26	348.47	1.79	20.0	328.47	10.0	338.47	20.0	328.47	1a
GW-2D	4/16/2012	350.63	348.69	1.94	50.0	298.69	40.0	308.69	50.0	298.69	3
GW-3S	4/10/2012	348.93	346.97	1.95	18.0	328.97	8.0	338.97	18.0	328.97	1a
GW-3D	4/17/2012	349.45	347.35	2.10	50.0	297.35	40.0	307.35	50.0	297.35	3
GW-4S	4/11/2012	354.80	352.82	1.98	24.0	328.82	14.0	338.82	24.0	328.82	1a
GW-4D	4/18/2012	355.00	353.14	1.86	44.0	309.14	34.0	319.14	44.0	309.14	3
GW-5S	4/11/2012	344.36	342.19	2.17	16.0	326.19	6.0	336.19	16.0	326.19	1a
GW-5D	4/17/2012	345.42	342.28	3.14	49.0	293.28	39.0	303.28	20.0	322.28	3
GW-6S	4/11/2012	349.48	348.07	1.41	20.0	328.07	10.0	338.07	20.0	328.07	1a
GW-6D	4/19/2012	349.65	347.87	1.78	52.0	295.87	42.0	305.87	52.0	295.87	3
GW-7S	4/12/2012	346.76	344.76	2.00	17.0	327.76	7.0	337.76	17.0	327.76	1a
GW-7D	4/18/2012	346.58	344.60	1.98	45.0	299.60	35.0	309.60	45.0	299.60	3
GW-8D	4/13/2012	340.69	338.83	1.86	47.0	291.83	37.0	301.83	47.0	291.83	3
MW-8	ca. 10/2002	342.80	339.12	3.68	20.0	319.12	10.0	329.12	20.0	319.12	1a
GW-9	3/19/2013	353.73	351.14	2.59	22.5	328.64	12.5	338.64	22.5	328.64	1a
GW-10	3/19/2013	354.33	351.73	2.60	25.0	326.73	15.0	336.73	25.0	326.73	1b
GW-11	3/20/2013	343.85	341.70	2.15	15.0	326.70	5.0	336.70	15.0	326.70	1b
GW-12	3/20/2013	337.11	334.60	2.51	15.0	319.60	5.0	329.60	15.0	319.60	1b
GW-13	8/21/2014	352.15	349.49	2.66	20.0	329.49	10.0	339.49	20.0	329.49	1b
GW-14	8/21/2014	351.37	349.07	2.30	20.0	329.07	10.0	339.07	20.0	329.07	1b
GW-15	8/22/2014	344.61	341.98	2.63	15.0	326.98	5.0	336.98	15.0	326.98	1b
GW-16	8/22/2014	337.28	335.01	2.27	15.0	320.01	5.0	330.01	15.0	320.01	1b

Notes:
1. All depths referenced from ground surface
2. Monitoring wells designated with "S" are shallow Type II wells; monitoring wells designated with "D" are deep Type III wells, with the exception of GW-8D which is a deep Type II well.

Table 2
Geotechnical Laboratory Data
Grain Size Distribution and Soil Classification
Phase 4 Hydrogeologic and Groundwater Quality Assessment
Central Carolina Tire Monofill Landfill
Harnett County, North Carolina
Permit # 43-04

Boring Number	Sample Depth, ft.	% Gravel >4.5 mm	%Sand 4.5 -- 0.075 mm	%Fines 0.075 mm>	%Silt 0.075 -- 0.005 mm	%Clay 0.005 mm>	Effective Porosity	USCS Class	Hydrogeologic Description
GW-1S	18.5-20	1.76	85.68	12.56	4.56	8.00	31%	SC	Clayey Sand
GW-2S	13-15	0.26	81.31	18.44	5.44	13.00	23%	SC	Clayey Sand
GW-3S	18-20	2.80	85.41	11.79	4.79	7.00	33%	SC	Clayey Sand
GW-4S	18-20	0.00	84.41	15.59	5.59	10.00	27%	SC	Clayey Sand
GW-5S	8-10	0.00	86.43	13.57	4.57	9.00	26%	SC	Clayey Sand
GW-6S	16-18	0.14	84.94	14.92	5.92	9.00	28%	SC	Clayey Sand
GW-7S	10-12	0.00	90.16	9.84	2.34	7.50	32%	SC	Clayey Sand
GW-8D	40-42	0.00	71.86	28.14	12.14	16.00	15%	SC	Clayey Sand
GW-1D	34-36	0.00	74.41	25.59	4.59	21.00	13.5%	SC	Clayey Sand
GW-2D	41.5-43.5	0.00	65.91	34.09	8.59	25.50	8%	SC	Clayey Sand
GW-3D	43.5-45.5	0.00	76.55	23.45	3.95	19.50	14%	SC	Clayey Sand
GW-4D	34-36	0.18	70.05	29.77	6.77	23.00	12%	SC	Clayey Sand
GW-5D	44-46	0.13	66.57	33.30	10.30	23.00	10%	SC	Clayey Sand
GW-6D	44-46	0.30	73.17	26.53	5.03	21.50	13%	SC	Clayey Sand
GW-7D	39-41	0.12	70.58	29.30	9.30	20.00	12.5%	SC	Clayey Sand

Notes to Above: Effective porosity values calculated from Textural Classification Triangle method referenced to A.I. Johnson, US Geological Survey Water Supply Paper 1662-D, 1967 (after C.W. Fetter, Applied Hydrogeology, 3rd ed. 1988)
Hydrogeologic descriptions based on field observations.

Table 3
Hydrogeologic Properties of Surficial Aquifer Sediments
Phase 4 Hydrogeologic and Groundwater Quality Assessment
Central Carolina Tire Monofill Landfill
Harnett County, North Carolina
Permit # 43-04

Piezometer Number	Hydrogeologic Unit	Hydrogeologic Description (1)	Effective Porosity (2)	Hydraulic Conductivity (k)		
				ft/min	ft/day	cm/sec
GW-1S	1a	Surficial Aquifer	31%	1.51E-02	2.17E+01	7.67E-03
GW-2S	1a	Surficial Aquifer	23%	2.00E-02	2.88E+01	1.02E-02
GW-3S	1a	Surficial Aquifer	33%	2.12E-02	3.05E+01	1.08E-02
GW-4S	1a	Surficial Aquifer	27%	4.50E-03	6.48E+00	2.29E-03
GW-5S	1a	Surficial Aquifer	26%	2.94E-02	4.23E+01	1.49E-02
GW-6S	1a	Surficial Aquifer	28%	2.40E-03	3.46E+00	1.22E-03
GW-7S	1a	Surficial Aquifer	32%	1.64E-02	2.36E+01	8.33E-03
MW-8	1a	Surficial Aquifer	29%	2.70E-03	3.89E+00	1.37E-03
GW-9	1a	Surficial Aquifer	29%	2.14E-03	3.08E+00	1.09E-03
GW-10	1b	Surficial Aquifer	29%	6.14E-04	8.84E-01	3.12E-04
GW-11	1b	Surficial Aquifer	29%	3.31E-03	4.77E+00	1.68E-03
GW-12	1b	Surficial Aquifer	29%	4.86E-03	7.00E+00	2.47E-03
GW-13	1b	Surficial Aquifer	29%	8.71E-04	1.25E+00	4.42E-04
GW-14	1b	Surficial Aquifer	29%	3.55E-03	5.11E+00	1.80E-03
GW-15	1b	Surficial Aquifer	29%	6.80E-04	9.80E-01	3.46E-04
GW-16	1b	Surficial Aquifer	29%	2.07E-02	2.98E+01	1.05E-02
			Geometric Mean:	**4.81E-03**	**6.93E+00**	**2.44E-03**

Notes
(1) Surficial Aquifer (Middendorf Formation) - very fine to medium variably clayey sand
(2,3) Effective porosity values for soils assigned based on laboratory testing (see Table 2)

Table 4
Horizontal Groundwater Gradient and Velocity Calculations: Surficial Aquifer
Phase 4 Hydrogeologic and Groundwater Quality Assessment
Central Carolina Tire Monofill Landfill
Harnett County, North Carolina
Permit # 43-04

Well No.	Hydrogeologic Unit	Hydraulic Conductivity (k) ft/min	ft/day	cm/sec	Top of PVC Elevation	Depth to Groundwater*	Groundwater Elevation*	Reference Elevation*	delta-Elev. in feet	Map Length in feet	Hydraulic Gradient (I)	Effective Porosity (n)	GW Velocity (V), ft/day	Geometric Mean Velocity, ft/day
GW-1S	1a	1.51E-02	2.17E+01	7.67E-03	352.95	15.29	337.66	337.0	0.66	138.16	0.005	0.31	0.34	
GW-2S	1a	2.00E-02	2.88E+01	1.02E-02	350.26	14.11	336.15	336.0	0.15	86.69	0.002	0.23	0.22	
GW-3S	1a	2.12E-02	3.05E+01	1.08E-02	348.93	12.33	336.60	336.0	0.60	84.59	0.007	0.33	0.65	
GW-4S	1a	4.50E-03	6.48E+00	2.29E-03	354.80	18.05	336.75	336.0	0.75	169.51	0.004	0.27	0.11	
GW-5S	1a	2.94E-02	4.23E+01	1.49E-02	344.36	8.76	335.60	335.0	0.60	73.51	0.008	0.26	1.33	
GW-6S	1a	2.40E-03	3.46E+00	1.22E-03	349.48	13.21	336.27	336.0	0.27	29.37	0.009	0.28	0.11	
GW-7S	1a	1.64E-02	2.36E+01	8.33E-03	346.76	10.99	335.77	335.0	0.77	74.71	0.010	0.32	0.76	
MW-8	1a	2.70E-03	3.89E+00	1.37E-03	342.80	6.79	336.01	335.0	1.01	43.35	0.023	0.29	0.31	
GW-9	1a	2.14E-03	3.08E+00	1.09E-03	353.73	17.00	336.73	337.0	0.27	44.11	0.006	0.29	0.07	
GW-10	1b	6.14E-04	8.84E-01	3.12E-04	354.33	17.51	336.82	336.0	0.82	78.36	0.010	0.29	0.03	
GW-11	1b	3.31E-03	4.77E+00	1.68E-03	343.85	8.45	335.40	335.0	0.40	12.12	0.033	0.29	0.54	
GW-12	1b	4.86E-03	7.00E+00	2.47E-03	337.11	9.56	327.55	327.0	0.55	32.28	0.017	0.29	0.41	
GW-13	1b	8.71E-04	1.25E+00	4.42E-04	352.15	14.70	337.45	337.0	0.45	32.51	0.014	0.29	0.06	
GW-14	1b	3.55E-03	5.11E+00	1.80E-03	351.37	13.31	338.06	337.0	1.06	43.82	0.024	0.29	0.43	
GW-15	1b	6.80E-04	9.80E-01	3.46E-04	344.61	8.22	336.39	335.0	1.39	21.62	0.064	0.29	0.22	
GW-16	1b	2.07E-02	2.98E+01	1.05E-02	337.28	11.22	326.06	327.0	0.94	12.85	0.073	0.29	7.51	0.30

Notes: Groundwater Velocity Calculated from Equation

V=KI/n where K = Hydraulic Conductivity in units of ft/day
I = Hydraulic Gradient in units of ft/ft
n = Effective Porosity (unitless)

Hydraulic Conductivity values from aquifer slug testing using the Bouwer-Rice method
Hydraulic Gradient values were calculated from the potentiometric surface map
Effective Porosity values derived from Table 2
*Groundwater elevations and potentiometric surfaces for reference elevations derived from water level observations made August 2014.

Table 5
Groundwater Field Data
Phase 3 Hydrogeologic and Groundwater Quality Assessment
August 27 and 28, 2014
Central Carolina Tire Monofill Landfill
Harnett County, North Carolina
Permit # 43-04

Well Identity	Well Depth (Feet BGS)	Well Diameter (Inches)	Top of Casing Elevation (Feet MSL)	Ground Surface Elevation (Feet MSL)	Depth to Groundwater (Feet BTOC)	Groundwater Elevation (Feet MSL)	Field Parameters					
							Temp. C^{o}	pH	S.C. umhos/cm	Turbidity (ntu)	ORP (mV)	DO (mg/L)
GW-1S	22.0	2.0	352.95	351.15	15.29	337.66	19.8	2.82	42	9.7	216.7	5.76
GW-1D	40.0	2.0	353.30	351.15	18.17	335.13	18.0	4.96	83.9	8.3	57.2	2.61
GW-2S	20.0	2.0	350.26	348.47	14.11	336.15	23.2	6.26	125	6.21	31.8	5.99
GW-2D	50.0	2.0	350.63	348.69	19.31	331.32	18.4	7.70	137.6	94.7	88.6	4.39
GW-3S	18.0	2.0	348.93	346.97	12.33	336.60	21.7	1.54	54	5.82	217.8	4.5
GW-3D	50.0	2.0	349.45	347.35	18.49	330.96	17.4	4.36	79.5	25.9	71.8	3.77
GW-4S	24.0	2.0	354.80	352.82	18.05	336.75	20.7	2.35	28	5.54	184.7	5.59
GW-4D	44.0	2.0	355.00	353.14	18.54	336.46	18.0	5.48	99.1	11	13.1	3.08
GW-5S	16.0	2.0	344.36	342.19	8.76	335.60	20.4	1.72	72	9.8	214.2	4.85
GW-5D	49.0	2.0	345.42	342.28	17.30	328.12	16.9	4.40	102.2	60.3	46.6	3.07
GW-6S	20.0	2.0	349.48	348.07	13.21	336.27	20.9	2.48	157	9.92	185	5.77
GW-6D	52.0	2.0	349.65	347.87	23.16	326.49	18.0	5.69	99.6	10.2	32.1	3.39
GW-7S	17.0	2.0	346.76	344.76	10.99	335.77	18.9	3.07	59	6.86	175.4	5.67
GW-7D	45.0	2.0	346.58	344.60	19.14	327.44	17.1	4.45	98.5	19.3	32.4	3.11
GW-8D	47.0	2.0	340.69	338.83	17.50	323.19	17.4	4.46	158.5	18.7	23.2	3.84
MW-8	20.0	2.0	342.80	339.12	6.79	336.01	19.9	4.07	48	4.8	120.3	3.4
GW-9	22.5	2.0	353.73	351.14	17.00	336.73	20.5	3.88	58	4.01	134.9	5.96
GW-10	25.0	2.0	354.33	351.73	17.51	336.82	21.1	3.61	45	8.33	136.9	4.35
GW-11	15.0	2.0	343.85	341.70	8.45	335.40	23.2	4.44	33	8.88	202.4	4.51
GW-12	15.0	2.0	337.11	334.60	9.56	327.55	22.9	6.04	299	6.17	-47.4	0.38
GW-13	20.0	2.0	352.15	349.49	14.70	337.45	21.4	6.18	88	194	130.9	5.09
GW-14	20.0	2.0	351.37	349.07	13.31	338.06	24.0	4.76	69	9.29	205.4	4.31
GW-15	15.0	2.0	344.61	341.98	8.22	336.39	25.7	5.17	48	9.94	142.3	6.22
GW-16	15.0	2.0	337.28	335.01	11.22	326.06	17.2	5.24	32.2	73.9	70.3	5.07

Notes: BGS = Below Ground Surface
MSL = Mean Sea Level
BTOC = Below Top of Casing
GW = Groundwater
mV = millivolts
S.C. = Specific Conductance
ntu = Nephelometric Turbidity Units
Monitoring wells designated with "S" are shallow Type II wells; monitoring wells designated with "D" are deep Type III wells.
ORP = Oxidation-Reduction Potential
DO = Dissolved Oxygen

Table 6
Summarized Historical Laboratory Analytical Results for Groundwater Samples
Phase 4 Hydrogeologic and Groundwater Quality Assessment
August 2014
Central Carolina Tire Monofill Landfill
Harnett County, North Carolina
Permit # 43-04

Well	Sampling	Volatile Organic Compounds by SW 846 8260B (ug/L)													
ID	Date	Acetone	Benzene	Bromodichloromethane	Bromoform	Carbon Disulfide	Chloroethane	Chloroform	Dibromochloromethane	4-Isopropyltoluene	Methyl t-butyl Ether	cis-1,2-Dichloroethene	Tetrachloroethene	Trichloroethene	Trichlorofluoromethane
GW-1S	4/30/2012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.82**	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**2.1**	ND	ND
GW-1D	5/1/2012	5	ND	**0.885**	1.96	0.641	ND	12.9	**6.5**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	1.7	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	0.58	ND	ND	ND	ND	ND	ND	ND
GW-2S	4/30/2012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.01	**8.82**	1.33	0.439
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	**22**	**4.0**	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	11	**16**	1.4	ND
GW-2D	5/1/2012	4.31	ND	**0.885**	ND	ND	ND	4.79	**0.763**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-3S	5/1/2012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**0.869 J**	ND	ND
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.4	**2.2**	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.2	ND	**8.0**	ND	ND
GW-3D	5/1/2012	5.09	ND	**2.04**	1.08	ND	ND	4.61	ND	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	1	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-4S	4/30/2012	ND	ND	**5.29**	0.831	ND	ND	5.94	**3.94**	ND	ND	ND	**1.7**	ND	ND
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**1.6**	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.54	ND	ND
GW-4D	5/1/2012	ND	ND	**1.92**	ND	0.823	ND	4.08	**1.54**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	1.2	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-5S	4/30/2012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**3.07**	ND	ND
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**2.0**	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**12**	2.7	ND
GW-5D	5/1/2012	4.36	ND	**6.55**	1.68	0.71	ND	11.5	**5.46**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-6S	4/30/2012	ND	ND	**5.9**	0.871	ND	ND	6.09	**4.59**	ND	ND	ND	ND	ND	ND
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-6D	5/1/2012	3.08	ND	**1.01**	0.937	0.811	ND	2.86	**1.08**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-7S	4/30/2012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.83	**7.37**	0.43	ND
	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.6	**13**	0.54	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.5	ND	**2.0**	ND	ND
GW-7D	5/1/2012	2.59	ND	**3.63**	1.22	ND	ND	7.17	**3.07**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	1.7	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	0.91	ND	ND	ND	ND	ND	ND	ND
GW-8D	5/1/2012	ND	ND	0.403	ND	ND	ND	0.716	**0.592**	ND	ND	ND	ND	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/28/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
MW-8	5/1/2012	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**3.32**	ND	ND
	4/3/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**3.6**	ND	ND
	9/10/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	**6.2**	ND	ND
GW-9	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-10	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.4	**54**	0.92	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.72	**58**	1.2	ND
GW-11	4/2/2013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
GW-12	4/2/2013	ND	**1.9**	ND	ND	ND	1.4	ND	ND	ND	ND	ND	ND	ND	ND
	8/27/2014	ND	0.97	ND	ND	ND	0.55	ND	ND	0.91	ND	ND	ND	ND	ND

Well ID	Sampling Date	Volatile Organic Compounds by SW 846 8260B (ug/L)													
		Acetone	Benzene	Bromodichloromethane	Bromoform	Carbon Disulfide	Chloroethane	Chloroform	Dibromochloromethane	4-Isopropyltoluene	Methyl t-butyl Ether	cis-1,2-Dichloroethene	Tetrachloroethene	Trichloroethene	Trichlorofluoromethane
GW-13	8/27/2014	ND	ND	ND	ND	ND	ND	ND	**0.65**	ND	ND	0.63	**1.4**	ND	ND
GW-14	8/27/2014	ND	ND	**1.6**	0.54 J	ND	ND	1.3	**2.0**	ND	ND	ND	ND	ND	ND
GW-15	8/27/2014	ND	ND	**0.7**	ND	ND	ND	ND	**0.79**	ND	ND	ND	ND	ND	ND
GW-16	8/27/2014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.61	ND	ND
NCAC 2L Std. (ug/L)		**6000**	**1.0**	**0.6**	**4.0**	**700**	**3000**	**70**	**0.4**	**NE**	**20**	**60**	**0.7**	**3.0**	**2000**

Notes:
Values in boldface exceed the corresponding 15A NCAC 2L .0202 groundwater quality standard for Class GA groundwater.
NCAC 2L STD = North Carolina Groundwater Standard established in Title 15A of North Carolina Administrative Code Subchapter 2L
J = Estimated value above laboratory method detection limit.
ND = None detected above laboratory method detection limit.
NE = No NCAC 2L standard or USEPA MCL established.