DNAPL SOURCE EVALUATION AT A PORTION OF THE CABOT CARBON/KOPPERS SUPERFUND SITE

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ABSTRACT

The Koppers, Inc. portion of the Cabot Carbon/Koppers Superfund Site is a woodtreating site in Gainesville, FL ("Site") that formerly used creosote. Based on historical evidence, four source areas were identified: (1) Former South Lagoon, (2) Former North Lagoon, (3) Former Cooling Pond Area (Process Area), and (4) Former Drip Track Area. The primary goal of this work was to define the vertical and lateral extent of dense non-aqueous phase liquid (DNAPL) creosote associated with the source areas. In addition, potential impacts to the Upper Floridan (UF) Aquifer were investigated.

The Site is underlain by a Surficial Aquifer that is about 20-25 ft thick. Underlying the Surficial Aquifer is the Hawthorn Group (HG) that ranges from approximately 115 to 125 ft in thickness and acts as a confining layer. The HG consists of three clay layers (upper, middle and lower) with silty-clayey sand (Upper HG and Lower HG) in between. Below the HG is the Ocala Limestone of the UF Aquifer. Characterization efforts in the Surficial Aquifer used a stepout approach to define the lateral extent of DNAPL and a step-down approach was used to determine the vertical extent of creosote constituents within the HG and the UF Aquifer. Use was made of previous investigations that included soil borings, test pits and monitoring wells. For this study, the lateral extent within the Surficial Aquifer was determined using a combination of Rapid Optical Screening Tool (ROSTTM) deployed on a Cone Penetration Testing (CPT) probe and Geoprobe® soil core with visual creosote observations. ROSTTM results demonstrated false positives, likely due to sandy calcite deposits in the Surficial Aquifer. Consequently, lateral creosote delineation relied primarily on Geoprobe® results. All four source areas within the Surficial Aquifer were delineated and the total volume of DNAPL-impacted source-area soil was estimated at 99,599 cubic yards.

To determine the vertical extent of creosote in the HG, multiple-cased monitoring wells were installed within each source area. During drilling, continuous split-spoon soil samples were collected and examined for the presence of creosote. If no creosote was seen toward the top of the middle clay, the well was completed as an Upper HG well and no further drilling was conducted in that source area. If creosote was seen, then a second well was constructed into the Lower HG. At three source areas, creosote penetrated the upper clay, but was confined to the Upper HG. Impacts below the Former North Lagoon in the HG were the deepest. Creosote beneath this source area was observed partially penetrating the lower clay. Subsequently, wells also were drilled into the UF Aquifer to assess impacts. UF well water quality data support the vertical penetration interpretation of the HG wells.

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INTRODUCTION

The Koppers portion of the Cabot Carbon/Koppers Superfund Site is located in Gainesville, FL ("Site") (see **Figure 1**). A focus of this study is the refinement of the Site conceptual model (SCM). The Site has been an active plant since 1916 and has been used primarily to preserve utility poles and timbers. Use of creosote decreased in the late 1960s and was totally phased out in 1992. Currently, copper chromated arsenate (CCA) is used at the Site. For this study, emphasis is on creosote. The Cabot Carbon/Koppers Site was added to the National Priorities List (NPL) in August 1983, and the Site has been studied since 1980.



Figure 1. Site Location Map, Koppers Portion of the Cabot/Koppers Superfund Site, Gainesville, Florida.

As a result of previous studies, it was believed that the Site was underlain by a Surficial Aquifer, about 20-25 ft thick, which is underlain by the Hawthorn Group (HG). The HG was thought to act as an effective confining layer that protects the underlying Upper Floridan (UF) Aquifer. Three wells completed in the HG in 1985 did not contain creosote constituents and an UF Aquifer well (FW-1) drilled in 1992 in the northeast portion of the Site (hydraulically down gradient from source areas) also did not contain creosote constituents. The initial Site groundwater remedy selected in 1990, based on this early SCM, included perimeter extraction wells in the Surficial Aquifer. This extraction system was installed in 1994 and began operation in early 1995. During this period of investigation, drilling generally stopped at the top of the HG to minimize the potential for cross contamination. Subsequently, in 2002-03, perimeter HG wells were drilled and creosote constituents were detected, suggesting that the HG was not as effective a confining bed as previously thought. This finding triggered additional investigational studies.

More recent studies [GeoTrans (1)], and the subject of this paper, have focused on refining the SCM by determining: (1) the lateral extent of DNAPL contamination in the Surficial Aquifer associated with the creosote source areas, (2) the potential extent of vertical DNAPL contamination in the HG and the UF Aquifer and (3) defining the three-dimensional distribution of dissolved contaminants within the UF Aquifer. The Floridan Aquifer is a drinking water aquifer and the Gainesville Regional Utilities' Murphree Wellfield (municipal water supply) is located approximately 2 miles northeast of the Site (**Figure 1**). The four creosote source areas that are investigated include: (1) Former South Lagoon, (2) Former North Lagoon, (3) Former Cooling Pond Area (Process Area), and (4) Former Drip Track Area (see **Figure 2**).



Figure 2. Site Map Showing Source Area Surficial Aquifer Wells and Direct-Push Borings with Source Area Delineations.

Both the Former North and South Lagoons ceased operation in the mid-1970s. Consequently, the driving DNAPL head for these two creosote source areas was eliminated approximately 30 years ago. Thus, a significant DNAPL mobility factor has been inactive for about the last 30 years. Creosote releases have had decades to migrate. Significant creosote was likely released, but significant creosote also has been trapped at residual saturation. Of the 85 Surficial Aquifer wells and piezometers across the Site, only one well (PW-1) historically has had a small amount of DNAPL creosote accumulate in it. After removal of creosote from this well, no additional creosote flowed into the well under natural hydraulic gradients. Based on these observations, part of the SCM for the Site is that creosote is primarily at residual saturation and large pools of DNAPL creosote are not anticipated. Defining the distribution of DNAPL and dissolved contaminants is one of the goals of this investigation.

SITE HYDROGEOLOGY

As part of the SCM, the underlying hydrogeologic units include the Surficial Aquifer, the HG, and the UF Aquifer (**Figure 3**). The Surficial Aquifer consists of approximately 20-30 ft of fine- to medium-grained sand with trace amounts of silt and clay interbedded with laterally discontinuous zones of clayey sands and sandy clays. The depth to water ranges seasonally from 3 to 15 ft below ground surface (bgs). The groundwater flow direction is toward the northeast and is controlled by land surface topography and localized discharge points, such as wetlands, creeks, drainage ditches, and the Surficial Aquifer pump-and-treat system. The Surficial Aquifer has low yields and is not a major source of potable groundwater.



Figure 3. Hydrostratigraphy of Site Deposits.

Underlying the Surficial Aquifer, the HG ranges from approximately 115 to 125 ft in thickness. It is comprised of interbedded and intermixed clays, silty-clayey sand, sandy clay, and occasional carbonate beds. The upper surface of the HG is a green-gray clay layer that is undulating and dips generally toward the northeast at the Site. This layer (Upper Hawthorn Clay) ranges from 0.5 to 7 ft in thickness. The average, laboratory-determined hydraulic conductivity of this clay layer is 6.7×10^{-8} cm/s [TRC (2)]. Below this clay is a clayey-sand zone (34 to 42 ft thick), which is referred to as the Upper Hawthorn Group (UHG). The UHG hydraulic heads are approximately 1-2 ft lower than hydraulic heads in the Surficial Aquifer. Below the UHG is a second clay layer (2 to 15 ft thick). Below this clay layer (Middle Hawthorn Clay) is another clayey-sand layer referred to as the Lower Hawthorn Group (LHG). The second clay layer appears to be a more effective confining bed, as hydraulic heads in the LHG are nearly 30 ft lower than the heads in the Surficial Aquifer. A third clay layer (20 to 38 ft thick) is found below the LHG. This layer contains 2-3 discernable clay layers (1-9 ft thick) separated by clayey sand/sandy clay. Below this clay layer (Lower Hawthorn Clay) is the UF Aquifer. The hydraulic head difference across the Lower Hawthorn Clay is approximately 90 ft (downward hydraulic gradient), suggesting that it is an effective confining bed.

The UF Aquifer, a source for drinking water, underlies the HG. The UF Aquifer at the Site consists of the Ocala Limestone and the underlying Avon Park Limestone. The Upper Transmissive Zone (UTZ) is a secondary water-producing interval for the UF Aquifer and is located in the uppermost portion of the Ocala Limestone. The thickness of the UTZ is variable, ranging from 50- to 100-ft. The Lower Transmissive Zone (LTZ) is the major water-producing interval for the Murphree Wellfield. The LTZ is located at the contact of the Ocala Limestone and Avon Park and is variable in thickness ranging from 20 to 100 ft. Approximately 85% of the Murphree Wellfield production is obtained from the LTZ and 15% is obtained from the UTZ [GeoTrans (3)]. The UTZ and LTZ are separated by approximately 100 ft of dense, lower-permeability carbonate deposits that produce limited quantities of water. The regional groundwater flow direction in the UF Aquifer (east to west) has been modified by withdrawals from the Murphree Wellfield, such that the average groundwater flow direction at the Site is to the north-northeast.

SOURCE DELINEATION APPROACH

The characterization approach consisted of building on previous work at the Site to determine the lateral extent of creosote in the Surficial Aquifer and the potential vertical extent of creosote in the HG and potential impacts to the UF Aquifer. The lateral extent within the Surficial Aquifer was determined using a combination of Rapid Optical Screening Tool (ROSTTM) deployed on a Cone Penetration Testing (CPT) probe and Geoprobe® soil core with visual creosote observations. Based on these observations in the field, other Geoprobe® locations were selected in order to bound the creosote lateral extent at all four source areas. This approach is referred to as a step-out approach.

To determine the potential vertical extent in the HG and UF Aquifer, monitoring wells were installed. The first HG well in each source area was located within the source area using results from the Surficial Aquifer study. During drilling, continuous split-spoon soil samples were collected and examined for the presence of creosote. If no DNAPL was observed immediately below the Upper Hawthorn Clay, then it was concluded that DNAPL did not penetrate the clay at this location. However, because creosote may have penetrated the clay at other locations, the most likely zone where DNAPL may have accumulated was targeted, which is the lower part of the UHG on top of the next clay layer. Therefore, drilling continued to the lower part of the UHG. If DNAPL was present there based on visual examination of the splitspoon soil sample, then the well was completed in the lower portion of the UHG. If no DNAPL was observed there, then the borehole was back filled and the well was completed in the upper portion of the UHG. LHG wells only were drilled if DNAPL was observed in the lower portion of the UHG. The logic for well completion in the LHG was the same as that just described for the UHG. This is referred to as a step-down approach. In addition, UF Aquifer wells subsequently were drilled to estimate potential impacts to this aquifer.

To minimize the potential for DNAPL short-circuiting at the UHG wells, telescopic drilling was conducted using multiple casings. **Figure 4** shows a well schematic for an UF Aquifer well, FW-6, installed as part of this investigation. A large-diameter isolation casing was set and grouted into the Upper Hawthorn Clay. Subsequently, a smaller diameter boring was extended into the UHG, where it was screened and completed as a monitoring well. These wells were screened in the lower portion of the UHG. The LHG wells also were completed using telescopic casing.



Figure 4. FW-6 Floridan Well Schematic.

SOURCE DELINEATION RESULTS

Surficial Aquifer

Monitoring wells, previously installed in the Surficial Aquifer, yield the following observations. Monitoring well M-1 is within the DNAPL source-area of the Former North Lagoon and is screened at the bottom of the Surficial Aquifer. Monitoring well MW-3BR is down gradient of the Former North Lagoon and also is screened at the bottom of the Surficial Aquifer. Neither of these wells contained/contains DNAPL, even though elevated naphthalene has been detected in both. Monitoring well M-21BR is located near (down gradient and down dip of) the DNAPL source area of the Former South Lagoon whereas MW-32B is down gradient. Both of these wells are screened at the bottom of the Surficial Aquifer and neither of these wells contained/contains DNAPL, even though elevated naphthalene has been detected. Monitoring well M-24B is located between the Former Tank Containment and Process Areas and naphthalene has been detected in groundwater from this well. This DNAPL source area contains PW-1³; M-25B is down gradient and has contained elevated naphthalene. These wells are screened at the bottom of the Surficial Aquifer and none of them contain DNAPL. Monitoring well M-15B is screened at the bottom of the Surficial Aquifer and is in or immediately adjacent to the Drip Track DNAPL source area; it does not contain DNAPL, even though elevated naphthalene has been detected in groundwater from this well. Consequently, based on the absence of DNAPL in wells in the Surficial Aquifer, there is no evidence that mobile DNAPL is present, even though naphthalene concentrations in source-zone wells imply the presence of creosote. This suggests that the creosote is at residual saturation and immobile. The focus of the direct-push study, therefore, was to define the lateral extent of this residual saturation in the Surficial Aquifer.

Direct-push ROSTTM has been successfully used at other creosote sites to identify creosote-impacted zones [Jones et al. (4)]. At the Site, however, the ROSTTM demonstrated fluorescence in areas known to be clean (no creosote). **Figure 5** shows a comparison between a ROSTTM and a Geoprobe® in a clean area. As may be seen, fluorescence occurs at a visually clean boring, suggesting that the ROSTTM results are unreliable. Minerals such as calcite and naturally occurring organic matter can fluoresce, possibly causing interference problems with the ROSTTM. Consequently, lateral DNAPL delineation relied primarily on Geoprobe® core (visual). For the Former North Lagoon, 8 ROSTTM and 12 Geoprobe® were installed. For the Former Cooling Pond Area, 10 ROSTTM and 9 Geoprobe® were installed. For the Former Drip Track Area, 6 ROSTTM and 11 Geoprobe® were installed.

<u>Former South Lagoon</u>. The DNAPL source location in the Surficial Aquifer for the Former South Lagoon is shown in **Figure 2**. The source area includes the locations of the former lagoons and beyond. Beneath the lagoons, vertical migration dominated until reaching the Upper Hawthorn Clay. At that location (base of the Surficial Aquifer), the creosote spread laterally until being trapped at residual saturation or finding weak (permeable) pathways through the clay. Therefore, the residual creosote distribution is thick under the lagoons and thin (at base of Surficial Aquifer) away from the lagoons.

³ PW-1 produces a small amount of DNAPL when water is pumped, but when pumping ceases and DNAPL is removed from the well, no DNAPL returns. This is consistent with DNAPL at residual saturation near PW-1.



Figure 5. Boring Log at Location CPT-07.

The boundary of the Former South Lagoon is consistent with the location of the former lagoon with the exception of impacts observed at CPT-40S, which may be related to the Former South Lagoon. The source area associated with the Former South Lagoon within the Surficial Aquifer is bounded by data from previous investigations and new information at CPT-44S, CPT-38S, CPT-39S, CPT-41S, CPT-02, CPT-42S, CPT-07, -07S, CPT-43S, and CPT-09.

<u>Former Process Area</u>. The DNAPL source location in the Surficial Aquifer for the Former Cooling Pond Area is shown in **Figure 2**. Unlike the former lagoons, in the Former Cooling Pond Area, creosote was observed sporadically with depth within the Surficial Aquifer. In determining source area versus non-source area, borings with minor creosote impacts were considered outside the source area. The boundary of the Former Cooling Pond Area is similar to the source area defined in 1999 Feasibility Study [TRC (5)]. The source area associated with the Former Cooling Pond Area within the Surficial Aquifer is bounded by data from previous investigations and new information at CPT-66S, CPT-69S, CPT-63S, CPT-25, 25S, CPT-64S, and CPT-65S.

<u>Former Drip Track Area.</u> Creosote was observed in seven borings (where CPT-19 and CPT-19S are at the same location). At several of these locations (**Figure 2**), creosote was only observed in the lower portion of the boring. This suggests that the Upper Hawthorn Clay was a partial barrier to vertical migration, causing some lateral creosote migration at the bottom of the Surficial Aquifer. The source area extends south (based on observations at CPT58S and CPT-59S) and east (based on observations at CPT-55S). In determining source area versus non-source area, borings with minor creosote impacts were considered outside the source area. The source zone associated with the drip track within the Surficial Aquifer is bounded to the north by CPT-22 and CPT-54S; to the south by CPT60S; to the east by CPT-23, CPT-61S and CPT-62S; and to the west by CPT-56S and CPT-68S.

<u>Former North Lagoon.</u> New information and data from previous studies have been used to delineate the Former North Lagoon source area as shown in **Figure 2**. As may be seen, the source area includes the locations of the former lagoon and beyond. Beneath the lagoon, vertical migration dominated until reaching the Upper Hawthorn Clay. At that location (base of the Surficial Aquifer), the creosote spread laterally until being trapped at residual saturation or finding weak (permeable) pathways through the clay. Therefore, the residual creosote distribution is thick under the lagoons and thin (at base of Surficial Aquifer) away from the lagoon. The source boundary extends to east based on the results from CPT-13, -13S and CTP-46S. The source area in the Surficial Aquifer near the Former North Lagoon is bounded to the east by the lack of creosote at CPT-49S, CPT-47S and CPT-45S (as well as data from previous investigations). It is bounded to the south by CPT-52S, CPT-53S and data from previous investigations. It is bounded to the west by CPT-17, CPT-16, CPT –51-S and data from previous investigations. Finally, it is bounded to the north by CPT-14, CPT-15, CPT-57S and data from previous investigations.

Volume of DNAPL-Impacted Soil. The surface projection of the estimated furthest lateral extent of prominent DNAPL and DNAPL staining at each of the four source areas within the Surficial Aquifer is shown in Figure 2. The estimated source areas are discontinuous in the sampled soil columns from the ground surface to the top of the UHG Clay. This presents challenges in estimating volumes of significantly impacted soil. The volume of significantly impacted-DNAPL soil is estimated as follows. The surface areas occupied by each of the four source-area lateral extent contours from Figure 2 are calculated. Next, the average depth of the Surficial Aquifer is estimated by averaging all of the representative boring logs from each source area. The estimated DNAPL-impacted soil volume is then calculated by multiplying the area by the depth and further multiplying by the estimated average percent of impacted soil column. The average percent of impacted soil column is a qualitative estimate based on a comparison of soil boring impacts versus non-impacts. The results show that the estimated volume of soil impacted with significant amounts of DNAPL ranges from approximately 10,000 cubic yards (CY) in the Creosote Drip Track Area to 35,500 CY in the Process Area. The total volume of DNAPLimpacted source-area soil in the Surficial Aquifer was estimated at 99,599 cubic yards. This estimate of impacted soil is a neat volume (i.e., the volume of soil containing DNAPL only and not the larger volume that would need to be excavated to remove (1) soil containing DNAPL and (2) soil due to construction limitations).

<u>PW-1 Creosote Recovery.</u> A pilot study was performed where groundwater was pumped from PW-1 (located in the Process Area) in an effort to increase the hydraulic gradient toward the well, thereby attempting to draw creosote to PW-1, the only well in the Surficial Aquifer where DNAPL had accumulated. By varying the pumping rate and monitoring the volume of DNAPL and groundwater extracted, it was determined that the pumping rate with the highest DNAPL yield was between 1.5 and 2.0 gpm. Over a period of 158 days, an estimated 335,169 gal of groundwater and 89.95 gal of DNAPL were extracted. The ratio of DNAPL to groundwater extracted for PW-1 is 0.000268. This indicates that the extraction system is not very efficient at removing DNAPL from the subsurface. For every 1 gal of DNAPL recovered, approximately 3,726 gal of groundwater needed to be extracted, treated, and disposed. The low DNAPL extraction ratio is consistent with other observations that the creosote in the Surficial Aquifer is at residual saturation and will not flow to a well under ambient conditions.

Hawthorn Group

The HG investigation (i.e., vertical extent) approach used the knowledge of contamination in the Surficial Aquifer as a guide for HG well placement. That is, in order to maximize the likelihood of finding creosote in the HG, wells were sited in the highly contaminated portions of each of the four former source areas. HG well locations are shown in **Figure 6**.



Figure 6. Site Map Showing Source-Area Hawthorn Group Wells and Upper Floridan Aquifer Multi-Port Wells with Source Area Delineations.

<u>Former South Lagoon.</u> Using this approach, HG-9S was drilled into the Former South Lagoon, where no creosote was observed in core from the lower portion of the UHG through the top of the Middle Hawthorn Clay. HG-9S was completed in the upper portion of the UHG and no LHG well was drilled as prescribed in the drilling protocol. Weekly to biweekly monitoring for about 2 yr indicates that HG-9S does not contain DNAPL. Thus, at the HG-9S location, DNAPL did not penetrate below the upper portion of the UHG and DNAPL in the vicinity of the HG-9S screen interval appears to be at residual saturation and immobile.

<u>Former Process Area</u>. For the Former Process Area, HG-11S was paired with PW-1; no creosote was observed in core from the lower portion of the UHG, so HG-11S was completed in the upper portion of the UHG in accordance with the approved approach. HG-15S also was drilled in the Former Process Area and had similar observations to HG-11S. HG-15S was completed in the lower portion of the UHG to provide vertical coverage across the UHG at this source area. Based on weekly to biweekly monitoring and bailing, both HG-11S and HG-15S contain DNAPL. Well HG-11S (the shallower well), yields less than 0.5 gal of DNAPL per week and the deeper well, HG-15S, yields less than 0.2 gal of DNAPL per week. Thus, at these locations, DNAPL did not penetrate below the UHG, and the UHG contains some mobile or potentially mobile DNAPL. The driving head of DNAPL appears low at this location.

<u>Former Drip Track Area.</u> For the Former Drip Track Area, HG-12S was drilled and creosote was observed in core from the lower portion of the UHG, where HG-12S was completed. As per the drilling protocol, HG-12D was drilled into the LHG and paired with HG-

12S. No creosote was observed in HG-12D core until the bottom of the LHG, where HG-12D was completed. Weekly to biweekly monitoring for about 2 yr indicates that HG-12D does not contain DNAPL. Based on weekly to biweekly monitoring and bailing, HG-12S contains DNAPL and yields less than 0.3 gal of DNAPL per week. Thus, at this well location, DNAPL did not penetrate below the UHG; the creosote observed in the core of HG-12D migrated laterally on the Lower Hawthorn Clay from some adjacent area. The creosote in the LHG at this location currently is not mobile (does not flow to a well), but some mobile or potentially mobile DNAPL is present in the UHG at this location, although the driving DNAPL head appears low at this location.

Former North Lagoon. Finally, for the Former North Lagoon, HG-10S was drilled and creosote was observed in the lower portion of the UHG, where HG-10S was completed. As per the drilling protocol, HG-10D was drilled into the LHG and paired with HG-10S. For HG-10D, creosote was observed in core from the lower portion of the LHG, where HG-10D was completed. HG-16S was drilled just down gradient and down dip (on the Upper Hawthorn Clay) of the Former North Lagoon and had similar observations to HG-10S. HG-16S was completed in the lower portion of the UHG and HG-16D was drilled. HG-16D had no creosote observed in core until the bottom of the LHG, where HG-16D was completed. Although not part of the source area delineation drilling protocol, a decision was made to install an UF Aquifer well, FW-6 at this location, which was outside the defined source area. Weekly to biweekly monitoring for about 2 yr indicates that HG-10D, HG-16D and FW-6 do not contain DNAPL. Based on weekly to biweekly monitoring and bailing, both HG-10S and HG-16S contain DNAPL, where the source area well, HG-10S, yields less than 0.5 gal of DNAPL per week and the down-gradient well, HG-16S, yields less than 0.3 gal of DNAPL per week. Thus, at the HG-10 location, DNAPL penetrated to at least the top of the Lower Hawthorn Clay and into the upper portion of the Lower Hawthorn Clay at the FW-6 location. Creosote in the LHG at these locations is not mobile, but some mobile or potentially mobile DNAPL is present in the UHG at these locations (associated with a thin, 2-3 in coarse-grained layer near the top of the Middle Hawthorn Clay).

<u>Creosote Recovery.</u> The amount of mobile or potentially mobile DNAPL near the top of the middle clay in the HG is not very thick and is associated with a thin, coarse-grained layer based on core observations. Five UHG wells (HG-10S, HG-11S, HG-12S, HG-15S, and HG-16S) accumulate DNAPL, which is removed weekly and later, biweekly. DNAPL recovery began on July 20, 2004; as of August 8, 2006, 136.06 gal of creosote had been removed or approximately 1.3 gal/week. The DNAPL yield has been low, but steady. LHG and UF Aquifer wells also are probed for DNAPL, but none has been observed.

UPPER FLORIDAN AQUIFER INVESTIGATION APPROACH

Although FW-6 did not contain DNAPL, it did contain elevated naphthalene concentrations. Ten other Site UF Aquifer wells (completed into the upper 20 ft of the aquifer) either did not contain naphthalene or contained naphthalene at low concentrations. Over time, naphthalene concentrations in FW-6 have generally declined suggesting that the elevated naphthalene concentrations at FW-6 may have been, in part, due to cross contamination. To evaluate potential impacts to the UF Aquifer, an additional field effort [GeoTrans (6)] was initiated that focused on the UF Aquifer. This effort consisted of installing 14 multiple-screened (using Westbay systems) UF Aquifer wells that straddled the UTZ interval of the Ocala Limestone beneath the Site. The 14 new UF Aquifer well locations are shown in **Figure 6**. As

may be seen, there are 4 source wells, 8 transect wells, and 2 boundary wells. A typical UF Aquifer well schematic is shown in **Figure 7**. To minimize potential cross contamination, the new wells are quadruple cased. These new wells supplement the previous 11 UF Aquifer wells at or in the vicinity of the Site. The objectives of this field program were: (1) to investigate the potential for groundwater impacts in the UF Aquifer down gradient of well FW-6 and down gradient of the four former source areas and (2) to utilize new information to confirm or update the SCM.



Figure 7. Upper Floridan Well construction Summary Log, July 2005 Through March 2006 UF Investigation.

UPPER FLORIDAN INVESTIGATION RESULTS

The over 2,000 ft of geologic core collected as part of this investigation allow the following observations: (1) the HG upper, middle and lower clay units are continuous and laterally extensive over the Site; (2) no free-phase or residual DNAPL impacts were detected below the top of the Lower Hawthorn Clay; (3) No free-phase or residual DNAPL impacts were detected in the UF Aquifer; (4) the UTZ is approximately 70 % unconsolidated, with 30 % classified as moderately consolidated; and (5) the estimated total porosity of the UTZ is high (typical of fine- to coarse-grained porous media) and the effective porosity is estimated to be in

the range of 10 to 15 % based on literature review of equivalent media [see e.g., Spitz and Moreno (7)]. The unconsolidated nature of the UTZ was not anticipated and resulted in a modification to the SCM.

The hydraulic-head data obtained in May 2006 from the new wells support the groundwater flow conceptual model for the Site. The following observations are based on these data: (1) horizontal hydraulic gradients at the Site are low; (2) vertical hydraulic gradients may be low (slightly downward), but are uncertain due to well drilling and construction (e.g., the potential inaccuracies of a few tenths of feet in the Westbay System pressure measurement port elevations are approximately equal to change in hydraulic head between ports); (3) the UTZ is heterogeneous, but the unconsolidated nature and karst features suggest the UTZ should be fairly well connected, both horizontally and vertically; and (4) the UF Aquifer potentiometric surface indicates a predominantly northeastern groundwater flow direction across the Site in the direction of the Murphree Wellfield and a predominantly northerly direction to the west of the Site.

Groundwater samples were collected from 14 new well locations at 4 discrete depths resulting in a total of 56 samples. The analytical results are generally consistent with the SCM. The following observations are made based on the water quality data: (1) no wide-spread constituent impacts to the UF Aquifer were identified (with the exception of low levels of benzene in two monitoring ports, organic constituents were either non-detect or below the Federal MCL drinking water standards; 51 of the 56 monitoring ports were either non-detect or below the Florida Groundwater Cleanup Target Levels (GCTLs) concentration limits); (2) no wide-spread constituent impacts were encountered down gradient of the four potential source areas (consistent with the HG results, water quality results from two of the source areas were non-detect for organic constituents; the remaining two source areas only contained low levels of naphthalene that exceed GCTLs); (3) historically, elevated organic constituent concentrations in FW-6 appear to be limited to the vicinity of this well and slightly down gradient; and (4) FW-12B was the only transect well with elevated constituent concentrations; concentrations in this well are anomalous with the highest concentrations in the lowermost two ports and non-detect in the upper two ports; two wells installed downgradient of this well demonstrate that impacts have not migrated off Site. Water quality data for March 2006 are summarized in Figure 8.

CREOSOTE PROPERTIES

Creosote samples originally were collected from wells HG-10S, HG-11S, HG-12S and HG-16D and sent to Texas Oil Tech Laboratories, L.P. in Houston, TX. Specific gravity was determined using ASTM D1298 and kinematic viscosity was determined using ASTM D 445. Additional creosote samples were collected from wells PW-1, HG-15S and HG-16S, and sent to Augustine Scientific to determine specific gravity and kinematic viscosity. Creosote samples from all of these wells, except HG-16D, which no longer produces creosote, also were provided to Augustine Scientific to determine interfacial tension. The results are shown in **Table 1** and discussed below.



Figure 8. UF Aquifer March 2006 Water Quality Results.

Table 1. Creosote density, absolute viscosity and interfacial tension measurements made by
Augustine Scientific Laboratory or Texas Oil Tech Laboratories (the latter marked by *).

		Absolute	Interfacial Tension
	Density	Viscosity (cp) at	(dynes/cm) at
Sample Location	(g/cm^3) at $60^{\circ}C$	40°C	22°C
Former Process Area			
PW-1 (Surficial Aquifer)	1.031	13.6	19.12
HG-11S (UHG)	1.069*	4.9*	17.80
HG-15S (UHG)	1.043	8.7	17.46
Former Drip Track			
HG-12S (UHG)	1.0923^2	13.9 [*]	21.30
Former North Lagoon			
HG-10S (UHG)	1.0936^{*}	11.2^{*}	20.25
HG-16S (UHG)	1.033	25.2	23.33
HG-16D (LHG)	1.0986^{*}	25.5^*	NA

<u>Density</u>. The original data were for specific gravity, which is the density of a substance divided by the density of water. Because water has a density of 1 g/cc, specific gravity is the same as density without the units. The density for Site creosote ranges from about 1.03 to 1.10 g/cc at 60°C, which is slightly denser than water. Because its density is close to that of water,

creosote does not experience as large a gravitational driving force for vertical migration as other DNAPLs such as chlorinated solvents (e.g., the densities of TCE and PCE are 1.46 and 1.62 g/cc, respectively [Cohen and Mercer (8)].

<u>Absolute Viscosity.</u> Viscosity is a measure of the fluid's internal friction. The original data were for kinematic viscosity provided in centistokes (cSt, where 1 cSt = 1 centipoise cc/g). Kinematic viscosity is the absolute viscosity divided by the fluid density. The absolute viscosity for Site creosote ranges from approximately 6 to 26 centipoise (cp) at 40°C, which is more viscous than water, which has an absolute viscosity of 1.14 centipoise (cp) at 15° C. Creosote generally has higher viscosity than other DNAPLs such as chlorinated solvents, and migrates more slowly under similar hydraulic gradients.

<u>Interfacial Tension</u>. The interfacial tension (IFT) refers to the tensile force that exists in the interface separating two immiscible fluids (e.g., creosote and water). It is provided in dynes/cm or N/m (where 1 N/m = 1000 dynes/cm). The IFT for Site creosote ranges from approximately 17 to 23 dynes/cm at 22°C. Lower values of IFT tend to decrease the spread of a DNAPL perpendicular to its primary migration direction and decrease the force needed for DNAPL to displace water, or vice versa, in saturated porous media.

<u>Wettability.</u> Based on a literature review, during initial DNAPL migration below the water table, creosote is the nonwetting fluid and its entry into the subsurface media will be resisted by water-filled pores. With time in the subsurface, it is possible for chemical reactions involving creosote, especially at low aqueous phase pH, to cause the media to become more intermediate-wet or DNAPL-wet along flow paths after contact with creosote. This condition leads to increased DNAPL trapping, hindering creosote recovery efforts. Low aqueous phase pH is not anticipated at the Site due to the buffering capacity of the calcium carbonate materials in the subsurface.

Wettability testing performed during this study utilized contact angle measurements and qualitative bottle tests, the two most common measurement techniques used for creosote. Results are generally consistent with those reported in the literature. Contact angles of creosote on Surficial Aquifer sand below water were indicative of water-wet conditions. Creosote contact angles on Hawthorn clay and glass slides below water typically ranged from 35° to 40° , indicative of water-wet conditions. Creosote wet the glass slide (contact angle ~170°) in the aircreosote system. Measured contact angles did not change with aging over 42 days, but rapid formation of a semi-rigid interfacial film on the creosote drops may have constrained creosote spreading over time.

To further test the water-wet results, qualitative bottle tests were performed. Based on these results, the Surficial Aquifer sand and commercial quartz sands were water-wet in all cases, including a test where the aqueous pH was maintained below 4.5 by the addition of HCl. Creosote adherence to glass vials, but not quartz sand, was observed in most of the tests. These and the contact angle test results demonstrating water-wet conditions are consistent with the field observations that mobile DNAPL creosote at the Site is only associated with a coarse-grained seam located above the Middle Hawthorn Clay.

CONCLUSIONS

This field effort is an example of development of a site conceptual model (SCM), using that SCM to design a data collection program that is phased and flexible, and then using the newly-collected data to update the SCM. Although the field program was dynamic and flexible

with decisions on Geoprobes[®] and wells made in the field, the field effort still had to be implemented in several phases, related primarily with the depth of the investigation. Additional wells within each phase were drilled based on Site conditions. Changes in the SCM included: (1) a better understanding of the HG, which is a confining bed, but has small-scale features that allow DNAPL penetration; consequently, creosote was found deeper than expected and (2) a better understanding of the UF Aquifer, which, beneath the Site, maintains karst features, but is 70 % unconsolidated, yielding relatively high total and effective porosities.

The four creosote source areas were delineated using a step-out and step-down approach. Within the Surficial Aquifer, direct-push technology was used. At the Site, the ROSTTM demonstrated fluorescence in areas known to be clean (no creosote). Minerals such as calcite and naturally occurring organic matter can fluoresce, possibly causing interference problems with the ROSTTM. Consequently, lateral DNAPL delineation relied primarily on Geoprobe® core (visual). Vertical penetration into the HG was determined via drilling, visual examination of core (continuous split-spoon soil samples), and well construction. A protocol was established prior to drilling and used to determine when to drill deeper. To minimize potential cross contamination, telescopic drilling was conducted using multiple casings. Based on this effort, creosote associated with the Former South Lagoon and Process Area did not penetrate the UHG; creosote associated with the Former Drip Track does not appear to have penetrated below the UHG, although some contamination was found near the bottom of the LHG and appears to have migrated there laterally (not vertically). The deepest penetration of creosote is associated with the Former North Lagoon, where creosote at residual saturation was found to have entered the upper portion of the Lower Hawthorn Clay. Consistent with the original SCM, mostly creosote at residual saturation was identified and only a thin (2-3 in thick) zone containing mobile creosote was located above the Upper Hawthorn Clay. This layer yields only low volumes of DNAPL.

The results of the HG study were confirmed by a subsequent study of the UF Aquifer. Multi-screened wells with quadruple casings were drilled. For the new wells, groundwater samples were collected from 14 well locations at 4 discrete depths resulting in a total of 56 samples. The analytical results are consistent with previous UF Aquifer results in that no DNAPL is present in the UF Aquifer and no wide-spread constituent impacts to the UF Aquifer were identified. Water quality results from two of the source area monitoring wells (Former South Lagoon and Process Area) were non-detect for organic constituents; the remaining two source area monitoring wells (Former North Lagoon and Drip Track) only contained low levels of naphthalene. Elevated organic constituent concentrations in previously-drilled FW-6 appear to be limited to the vicinity down gradient of this well. Natural attenuation within the UF Aquifer, as evidenced by concentrations in down-gradient boundary wells, indicates that impacts have not migrated off Site.

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