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Proven Soil, Sediment, and Groundwater Remediation Technologies

VIA E-MAIL: Mitch.Brourman@hanson.biz

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Subject: Phase I ISBS - Field Pilot Study Report
Cabot Carbon/Koppers Superfund Site in Gainesville, Florida
Adventus Project No. AAI6-189

Dear Mr. Brourman:

This report describes implementation and performance monitoring activities conducted for pilot-scale field validation of the ISBS (in situ biogeochemical stabilization) technology at the Cabot Carbon/Koppers Superfund Site in Gainesville, Florida. Specifically, the report summarizes field observations obtained during September 2007 and January 2008, provides analytical results for core samples collected in September, and identifies planned activities and locations for ongoing work activities. A detailed description of overall project activities is provided in the Final Field Activity Plan (FAP), Revision 3 (Adventus Americas, Inc., 2008), which has previously been provided to both USEPA and FDEP..

As discussed in the FAP, the pilot scale field testing of the ISBS technology will be conducted in the former North Lagoon Area (Figure 1) using two different delivery methods (i.e., direct push and injections via temporary wells) to meet the following objectives:

- Validate the ability of the ISBS reagent to stabilize non-aqueous phase liquid (NAPL) residuals; and
- Confirm the effectiveness of the selected construction methods to properly introduce the ISBS reagents into the subsurface.

SITE BACKGROUND

The Koppers portion of the Cabot Carbon/Koppers Superfund Site encompasses approximately 90 acres in a relatively flat industrial and commercial area within the City limits of Gainesville, Florida. Elevation ranges from 165 to 185 feet above mean sea level. The main historic and current processing facilities are located within the

southeastern corner of the Site. This area includes a tank farm, the cylinder drip tracks, the treating cylinders' wastewater system, and drying kilns. A cooling water pond was formerly also located in this area. The central and northern portions of the Site have been cleared and graded, and they are currently used as storage areas.

Two historic lagoon areas, referred to as the former North Lagoon and former South Lagoon, were used to manage wastewater generated by the treatment processes. The former North Lagoon reportedly operated from 1937 until the mid-1970s. The operational period of the former South Lagoon is not known. Both the former North Lagoon and former South Lagoon have been closed, covered and graded.

PHASE I ACTIVITIES

A generalized list of Phase I activities that have been conducted to date is as follows.

During September 2007:

- Pre-construction baseline soils sampling
- Installation NAPL monitoring wells
- Installation of temporary injection points (TIP wells) for use in the injection of ISBS reagents.
- Pre-construction baseline soils analysis
- Initiated periodic NAPL monitoring at NAPL and TIP wells

Borings installed as part of these activities are shown on **Figure 1.**

During January 2008:

- Installation of an additional pre-construction soil boring.
- Installation of an additional monitoring well ZOD-1 at the Zone of Discharge (ZOD) perimeter.
- Initiation of groundwater monitoring based on the February 5, 2008 FAP.
- Injection of ISBS reagents at the TIP and Direct Injection Point (DIP) areas.
- Installation of post-injection verification borings.

Borings installed as part of these activities are shown on **Figure 2,** with the exception of ZOD-1, which is shown on **Figure 3.**

The following additional/ongoing project activities are also described in this report:

- Soil core leachable Constituent of Interest (COI) assessments
- Post-treatment monitoring locations

SEPTEMBER 2007 FIELD ACTIVITIES

GeoTrans, Inc. (GeoTrans) was contracted by Beazer East, Inc. (Beazer) to assist Adventus with ISBS implementation activities at the site. **Appendix A** is the GeoTrans report on field activities. In addition to the information noted in the GeoTrans report, Adventus has noted the following changes from the FAP:

- Sumps were not installed in the TIP or ISBS wells, in order to avoid the potential of over-drilling through the upper clay.
- Boring and planned ISBS reagent injection locations were moved north and east, in order to perform the pilot in areas with adequate NAPL impact.

Additional documentation of field activities is provided by way of project photo-documentation. Photographs of soil cores and well completions are provided in **Appendix B. Table 1** provides a listing of soils samples collected for laboratory analysis during the Phase I Field activities. Note that the TIP-3 core was collected and later disposed while in the field, as 1) part of the interval sampled at TIP-3 was later recognized to be 'slough', and 2) the TB-1 core interval sample had more clearly discernable NAPL present. Laboratory results obtained to date are included as **Appendix C**.

Table 1. Pre-Construction Baseline Sampling Soil Cores Submitted for Analysis

Boring ID	Depth Interval (feet bgs)	Date Collected	Comments
TIP-3	10.5 to 12.5	9/7/2007	Not analyzed
TIP-4	10 to 12	9/7/2007	
TB-1	13 to 15	9/7/2007	
DB-1	15 to 17	9/7/2007	
NISBS-2	13 to 15	9/10/2007	
NISBS-1	20 to 21.5	9/10/2007	
DB-2	18.5 to 20.5	9/10/2007	

Field and Technical Services (FTS), also under contract to Beazer, has been obtaining water and elevation/thickness data since shortly after the NAPL and TIP wells were installed. To date, no measurable NAPL thickness has been detected in any of these wells. However, traces of NAPL have been frequently reported in ISBS-1, and have recently been reported in ISBS-2 (prior to ISBS field implementation).

Appendix D provides a summary of these measurements through February 19, 2008.

JANUARY 2008 FIELD ACTIVITIES

As a point of reference for subsequent analyses of the influence of ISBS treatment protocols, one additional pre-construction boring, designated as DB-3 was installed. The location of DB-3 is also depicted on **Figure 2**. The core was collected using GeoProbe MacroCore Tooling, and was contained in acetate sleeves. The core was not logged in the field, as it was shipped intact within the core sleeves to Dr. Tom Al at the University of New Brunswick. The purpose of this core is to provide a reference sample of initial (pre-injection) conditions, as supplemented by the detailed GeoTrans logs contained in **Appendix A**. Samples were approximately 1-1/2" in diameter and were packed in 2' sections inside of 3" diameter PVC pipe for protection. The following intervals of sample were submitted to Dr. Al:

- 18 to 22' (two tubes)
- 16' to 17'5" (Bottom 7" from 14 to 18' core was not recovered)
- 14 to 16'
- 12' to 12'10.5" (Bottom 13.5" of the 10' to 14' core was not recovered)
- 10' to 12'
- 6'3" to 8'3" (Bottom portion of 5' to 10' core was not recovered)

Shallower samples were not submitted, as they are not within the zone over which ISBS reagents were injected. Photos of the soil cores within the macro-core tubing are included in **Appendix E**. Because the macro-cores were not opened, the DB-3 core was not logged. However, clay was noted as being present at the bottom of the deepest core interval, at a depth of 22'

In accordance with the Florida Department of Environmental Protection (FDEP) Final Order Granting a Variance (FDEP, 2008), an additional monitoring well was installed on January 22, 2008 in the surficial aquifer approximately 150 feet downgradient of the ZOD, where injections were performed. The monitoring well, designated ZOD-1, is shown on **Figure 3**. A boring log and well construction log are included in **Appendix F**, and a photo of the completed well is shown as **Figure 4**. Following its installation, ZOD-1 was developed by pumping 160 gallons of water from the well at a flow rate of approximately 2.5 gpm. This was also conducted on January 22, 2008.

Groundwater sampling was conducted on January 16 and January 23, 2008. The purpose of the sampling is to satisfy the requirements of the Final Order, which are essentially as follows:

- To demonstrate that the primary analytes (antimony, arsenic, beryllium, cadmium, chromium, lead, mercury, selenium, sodium, and thallium) do not exceed FDEP groundwater standards (the MCLs) within the zone of discharge (150') for more than 12 months.
- To demonstrate that the primary analytes return to meeting their MCLs or natural background levels (whichever is less) after 12 months.
- Secondary parameters (aluminum, chloride, iron, manganese, color, pH, and TDS) are included for monitoring the zone of discharge.

Groundwater flow within the surficial aquifer is reportedly to the northeast at a gradient of approximately 21 ft/day (GeoTrans, 2004). For reference, **Figure 3** depicts the relative locations of the surficial wells sampled. Sampling logs and laboratory analytical results are provided in **Appendix G,** and results are summarized in **Table 2**.

Figure 4. ZOD-1 Completion Photo

Note that monitoring well ZOD-1 was sampled as soon as practical after it was installed, at 09:55 on Wednesday, January 23, 2008. The timing of the initial

sampling was shortly after injections had been initiated (below). However, given the low rate of ISBS reagent injection and the relative distance between the point(s) of injection and well ZOD-1, it is inconceivable that the injections would have influenced the results at ZOD-1 within such a short time period.

The groundwater results of the "variance analytes" are summarized in **Table 2** and may be briefly described as follows:

- For the primary analytes:
  - None were detected above the MCLs.
  - Sodium was detected in M-1 and ZOD-1 at levels above the laboratory reporting limit.
  - Any other reported detections were at levels below laboratory reporting limits, and are estimated concentrations.
- For the secondary analytes and field parameters, the most apparently notable observation was that the water in ZOD-1 was recorded as 'clear/grey' This observation is consistent with its recent installation and with the relatively high turbidity value during sampling.

In addition to the above groundwater analytical results, some in-well parameters were obtained by FTS from the ISBS wells on February 8, 2008, as shown in **Table 3.**

Table 3. ISBS Well Field Readings

	ISBS-1	ISBS-2
Temp ^{o}C	22.6	22.6
Turbidity (NTU)	24.7	24.7
DO (mg/L)	1.83	1.83
pH	6.02	6.02
ORP	-77.4	-77.4
Conductivity (mS/cm)	0.264	0.264

ISBS reagent injections were performed on January 22 through January 26, 2008 in the TIP and DIP Areas. The Adventus Group subcontracted Innovative Environmental Technologies (IET) of Pipersville, PA to perform the injections. Additionally, IET subcontracted Preferred Drilling Solutions (PDS) of Clearwater, FL to perform the GeoProbe work necessary for the well installations, soil borings, and advancing of injection tooling. IET's field report on the site injection activities is

included as **Appendix H,** and the Adventus injection summary is included as **Table 4**.

As a summary, the TIP injections were to be performed through two wells (TIP-3 and TIP-4) with a 10% RemOx EC solution. The DIP injections through GeoProbe tooling at 10 locations (DIP-1 through DIP-10) with a 4.5% RemOX EC solution.

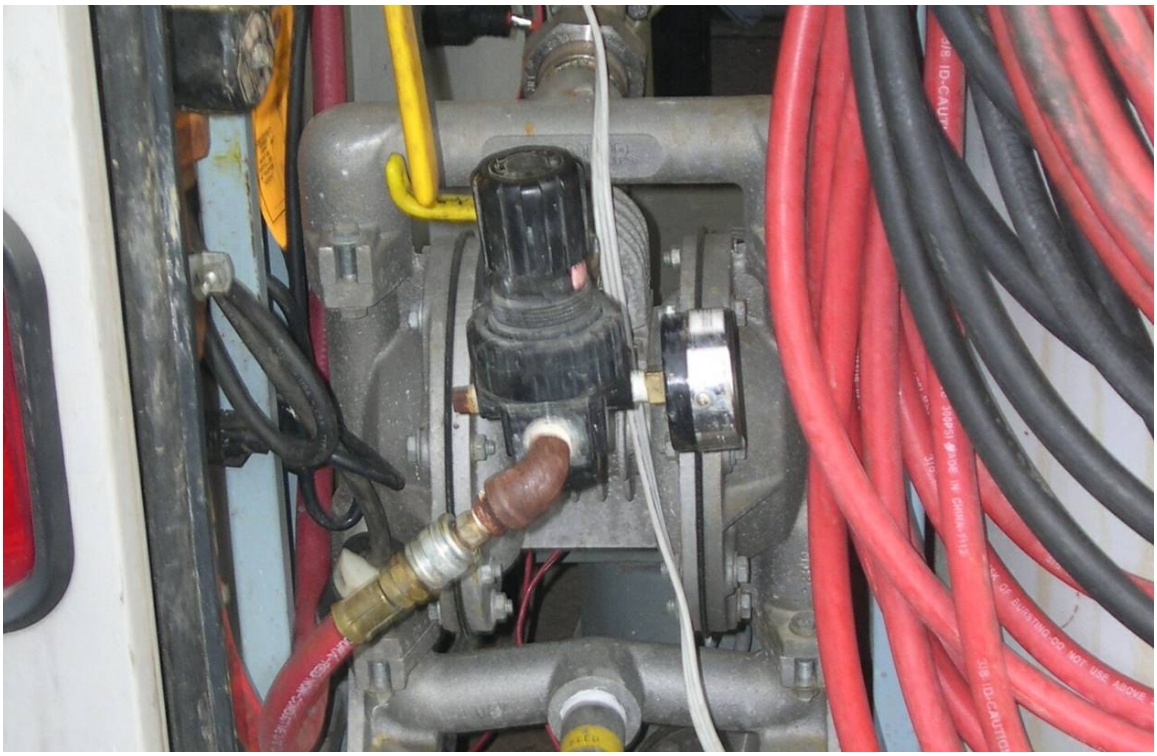
In performing the TIP injections, only a small volume of injectate (approximately 40 gallons) was successfully injected into TIP-4. ISBS reagent was successfully injected into TIP-3 (a total of 542 gallons). Relatively high injection pressures (*e.g.*, 200 psi) were observed at both TIP wells. Accordingly, a larger well screen slot size and coarser sand pack may be desirable for future injections through temporary wells. NAPL staining was evident in the geologic logs from both borings (**Appendix A**), making it otherwise difficult to surmise the differences in injectate acceptance.

Most of the information below is specific to the DIP injections, and supplements the information contained in the IET report:

- Injections proceeded at each DIP location from the deepest to the shallowest interval (bottom-up). When using the proprietary IET tooling (as shown in the IET report), this was an essential part of the process, as the tooling works by:
  1. Advancing rods to the final desired depth.
  2. Retracting the rods a short distance.
  3. Introducing a pulse of air to open the injection tool
  4. Injecting the amendments horizontally into the formation via vertical ports in the tooling .
- Given the water table depth of approximately 12' (**Appendix D**), and a depth to clay of just over 20' (**Appendix A**, logs from N-ISBS-2 and DB-1), the injection intervals were adjusted and the target volume of ISBS reagent injected at each location reduced from 620 gallons to 525 gallons.
- The final number of DIP borings increased from a planned 10 to 16 (**Figure 2)**.
- A small air-diaphragm pump was used to keep the injection flow rate as low as practical (**Figure 5**). Injection pressures generally ranged between 25 and 75 psi and were adjusted to achieve minimal maintainable flow rates, which ranged from approximately 2 to 10 gallons per minute (gpm), and averaged about 6 gpm. The air diaphragm pump was an essential piece of equipment, given the relatively high solids and low flow rate requirements of the job.

- Injections were completed using multiple rods in the ground concurrently (**Figure 6** – note multiple pipes in ground with valves closed). This was done to allow pressure to safely dissipate before pulling the tooling up to the next interval at a given location.
- In addition to the use of air pulses as described in the IET report, short air pulses were occasionally used at the first indication of daylighting (i.e., injectate coming to the surface). This worked particularly well at location DIP-5S, where the air pulse effectively terminated the daylighting, and allowed the injection to be completed.

Figure 5. Air Diaphragm Pump in IET Trailer



- Relatively speaking, the amount of daylighting increased as the work progressed, and was more frequent in injections at shallower depths. Accordingly, only deeper injections were performed at the last few injection points – which were also outside of the perimeter of the other injection points. (**Figure 2,** DIPs 13 to 16)
- All daylighted material was neutralized on site, typically using a mixture of water, dilute peroxide, and a dilute acid (vinegar or diluted hydrochloric acid). The greatest amount of daylighting observed occurred while injecting at DIP-

12. A summary of the DIP-12 daylighting neutralization is included as **Appendix I.**

- Composted cow manure was also used to neutralize daylighted RemOx EC, as the large amounts of organic matter within the manure are well-suited to safe and effective neutralization. In addition, neutralized manganese with composted manure effectively improves soil tilth and fertility, enhancing site restoration efforts.

Following the completion of ISBS reagent injections on January 26, 2008, seven verification borings (VBs) were installed on January 27, 2008 at the locations shown on **Figure 2**. Field screening of these borings was conducted to look for visual evidence of the potential presence of injected ISBS reagents within the cores. Summary screening logs are presented in **Appendix J**, and photographs of the cores are presented in **Appendix K**.

Figure 6. Injection Rods at Multiple Locations Concurrently

Prior to conducting the verification borings, it was envisioned that verification would be accomplished solely through the use of direct observation of injected purple color, as the RemOxEC and its sodium permanganate are a very strong purple in color. In addition, when this color was not immediately or directly evident in some of the site verification borings. RemOxEC neutralization solution as a potential indicator. In subsequent discussions with Carus Corporation representatives, we found that permanganate is oxidized from the strong purple color to black manganese dioxide in the course of about an hour in the presence of air and high oxidant demand.

Use of the neutralization solution in this way is based on the generation of visible gas bubbles in the neutralization reaction. The permanganate ion itself, MnO4, would generate bubbles of oxygen in the presence of the neutralizing agent as: 2MnO4- + 5H2O2 + 6H+ → 2Mn++ + 5O2 + 8H2O. In the presence of an organic compound (R), MnO4 reactions yield an oxidized intermediate (Rox) or CO2 plus MnO2, as R + MnO4- → MnO2 + CO2 or Rox. In the case of RemOxEC, this would be an intermediate step, as the ultimate goal is the generation of a Birnessite (an oxide of Mn and Mg) mineral crust, as (Na,Ca,K)(Mg,Mn)Mn6O14.5H2O.

The presence of MnO2 (Resulting from the R/MNO4- reduction) would be also be observable (as oxygen bubbles) in the presence of the neutralization solution, as MnO2 + 2H2O2 --> MnO2 + O2 + 2H2O, or more accurately as 2H2O2 --> O2 + 2H2O (because the MnO2 effectively acts as a catalyst). The bubble formation is not unequivocal, of course, as there are other reactions that may result in gas evolution. Accordingly, bubble formation on soil cores treated with neutralizer is used as an indicator of the potential presence of un- or partially- reacted permanganate.

To enable further discussion of the observations obtained from the verification borings (or VBs), **Table 5** provides an estimated injection radius of the verification borings from the nearest injection points. The most definitive information to be obtained from this data set can be drawn where purple RemOx EC intrusions are directly observed.

Such intrusions were observed in 3 of the seven VBs, VB-2, VB-3, and VB-7. In this regard:

- VB-2, VB-3, and VB-4 are a series of borings extending from the TIP-3 in the TIP area to DIP-2 in the DIP area. They suggest that the ROI from TIP-3 is at least 13’ and the ROI from DIP-3 is less than 7’.
- VB-7 is located within the DIP grid area, so specific conclusions about where material may have come from (especially given the large volume injected at DIP-16) are difficult to make.

- Generally, the most purple was observed at the bottom of these borings along the top of the clay surface, seemingly along more permeable materials, at depths slightly deeper than the injection intervals.

Based on the observations above, approximate boundaries of the TIP and DIP areas have been added to **Figure 7**. Less definitive, but still seemingly useful, is the neutralization reaction test. Some general observations from that are as follows:

- Black streaks in some cores were seemingly of NAPL, as the neutralization reagent resulted in product bubbles floating up in it (without bubble formation). In other cases (e.g., VB-7) , the black streaks may well have been MnO_2, a black oxide, as they reacted to the neutralizer.
- In one case, at VB-6, a neutralizer reaction was noted in surficial soils. This may be the result of previously neutralized daylighting from DIP-12 and DIP-11. In those areas, both neutralizer and manure were used to both neutralize RemOx EC and restore surficial soils.
- More specific observations are difficult to make without comparative testing on reference or control core (s).

Reasons for the apparently greater ROI for TIP vs DIP are injections are not definitively identifiable. However, some factors may include the varying injectate densities, injection volumes, and injection pressures. The Carus Chemical MSDSs show a specific gravity of RemOx EC (4.5%) of 1.05 to 1.10, and a specific gravity of 1.15 to 1.17 for the RemOx L-D (20%). The 10% RemOx EC solution that was prepared in the field would be expected to have a comparably elevated specific gravity. For reference, these MSDSs are included as **Appendix L**.

Shortly after completion of injection and verification activities, Field and Technical Services (FTS) staff working at the site informed us of the following (1/31/08):

> Water appearance was normal at ISBS-1&2. There was no water in TIP-4 (only purple sludge). The water in TIP-3 was purple with purple sludge at 9.10 feet. When I gauged UHG-EW01 (Key well) the entire water column was stained purple. The well screen in this well is located from 54.5 feet to 59.5 feet. This is a 64 foot deep extraction well. HG-10S did not have any purple stain and appeared normal with DNAPL in the bottom foot of the well.

And this on 2/6/08:

> Attached is a photo of the water in UHG-EW01. HG-10S, HG-10D, HG-18S, and HG-19S (all in close proximity to UHG-EW01 and injection area) contain no signs of purple.

A photo of the water in UHG-EW-01 is included as **Figure 8**, and relevant well logs are included as **Appendix M**. The recovery well log (i.e., UHG-EW-01) shows the clay at the base of the surficial aquifer to be 2 to 2.5' thick, with a sand intrusion. It also shows that a surface casing was set into this clay and that all casings were

grouted. In addition the water level in UHG-EW-01 is within a foot of that in adjacent Upper Hawthorne Group wells (**Figure 3**).

Thus, it shows no clear pathway for the RemOx EC to reach the Upper Hawthorne Group from the surficial aquifer. Some factors that may have enabled the RemOx EC to pass from the surficial aquifer into the Upper Hawthorne Group in this area may include:

- The thin clay with sand intrusions and oxidized mineral faces, is likely discontinuous. Note that the HG-18s/HG-19s log seemingly shows the clay to be only 6” thick.
- The relatively high density of the RemOx EC solution and evidence from the VBs that it followed the clay (discussed above), coupled with the presence of NAPL and tarry materials within the zone of injection may have effectively resulted in preferential flow paths towards discontinuities in the clay.

Figure 8. Water in UHG-EW-01 Following Injections

Although RemOx EC was not intended to be injected into the Upper Hawthorne Group during this initial pilot test, its presence at UHG-EW-01 is not seen as problematic in any way. This is because full-scale application of the technology would presumably entail treatment of the Upper Hawthorne Aquifer. The same mechanisms that make this treatment approach suitable for NAPL present in the surficial aquifer (i.e., oxidation and encrustation) also make it suitable for the Upper Hawthorne. The mineral crust formation properties of this injectate are designed to seal whatever cracks provided the pathways for its vertical migration in the first place.

Other Observations

All of the various borings conducted as part of the January 2008 work were properly abandoned. The DIP borings and DB-3 were abandoned using standard bentonite chips and/or HoleBlok. A photo of the HoleBlok being added to a boring is included as **Figure 9**, and an information sheet on the product is included as **Appendix N**. A total of 11 bags of HoleBlok and 2 bags of bentonite chips were used in the course of abandoning these borings. The verification borings were generally abandoned using neat cement, with the exception of VB-1. VB-1 was partially filled with bentonite chips, and neat cement grout was utilized from the top of the chips to the surface.

Figure 9. HoleBlok Addition to a DIP Boring

Investigation derived waste (IDW) disposal was handled by FTS in support of Adventus operations. FTS IDW disposal activities addressed proper disposal of soil cuttings, development water, and personal protective equipment (PPE). In addition, FTS properly neutralized RemOx EC product containers at the site prior to off-site disposal.

Following completion of injection and surveying activities, FTS staff addressed heavy rutting in the area with some grading, topsoiling, and seeding in the injection areas.

In accordance with the Adventus Health and Safety Plan for the site, PID readings were obtained at intervals in the breathing zone of site workers, especially during periods when borings were being advanced (i.e., worst-possible conditions). No readings above the site background of 0.0 PPM were observed.

ONGOING WORK ELEMENTS

Soil core leachable COI assessments are currently being conducted. Results will be reported in a subsequent report.

In accordance with the final variance, groundwater sampling will continue to be conducted at M-1, M-14, and ZOD-1 for one year following injection. The next such sampling event was conducted concurrently with the March 2008 ISBS soil core collection. Thereafter, sampling will be conducted quarterly for one year from the time of the injections.

In addition, due to the observed presence of ISBS reagents in UHG-EW-01 (as indicated by purple coloration) we have initiated concurrent monitoring of UHG-MW-2S, HG-10S, HG-10D, UHG-MW-16S for the same variance parameters and analytes as for M-1, M-14, and ZOD-1 (**Figure 3**) These data will serve to document that the impacts to the Upper Hawthorne Group are spatially limited and, as described above, potentially beneficial in their ability to block vertical migration pathways.

Post-treatment monitoring cores were collected at 8 and (optionally) at 16 weeks following ISBS reagent injections. Accordingly, based on injections having been conducted the week of January 20, 2008 the Phase II cores were collected the week of March 16, 2008 and the optional Phase III cores would be collected the week of May 11, 2007. The approximate, planned locations for collection of these cores are as shown on **Figure 10** (for TIP locations) and **Figure 11** (for DIP locations). Additional reports on these activities will be prepared following completion of the related work efforts.

References

Adventus Group, 2008. Final Field Activity Plan, Revision 3: Field-Scale Testing of in-situ Biogeochemical Stabilization, Cabot Carbon / Koppers Superfund Site, Gainesville, Florida (FAP), dated February 5, 2008.

FDEP, 2008. Florida Department of Environmental Protection Final Order Granting a Variance, OGC Case Number 07-1825, Done and Ordered January 14, 2008 by Janet G. Llewellyn, Director, and provided to James G. Mueller, President of Adventus Americas, Inc. on January 16, 2008 by Cathy McCarty, DEP.

GeoTrans, 2004. Addendum 6: Groundwater Flow and Transport Model, Draft Report, Koppers Inc. Site, Gainesville, Florida, October 5, 2004.