DEMONSTRATION OF DISTRIBUTION OF ACTIVATED CARBON IN FINE-GRAINED GEOLOGY RESULTING IN BTEX AND NAPHTHALENE CONCENTRATION DECREASES IN SOILS (AQUIFER SOLIDS) LEADING TO REGULATORY CLOSURE: NO FURTHER ACTION

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BACKGROUND/OBJECTIVES

Remediating contaminants sorbed to low-permeability, fine-grained clays is a complex task, requiring a deep understanding of initial contaminate entrainment and the subsequent long-term diffusion-controlled release back into transmissive zones. Without appropriate intervention, source depletion may require decades to centuries. Our work at a former retail petroleum site (site), which had been an open case for over 20 years, exemplifies this complexity. The mean initial benzene concentration was 383 μg/Kg, while m/p-Xylene was 20 mg/Kg in aquifer solids. Geologically, the site is characterized by 15-20 feet deep silty and sandy clays with occasional chert layers overlying Upper Mississippian aged Salem and Warsaw limestones. The soils were soft to wet, beginning approximately 6-8 feet below the ground surface (bgs). In situ injection of an activated carbon slurry was selected to enhance permeability, alter the diffusion gradient, and increase the advection-dispersion of site clays and silts.

APPROACHES/ACTIVITIES

The site was injected using a positive displacement pump at a volumetric flow rate of approximately thirty-five gallons per minute. Injections were completed at specific depths rather than across intervals. Injections were initiated at about 6 feet and continued in a top-down manner. Vertical injection intervals were spaced every two feet. Individual injection points were horizontally spaced five feet apart. At one month post-injection, twelve continuous soil borings were advanced next to existing site monitor wells, and an additional twenty-eight borings were advanced throughout the injected area for a total of forty soil borings. One hundred twenty soil samples were analyzed for BTEX and naphthalene. The soil cores were visually inspected for activated carbon inclusions and by brightfield microscopy. The inclusions were logged lithology. Pictures were taken to document the distribution of carbon in various soil types and along bedding interfaces. A survey was used to accurately define the locations and elevations of all wells and soil bores. Site remedial progress was characterized by post-injection water samples collected from 42 monitoring wells, installed in a grid pattern, distributed within ≈ 18,000 square feet. ArcGIS and RockWorks17 were employed to present the logged core data. At 40 months, the site was again extensively cored, and soil and aquifer samples were collected and analyzed for site contaminants. The Commonwealth of Kentucky independently collected and logged cores for activated carbon inclusions. In 2020, 2022, and 2023, additional soil cores were collected as directed by the regulatory agency.

RESULTS/LESSONS LEARNED

Core log descriptions and photographs document the presence of activated carbon in each of the forty soil borings, indicating carbon distribution throughout the injection field. Laboratory analysis confirmed activated carbon inclusions in the soil cores. Both visual examination and ArcGIS and RockWorks17 models offer corroborating depictions of carbon distribution. Mass and probability calculations further support distributional models. No significant balling, clumping, or generalized distribution failures were noted in this study. Groundwater data and soil sampling demonstrated reduced petroleum impact. All examined site contaminants (BTEX and naphthalene) sorbed to the soils and aquifer materials significantly decreased, as the Wilcoxon-Mann-Whitney test shows. This study indicated that the injection of activated carbon resulted in the remediation of fine-grained media. The site received a regulatory no further action determination in 2022.

FORMER UST FACILITY, RUSSELL SPRINGS, KY

- UST Closure 2000 and 2001 (in-place)
- Site Investigations 2002 thru 2013
- No previous remediation efforts, besides tank closure, before BOS 200® in situ injection.
- Benzene concentrations
- Soil high ≈ 16 ppm
- Water high ≈ 9 ppm
- Bedrock ≈ 18 ft in the treatment area
- 15-20 feet deep silty and sandy clays with occasional chert layers overlying Upper Mississippian aged Salem and Warsaw limestones.
- The soils were soft to wet, beginning 6-8 feet below the ground surface (bgs).

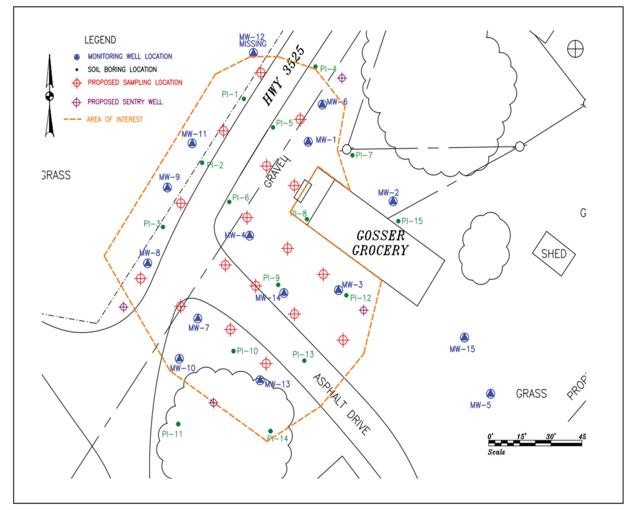


Illustration 1. The former UST facility had pumps directly in front of the marked building. The tanks were to the south on the side of the building. The release occurred at the pump island. Significant contamination in the near-surface soils (1 to 4 ft) around the pump island was left in place and intentionally not treated. Additional contamination was untreated under Hwy 3525.

STRATIGRAPHICFENCEMAPSHOWINGINTERCALATED CLAYS AND CLAYEY SANDS

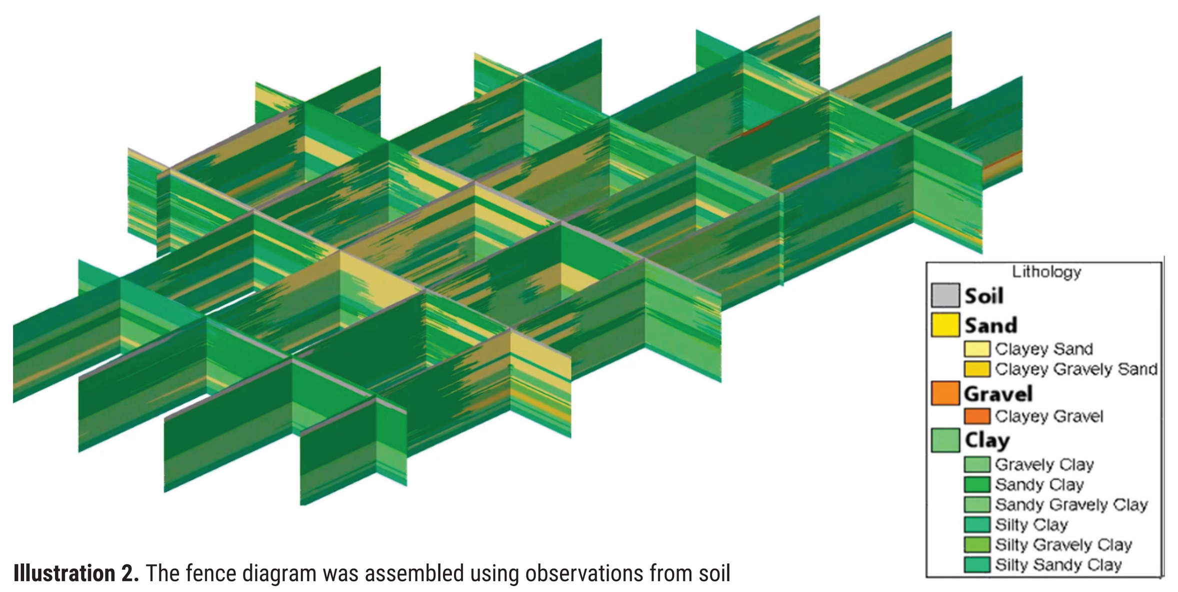


Illustration 2. The fence diagram was assembled using observations from soil core logging, ArcGIS, and RockWorks 17. The clay sands and clayey gravely sands were heaviest around the pump island, the point of the release.

IN SITU INJECTION POINTS MAPPED

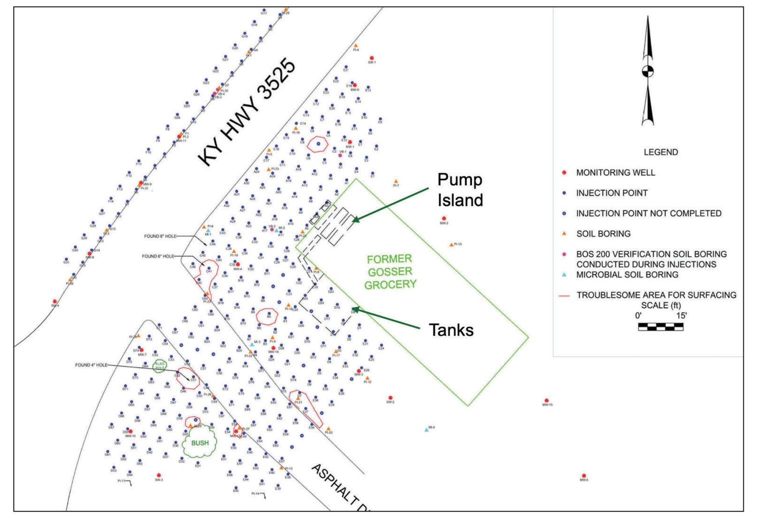


Illustration 3. The in-situ injection points for BOS 200® were laid out on a triangular grid with 5 ft centers. Injection proceeded from the surface to the bedrock, injecting at two-foot intervals. The injection intervals were interlaced between adjacent points.

Interlaced injection intervals

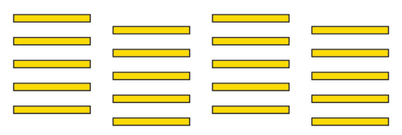


ILLUSTRATION OF THE SOIL CORES COLLECTED AND MODELED STRATIGRAPHY

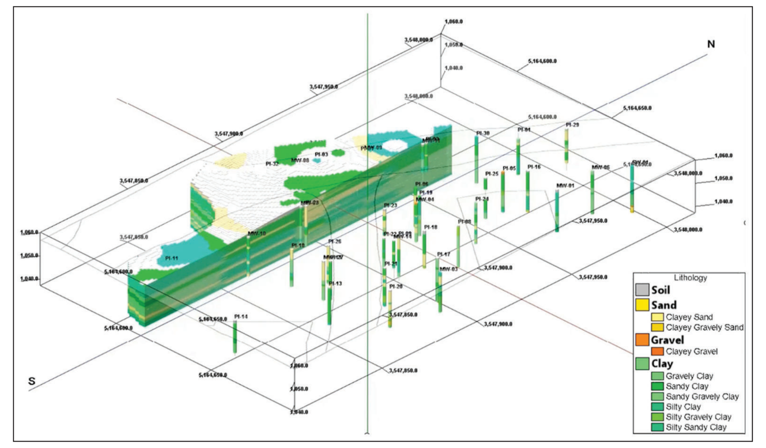


Illustration 4. Over 40 soil cores were logged. The resulting data were used in ArcGIS and RockWorks17 to build a stratigraphy model. The model was used to inform in situ injectate loading.

MODEL OF ACTIVATEDCARBON INCLUSIONSASSEEN IN CORES LOGGED

Observed BOS 200® Inclusions

- Suspect Carbon
- Specks
- Spots
- Smears
- Even Distribution
- Heavy Distribution
- Vertical Seams
- Horizontal Seams

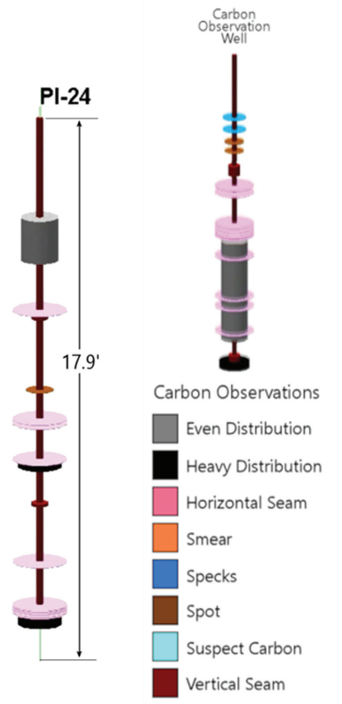


Illustration 5. At 40 months, the site was extensively cored and logged for activated carbon inclusions. The observed inclusions were cataloged and modeled using ArcGIS and RockWorks17.

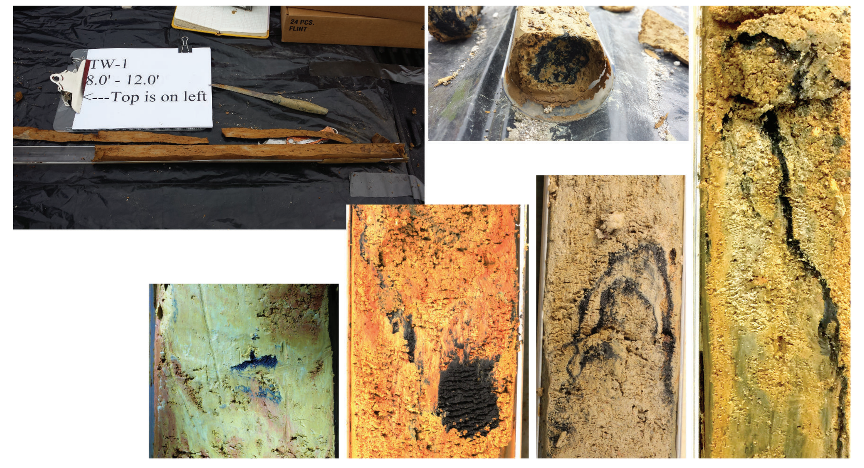
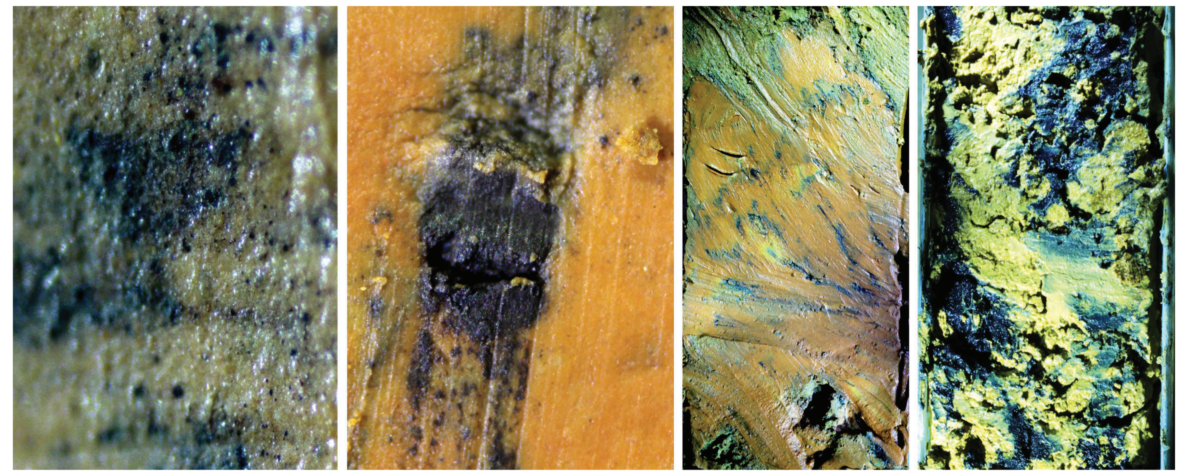


Illustration 6. While examining the core for BOS 200®, the cores were inspected visually and with a brightfield microscope. Photographs were taken to help catalog the types of inclusions.



QUANTIFICATION OF CARBON SIGHTINGS

Carbon Count by # of Inclusion within 40 Cores by Depth		6-8 FT	8-10 FT	10-12 FT	12-14 FT	14-16 FT	Sum of Inclusions per Category	Percent of Total Sightings
Carbon Present	X≥1	32	32	31	26	29	150	55%
% by Interval	%	80%	80%	77.50%	65%	72.50%		
	X≥2	14	20	15	7	18	74	27%
	%	35%	50%	37.50%	17.50%	45%		
	X≥3	4	9	5	3	11	32	12%
	%	10%	22.50%	12.50%	7.50%	27.50%		
	X≥4	2	3	1	0	4	10	3%
	%	5%	7.50%	2.50%	0	10%		
	X≥5	1	1	1	0	1	4	1%
	%	2.50%	2.50%	2.50%	0	2.50%		

Visual Carbon: Sum of Cores		6-8 FT	8-10 FT	10-12 FT	12-14 FT	14-16 FT	Total	
TOTAL Sightings per depth for all cores:		53	65	53	36	65	272	
% OF TOTAL:		19%	24%	19%	13%	24%		

Illustration 7

Top Chart Summary
Each core had between 65 to 80% probability of visually demonstrating carbon (Row data highlighted in yellow). 55% of all inclusions were single, while 1% demonstrated 5 or more inclusions. See "Percent of total sightings" column.

Bottom Chart Summary
Each of the 5 intervals demonstrated between 13 to 24% of the total carbon identified (20% would be equality)

Even Distribution
Demonstrates that BOS 200® is reasonably evenly distributed both vertically and horizontally.

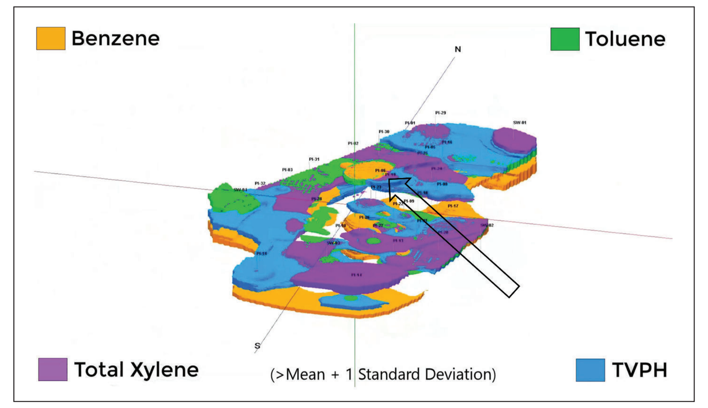
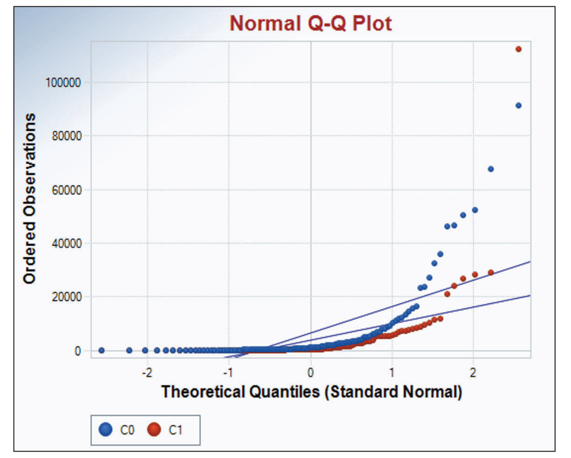


Illustration 8. The colors are concentrations of BTEX. If the concentration is greater than the mean concentration for the constituent plus one standard deviation, then the area is presented in color or that constituent.

In the area of the original release, the pump island, significant contamination in the near-surface soils (1 to 4 ft) was left in place. This contamination continued to impact groundwater post-treatment. Having this source in place was intentional. We were interested in examining the influence of a continual contamination source on the BOS 200®.

ETHYLBENZENEINAQUIFERSOIL40MONTHS POST IN SITU INJECTION OF BOS 200®

Wilcoxon-Mann-Whitney Test
Co, site initial, C1, site post-emplacement



Raw Statistics		Pre-emplacement	Post-emplacement
Number of Valid Observations		120	120
Number of Distinct Observations		115	109
Minimum		0.25	0.25
Maximum		91100	112000
Mean		6285	3628
Median		866.5	215.5
SD		14165	11431
SE of Mean		1293	1044
H0: Mean/Median of Pre-emplacement <= Mean/Median of Post-emplacement			
Sample 1 Rank Sum W-Stat		16133	
Standardized WMW U-Stat		3.109	
Mean (U)		7200	
SD(U) - Adj ties		537.8	
Approximate U-Stat Critical Value (0.05)		1.645	
P-Value (Adjusted for Ties)		9.38E-04	
Conclusion with Alpha = 0.05			
Reject H0, Conclude Pre-emplacement > Post-emplacement			

Illustration 9. At 40 months post-in situ injection of BOS 200®, soil samples were collected and analyzed for BTEX, Trimethylbenzene, and naphthalene. The results were compared to the pre-injection soil sample. 120 soil samples from each dataset were examined by the Wilcoxon-Mann-Whitney test. For ethylbenzene, the mean was 1.7-fold lower, the median 4-fold lower, and the p-value ≈ 0.001.

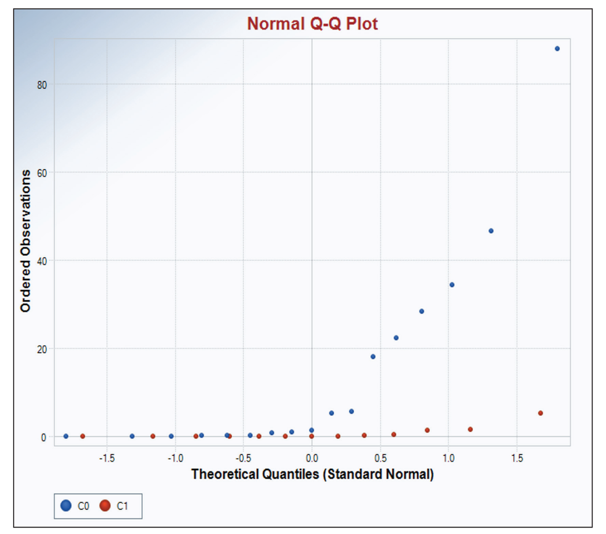
BTEX PLUS AT 40 MONTHS POST-EMPLACEMENT

Constituent	Median Difference	p value	1/2-life in years
Benzene	3.6-fold lower	0.0009	0.48
Toluene	1.5-fold lower	0.0018	1.16
Ethylbenzene	4.0-fold lower	0.00089	0.43
m/p Xylene	2.2-fold lower	0.0091	0.79
o-Xylene	2.5-fold lower	0.019	0.69
1,2,4-TMB	1.2-fold lower	0.0289	1.44
Naphthalene	3.5-fold lower	0.0018	0.50

Illustration 10. Using the methodology described in illustration 9, the measured decrease in constituent concentrations between pre- and post-in situ injection is significant. The half-life calculations were based on the same data.

ETHYLBENZENE IN AQUIFER SOLIDS FROM 2ND INDEPENDENT DATASET COMPARING 2018 TO 2020

Wilcoxon-Mann-Whitney Test
2018 (C0) to 2020 (C1)



Raw Statistics			2018	2020
Number of Valid Observations			17	13
Number of Missing Observations	Non-detects		8	12
Number of Distinct Observations			17	12
Minimum			0.00295	0.0025
Maximum			87.9	5.25
Mean			14.8	0.672
Median			1.23	0.0254
SD			23.77	1.476
SE of Mean			5.766	0.409
H0: Mean/Median of 2018 Samples <= Mean/Median of 2020 Sample				
Sample 1 Rank Sum W-Stat			322	
WMW U-Stat			169	
Mean (U)			110.5	
SD(U) - Adj ties			23.89	
WMW U-Stat Critical Value (0.05)			150	
Standardized WMW U-Stat			2.428	
Approximate P-Value			0.0076	
Conclusion with Alpha = 0.05				
Reject H0, Conclude 2018 Samples > 2020 Samples				

Illustration 11. Additional samples were collected during roughly the same timeframe by the primary contractor and sent to a different laboratory than the data presented in illustrations 9 & 10. Ethylbenzene analytical results support the analysis given in 9 & 10.

INDEPENDENT DATASET COMPARING 2018 TO 2020

Constituent	Median Difference	p value
Benzene	27-fold lower	0.007
Toluene	122-fold lower	0.0018
Ethylbenzene	48-fold lower	0.00089
m/p Xylene	635-fold lower	0.0091

Illustration 12. This dataset was much smaller (x ≈ 25) than the dataset in 9 & 10. The samples were collected by the primary contractor for regulatory compliance. Given the small sample size and the inability to replicate a collected soil sample, the median fold difference should only be seen as confirmation of the data in 9 & 10, not as being reliable in magnitude and direction. These samples were only analyzed for BTEX.

SUMMARY

- Distribution of activated carbon by in situ injection is demonstrated.
- Distribution statistics indicate that carbon inclusion occurrences are predictable, but inclusion types vary greatly.
- Observations indicate that carbon often tracks the interface between different soil textures.
- Extensive sampling of the aquifer soils (soils) demonstrates significant decreases in BTEX and other petroleum constituents.
- Groundwater sampling also demonstrated significant decreases and was the basis for Site No Further Action. No groundwater data was presented, as the purpose of this poster is to present soil (aquifer solids) data.
- Significant contamination was not treated in the soils from 0 to ≈ 5 ft around the historic pump island and under the highway. Despite this the site did remediate and received regulator No Further Action.