EVIDENCE OF EFFICACY OF ACTIVATED CARBON INJECTION FROM HYDROCARBON SITES A CROSS-SITE EXAMINATION OF FIELD DATA ASSESSING THE EFFECTIVENESS OF ACTIVATED CARBON INJECTIONS WITH EMPHASIS ON SUBSURFACE DISTRIBUTION, DECREASES IN CONTAMINATE CONCENTRATIONS IN AQUIFER MATERIALS, MICROBIAL POPULATION CHANGES, GASES PRODUCTION, DIFFERENTIAL ISOTOPES, AND MICROSCOPIC LOCATION OF MICROBES.

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INTRODUCTION

BOS 200[®] is an activated carbon-based remediation product for treating petroleum hydrocarbons in the subsurface. It was the first activated carbon-based product for hydrocarbons on the market, and it has been employed on hundreds of sites for over twenty years. Data has been collected on the efficacy of BOS 200[®] from sites across the U.S. and multiple other countries. RPI has collected some of the data, but much of the data has been provided by contractors and states. The purpose of this poster is to present some of that data.

DECREASE IN ELECTRON ACCEPTORS POST-BOS 200[®] EMPLACEMENT



DECREASE IN TPH & BENZENE POST-BOS 200+[®] EMPLACEMENT



The red arrow marks the injection of BOS 200[®]. As denoted by the blue arrow, the PHC concentrations in the groundwater decrease rapidly as the PHCs absorb in the AC of the CBI. The orange arrow marks the beginning of the re-equilibration of the lower heat of adsorption benzene versus the higher heat of adsorption PHCs. Biodegradation initiates early post-BOS 200[®] emplacement but does not dominate the PHC concentration pattern until the final stages of site remediation (approximately noted by the green arrow).



Electron acceptors at a site where BOS 200[®] was installed. Nitrate concentrations dropped first, followed by a slight rise in nitrite. Sulfate concentrations persisted longer. Benzene concentrations were added to the graph for comparison purposes.

INCREASE IN GASES LINKED TO MICROBIAL METABOLISM

Prior to injection, which was completed in June of 2015, gases, except for methane, were not detected above detection limits. Three months post-CBI emplacement, the concentration of gases linked to microbial metabolism like methane, n-Butane, and iso-Butane rose. Gases such as cis-2-Butene, propane, ethane, t-2-Butene, 1-Butene, and iso-Butylene (data not displayed) exhibited similar patterns.

NAPHTHALENE IN AQUIFER SOIL AT **40 MONTHS**



The left graph shows that naphthalene decreased in concentration in aquifer solids post-CBI, in situ emplacement. The raw statistics, presented in the table on the right, record decreases in measures of central tendency and variance for the 2020 naphthalene dataset. Wilcoxon Mann Whitney test demonstrates that there is less than a 0.002 chance that an additional collected sample from the 2020 data would be as large or larger than the 2016 mean/median. Naphthalene was not the only constituent examined. Samples were collected before and after CBI emplacement and analyzed for BTEX, naphthalene, and trimethylbenzene. The graphs and the raw statistics for the other constituents were consistent with those presented for ethylbenzene. The next table presents a summary of the data for all constituents examined. The median difference was between the 2016 and 2020 datasets.

HALF-LIFE OF PHCS IN SOIL AT 40 MONTHS **POST-EMPLACEMENT**

Constituent	Median difference from initial concentration	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

The table presents PHC concentrations in aquifer solids post-BOS 200[®] in situ emplacement. The values presented in the table record change in the 2020 data versus the 2016 data. Samples were collected before and after BOS 200[®] emplacement and analyzed for BTEX, naphthalene, and trimethylbenzene. Table presents a summary of the data for all constituents examined for which naphthalene was given as an example. The number of samples for each dataset was 99 or more.

Raw Statistics	Pre-emplacement	Post-emplaceme		
Number of Valid Observations	99	99		
Number of Missing Observations	1	1		
Number of Distinct Observations	95	93		
Minimum	39.2	0.25		
Maximum	24900	35000		
Mean	3806	2148		
Median	1550	1010		
SD	5481	4114		
SE of Mean	550.9	413.5		
H0: Mean/Median of Pre-emplacement <	= Mean/Median of Post-em	placement		
Sample 1 Rank Sum W-Stat	11027			
Standardized WMW U-Stat	2.916			
Mean (U)	4901			
SD(U) - Adj ties	403.2			
Approximate U-Stat Critical Value (0.05)	1.645			
P-Value (Adjusted for Ties)	0.00177			
Conclusion with Alpha = 0.05				

THE MICROBIAL POPULATION INCREASES **16S QUANTIFICATION**



The total number of bacteria increase post-emplacement of BOS 200[®] relative to controls.

QUANTARRAY[®]-PETRO DATA 5 MONTHS POST-BOS 200[®] EMPLACEMENT



QuantArray[®]-Petro data from a site where CBI was injected. Microbes having selected genes associated with both aerobic and anaerobic petroleum hvdrocarbon metabolism increased in number relative to background. The increase was higher at 5 months postemplacement than at 1 month.

$\delta^{13}C \ge 2^{\circ}/_{\circ\circ}$ FROM AQUIFER MATERIALS



Soil samples were collected from a BOS 200[®] emplacement on a petroleum release site. Points below the red line are upgradient of the BOS 200[®] emplacement. Points above the red line are samples collected with the PBR emplacement. The difference between three of the four points exceeds $\delta 13C \ge 20/00$. This is also consistent with published values for nitrate, sulfate-reducing cultures, and methanogenic cultures (2 to 3.5 o/oo). Mancini et al., 2003, Fischer etal., 2008. $\delta 13C \ge 20/00$ is indicative of biodegradation (Hunkeler, 2008).



THE MICROBIAL POPULATION IS ENRICHED IN THE **SEAMS OF ACTIVATED CARBON IN PREFERENCE TO** NATIVE SOILS (AQUIFER SOLIDS)





These pictures were taken with a confocal microscope at 10x. The fluorescence is from bacteria embedded in clay aquifer solids collected from a petroleum hydrocarbon site post-BOS 200[®] in situ injection. The dark areas are clay and demonstrate less fluorescence due to having fewer bacteria. The bright regions have more fluorescence and are BOS 200[®] activated carbon. The BOS 200[®] has more bacteria on its surface than does the surrounding clay soils.

CONCLUSION

This poster has presented a compact summary of the data types supporting the degradation of PHCs post-BOS 200[®] emplacement. PHC concentrations decrease. Supplied electron acceptors are consumed. Gases associated with microbial degradation are produced. The half-lives of PHCs in the soil and aquifer materials are notably improved – degradation occurs faster than that reported in the literature. The total bacteria increase and genes associated with PHC degradation are identified in the microbial population post-BOS 200[®] emplacement. The carbon isotope data is indicative of biodegradation. The increased microbial growth on the BOS 200[®] activated carbon base in preference to soil is evident in confocal images.