EVIDENCE OF THE PROLIFERATION OF NATIVE PETROLEUM REDUCING BACTERIA SUBSEQUENT TO APPLICATION OF CONTROLLED IN-SITU CHEMICAL OXIDATION

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ABSTRACT: Rapid remediation of petroleum contaminated soil and groundwater at a gasoline station in Florida occurred following treatment using a controlled in-situ chemical oxidation process. Two main processes were thought to be responsible for the rapid and substantial decreases in petroleum contaminant mass in both the soil and groundwater at a site in Bonifay, Florida. Soil and groundwater sampling confirmed a significant increase in petroleum reducing bacteria following the injection of a controlled in-situ chemical oxidation process. Soil and groundwater contaminants had impacted significant areas on the site owner's property and areas beneath an adjacent highway where underground fiber optic, water, and storm sewer utilities exist. A remedial strategy had to be selected which would assure that these utilities would be protected from physical and corrosive damage during any remediation process. One chemical oxidation process that could rapidly reduce/oxidize petroleum contaminants (BTEX, MTBE and PAHs), that would not adversely effect utilities, undermine roadway structures, and which could also enhance biologic degradation of residual contaminants was chosen. This process (the BIOX® Process – an In-Situ Chemical Oxidation/Biologic Enhancement process) already had a FDEP Underground Injection Control variance for use at petroleum sites in Florida. Time and cost limitations eliminated consideration of other conventional and innovative technologies. Post injection soil and groundwater analytical results confirm that soil contaminants were reduced below the FDEP's CTLs and that dissolved groundwater contaminants were reduced below the FDEP's Natural Attenuation default CTLs rapidly in most wells. Ringed petroleum contaminants (BTEX, PAHs) and MTBE concentrations decreased and long chained hydrocarbons (TRPHs) remained following injection of the BIOX® reagent. An environment rich in organic material and dissolved oxygen with a neutral pH was then present (well suited for biologic reduction). Laboratory data confirmed that substantial and sustained increases in population of native petroleum reducing bacteria had occurred. These results have also been repeated at another petroleum cleanup site and similar results can be anticipated where similar chemical oxidation/biologic enhancement treatments are to be performed.

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INTRODUCTION

A remedial design to rapidly address or eliminate petroleum contaminants in soil and groundwater was necessary in order for remediation to continue. AET was tasked to eliminate petroleum contaminants which still were being detected at unacceptable levels in the groundwater at a former gas station following years of assessment and remedial efforts which were unable to eliminate or even substantially reduce petroleum contaminants sorbed to tight silty/clayey soil at this site. Attempts to pump and treat or enhance biologic degradation in-situ with horizontal trenches provided some benefits but the remediation system operation had many problems and was discontinued. Once AET, LLC took over site remediation, it was decided that one remedial technology (remediation process) was on the FDEP BPSS's web site which could potentially reduce soil and groundwater contaminant concentrations quickly, safely, cost effectively and which already had been issued an Underground Injection Control Variance by the Florida Department of Environmental Protection for use at sites contaminated with petroleum products. AET received approval to inject chemical oxidants using the BIOX® Process with the optimistic goal of remediating the remaining soil and groundwater contaminants in and around active underground petroleum storage tanks and pump islands. Assessment and remediation reports indicated that an area of approximately 5,000 cubic yards of soil and groundwater required treatment.

SITE CONDITIONS

High concentrations of petroleum contaminants (BTEX, MTBE and Napthalenes) were present in the soil and groundwater primarily on the eastern portion of the property and migrating primarily to the northeast. In addition other locations across the site have elevated levels of dissolved petroleum contaminants that are above the GWCTLs and need to be addressed. It was agreed that the site's difficult lithology (silt, silty clays, and clay), inherent limitations of standard remediation techniques and the general condition of the operating gas station/store that the injection of BIOX® was a reasonable alternative that FDEP could accept with written justification in a Limited Scope Remedial Action Plan (LSRAP).

The BIOX® process is an accepted chemical injection technique that can be used at active sites and near underground utilities. The process initially chemically degrades petroleum contaminants. Such chemical destruction is buffered and can be accomplished at a pH >7 and is designed to continue for several months. The process generates oxygen

which is expected to raise dissolved oxygen levels and enhance natural biologic degradation surrounding the initial inject points while the chemical oxidation is also occurring. Once the BIOX® reagent concentration reaches a level where chemical oxidation is no longer the primary mechanism of petroleum contaminant destruction, it will still be slowly reacting and releasing oxygen to the groundwater for several more months. This stimulates growth of natural organisms which use the oxidized petroleum contaminants as food to further reduce residual petroleum contaminants that are slowly released from the petroleum contaminated soil. This innovative treatment process rapidly reduces petroleum contaminant concentrations in the soil and groundwater and continues to reduce any residual petroleum contaminants leaching from the soil for several months.

The initial goal of the LSRAP was to reduce groundwater contaminant concentrations to the "Natural Attenuation" default cleanup criteria established in Table V of Chapter 62-777, Florida Administrative Code within six months and ultimately (one year or less) to the "Groundwater of Low Yield/Poor Quality" cleanup criteria in Table I of Chapter 62-777, F.A.C.

BIOX® APPLICATION ACTIVITIES

Application of the chemical oxidant BIOX® was initiated at the site on July 15, 2002 and was completed on August 2, 2002 (three (3) weeks total). The liquid oxidant mixture was injected at five (5) foot centers at predetermined areas across the site. A maximum radius of influence of up to five (5) feet was determined based on the tight soil types associated with the site. The BIOX® reagent was injected using a GeoProbe^{R} direct push technology (DPT) rig.

A total of approximately 13,027-gallons of BIOX® reagent were injected at 223 points across the site. Four (4) discrete areas of the site were treated. Area #1, located around the underground storage tank pit, the eastern pump island and in the vicinity of MW-22 along the east right-of-way of McGee Road, was treated with approximately 11,650-gallons of the BIOX® reagent at 177 injection points. Area #2 of the site, located along the south, southwest and west sides of the existing building, was treated with approximately 431-gallons of reagent at 15 injection points. Area #3, located along all four (4) sides of the northern pump island, was treated with 810 gallons of reagent at 23 injection points and Area #4, located around monitor wells, MW-33 and MW-28, was treated with 136-gallons of reagent at 8 injection points. **Figure 1** shows the locations of the injection points installed at the site and the groundwater monitoring wells. The volume of the BIOX® reagent introduced into the individual injection points ranged from 17-gallons to 250 gallons. The degree of treatment was based on the mass of contaminants known to be present in the respective treatment areas as well as the degree of reaction observed during injection process.

POST INJECTION SOIL & GROUNDWATER SAMPLING & ANALYSES

Additional groundwater and soil samples were collected at the site on August 1 and 2, 2002, respectively. Groundwater samples were collected from monitor wells CW-3, CW-4, MW-8, MW-12 and MW-30 and analyzed for BTEX, MTBE, PAHs and TRPHs (FL-

PRO). Soil analytical samples were collected adjacent to monitor wells CW-4, MW-29 and MW-30 at 1-ftbls and 2-ftbls for TRPH and bacterial analysis. Groundwater sample collection activities performed under a FDEP Work Order # were collected prior to injection of chemical oxidants and have been collected as close to quarterly as possible since July of 2002 from monitoring wells, MW16, MW17, MW18, MW21 MW28, CW1, CW2, CW3 and CW4. All nine (9) monitoring wells were analyzed for the presence of BTEX, and MTBE. In addition, CW1 through CW4 were analyzed for the PAHs, Sulfates, Nitrate-Nitrogen, Iron, Lead and Total Dissolved Solids (TDS). The work order called for the collection and analysis of soil and additional groundwater samples during the third month (i.e., November 12, 2002) of post remedial action monitoring. A decision was made between AET and the FDEP Project Manager to wait a few more months before collection of the soil and additional groundwater samples. Groundwater samples have been collected on June 25, 2002, September 5, 2002, October 1, 2002, November 12, 2002, April 5, 2004, and July 27th, 2004. **Table 1** summarizes bacteriological data collected. **Chart 1** shows the average groundwater analytical results for the milestone compliance wells.

Conclusions

1) AET, LLC has collected pre and post chemical oxidation/biologic enhancement treatment data which confirms that:
   A) Groundwater petroleum contaminant concentrations have been significantly reduced in most monitoring wells both onsite and offsite within three to six months,
   B) Levels of BTEX, PAHs and MTBE were dramatically reduced in all wells, except for two source wells where additional (possibly continuing) problems could be occurring. The reduced contaminant concentrations have remained near or below the FDEP Natural Attenuation Default Cleanup Target Levels. However continued reduction in these wells appears to still be continuing.
   C) Soil contaminant concentrations have been significantly reduced and such reduction has been maintained for one year. Total recoverable petroleum hydrocarbon (TRPH) concentrations have been reduced significantly at all locations and depths where sampling was performed. Only one source soil sample (highly contaminated area – CW-3) had petroleum contaminants (benzene) still above the leachability soil cleanup target level, at a depth just into the shallow water table. No contaminant concentrations above the SCTL's were detected in vadose zone soil.
   D) Petroleum reducing bacteria counts increased from average counts of ~447, 66,889, 22,917 and 2,353 (July/August 2002, February 2003, September 2003 and July 2004 respectively) from nine locations. This data confirms a sustained and substantial increase in petroleum reducing bacteria counts following remediation using controlled chemical oxidation and biologic enhancement treatment at this site.
   E) AET has documented that total BTEX, in five milestone wells, have been reduced to levels below that were to be achieved in up to three years, during the first year of Post Active Remediation Monitoring.

REFERENCE: Florida Department of Environmental Protection, Chapter 62-770 and Chapter 62-777, Florida Administrative Code.

FIGURE 1

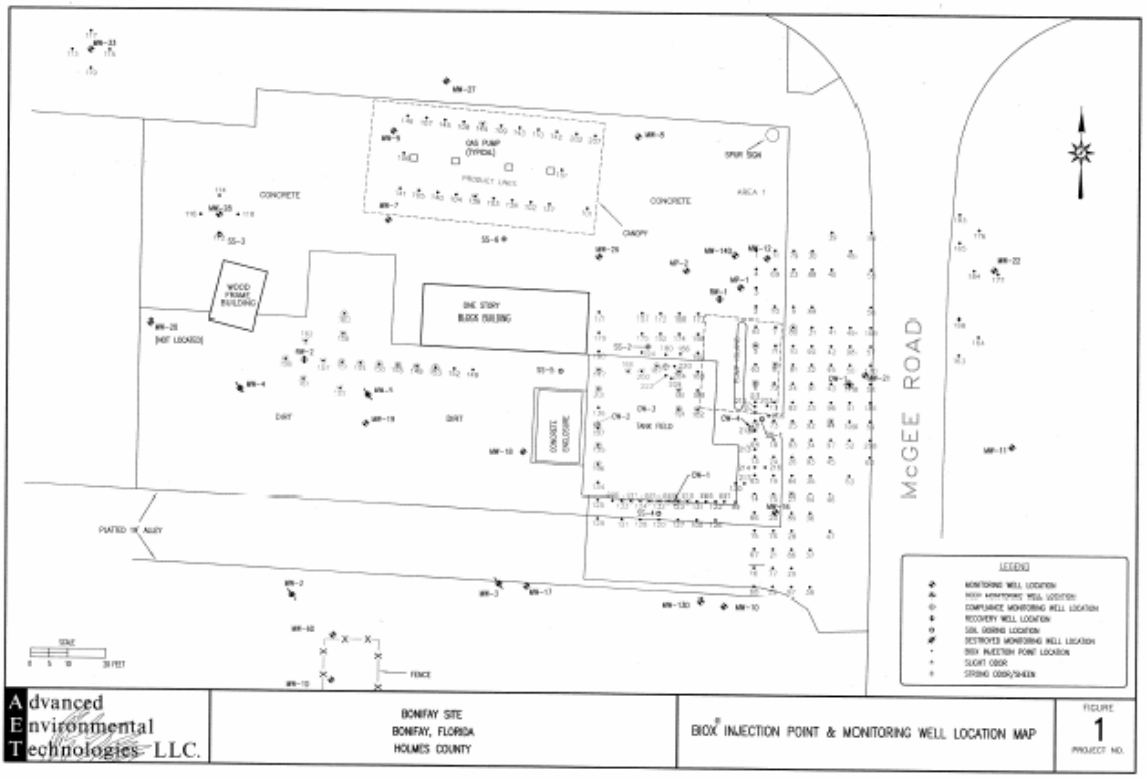

TABLE 1: BACTERIOLOGICAL ANALYSIS SUMMARY

Facility Name: **Bonifay Oil** **Facility ID#: xxxxxxx**

Bonifay, FL
Holmes County

Sample Location/Depth	Date	Petroleum Reducing Bacteria Recovered (Total Colonies)
CW-4 (1') Final day of BIOX® Injections	08/02/02	245
Post BIOX® Injections	02/11/03	99,000
1st Year post BIOX® Injection	08/19/03	23,000
2nd Year post BIOX® Injection	07/27/04	740
CW-4 (2') Final day of BIOX® Injection	08/02/02	470
Post BIOX® Injections	02/11/03	56,000
1st Year post BIOX® Injection	08/19/03	3,000
2nd Year post BIOX® Injection	07/27/04	960
CW-4 (3') Pre-BIOX® Injection	07/16/02	567
Post BIOX® Injections	02/11/03	32,000
1st Year post BIOX® Injection	08/19/03	13,000
2nd Year post BIOX® Injection	07/27/04	1,830
MW-29 (1') Final day of BIOX® Injections	08/02/02	163
Post BIOX® Injections	02/11/03	8,000
1st Year post BIOX® Injection	08/19/03	13,000
2nd Year post BIOX® Injection	07/27/04	3,570
MW-29 (2') Final day of BIOX® Injections	08/02/02	30
Post BIOX® Injections	02/11/03	23,000
1st Year post BIOX® Injection	08/19/03	18,000
2nd Year post BIOX® Injection	07/27/04	1,540
MW-29 (3.5') Pre-BIOX® Injection	07/16/02	118
Post BIOX® Injections	02/11/03	24,000
1st Year post BIOX® Injection	08/19/03	12,000
2nd Year post BIOX® Injection	07/27/04	690
MW-30 (1') Final day of BIOX® Injections	08/02/02	707
Post BIOX® Injections	02/11/03	6,000
1st Year post BIOX® Injection	08/19/03	37,000
2nd Year post BIOX® Injection	07/27/04	2,180
MW-30 (1.5') Pre-BIOX® Injection	07/16/02	1,788
Post BIOX® Injections	02/11/03	55,000

1st Year post BIOX® Injection	08/19/03	28,000
2nd Year post BIOX® Injection	07/27/04	2,630
MW-30 (2') Final day of BIOX® Injections	08/02/02	377
Post BIOX® Injections	02/11/03	299,000
1st Year post BIOX® Injection	08/19/03	14,000
2nd Year post BIOX® Injection	07/27/04	1,120
CW-3 (1') 1st Year post BIOX® Injection	08/19/03	97,000
2nd Year post BIOX® Injection	07/27/04	6,300
CW-3 (2') 1st Year post BIOX® Injection	08/19/03	4,000
2nd Year post BIOX® Injection	07/27/04	3,330
CW-3 (3'-4') 1st Year post BIOX® Injection	08/19/03	13,000
2nd Year post BIOX® Injection	07/27/04	3,350

CHART 1