

# **COUPLED CHEMICAL OXIDATION AND ENHANCED BIOREMEDIATION PILOT TEST - PETROLEUM HYDROCARBON PLUME MIGRATING IN FRACTURED ROCK**

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## **Abstract**

Fuel storage and dispensing operations at an active facility in western Alberta resulted in diesel and gasoline release to the subsurface. The fuel entered an alternating sequence of siltstone/mudstone and sandstone units and a non-aqueous phase liquid (NAPL) plume of approximately 175 meters in length and 100 meters in width has formed. The primary drivers for remediation are the protection of nearby local water supply wells (and the regional aquifer) and the prevention of further off-property impacts. The current thrust is to better understand the hydrogeology and contaminant distribution while in parallel arresting or otherwise attenuating the lateral and vertical migration of the NAPL plume and petroleum hydrocarbon constituents in groundwater. A NAPL interdiction system involving 16 bedrock recovery wells has been installed at the leading edge of the NAPL plume. Bench-scale and pilot tests have been conducted to assess the viability of reducing dissolved-phase contaminants not captured by the interdiction wells or which may otherwise migrate vertically downward into the bedrock at any location within the plume.

A conceptual-model driven approach to characterization and remediation was adopted by UFA in 2005 and has been instrumental in accelerating the project. The conceptual model pointed to the value of pursuing the integrated strategy of physical interdiction and chemical oxidation coupled with enhanced aerobic biostimulation.

Chemical oxidation and enhanced aerobic biodegradation, more specifically technology based on base-activated sodium persulfate and solid peroxide oxygen-release chemical processes, were selected for bench and pilot testing. A Total Oxidant Demand (TOD) treatability test was conducted using Klozur® OBC. Two different bedrock materials and two different particle sizes were tested. The two particles sizes allowed evaluation of surface area influence on oxidant demand – a relationship that might be expected when comparing porous media flow to fracture flow. Following TOD testing, a pilot test was designed to evaluate slurry injection characteristics and subsurface behavior of Klozur® OBC and the timed-oxygen release product PermeOx® Plus. The pilot test involved baseline characterization of a wide suite of parameters of interest, process monitoring during and after injections, and performance assessment to evaluate destruction removal efficiency. Over 30 single and multiple-level well installations were utilized. Other technologies employed before and after pilot testing included continuous coring, UV fluorescence screening, gamma and conductivity borehole logging (for stratigraphic

definition and injectate tracking), hydraulic tests and automated fluid level monitoring, Goresorber™ passive detection modules, and phospho-lipid fatty acid (PLFA) and stable carbon isotope analyses of C<sup>13</sup> enriched benzene-baited Biotraps®. This pilot test program was effective in testing the conceptual model for the site as well as the efficacy of pressurized chemical slurry injection in the fractured bedrock system, and reduction removal efficiency for the dissolved-phase petroleum hydrocarbons.

## **Project Objectives**

This coupled chemical oxidation – enhanced bioremediation pilot test project was undertaken to meet five key objectives. These objectives were:

- Enhance the current site conceptual model;
- Test the site hydraulic characteristics under chemical injection conditions;
- Determine the geochemical effects of injecting Klozur® OBC and PermeOx® Plus;
- Evaluate the efficacy (under field conditions) of the proposed remedial strategy; and
- Collect enough data for design of the full scale injection program.

## **Project Background**

Fuel storage and dispensing operations at an active facility in western Alberta resulted in diesel and gasoline release to the subsurface over a number of years. Multiple rounds of drilling and well installation from 1998 through 2003 resulted in the installation of a multiphase extraction system (on-site) to attempt to remediate impacted soil and groundwater. This system consisted of 13 recovery wells and 8 injection wells and was operated sporadically between 2003 and 2005. Marginal impact was observed by operating the system (3,399,000 L groundwater and 912 L PHC were recovered).

In 2006, additional characterization of the site (on and off property) was undertaken with a view to creating a more detailed site conceptual model. Undertaking a site conceptual model approach for this site resulted in a more detailed understanding of the problem at hand.

Based on updated site characterization information, it has been determined that the fuel entered an alternating sequence of siltstone/mudstone and sandstone units and a non-aqueous phase liquid (NAPL) plume of approximately 175 meters in length and 100 meters in width has formed. This sequence of alternating bedrock units is highly fractured, presents non-uniform groundwater flow characteristics and sits above a domestic use aquifer. The NAPL and dissolved phase hydrocarbon plumes continue to migrate to the south of the property.

Therefore, the primary drivers for remediation are the protection of nearby local water supply wells (and the regional aquifer) and the prevention of further off-property impacts.

## **Proposed Remedial Strategy**

Based on the updated site conceptual model, it was determined that migration of the NAPL and dissolved phase plume to the south was the most urgent remedial driver. Based on this assertion, a remedial strategy was developed to arrest this plume migration.

The site conceptual model indicated that a single remedial technique would most likely not be effective in arresting both the NAPL plume migration and the dissolved phase plume. Therefore, a remedial strategy consisting of physical interdiction, chemical oxidation and enhanced bioremediation was proposed.

To provide physical recovery of NAPL and limit southerly migration of fluids in general, an interdiction line consisting of 16 recovery wells, utilizing pneumatic, downhole pumps, connected to a groundwater remediation system was installed in the fall/winter of 2006/2007.

It is proposed to supplement the physical recovery of NAPL and groundwater at the leading edge of the NAPL plume (NAPL/dissolved phase interface) with a zone of chemical oxidation. This chemical oxidation would be undertaken by injecting Klozur® OBC into the contaminated zone. Klozur® OBC is a base activated persulphate product supplied by FMC Corporation.

To supplement the chemical oxidation zone and effect remediation of the leading edge of the dissolved phase plume (and potentially provide a permeable reactive barrier at the leading edge of the plume), it has been proposed to inject PermeOx® Plus. PermeOx® Plus is a timed oxygen release compound consisting of engineered calcium peroxide. PermeOx® Plus is also supplied by FMC Corporation.

By utilizing the above described three-pronged approach, it is proposed that the leading edge of the contaminant plume can be effectively mitigated.

## **Pilot Test Strategy**

Once the conceptual remedial strategy was decided upon, a pilot test strategy was developed. Because of the complex nature of the subsurface conditions at the site, it was decided that a pilot test phase of the project would be valuable to evaluate the efficacy of the proposed remedial strategy before full scale implementation.

To effectively evaluate the remedial strategy under pilot scale conditions, it was determined that additional intensive baseline characterization would be conducted in a limited area that would serve as the pilot test area. This additional characterization was conducted in a systematic manner such that it was not only valuable for the pilot test, but also provided a wealth of additional information for the site conceptual model.

In conjunction with the baseline characterization activities, core materials from the pilot test area were subjected to bench scale testing of total oxidant demand. This information, combined with contaminant loading provided the information necessary to calculate oxidant concentrations for injection.

Based on the characterization information, a combination of nine locations/depths were chosen for injection of Klozur® OBC and PermeOx® Plus. During chemical injection and for a period of 10 days following injections, process monitoring was conducted to measure the initial effects of the chemical injections.

A performance monitoring program was also undertaken for three months following the injections to evaluate the longer term effects of the chemical injections. Once the performance monitoring phase was complete, the data collected during baseline, process and performance monitoring programs was compiled and analyzed to determine the contaminant destruction and removal efficiencies.

### **Site Conceptual Model Based Pilot Test Characterization**

To ensure the pilot test injections were properly evaluated, a wide variety of characterization tools were used. To provide detailed geological information a combination of solid stem auger sampling and continuous coring and logging was used. This was supplemented by conducting geophysical (electrical conductivity and natural gamma) logging of all new and existing boreholes in the pilot test area. This information was used to produce numerous geological cross-sections to aid in interpreting subsurface characteristics.

To evaluate hydrogeologic characteristics of the pilot test area, a combination of discrete screen length conventional groundwater wells and Solinst Multi-Level Sampling (MLS) wells were installed. These wells were subjected to regular manual water level gauging, groundwater sampling, slug tests and continuous water level gauging using pressure transducers (corrected for atmospheric pressure and rainfall events).

Geochemical information was collected from over 30 monitoring wells during all three phases of the pilot test (baseline, process and performance monitoring). This included field determination of groundwater temperature, pH, dissolved oxygen, total dissolved solids, electrical conductivity, specific conductance, oxygen reduction potential and persulphate concentration. Groundwater samples were collected and submitted for laboratory analysis of benzene, toluene, ethylbenzene, xlyenes, petroleum hydrocarbon fractions (F1 and F2), pH, alkalinity, carbonate, electrical conductivity, chloride, fluoride, total organic carbon, dissolved organic carbon, nitrate, nitrite, sulphate, calcium, magnesium , sodium, potassium, iron and manganese.

In addition to the above conventional geochemical characterization methods, Gore Sorber® Modules for VOC detection and quantification were used to detect ultra-low levels of petroleum hydrocarbons in MLS well installations. This technology allowed for the detection of the presence of hydrocarbons in groundwater where standard

laboratory analytical techniques would only provide a detection limit of 0.5 ppb. This information is not useful from a regulatory compliance standpoint, but can be used to indicate hydrocarbon migration prior to exceeding regulatory limits for groundwater ingestion.

Finally, to directly evaluate biological activity and effects of chemical injection, BioTraps®, provided by Microbial Insights were used. Biotraps® consist of porous beads in a permeable container that is inserted into a groundwater monitoring well, in direct contact with groundwater. Bacteria present in the groundwater attach to the porous beads and are thereby captured for analysis. The Biotrap is then returned to Microbial Insights for analysis of PLFA. This provides specific information not only about the relative amount of bacteria on the beads, but also the relative abundance of different structural groups. The beads can also be baited with C<sup>13</sup> labeled substrate (in this case C<sup>13</sup> labeled benzene), to allow for direct measurement of contaminant utilization, determination of actual field rate constants and direct measurement of the amount of contaminant converted to dissolved organic carbon.

### Pilot Test Results

The pilot test consisted of injection of Klozur® OBC and PermeOx® Plus at three locations, as described earlier. At each location, chemical was injected into three different geological horizons. The uppermost horizon (A) was injected with a 20 wt% solution of Klozur OBC. The middle horizon (B) was injected with Klozur OBC or PermeOx® Plus (10 wt%) depending on location. The lower horizon (C) was injected with PermeOx® Plus (10 wt%). Figure 1 illustrates the injection locations and details the chemical volumes injected into each geological horizon.

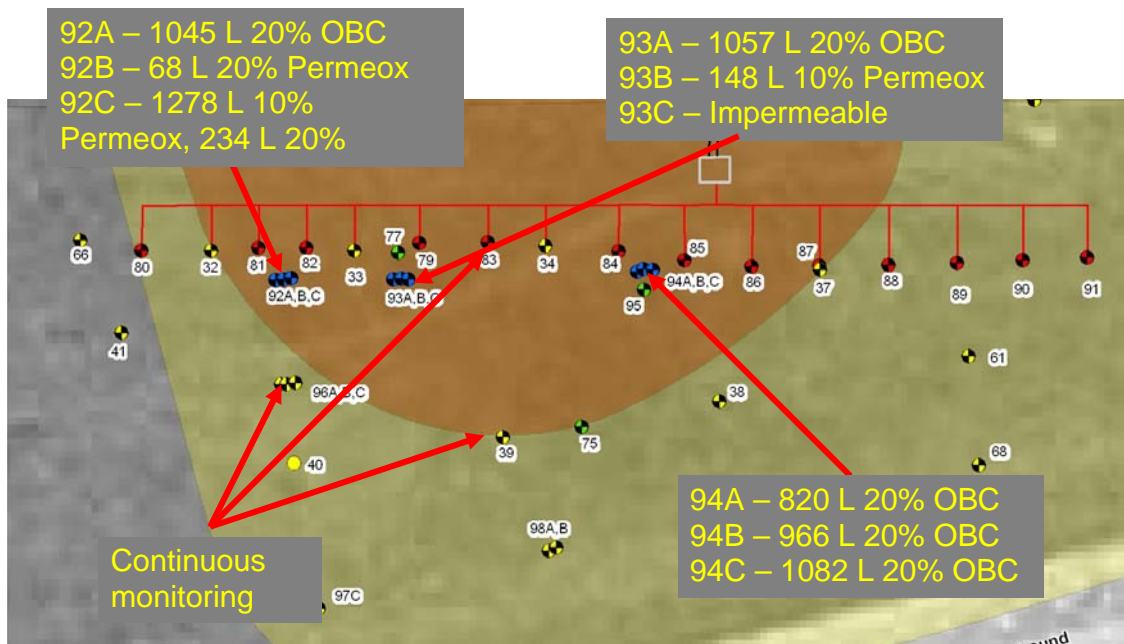
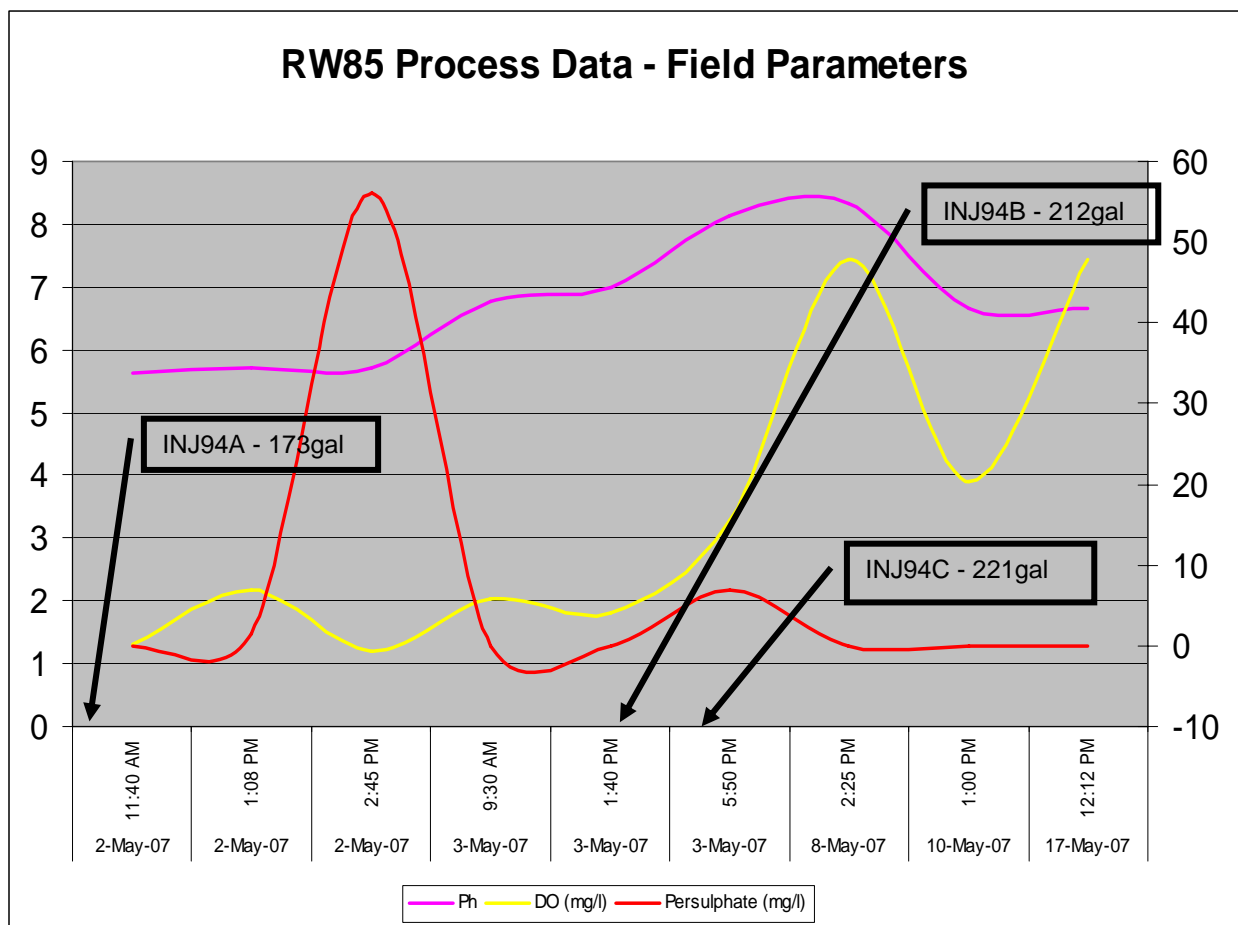


Figure 1: Pilot Test Injection Details

Chemical injection took place over an eight day period in May 2007. Throughout the injection period and one week after injection, process monitoring data was collected. Process monitoring data for each well consisted of a combination of field determined parameters (groundwater temperature, pH, dissolved oxygen, total dissolved solids, electrical conductivity, specific conductance, oxygen reduction potential and persulphate concentration) and laboratory determined parameters (benzene, toluene, ethylbenzene, xlyenes, petroleum hydrocarbon fractions (F1 and F2), pH, alkalinity, carbonate, electrical conductivity, chloride, fluoride, total organic carbon, dissolved organic carbon, nitrate, nitrite, sulphate, calcium, magnesium , sodium, potassium, iron and manganese). Not all laboratory analytes were measured at each location during the process monitoring stage. Figure 2 illustrates the typical field determined process monitoring data that was collected.

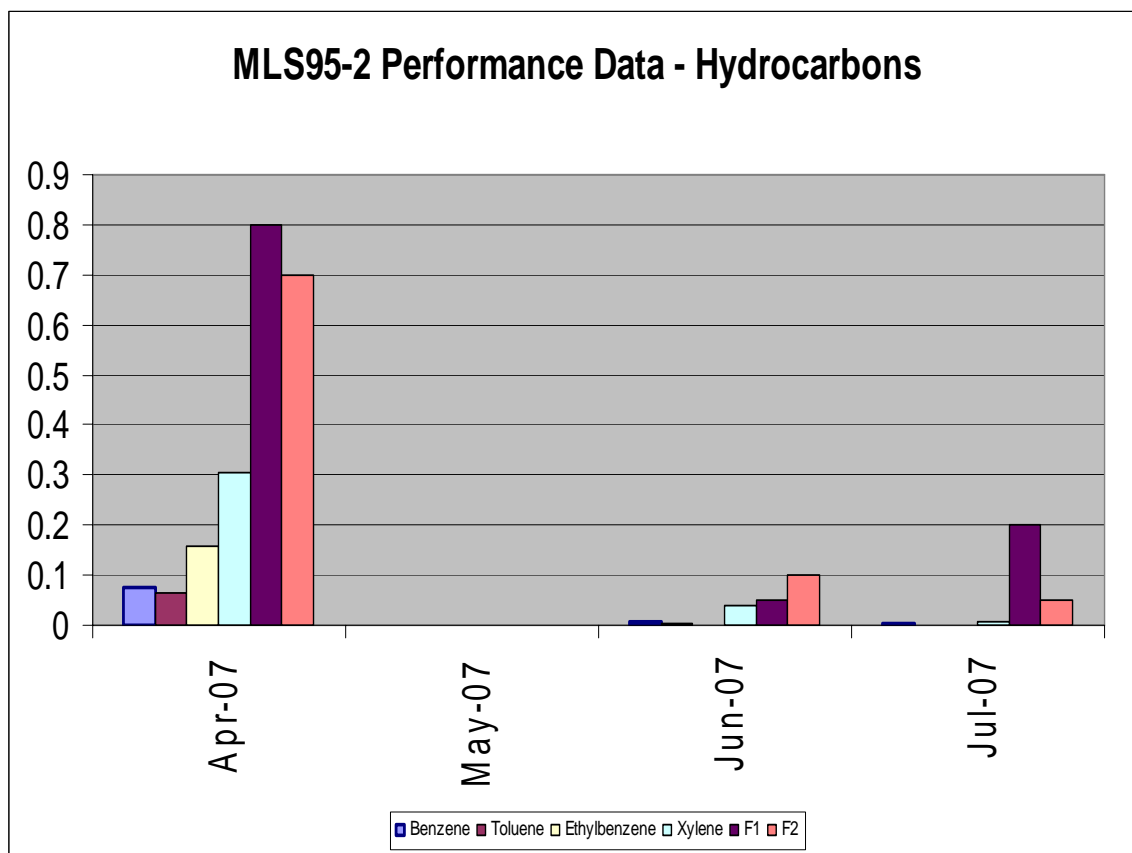


**Figure 2: Typical Process Monitoring Data**

The process monitoring period was designed to capture immediate hydrogeological and geochemical changes brought about by injection of the oxidants into the various geological units. Near-field (within 3-5m of injection) hydraulic response to injection was noted during process monitoring. Geochemical response was noted up to 20 m distant from injection points during the process monitoring stage.

After the process monitoring period was complete, a three month performance monitoring program was undertaken. To ensure consistency in data, the same combination of monitoring points and parameters that had been used in the baseline monitoring and the process monitoring was employed for performance monitoring.

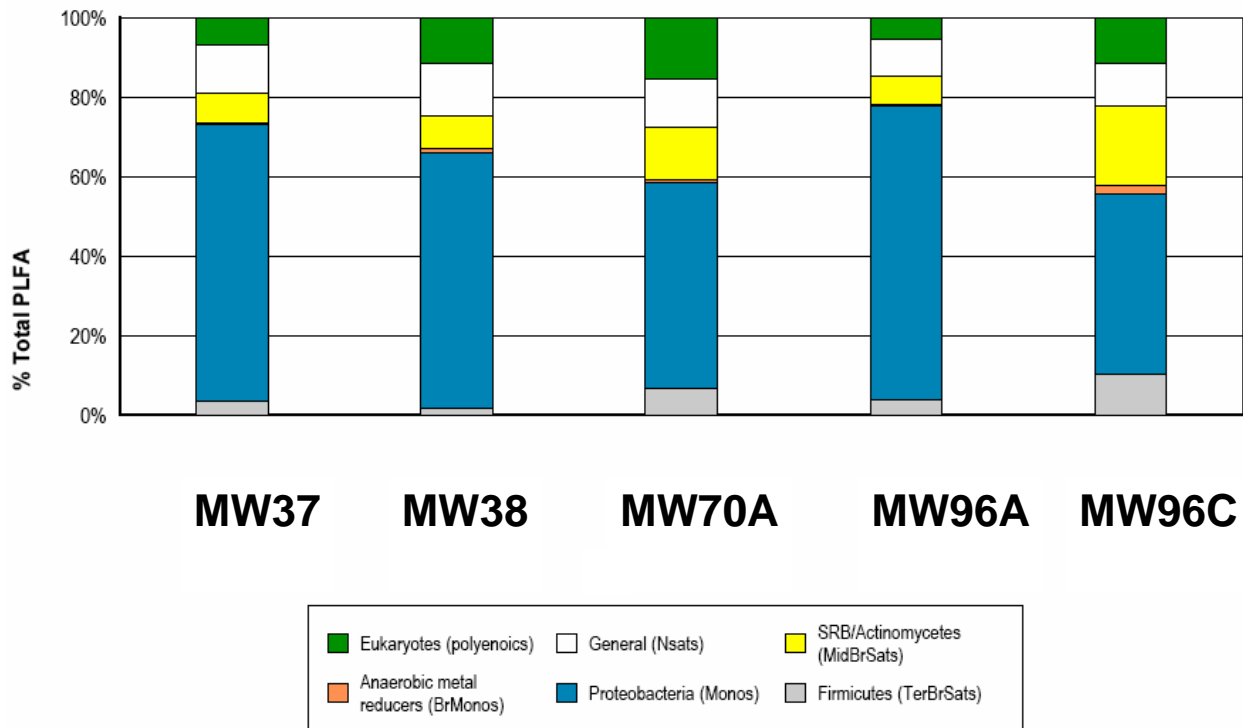
Three months after injection, the performance monitoring data indicated a lasting geochemical response. Levels of oxygen, TOC, DOC, TDS, sulphate and iron were elevated in the majority of monitoring points in the pilot test area. More importantly, hydrocarbon levels were significantly lower in the pilot test area. Figure 3 illustrates the typical hydrocarbon performance data that was collected during this stage of the program. Levels of BTEX, F1 and F2 declined significantly after injection. There is some rebound of F1 and F2 hydrocarbons, however this response was expected.



**Figure 3: Typical Performance Monitoring Data**

In addition to the hydrogeological and geochemical parameters monitored during the performance monitoring program, BioTraps® were installed at five monitoring points (consistent with the baseline monitoring program). These BioTraps® were baited with C<sup>13</sup> labeled benzene. The BioTraps® were incubated in-situ for 30 days, and then were sent to Microbial Insights for analysis.

Figure 4 illustrates the community structure as determined by % PLFA analysis. These results indicate that the larger fraction of the microbial population is Proteobacteria. These are normally well suited for hydrocarbon destruction.



**Figure 4: Relative Biological Community Structure**

In addition to the standard PLFA analysis, Microbial insights also determined the relative concentration of  $C^{13}$  in the biomass, estimated a first order rate constant for the degradation of benzene, determined the relative concentration of  $C^{13}$  in the dissolved organic carbon and determined the functional genes.

Figure 5 illustrates the post injection biological data obtained from the BioTrap analysis. This information illustrates that the naturally occurring bacterial population was able to utilize benzene as a carbon source, the benzene utilization rates ranged from 0.023 mg/day to 0.043 mg/day and that the benzene was broken down into small chain hydrocarbons that appear as dissolved organic carbon in the analysis. This relates well to the increases in dissolved organic carbon observed at other monitoring points during the performance monitoring period of the pilot test.

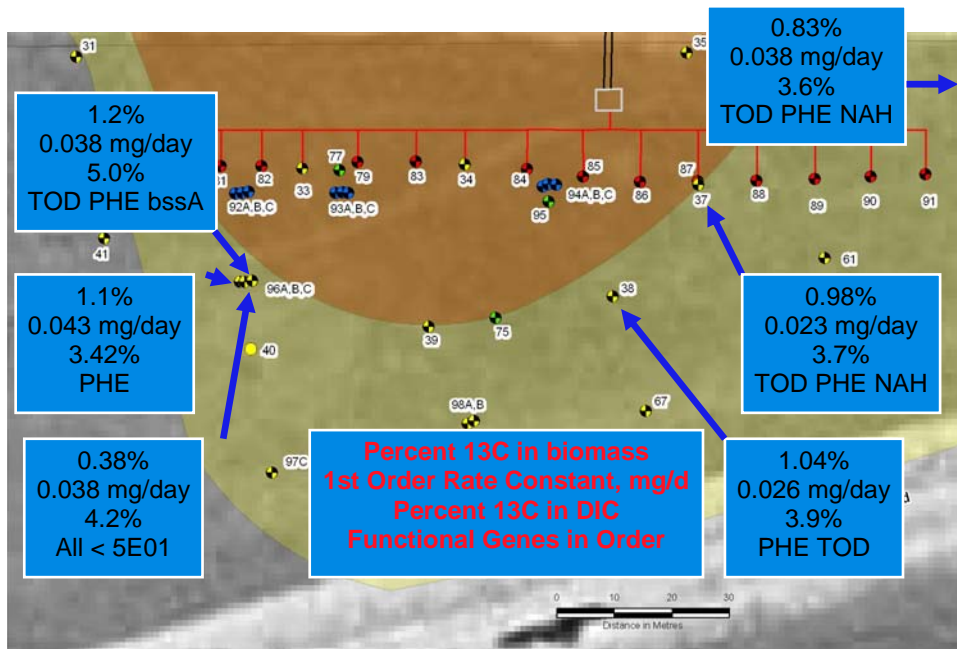


Figure 5: Post Injection Biological Data

## Conclusions

The following conclusions can be drawn from the pilot test:

1. Bench scale testing is a valuable first step to properly determine chemical concentrations for field testing;
2. Hydraulic effects were localized and short lived (relative to the test area/period);
3. Geochemical effects were broad and long lived (relative to the test area/period);
4. Biological effects were broad and long lived (relative to the test area/period); and
5. Injection of Klozur® OBC and PermeOx® Plus were effective in reducing petroleum hydrocarbon concentrations when injected into the contaminant plume.

## Were Objectives Met?

This coupled chemical oxidation – enhanced bioremediation pilot test project was undertaken to meet five key objectives. All five objectives of the pilot test were met:

1. The data collected has improved the Site Conceptual Model;
2. Hydraulic effects were observed and recorded;
3. Positive geochemical effects were apparent;
4. Results indicate destruction of contaminants; and
5. Full scale remedial design is currently underway.