Extracts from:
Testing of Selected Biosorbents

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Note: This copy of the SAIC 2004 report has been modified.

Abstract

A number of products have been introduced to the market over the past few years touting their ability to sorb spilled oil and the capability to biodegrade the retrieved oil in-situ. While the number of products which would fit this description is not large, this ability has the potential to help reduce one of the costly side effects of oil spill response – ultimate disposal.

The purpose of this project is to test two different products identified as biosorbents for their ability to sorb and breakdown petroleum products spilled on land. An initial literature review identified a number of products available in the North American market. A subset of these products is available in Canada. This project provides initial testing of the effectiveness of selected products, focusing two biosorbents available in Canada. The results of the bench scale biodegradation results are presented. Descriptions and discussions of the analytical techniques used are also detailed within the report.

1 Introduction

Sorbent products have traditionally been used as a means of remediating small spills such as pooled oil from land-based spills or as a final polishing step for cleaning large spills on water. Certain products, marketed as biosorbents, also possess the claimed ability to treat any oil sorbed through a biodegradation process. Performance issues related to this specific land based application for sorbents has not been formally addressed through recognized comparison testing.

Biosorbents are designed for treating spills on land through the process of sorption followed by a biodegradation process which would eliminate the need for further collection and disposal. This eliminates one of the traditional limitations related to the use of sorbents, specifically waste issues. As with any process, there are limitations to the effectiveness of these products. Specific soils conditions such as moisture content must be maintained while the treatment process is underway. The maintenance of these specific conditions encourages the propagation of the microbes responsible for the degradation of the hydrocarbons. The objective of this study was to gather data and information in order to compare two biosorbent products that are marketed and sold within Canada. As part of this objective, the goal was also to develop a reproducible method to test progress of the biodegradation rates of the biosorbent products within a controlled soil.

2 Background

SAIC Canada has been involved in sorbent testing over the past five years. The standard protocol used for the majority of testing, ASTM F726-99 Standard Test Method for Sorbent Performance of Adsorbents, was designed to quantify the performance testing of products used for spills on water or "pooled" land based spills. This protocol does not, unfortunately, address the unique operational characteristics of these biosorbents.

A previous project reviewed commercially available products that claim to be able to promote the biodegradation of contaminants in soil and water (SAIC Canada, 2004). These products included treated sorbents, biological enhancers and microbial liquids and powders. A listing was developed through a search on the Internet using a suite of search engines. Also, there were various discussions with several distributors and manufacturers of biodegradation products and spill treating agents. Interest in the use of these products has led to the development of this study which attempts to quantify their performance by tracking the degradation of petroleum hydrocarbons over time in soil.

3 Materials and Methods

3.1 Materials

In this study, the two products chosen are used for the treatment of spills on soil. The two products chosen are commercially available within Canada.

3.1.2 Enretech-1

Enretech-1 (Enretech, 2003) is described as a dual purpose oil/fuel absorbent and bioremediation agent for use directly on direct spills or on hydrocarbon contaminated water. It contains naturally occurring bacteria and micro-nutrients indigenous to the cotton plant which, when kept moist and given a hydrocarbon food source, propagate to break down the contaminant. Average reductions of total hydrocarbons (TPH) are claimed to have averaged 82% in 77 days. Supplementary nitrogen, and other nutrients, were incorporated into the fibres through a patented manufacturing process. The biosorbent is a light brown fine powder similar to talc (see Figure 2).

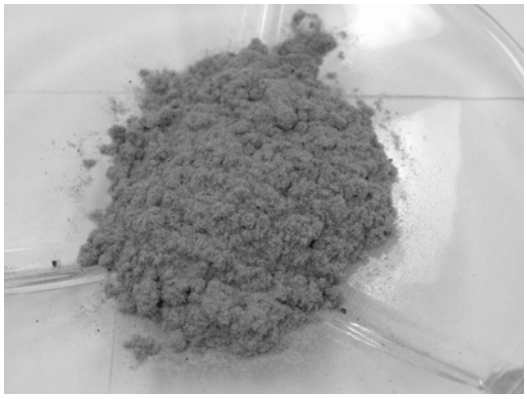


Figure 2: Enretech-1 Biosorbent

3.2 Experimental Plan

The first step in the experimental plan was the construction/modification of ten test cells. Ten plastic containers (Tupperware) with a maximum capacity of 8 L each were acquired. To avoid cross contamination 10 sampling shovels were also purchased and assigned to individual cells for use during testing. Holes were cut through the lid (5 x 5 cm diameter) and along the sides just below the lip of the container (12 x 3 cm diameter) for aeration. In order to avoid any contamination, both the containers and the shovels were initially sterilized with methanol before commencing the experiment.

The next phase was the preparation of the oil mixture. A total quantity of approximately 1.4 L solution was prepared. Three different fractions of hydrocarbons were chosen; a light, a medium, and a heavy oil. The mixture of hydrocarbons was composed of diesel, a medium crude oil, and a heavy crude oil. Target weights of the composition were 15%, 70%, and 15% for the respective oils. This recipe was chosen to provide a wide range of hydrocarbons for the experiment. By creating 1.4 L of mixture, there was enough volume of the prepared hydrocarbon mixture to reach the initial target concentration of 20,000 ppm in the volume of soil required for the experiments.

The soil used in each of the test cells was commercially available topsoil. Approximately 60 L (3 bags) of topsoil was used to generate ten test cells. This topsoil was added to a clean metal drum (washed, rinsed, and sterilized with steam) which was then placed on a drum mixer for approximately 30 minutes of tumbling. A moisture content test was then performed on the soil. To test the moisture content approximately 100 g of mixed soil weighed in pre-weighed oven proof container. The container was then placed in an oven at 60°C until it was completely dried (approximately 24 hours). As soon as the soil was dry and removed from the oven, it was left to cool until it reached room temperature. Once the container and the soil reached room temperature, the container was reweighed with the dried soil. The following formula was used to determine the moisture content of the soil (see Equation 1):

Equation 1: Moisture Content Formula

$$MC = \frac{(WS - DS)}{WS} * 100 \qquad (1)$$

where MC = Moisture Content
WS = Weight of Wet Soil
DS = Weight of Dry Soil

To maintain a 30% moisture content (by weight) of the soil, water was added to the drum. The drum was then re-mixed for approximately 30 minutes. From this drum, 2.5 kg of soil was removed and placed in a mixer (Ross model LDM-2). Within the mixer, the oil and the biosorbent (if required) was added and mixed thoroughly for approximately 15 minutes. This mixing step was added so that the soil within each test cell would be completely homogenized with both the oil and the biosorbent.

The duration of the experiment was selected to be 12 weeks. This time period was chosen as it exceeded some of the manufacturer's performance claims from the previous study, and would provide a good indication of performance under controlled conditions.

During the course of the experiment, soil moisture content was monitored on a periodic basis. When the moisture content dropped below 25%, additional water was added to bring the moisture up to 40% by weight. This moisture range was selected based in part upon recommendations by the manufacturers.

3.3 Test Cells

The oil mixture that was prepared for this experiment is detailed in Table 1. The heavier oil was added to the plastic bucket first, followed by the medium oil and then the lighter oil was added. To mix the hydrocarbon mixture, a paint mixer attached to a drill was used. By using the paint mixer and drill, the hydrocarbons were thoroughly mixed (a homogenous oil mixture was created). To help in the identification of the hydrocarbons, the viscosity of each oil used is provided in Table 1. The actual percentage of each type of oil is also presented.

Table 1: Actual Oil Composition

Oil Type	Viscosity Range (cP)	Weight of Sample (g)	Composition (%)
Diesel	0 -10	218	15
Medium	200 - 300	1010	69
Heavy	1500 - 1800	230	16

Once the soil and the oil mixture were prepared, the two were combined within a mixer along with the specified biosorbent. Table 2 details the soil, oil mixture, and biosorbent content for each of the test cells. Figure 3 depicts a typical test cell. For quality control and quality assurance purposes a blank (soil only, no biosorbent, no oil) and control test cells (soil and oil, no biosorbent) were also prepared. For each specific biosorbent, there were three test cells prepared (triplicates). By preparing the test cells in triplicate, errors within the soil samples could be reduced. Triplicates also aided in the reproducibility of the test results.

Table 2: Test Cells Set-up

Test Cell	Soil (grams)	Oil Mixture* (grams)	Biosorbent Type	Biosorbent (grams)
4	2499.9	50.4	Enretech-1	95.3
5	2499.9	50.4	Enretech-1	95.1
6	2500.0	50.4	Enretech-1r	95.1
7	2500.0	50.4	-----	-----
8	2499.9	50.4	-----	-----
9	2500.0	50.4	-----	-----
10	2499.9	------	-----	-----

* 55 mL of oil mixture = 50.4 grams

Also at week 6, 32.0 g of additional biosorbent was added to each of the respective first 6 test cells. More biosorbent was added to increase the rate of degradation of the hydrocarbons.

Figure 3:
Soil test Cell

3.4 Analytical Methods

Standard analytical testing was performed by an outside CAEAL accredited laboratory. The laboratory test methods involved the following two protocols:

- BTEX, PHC F1 (CCME) EPA 8260, CWS PHCs – P&T GC-MS/FID
- PHC F2-F4 (CCME) CWS- Tier 1 Method, GC-FID

The analysis is divided into hydrocarbon fractions, indicated by F1 through F4, designated by carbon number ranges as per the CCME, 2001 Canada-Wide Standards for Petroleum Hydrocarbons (PHC) in Soil. As an example of target levels, Table 3 lists the Tier 1 numerical levels for Industrial land use, fine-grained (≤75 µm) soil.

Table 3: Summary of Tier 1 Levels (mg/kg) for Surface Soil

Parameter	Criteria (mg/kg)
PHC Fraction 1 (C6 to C10)	660
PHC Fraction 2 (>C10 to C16)	1500
PHC Fraction 3 (>C16 to C34)	2500
PHC Fraction 4 (>C34)	6600

Samples were sent for outside analysis at three stages throughout the experiment:

- At the beginning of the experiment to obtain initial values;
- In the middle to monitor the performance of the biodegradation rate at the half way point; and,
- At the 12th week to obtain final results.

4 Results and Discussion

The analytical results are presented here in two separate categories: Enretech-1 and the control test cells. Each were monitored and tested throughout the entire 12 week experiment.

4.2 Enretech-1

Test cells 4, 5, and 6 were filled with soil, oil and Enretech-1 biosorbent. The results of test cells 4, 5,and 6 from the analysis over the 12 weeks is documented in Table 5 and illustrated in Figure 6. The result of the Enretech-1 test indicate that losses and/or degradation of lighter hydrocarbons (F1 or “C6-C10”) occurred quite readily for all cells as shown in the C6-C10 row of Table 5.

Again, as each successive family of larger hydrocarbons was analysed it became apparent that the degradation effect diminished. The data has been graphed and appears below in Figure 6.

Table 5 Enretech-1 Degradation Results

	Cell 4			Cell 5			Cell 6		
	Initial	Week 6 (avg)	Week 12	Initial	Week 6	Week 12	Initial	Week 6	Week 12 (avg)
C6-C10	800	20	<20	1600	20	<20	1600	20	<20
C10-C16	13000	3770	1800	10000	6000	1900	16000	8100	1900
C16-C34	9500	6700	7600	7000	8700	7400	12000	11000	7270
C34-C50	2500	820	1800	1700	400	1700	2800	1900	1670
TOTAL:	**25800**	**11310**	**11200**	**20300**	**15120**	**11000**	**32400**	**21020**	**10840**

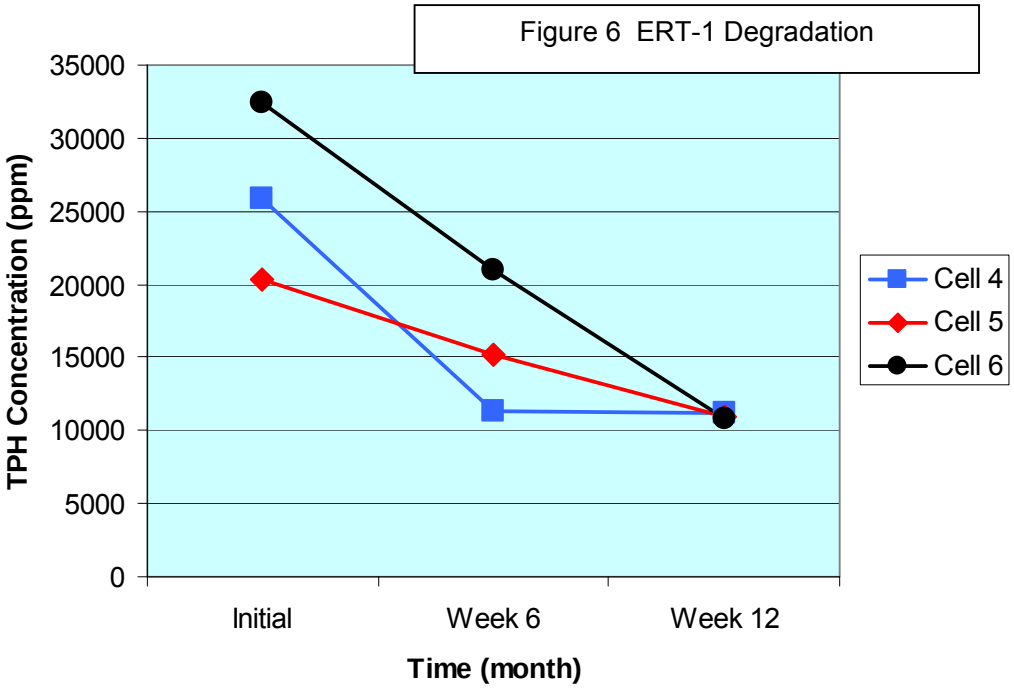


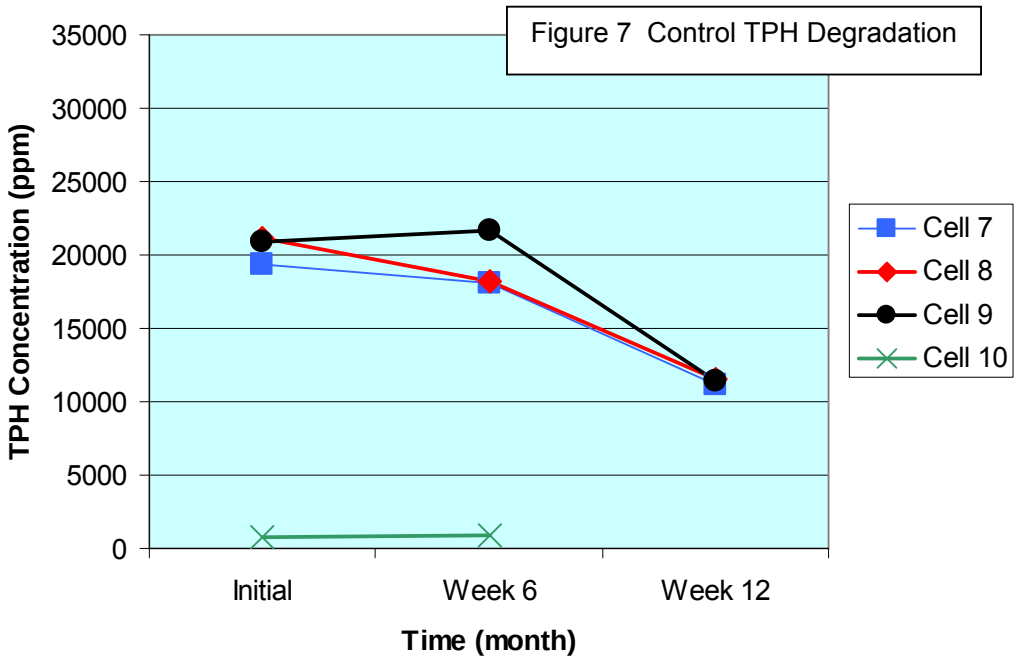
Figure 6 illustrates the analytical results of test cell 4, 5, and 6. From these three test cells, test cell 5 and 6 have very similar trend lines. Over the 12 weeks, the average concentration of total hydrocarbons in the test cells decreased by 56%. As with the first set of test cells, one test cell had results that were different. In this batch, test cell 4 has a slightly different trend line. As previously mentioned the reasons for this discrepancy are varied. It could be due to the soil type, the moisture content of the soil, the sample particles and/or the non-homogeneity of the soil and oil mixture.

4.3 Control

The control samples were test cells 7, 8,and 9. These test cells had oil mixture added but no biosorbents. The results of the analysis can be found in Table 6. The results of the control, similarly to the previously tested biosorbent cells, showed rapid elimination of the lighter hydrocarbons, followed by progressively slower degradation of the larger hydrocarbons. Given the high organic content of the soil, naturally occurring microbes would be expected in abundance. The results seem to indicate very good natural attenuation using this particular soil type. When graphed, the results show very good degradation within the testing period (see Figure 7).

Table 6 Control

	Cell 7			Cell 8			Cell 9		
	Initial	Week 6	Week 12	Initial	Week 6	Week 12	Initial	Week 6	Week 12
C6-C10	1200	40	<20	1200	20	<20	1200	20	<20
C10-C16	9400	7600	2100	10000	6600	2100	9800	7800	2100
C16-C34	6800	10000	7400	7700	10000	7700	7700	12000	7600
C34-C50	1900	430	1600	2200	1600	1700	2200	1900	1700
TOTAL:	**19300**	**18070**	**11100**	**21100**	**18220**	**11500**	**20900**	**21720**	**11400**



The results of the blank sample have also been presented with the results of the control test cells (see Test Cell 10, Figure 7). The blank test cell contained no biosorbent and no oil mixture. Although the soil registered a slight concentration of hydrocarbons, this could be due to interference of the organic matter within the soil to the analysis.

Figure 7 illustrates that test cells 7, 8, and 9 over the 12-week period had similar trend lines in the degradation process of the hydrocarbons. Initially there was little movement however losses were detected during the second half of the experiment. As previously mentioned this could be due to the high organic matter within the soil that tends to have a high indigenous microbe population that might use the hydrocarbons as a carbon source.

(Editor's Note: The literature seems to show that the bioremediation rate in natural attenuation systems initially lags behind bioaugmentation treatment, but catches up around the 3-6 month mark. After this, there is no apparent distinguishable difference between the two treatment regimes. This is thought to be due to the naturally-occurring bacteria having to adapt to the new "food source" and build up its biomass.

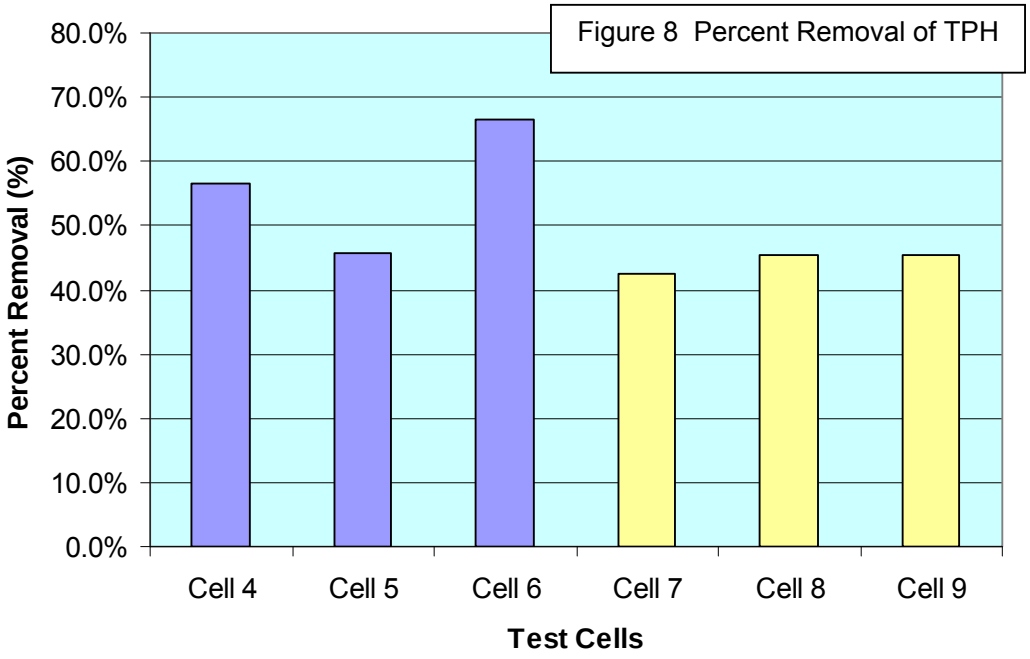


Figure 8 illustrates the percent removal of the total petroleum hydrocarbons for test cells 4 to 9. Test cells 4 through 6 (Enretech-1) averaged 56% removal, and test cells 7 through 9 averaged 45% removal.

5 Conclusions and Recommendations

The analytical results of this initial series of testing showed that the biosorbent product Enretech-1 was effective at reducing the TPH within the cells by an average of 56%. In comparison, the control managed degradation rate averaging 45% without any additional amendments.

The main assumption being made during the course of this study was that the disappearance of TPH was due to biodegradation. Additional factors such as evaporation must be considered, especially when considering the range of oil products used to create the stock oil solution used in these tests. The effects of physical processes such as evaporation were addressed through the use of the control cells. The difference between the control cells and the cells containing biosorbent averaged 10% which is not to say that the biosorbent did not help. It is simply a bit disappointing that this difference was not more dramatic. As indicated earlier, the presence of naturally occurring microbes may have contributed to these losses. Additional testing is recommended to isolate the cause of the losses of TPH, by adding controls with sterilized soils.

(Editor's Note: It would be interesting to conduct this comparison using field scale soil samples (ie: 2-3 m^3) as a number of other factors then come into play (ie: anaerobic pockets) - factors which more closely resemble real-life conditions when treating contaminated soils.)

6 References

1. Canadian Council of Ministers of the Environment, Canada-Wide Standards for Petroleum Hydrocarbons (PHC) in Soil, Winnipeg, Manitoba, 7p., 2001.

2. Enretech Australasia Pty. Ltd., Enretech-1 MSDS, Moss Vale, NSW, Australia, http://www.enretech.com.au/Downloads/MSDS-ERT1.pdf. (accessed November 2003)

3. SAIC Canada, Review of Commercially-Available Products Purported to Promote Bioremediation, Environment Canada, Ottawa, ON, 25 p., 2004.

ADDENDUM A:

The following are comments by Enretech Australasia Pty Ltd., who are manufacturers of the Enretech-1 technology and have extensive experience in its application.

It is acknowledged by the researchers in this report that there is probably loss of product via evaporation and not bioremediation - particularly in the C6-C10 range. We agree with this, and add that a certain amount of the C10 - C16 will also be lost due to vapour release.

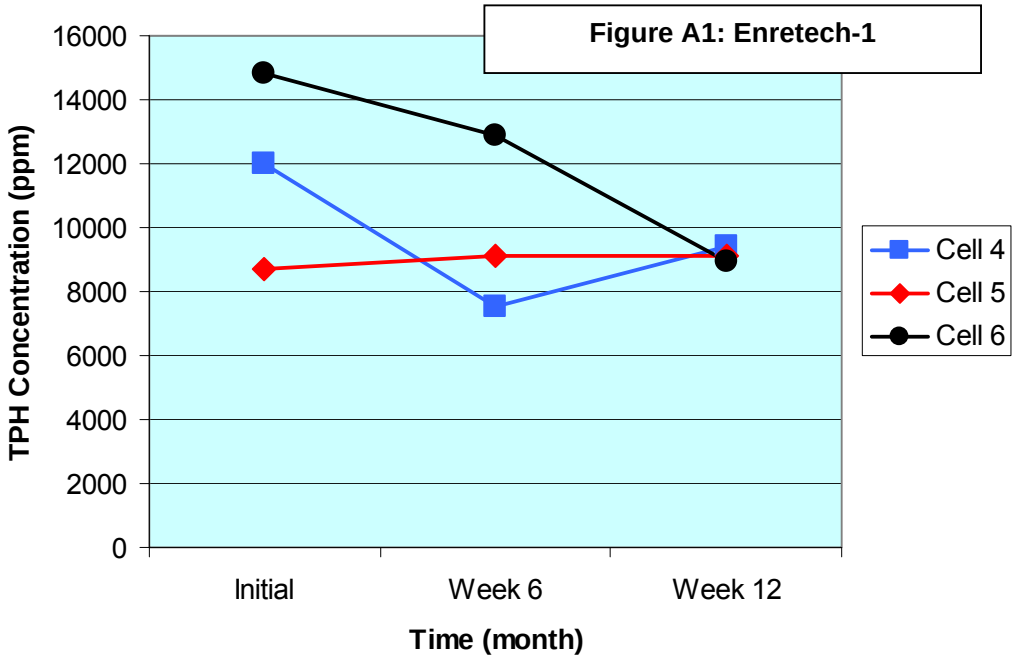
Accepting this possibility, we suggest that, to get a true indicator of the bioremediation rate of Enretech-1 and the control, the data for both the C6-C10 and C10-C16 TPH should be removed from the tables and the remaining C16-C34 and C34-C50 results re-analysed. Doing this provides the following observations:

1. There is significant variation in the remediation rates between all cells, with many actually increasing their TPH levels after 6 weeks. This increase is commonly found and is likely due to the release of biogenic compounds which are detected by the analytical method as TPH.

2. The Control cells showed minor amounts of degradation with a maximum of 6.1% (Figure A2), whereas the ERT1 showed much more dramatic reductions up to 39.6% (Figure A1). Reduction percentages are summarized in Figure A3.

3. All 3 ERT1 test cells (4-6) ended up at the same TPH concentration after 12 weeks (around 9300 ppm). Coincidence, contamination or test protocol anomaly?

4. Best remediation results occurred when starting with the highest TPH levels. This is a trend we have observed in the field, but are uncertain as to a mechanism explaining why.



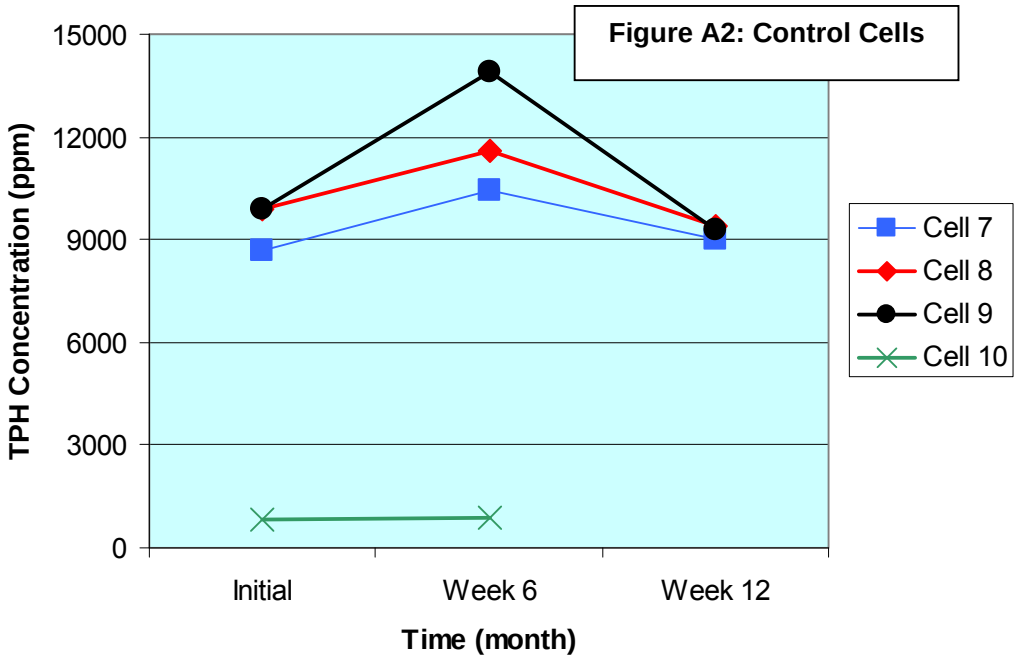


Figure A2: Control Cells
15000
12000
9000
6000
3000
0
TPH Concentration (ppm)
Initial
Week 6
Week 12
Time (month)
Cell 7
Cell 8
Cell 9
Cell 10

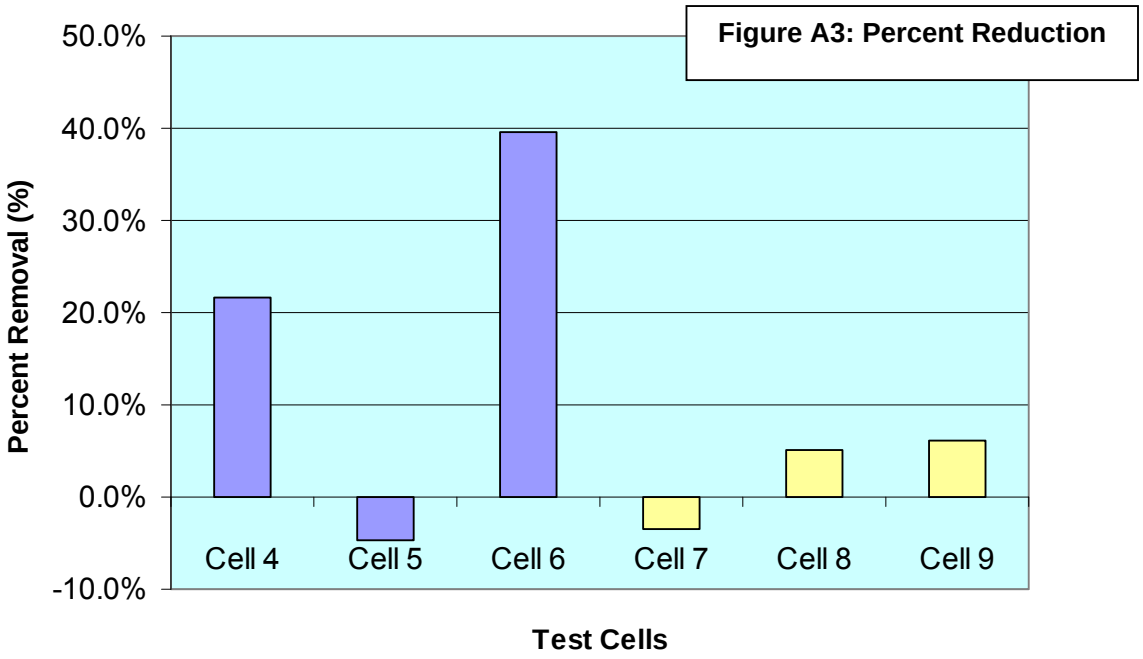


Figure A3: Percent Reduction
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
-10.0%
Percent Removal (%)
Cell 4
Cell 5
Cell 6
Cell 7
Cell 8
Cell 9
Test Cells