When it comes to Remediation, LNAPL is a Four-Letter Word: Activated Carbon may provide an answer

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Abstract

Products based on activated carbon have been offered by Remediation Products Inc. (RPI) for over fourteen years. There has been a recent interest in "Carbon Based Injectates" with many people and organizations offering opinions on applications and limitations. Several questions have come to the forefront of this technology.

1. Are compounds adsorbed into the microporous structure of carbon bioavailable?

2. Is regeneration/reactivation of the carbon through biological mechanisms viable?

3. Do sorption limitations of activated carbon prevent its application to LNAPL?

RPI's laboratory has been evaluating various carbons, blends of microorganisms purported to degrade petroleum hydrocarbons, and numerous supplements and substrates to generate several lines of evidence to support or negate the in- situ application of activated carbon for treatment of LNAPL. The testing program included multiple blends of organisms from several different vendors that are cultured to degrade petroleum hydrocarbons, and several different substrates. Controls were designed to evaluate experimental losses and provide performance profiles for changes due to simple adsorption by the activated carbon. These metrics defined a baseline that was used to evaluate overall NAPL and compound specific degradation rates. Commercial gasoline and diesel fuels were employed in the testing.

Preparation of Carbons Pre-loaded with Diesel fuel

1. To a 1-liter media bottle half filled with reagent water was added a weighed amount of carbon. The bottle was placed in a rotator at 6 rpm for 2 days to fully saturate the carbon with water.
2. An excess of diesel fuel was added and the bottle allowed to mix on the rotator for several days. This allowed enough time for adsorption of LNAPL to reach equilibrium.
3. The bottle was allowed to stand so that phases could separate.
4. As much excess diesel fuel was siphoned off as practical and paper towels were used to wick additional fuel from the surface of the water. Carbon had settled to the bottom.
5. The contents were vacuum filtered to recover the carbon. Cold methanol was used to wash the carbon and remove any fuel from the outer surface.
6. The saturated carbon was dried at room temperature, weighed, and placed into an amber glass bottle for storage pending use in the bench.

BOS 200® (coal based) Carbon

1. Based on the analysis of 9 samples, average loading of diesel is 58% (wt.).
2. Each nominal dose of 0.5 gms prepared material contains 305 mg carbon and 178 mg of diesel fuel. The balance is water.

Wood Based Carbon (Char)

1. Based on the analysis of 9 samples, average loading of diesel is 29% (wt.).
2. Each nominal dose of 0.5 gms prepared material contains 176 mg carbon and 51.8 mg of diesel fuel. The balance is water.

Sample Analysis

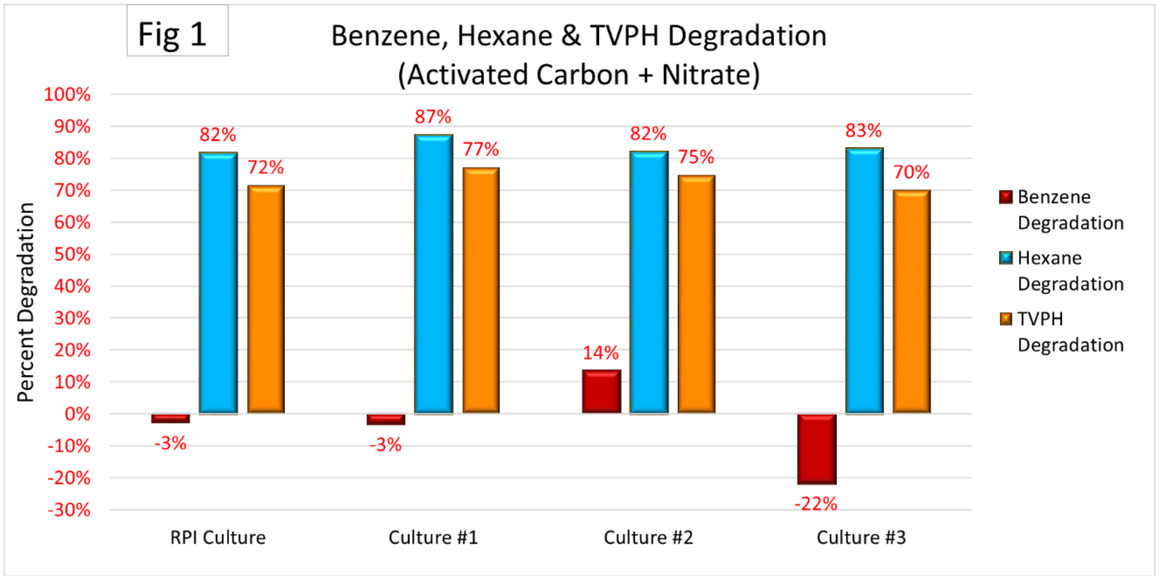
Septa sealed 150 ml serum vials were used to prepare test bottles. Multiple bottles were prepared for each evaluation. This was done because at various times during the testing, bottles were sacrificed for analysis. The aqueous phase was analyzed using the following methods.

- An extended list of volatiles by method 8260B.
- Low molecular weight hydrocarbon gases using RSK 175. The method is calibrated for 13 gases.
- Both inorganic and organic anions by SM 300. The organic anions consist of a suite of volatile fatty acids.
- Ammonia nitrogen using SM 4500-NH_3.
- pH.

Carbon added to the test bottles was isolated by vacuum filtration, extracted, and the extracts analyzed by Method 8260B for an extended list of volatile compounds.

Are compounds absorbed into the microporous structure of carbon bioavailable?

Data is presented both from the gasoline study and that involving diesel fuel preloaded onto activated carbon and wood based carbon (char). A set of three figures are presented from the work with gasoline grouping specific amendments and looking at the effects of different blends of microorganisms after four months. In each case, BOS 200® carbon was employed. For example, Figure 1 shows nitrate only (no other terminal electron acceptors present) with benzene, hexane, and TVPH-GRO data presented.



The first thing to notice is that very little degradation of benzene took place. In each case a significant amount of the total TVPH-GRO and hexane were degraded and this provides insight into how the nitrate is being used. It appears from the data that a substantial portion of the aliphatic fraction is being degraded and the extensive degradation of hexane supports this conclusion. Figure 2 reflects the effect of now adding nitrate and sulfate.

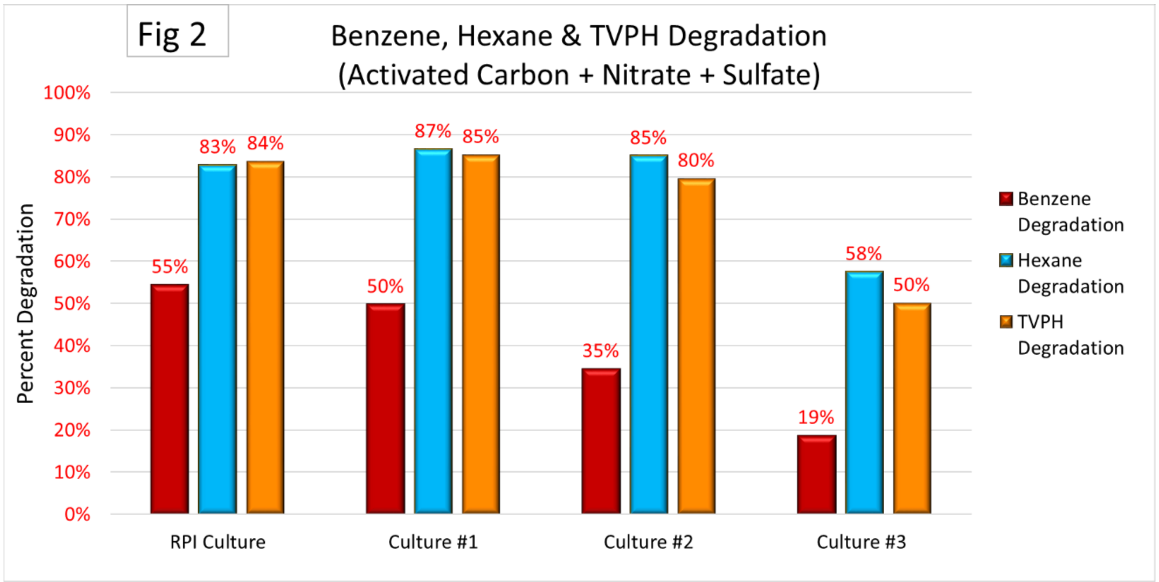


Fig 2

Benzene, Hexane & TVPH Degradation
(Activated Carbon + Nitrate + Sulfate)

Results are significantly different in that the aromatic fraction of the gasoline is now being degraded along with the aliphatic fraction. Degradation of benzene and TVPH has increased significantly. Addition of sulfate appeared to suppress aliphatic degradation in the Culture 3 however RPI believes this result is likely due to an analytical issue or simple scatter in the data rather than a true biological effect. Figure 3 displays the results obtained when complex carbohydrate and a consortium specifically designed to degrade the carbohydrate to smaller sugar fragments is added.

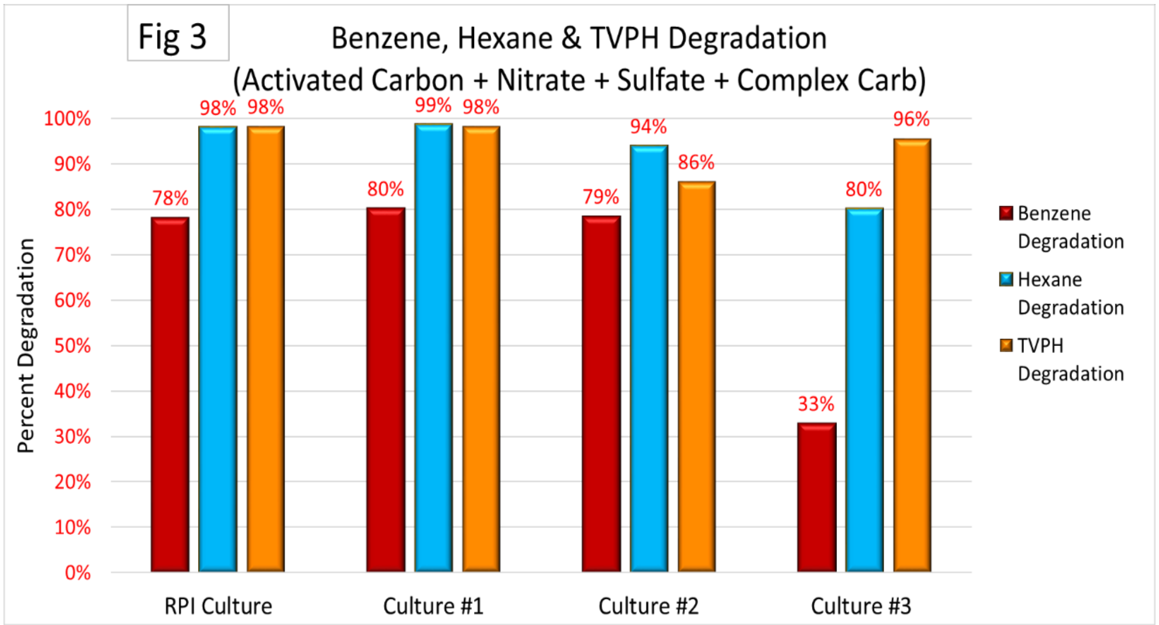


Fig 3

Benzene, Hexane & TVPH Degradation
(Activated Carbon + Nitrate + Sulfate + Complex Carb)

Regardless of the consortia used, substantial improvement in performance was realized. Degradation of the aromatic and aliphatic fractions rose significantly and data involving the Culture 3 also improved although it still lagged other blends of organisms tested.

Figure 4 is a comparison between RPI's consortia and the Culture 3 used with the diesel preloaded BOS 200® carbon and preloaded wood based carbon (char).

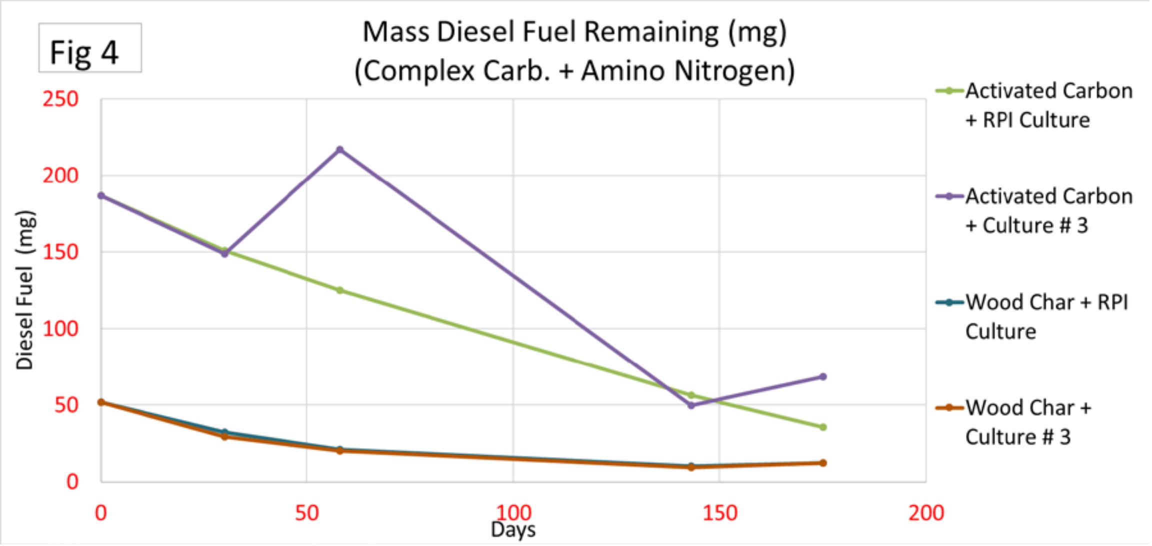


Fig 4

As with the gasoline work, the Culture 3 appears to have more variance in the data although performance is comparable. Interestingly results when char is used literally lay on top of each other so the consortia makes no difference. RPI believes this is due to the much lower ability of the char to absorb diesel so there is substantially less mass involved for the organisms to consume. Very similar data is shown in Figure 5 where different amendments are explored using RPI's consortia and BOS 200® carbon. Consistently across carbons and consortia, it was found that whenever a polymeric substrate capable of functioning as an electron donor was present, performance was enhanced.

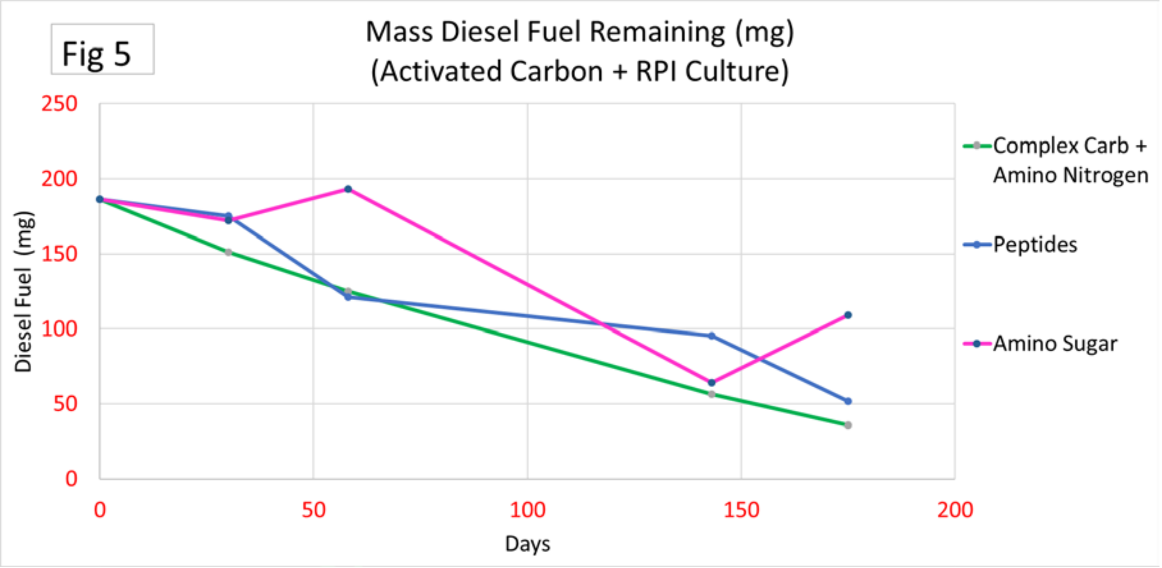


Fig 5

The most striking difference evident in the Figure 4 data is the fact that approximately 135 mg of diesel was degraded in the BOS 200® carbon while only 37 mg was degraded within the wood based char over the four-month test. This has significant ramifications with respect to applicability to LNAPL DRO sites and is further discussed in the section pertaining to activated carbon and its application to LNAPL.

Combined data from the gasoline and diesel fuel studies provide compelling evidence to support a conclusion that compounds adsorbed into the microporous structure of activated carbon are indeed bioavailable.

Is regeneration/reactivation of the carbon through biological mechanisms viable?

The data addressing this question stems from Gasoline spiked into test vials (500 ppm spike – 75 mg gasoline) rather than preloaded carbon as described above related to the study of diesel fuel. Test vials across treatments were sacrificed at various times (one month and six months) so that a complete analysis of both the aqueous phase and the carbon could be completed. After one month, the carbon was recovered by vacuum filtration and washed on the filter. Then it was extracted to remove all sorbed VOCs, again vacuum filtered and washed. Finally, the carbon was re-suspended in reagent water and a fresh 500 ppm spike of gasoline added. After equilibration, the water was analyzed for VOCs and TVPH-GRO. This data is shown in Figure 6 where the 0% line represents TVPH-GRO control values.

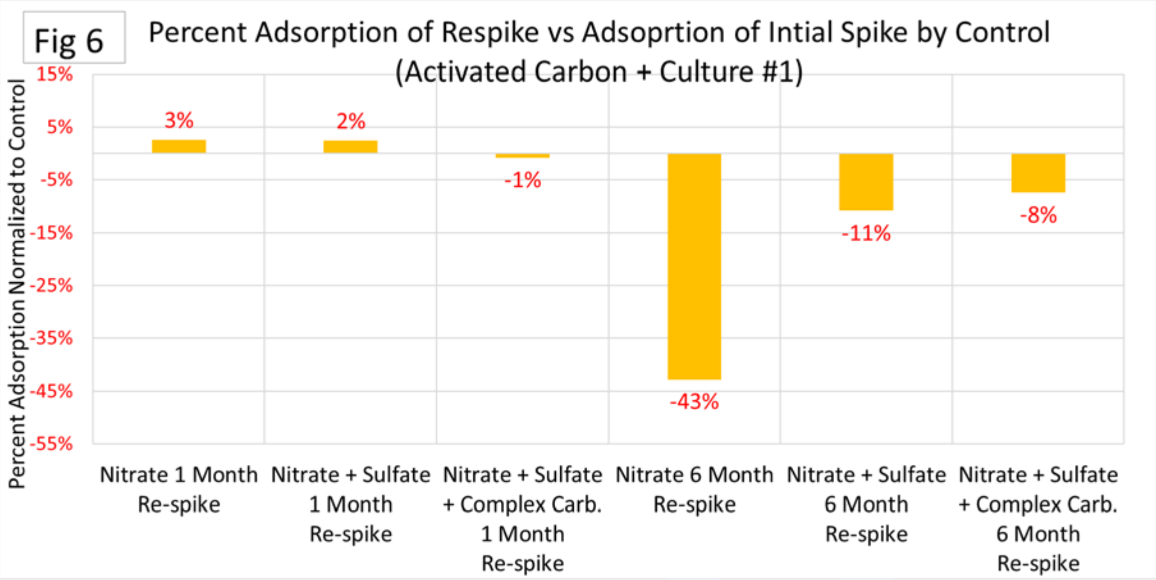


Fig 6 Percent Adsorption of Respike vs Adsoprtion of Intial Spike by Control (Activated Carbon + Culture #1)

It is apparent from the first three plots (one month data) that complete adsorption capacity was recovered regardless of amendments added. This makes sense given all sorbed VOCs had been removed prior to the re-spike. The significance of this is that biological activity occurring in this first month did not interfere with the carbon's adsorption capacity.

The next set of values were obtained after allowing biological activity to continue for 6 months. A small sample of the water was collected to determine the residual concentrations of VOCs and TVPH-GRO and then the bottle was re-spiked at 500 ppm (75 mg of gasoline). The bottles were mixed for a few days to allow equilibrium to be established and the water sampled again to measure the percent absorption of the new spike. Now we see adsorption capacity is affected by the amendments added. The nitrate only vial showed over 40% less adsorption capacity than was available initially in the control. Significantly, when sulfate is added to the nitrate, a substantial improvement is observed as now the adsorption capacity is just 11% below that in the controls. When complex a carbohydrate donor is added a further improvement is noted and virtually all the original adsorption capacity is recovered. This is an astonishing result as this last treatment embodied the biological activity associated with degradation of the gasoline and the activity associated with degradation of the complex carbohydrate. This represents a worst case as significant biofilm formation occurred and conventional wisdom suggests that such biologic activity would have plugged pores and reduced adsorption capacity.

Figure 7 shows the same data a bit differently as performance of benzene is added and the data is not normalized to a control.

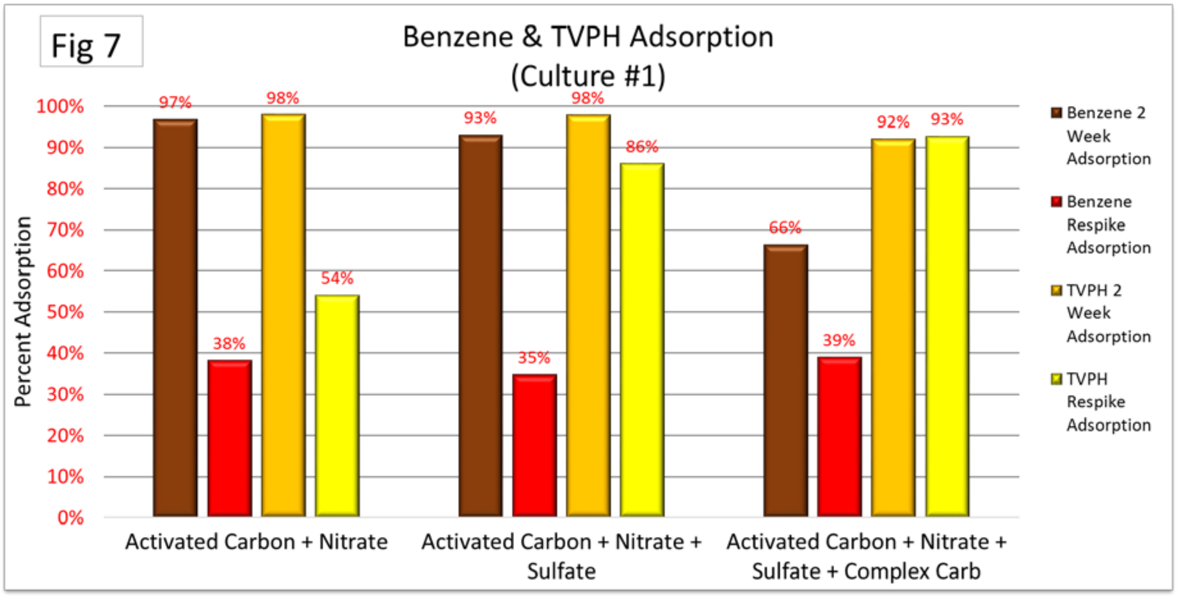


Fig 7

The brown bars represent the percent adsorption of benzene on the initial spike and the red represents the adsorption of the second spike after six months. Similarly, the darker yellow is adsorption of TVPH-GRO initially and the yellow adsorption of the second spike at six months. The last data set clearly demonstrates that addition of substrate donors interferes with the initial sorption of the gasoline and some of its constituents although after extended time and the associated degradation, initial sorption capacity is almost completely recovered.

Do sorption limitations of activated carbon prevent its application to LNAPL?

The question of whether activated carbon is suited to applications at LNAPL sites has a couple of parts. First, the saturated adsorption capacity is critical because the widely-held view that “you cannot put enough carbon in the ground” must be answered. Secondly it also turns on whether the sorbed hydrocarbons are bioavailable. Thirdly, it depends on the kinetic rates of degradation and lastly whether biological regeneration of the carbon is a viable process. Each of these aspects are discussed below.

1. The saturation adsorption capacity for fuel hydrocarbons is widely considered to be around 25% (wt.) by the environmental industry. RPI carefully measured this parameter for its BOS 200® carbon and it is 58% (wt.), double what was presumed.
2. Compelling data has been presented in this paper to support the fact that adsorbed hydrocarbons including gasoline and diesel range hydrocarbons are bioavailable even when located in the microporous structure of the carbon.
3. Given the data supporting bioavailability, there is no longer a need to have enough carbon in the ground to account for every pound of hydrocarbon. We now have kinetic data that says mass removal will increase as a function of the amount of carbon emplaced but that there is no "magic" amount of carbon needed. Rather it becomes a matter of project goals and how quickly they must be met. Diesel fuel degradation data presented here suggests that somewhere between 0.5 gm to 1 gm of hydrocarbon can be degraded per gram carbon per year.
4. Compelling data is also presented suggesting that biological regeneration of the carbon is a viable process. The mass removal rate per gram-carbon/year coupled with the fact that new adsorption of hydrocarbons can be occurring makes a strong case for using activated carbon to clean up LNAPL sites. Mass removal rates and saturation adsorption capacity associated with wood based carbon (char) do not appear to be advantageous as over four times as much carbon would need to be used to achieve the same result as that observed with BOS 200® coal based carbon. The type of carbon used matters.

Further Lines of Evidence of Biological Activity

Data presented is dominated by changes in concentrations or mass of specific compounds or hydrocarbon ranges including GRO and DRO. The underlying presumption has been that biological activity is responsible for the changes noted. Data specific to various degradation pathways was collected to support the fact that biological activity was ongoing. Fermentation of hydrocarbons produces alcohols and fatty acids. Although it is not clear exactly which microorganisms were present in each of the consortia tested there are clear differences. For example, generation of lactate and acetate in the complex carbohydrate amendment chemistry resulting from RPI's consortia compared to Culture 3 suggest very different pathways are evident. The RPI consortium did not generate much acetate but did generate lactate while the Culture 3 generated substantial amounts of acetate but almost no lactate. Another suite of byproducts of fermentation are well known to all; alcohols. Although not plotted generation of alcohols was common across treatments and consortia. Ethanol, t-butanol, and n-butyl alcohol were commonly formed to various extents.

A good deal of other evidence was gathered including nitrate consumption, other fatty acid generation, low molecular hydrocarbon gas generation, and other biological volatile compounds like acetone, and acetaldehyde. The best lines of evidence for biological activity are those that can be seen. The first photograph (below) shows several of the bottles and the various colors observed. Some bottles are relatively clear while others are yellow or pale yellow and others are pink to violet. All test bottles contained trace metals and the yellow tinted bottles are likely due to iron oxidation while the pink and violet are due to manganese or cobalt. Visible evidence that consortia are sometimes using metals as terminal electron acceptors which is widely accepted within the industry. The second picture shows a glob of carbon encased in bubbles and a clear mucus-like substance.

Biofilm formation in several of the test bottles was so extensive that the grains of carbon or the char were completely surrounded by goo and liquid in the bottle had the viscosity of egg-drop soup.

Although not confirmed, the bubbles are thought to be primarily carbon dioxide. There were multiple instances of foaming or effervescence when bottles were opened. Also, at various times, pressure had to be vented to prevent rupture of the crimp seal. These photos were of bottles in the diesel study.

Conclusions

1. BOS 200® coal based carbon appears to have the necessary properties coupled with a viable degradation mechanism to realistically address LNAPL impacted sites.
2. Fuel hydrocarbons including gasoline and diesel fuel are effectively adsorbed by activated carbon and those sorbed compounds can be degraded biologically, even those sorbed within the microporous structure.
3. Biological regeneration of activated carbon to recover substantial amounts of the original sorption capacity is an important and open question. Other studies have produced mixed results and the consensus is that some amount of adsorption capacity can be recovered however it is a small fraction of the original so is not a realistic mechanism. Results disclosed in these studies conducted by RPI disputes this “consensus view” and the data presented suggests that a substantial amount (over 90%) of the original adsorption capacity can be recovered. Further, the more effective the overall biological degradation biochemistry is, the more effective the recovery of adsorption capacity becomes.
4. Nitrate does not appear to be a very effective electron acceptor for degradation of benzene and other aromatics. Rather, nitrate seems to be an effective vehicle to support degradation of aliphatic hydrocarbons.
5. The combination of nitrate with sulfate improves performance and both the aliphatic and aromatic fractions of petroleum hydrocarbons are now degraded.
6. Addition of substrate electron donor materials, and particularly complex carbohydrates (such as starch) or peptide containing materials in conjunction with consortia focused on degrading the complex carbohydrate into smaller substrate molecules significantly improves performance and rates of degradation across the board.