WHEN IT COMES TO LNAPL, ACTIVATED CARBON MAY REPLACE NSZD AS THE BEST AVAILABLE CLOSING TECHNOLOGY

RPI GROUP

ABSTRACT

Products based on activated carbon have been offered by Remediation Products Inc. (RPI) for over nineteen years. There has been a recent interest in "Carbon-Based Injectates" with many people and organizations offering opinions on applications and limitations. At this point, industry has accepted that compounds absorbed into the microporous structure of carbon are bioavailable and that subsequent degradation results in biological regeneration/reactivation of the carbon. Work at RPI indicates that a correlation exists between the surface area of activated carbon and the biological degradation rate of adsorbed hydrocarbons. Fundamentally, this presents a new way to think about designing treatment strategies, incorporating carbon, for remediation of LNAPL impacted sites.

The industry has long pointed out that the amount of hydrocarbon mass present at most LNAPL sites cannot be treated with activated carbon because it is not possible to put enough carbon in the ground to adsorb it. RPI has developed a design strategy based on kinetic mass removal rates rather than adsorption capacity, thus circumventing this objection.

This presentation will include results from research at RPI underpinning the basis of this approach and the performance of this design approach implemented at multiple sites in the USA. The research involved testing performed with GAC that had been preloaded with diesel fuel. Overall biological activity was enhanced with nutrients and a long-term complex carbohydrate substrate.

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.

PREPARED CARBON MASS LOADING BOS 200® CARBON

1. Based on the analysis of 10 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.

SAMPLE 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-NH3.
- pH.

Spent carbons were vacuum filtered, extracted, and the extracts analyzed by Method 8260B for volatiles and the diesel fuel determined by GC/MS using a semi-volatile method.

DIESEL BENCH SETUP

Previous work with gasoline demonstrated that degradation of fuel hydrocarbons is significantly enhanced by addition of a complex carbohydrate, yeast extract, and an enhanced blend of microbes. This chemistry was included in the diesel bench study, and data from this treatment is discussed in the next section.

Measured amounts of food-grade starch, yeast extract, and a blend of microbes designed to degrade fuel hydrocarbons and the starch, along with 0.5 gms of the diesel-loaded F-400 activated carbon, were added to small serum vials (150 ml). One ml of the microbial blend was added and reagent water added to fill the vial, leaving minimal headspace. Vials were closed with rubber septa and crimp seals. At each sample event, bottles were sacrificed, and samples collected for analysis. Based on preliminary work, each 0.5 gms of diesel loaded carbon contained 178 mg of diesel fuel and 305 mg of activated carbon. Serum vials were mixed a couple times each day by inversion and maintained in an incubator at 30 degrees C.

DISCUSSION OF THE DIESEL BENCH TEST RESULTS

The extent of biological activity in the vials is readily seen in the picture, which shows what appears to be 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 were 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.

Figure 1 shows a plot of diesel fuel remaining on the carbon as a function of time, where the vertical axis is mass of diesel remaining and the horizontal axis is time in days. The most striking feature is that results showed zero-order kinetics for degradation of diesel fuel adsorbed in the activated carbon, suggesting that the rate of degradation is independent of concentration. This situation commonly occurs when a reaction is catalyzed by attachment to a solid surface (heterogeneous catalysis) or an enzyme. In our case, both are likely occurring, but the available surface area of the activated carbon is controlling the mass removal rate. Rather than designing the site remediation by basing the carbon loading on adsorption isotherms (the industry standard), we can now base design on kinetic rates of degradation, and the rate of degradation can be manipulated based on the amount of carbon employed. In other words, given the initial hydrocarbon mass distribution within a plume, we can choose the length of time needed to approach a targeted goal, and the time chosen determines the amount of carbon needed.

The kinetic data 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 roughly one gm of hydrocarbon can be degraded per gram carbon per year.

APPLICATION TO LNAPL SITES

This kinetic design approach has been implemented at numerous sites over the last five years. Contaminant mass removal rates observed at these sites are five to ten times greater than those realized under comparable NSZD scenarios. At the oldest site, kinetic design predicted elimination of measurable LNAPL in 18 to 24 months. The contaminant here is condensate that is rich in aromatic content, so benzene concentrations are high. One of the more highly impacted areas is now monitored by recovery well 9, and with depth to GW between 14 ft and 16 ft, around 0.36 feet of NAPL persisted in the months prior to installation of BOS 200+ in October of 2017. Post-injection data is shown on Figure 2. Because of COVID, the site has not been sampled since September 23, 2019, although another set of samples are planned in late May 2022.

The vertical axis is depth to water (DTW) in feet (BTOC), the secondary axis is PSH thickness (ft) and the horizontal axis shows monitoring dates and implementation of treatment is depicted as the vertical line. Shortly after injections were completed, GW rose over four feet, so it is surprising to see any measurable NAPL at the first post-injection monitoring event. The September 2019 sampling event is roughly 22-months post injection. Measurable NAPL should be minimal or non-existent and 0.02 ft of NAPL was observed. It is worth noting that DTW is 17-feet, deeper than has been observed in over two years, so it represents the best opportunity to detect even trace amounts of PSH. Further, benzene is below the MCL, suggesting that minimal hydrocarbon mass remains.

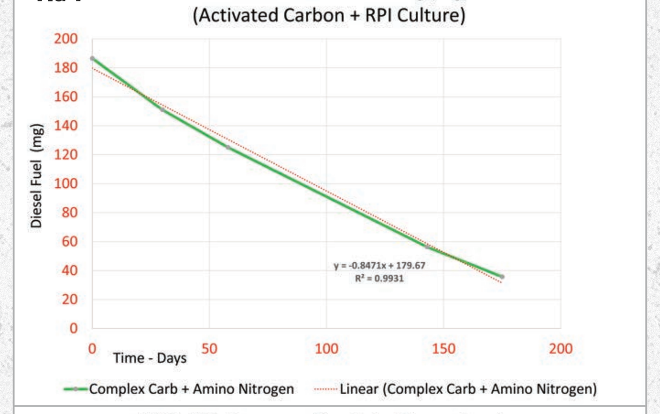
Eighteen wells were tracked post injection for NAPL and selected data including pre-inject benzene, and those wells where benzene is below the MCL in September 2019, NAPL values in the fall of 2017 and in the fall of 2019, and notations where sulfide and/or ammonia is generated are recorded on Table 1. Benzene ranges from 1350 ppb to a low of 0.7 ppb while most are in the hundreds of ppb. Of the seventeen wells that started above the MCL, ten are below the MCL as of September of 2019.

Based on chemical data, the "sheen" noted at three of the wells in 2019 is likely not related to PSH but rather to biological activity. This leaves three wells with PSH detected: RW-07, RW-09, and MW-02. MW-02 is surrounded by utilities and a pipeline so that no injections were installed anywhere near the well. It is in the heart of the source, far removed from a property boundary and is expected to exhibit measurable PSH for a while.

Generation of sulfide and ammonia is noteworthy as sulfide is a byproduct of sulfate reduction through degradation of hydrocarbons and ammonia is needed for cell growth. Ordinarily, sulfide is not observed when petroleum hydrocarbons are treated using BOS 200 because the blend of microbes added contain some that are sulfide oxidizers and elemental sulfur is produced. This element is insoluble in water and very stable. However, when NAPL is involved, rates of sulfate utilization can exceed the rate of sulfide oxidation and sulfide is observed. The sulfide will not persist and is a positive indication of COC degradation.

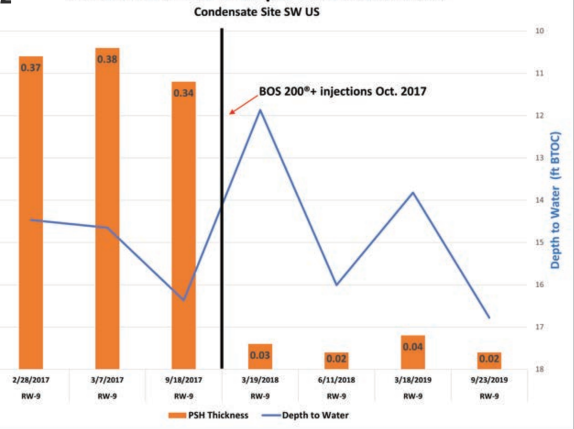
Mass removal rates estimated for this site using guidance detailed in the ITRC document suggested a value of around 730 gms-PSH/m2-yr while that estimated from site data is 5,065 gms-PSH/m2-yr. Should trends evident in data from the previous monitoring up to the fall of 2019 be confirmed in the scheduled monitoring event in May, it is expected the site will be closed.

FIG 1



Mass Diesel Fuel Remaining (mg) (Activated Carbon + RPI Culture)

FIG 2



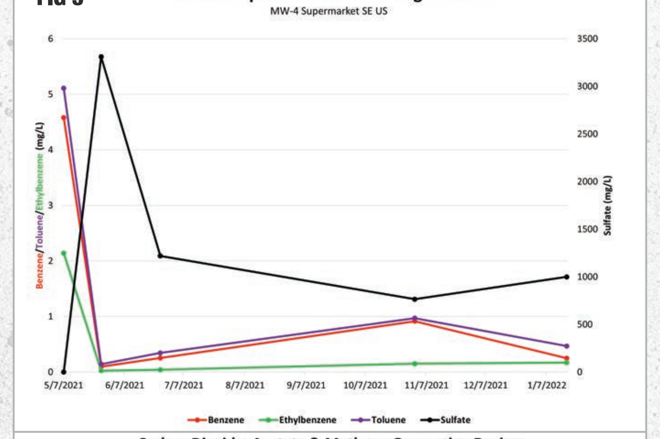
NAPL Thickness vs Depth to Groundwater

TABLE 1

ID	Benzene Pre-Inj (ug/L)	Benzene < MCL 9/2019	NAPL 9/2017 (ft)	NAPL 9/2019 (ft)	Sulfide Present	NH_3 Generation
MW-02	246			0.66	X	X
MW-04	23.4	X	0.07	Sheen		X
MW-06	125	X				
MW-11	22.5	X				
MW-20	341		0.01		X	X
RW-05	1350	X	0.06	Sheen		X
RW-07	387		0.19	0.02	X	
RW-08	256	X	Sheen			X
RW-09	311	X	0.34	0.02		
RW-10	0.69	X	Sheen			X
MW-16	21.0	X			X	X
MW-29	103		Sheen			X
MW-32	11.4	X				X
MW-33	153		Sheen			
MW-03	309					X
RW-01	141			Sheen	X	X
RW-02	28.0	X				X
RW-04	340		Sheen			X

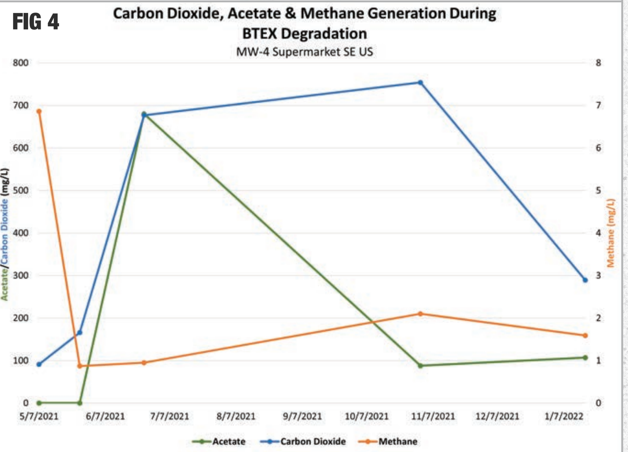
Note: analytical data does not support hydrocarbons are the source of "sheen" at highlighted entries.

FIG 3



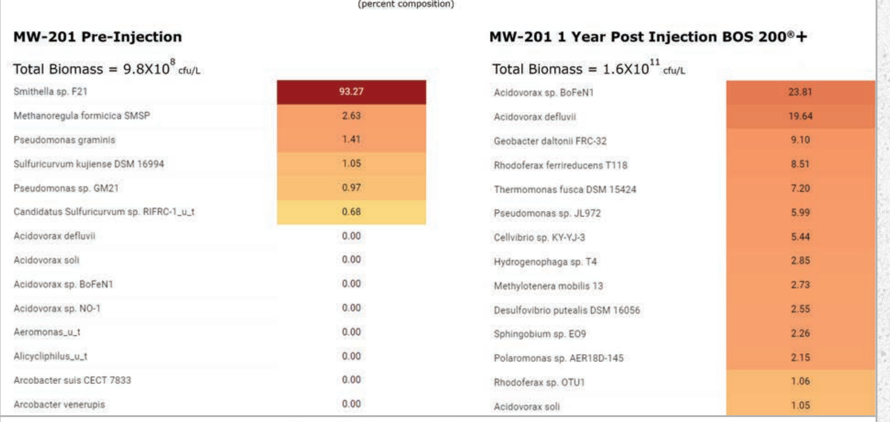
Sulfate Depletion from BTEX Degradation

FIG 4



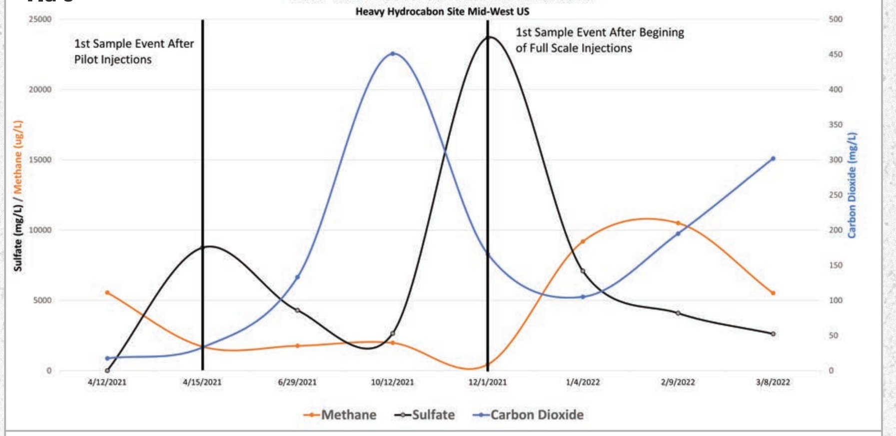
Carbon Dioxide, Acetate & Methane Generation During BTEX Degradation

FIG 5



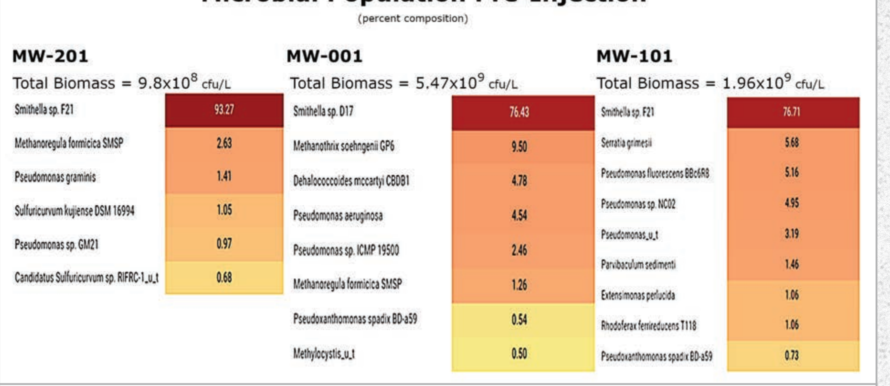
Microbial Population

FIG 6



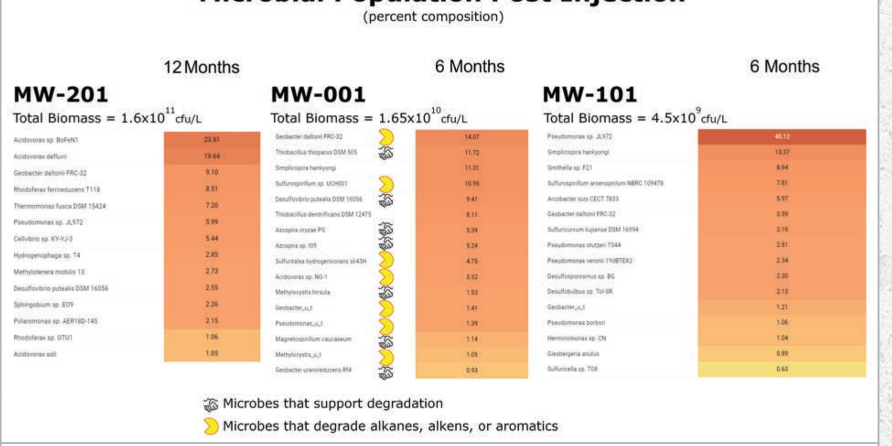
MW-201 Dissolved Gases and Sulfate

FIG 7



Microbial Population Pre-Injection

FIG 8



Microbial Population Post Injection

FIG 9

Significant Increase in Richness and Evenness

APPLICATION TO LNAPL SITES CONT.

Former UST Site in Tennessee

The geologic setting at this site consists of stiff to soft clay and the depth to GW is 17-feet bgs. Gasoline impacts have managed to penetrate nearly twenty feet below the water table. Dissolved benzene and soil TVPH values are certainly suggestive of LNAPL although no PSH has been observed. Total petroleum hydrocarbon impacts in soil range from 1,000 to 5,000 ppm at most locations across the smear zone. BOS 200+ was installed at this site in May of 2021.

Figure 3 plots typical gasoline contaminants (B,T, and E) versus sulfate. A classic pattern of adsorption is evident, and the sulfate response is consistent with high sulfate demand that is common at heavily impacted sites. Initial drop in B, T, and E is due to installation of an activated carbon-based product where concentration in GW fall below what is expected based on design and this is followed by contaminants bound to soil leaching into GW as a new equilibrium is established. Because site soils are clay, this process takes longer, and the rise observed in November 2021 results from this equilibration process. Dissolved sulfate derived from magnesium sulfate is responsible for the rapid rise and sulfate demand results in the following decline. BOS 200+ also includes gypsum which is a second source of sulfate. Gypsum is not very soluble but easily supports a sulfate concentration of around 1,000 to 1,500 ppm. As the readily available sulfate is consumed, sulfate then re-establishes a new steady state around gypsum saturation, and this is evident in the graph.

The rest of the story is shown on Figure 4 which depicts CO^2, methane, and acetate data over time. Again, the initial methane drop is due to installation of BOS 200+: a combination of adsorption and dilution. As microbial activity commences, generation of CO^2 and acetate begins. It is well known that sulfate reduction results in production of CO^2 and fermentation of the starch in BOS 200+ produces acetate, which is utilized by many microbes.

This installation is young and the full signature of BOS 200+ is developing. Because acetate is utilized by such a broad spectrum of microbes, its concentration cannot continue to rise and soon gets to a point where rates of production are essentially equal to its rate of assimilation. Carbon dioxide follows a similar pattern as generation is high while elevated concentration of dissolved sulfate persists but then falls off in line with the new equilibrium associated with dissolution of gypsum. Site closure criteria is risk-based and currently benzene is below the targeted standard of 885 ppb.

Industrial Manufacturing Facility in the Midwest

A heavy industrial manufacturing facility in the Midwest, impacted by oils in the C14 to C40 range, attempted to excavate contaminated soils as a partial remedy in 2015. Essentially, all soil that could be removed was excavated. There are access limitations that prevented complete removal. Observation of LNAPL in an off-site well triggered additional investigation to delineate remaining mobile NAPL. Soil borings combined with a laser induced fluorescence survey were completed in 2016, and the plume was found to be moving toward a river. The goal is elimination of mobile NAPL. Soil impacts within a ten-foot depth horizon of from 5,000 to 25,000 ppm (0.5 to 2.5% wt) are widespread. Adsorption capacity of BOS 200® with NAPL from the site was estimated to be approximately 30% (wt.) and the NAPL solubility in water was determined to be just under 1-ppm.

This is a very challenging site. Because of site NAPL characteristics, there are no VOCs, and the low solubility in GW means no direct measurement of changes in contaminant mass is realistic. The best chemical indications will stem from measuring generation of gases such as carbon dioxide and methane and utilization of sulfate. Another avenue is to collect samples for biological evaluation using metagenomic sequencing (MGS) to track changes in microbial communities and measure biomass.

Figure 3 shows control data (pre-injection) and 1-year post-injection data from MW-201. The microbial community prevalent before injection of treatment is characterized as a functional but modest syntrophy degrading alkanes and aromatics and producing methane. As detailed in the figure, the community primarily consists of smithella, is not very diverse, and total biomass is low, so rates of degradation are not high. The community observed is completely consistent with chemical data as terminal electron acceptors are sparse and methane concentrations across the plume are elevated. For example, at MW-201, sulfate was 0.34 ppm, CO2 was non-detect, and methane was 4260 ppb prior to injection.

One year later, the microbial community has completely changed, smithella does not even make it in the top 99%. It now consists as a diverse and more evenly populated community with multiple sulfate reducers, sulfide oxidizers, and hydrocarbon degraders capable of assimilating alkenes and aromatics. In addition, there are several microbes capable of using methane as the sole carbon source. Finally, total biomass has increased by over two orders of magnitude.

A pilot study was conducted at this well around April 2021, and then full-scale expansion occurred in November 2021. Plots of the methane, CO^2, and sulfate are depicted in Figure 4. Because the sulfate demand is extreme, BOS 200+ slurries are prepared using water that is nearly saturated with magnesium sulfate. TDS of the slurry is around 30,000 ppm and is designed to prevent any dehydration of added microbes. Baseline methane is 550 ppb. Initial decline is due to a combination of adsorption and dilution from injections. Hydrocarbon degradation via sulfate reduction generates CO^2 and sulfide. Carbon dioxide is very low initially but begins to rise shortly after injections. Sulfate is added in two forms, gypsum, and magnesium sulfate. Sulfate demand is high because of the contaminant mass present in the saturated zone. Magnesium sulfate is highly soluble and readily bioavailable which accounts for the relatively rapid decline. As dissolved sulfate falls, it begins to be replenished by dissolution of gypsum.

The left vertical axis is associated with sulfate and methane; however, sulfate values are in ppm and methane values are in ppb. Right axis is just carbon dioxide in ppm. There is a clear impact exhibited in the well from full-scale injections stemming from expansion of the pilot study area. Addition of fresh BOS 200 activated carbon results in adsorption of both methane and CO2 and some dilution. This depression is followed by generation of methane and CO^2 along with utilization of the readily available dissolved sulfate, the same pattern as was observed pre- and post injection during the pilot study.

Microbial MGS was also performed on samples from MW-001 and MW-101 within the NAPL plume. Figure 5 shows pre-injection control data for all three wells: MW-201, MW-101, and MW-001. It is clear from the data that baseline microbial communities were similar across the plume consisting primarily of smithella and with biomass on the low end of what is considered to be effective abundance. Figure 6 shows 6-month post-injection data, biomass has increased significantly, and the communities are diverse syntrophy that's degrading hydrocarbon contamination consistent with the previous discussion regarding performance at MW-210.

Plotting the diversity and richness of the microbial communities present in controls versus post-injection results in the data depicted on Figure 7. Using Wilcoxon Rank Sum Test to evaluate the difference results in a statistical value of -1.964, which is significant at the 0.05 level. Just another way in which to validate the compete change noted in microbes thriving after installation of BOS 200+.

CONCLUSIONS

Industry is correct when pointing out that impacts at many petroleum hydrocarbon sites are extreme and would require infeasible amounts of activated carbon for complete adsorption. This position rests on the premise that full adsorption is required for successful application of this technology, and this thinking is flawed. BOS 200+ has been shown to create a healthy and diverse microbial community that enhances mass removal rates as a function of the activated carbon surface area upon which it is staged.

Remedial design based on kinetic modeling has the potential to substantially reduce the time required for closure of LNAPL sites. Mass removal rates realized at the condensate site were approximately seven times higher than NSZD rates estimated using procedures detailed in the ITRC NSZD Guidance document. Kinetic design allows the design activated carbon loading to be fixed based on the time selected to achieve cleanup goals: elimination of measurable LNAP is often the case. Current wisdom is that NSZD is the best technology for cleanup of residual LNAPL sites or those with soil impacts measured in percent rather than ppm. Performance of BOS 200+ at such sites demonstrates the potential of enhancing NSZD with activated carbon treatment coupled with design based on degradation kinetics.