Modeling Residual LNAPL and Impacts to Groundwater using a Kinetic Approach

Background

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. This presentation will include results from research at RPI underpinning the basis of this approach and the performance of this design approach implemented at a site in the Gulf Coast. 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.

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.

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. Diesel fuel degradation data presented here suggests that roughly one gm of hydrocarbon can be degraded per gram carbon per year.

The site is an active pipeline and bulk storage facility in the Gulf Coast Region. Crude oil was released in 2011. Two LNAPL plumes encompassing 8,800 m² persisted after emergency recovery efforts, limited excavation, and operation of a dual-phase mechanical system for just under three years. RPI's BOS 200+ activated carbon technology was injected in 2017.

An extensive sampling program was completed to explore the distribution of LNAPL/TPH within each plume. The adjacent figure shows grid locations for soil borings advanced during this work. In addition, locations of monitor wells and selected utilities are shown. Analytical TPH results from samples taken at each boring are provided in the lengthy table along the bottom of the Poster. Units for TPH are mg/kg (ppm).

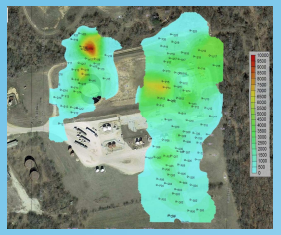
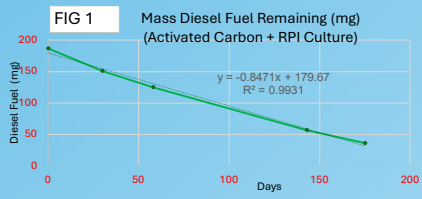
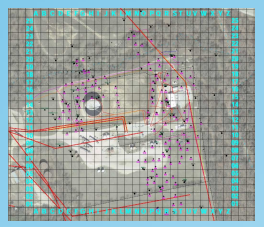


FIG 1





Depth to groundwater is shallow in the west plume and tends to increase as you move to the east. This is consistent with the bedrock contour and is seen in the distribution of TPH in the bottom table. Red highlighting are values of TPH greater than 5000 ppm, orange are values between 500 ppm and 5000 ppm, and blue are values less than 500 ppm. Contamination in the east plume is significantly deeper and affects a thicker zone than that found in the west. The highest TPH in the west plume is at H19 (11,100 ppm) at a depth of 7 feet and that in the east plume is at P14 (8380 ppm) at 33 feet. P14 is near MW-2 and DTW has not exceeded 25 feet in the last 14 years. A portion of the NAPL at this location is clearly submerged.

The heat map shows the extent of impacts to soil above Csat (roughly 250 ppm). Targeted cleanup was elimination of measurable NAPL. Dissolved benzene was of interest; however, it was not part of the regulatory mandate.

Several design options were evaluated and a cleanup time of from eighteen to twenty-four months was selected. Over 1000 injection points were completed within a 5-month period in late 2017.

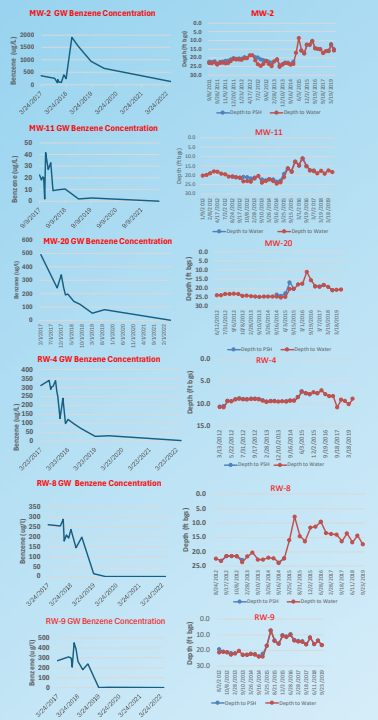
ID	Benzene pre-inj (ug/l)	Benzene < MCL 2022	NAPL 9/2017	NAPL 9/2019	NAPL 5/2022	Carbon Dioxide (mg/L)	Methane (ug/L)
MW-02	246	122	0.02	0.66	0.01	354	11000
MW-04	23.4	X	0.07	sheen	ND	216	13200
MW-06	125	X			ND	243	16800
MW-11	22.5	X			ND	138	6710
MW-20	341	X	0.01		ND	223	10900
RW-05	1350	X	0.07	sheen	ND	259	14900
RW-07	387	X	0.19	0.02	ND	206	12700
RW-08	256	X	sheen		ND	194	10300
RW-09	311	X	0.34	0.02	ND	198	15600
RW-10	0.69	X	sheen		ND	239	10300
MW-16	21	X			ND	257	7340
MW-29	103	X	sheen		ND	164	10200
MW-32	11.4	X			ND	199	4320
MW-33	153	X	sheen		ND	189	14700
MW-03	309	X			ND	244	11600
RW-01	141	X		sheen	ND	231	5120
RW-02	28	X			ND	265	8610
RW-04	340	X	sheen		ND	301	10100

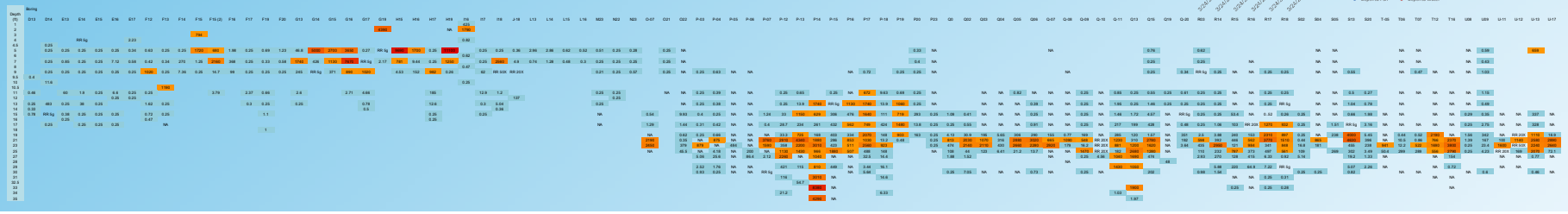
Note: Updated to May 2022 data

PSH values in ft. -

Eighteen wells were tracked key data is provided in the above table. Baseline values of benzene in groundwater is provided and post-injection NAPL measurements are shown for 2017, 2019, and May 2022. Values for carbon dioxide and methane are from the most recent sampling event. As of May of 2022, benzene in all but one well had fallen to a value below the MCL. The value shown in red at MW-2 is the benzene in groundwater in May 2022.

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 in the east plume, so it is not surprising that this well remains with measurable PSH .





Shortly after completing injection work, the DTW had risen nearly four feet, so it is somewhat surprising that any measurable PSH was noted in late 2017. The collection of graphs to the left show depth to water and depth to PSH at six different locations. For each location, there is a corresponding plot of benzene in groundwater. Groundwater elevation data clearly indicates that the water table had risen, and this has interfered with measurement of LNAPL at many of the locations.

During the sampling work in the summer of 2017, historical data was reviewed to look for a fingerprint of groundwater in contact with NAPL versus groundwater with soil impacts below Csat. A good correlation between benzene in groundwater was found to predict when NAPL was present even though it was not visible in monitor wells. The magic number was 50 ppb benzene.

Monitoring activity at the site was suspended due to COVID after the September 2019 event and was not sampled until 2022. The September 2019 event fell within the 18-to-24-month design prediction and the benzene data and PSH measurements suggests we were getting close. Based on the 2022 data, an NFA has been requested and is under review by the agency.

CONCLUSIONS

1. **NSZD can be accelerated using RPI's BOS 200+.**
2. **Using a kinetic design instead of a carbon demand design reduces cost significantly.**
3. **Chemical markers can be used to track contaminant mass removal.**