

CASE STUDY



Excavation and ISCO followed by *In Situ* Sorption and Biodegradation at a Petroleum Site

Site Type: Contaminated groundwater (TPH) in Kansas

Project Type: Excavation and ISCO followed by Sorption and Enhanced Aerobic Biodegradation

PROJECT SUMMARY

Location: Kansas

Client: Confidential

Contaminants: TPH (gasoline range and diesel range)

Project Practice Area: Excavation and ISCO followed by Sulfate Enhanced Bioremediation and Sorption

Products Supplied: TersOx™ NPS, TersOx™ Liquid, TersOx™ Powder, TersOx™ Nutrients-QR, and NutriBind® HDPAC

Our Contribution:

- Minimized surface disturbance by using chemical oxidants with limited excavation
- Oxidized a large percentage of the TPH left behind after excavation with ISCO
- Restored water quality by finishing remediation with enhanced aerobic biodegradation

Highlights:

Contaminants: TPH (gasoline range and diesel range)

Location: Kansas

Remediation Approach:

- Minimal excavation
- Application of base-activated TersOx™ NPS (a persulfate) through passive infusion gallery and DPT points
- Promoted sorption and aerobic bioremediation and of remaining TPH with a combination of TersOx™ Liquid, TersOx™ Powder, TersOx™ Nutrients-QR, and NutriBind® HDPAC

Site description:

The roughly 2.5-acre site is occupied by a one-story, 26,000 ft² building, with most of the remaining area covered in asphalt. The site is occupied by retail auto sales and an auto-repair shop, and the site was active throughout the remediation. Based upon data gathered during preliminary investigations, it appeared the source of the TPH was a leaking pipe and not a leaking tank. A map is provided in Figure 1 that shows the site layout, the dominant groundwater flow direction, and the monitoring stations used as indicator wells. A map showing the TPH contamination contours is presented in Figure 2.

Remedial Approach:

It was surmised that the TPH impacts could be remediated by limiting the excavation to the area around the leaking pipe, using injections and infiltration to remediate areas outside the excavation, thereby minimizing surface disturbance.

The project timeline is shown in Figure 3.

Project field events consisted of:

- Sampled monitoring wells to establish baseline TPH concentrations, DIC isotopic ratios ($\delta^{13}\text{C}$), and bacterial populations via NGS.
- Excavated limited area and removed contaminated soil.
- Installed infiltration gallery for ISCO amendments.
- Applied base-activated persulfate with Tersox™ NPS through both infiltration gallery and DPT points.
- Post excavation/ISCO sampling for TPH concentrations, DIC isotopic ratios ($\delta^{13}\text{C}$), and NGS bacterial populations.
- Injection of TersOx™ NPS, TersOx™ Liquid, TersOx™ Powder, TersOx™ Nutrients-QR, and NutriBind® HDPAC through DPT points to sorb and aerobically bioremediate remaining TPH.
- Post-aerobic amendments sampling for TPH concentrations, DIC isotopic ratios ($\delta^{13}\text{C}$), and NGS bacterial populations.

Technology: Used ISCO to minimize surface disturbance of excavation. Applied NGS to identify many species of active bacteria degrading wide range of hydrocarbons. Enhanced aerobic biodegradation and sorption of remaining contaminants. Used four indicator wells shown in Figure 1 to direct remediation. Figure 4 shows one of the first injections occurring on the asphalt covered site, with the employees' cars parked in the background.

Investigative Technology:

- Documented degradation of TPH with isotopic measurements of DIC.
- Assessed bacterial diversity and population density using NGS to survey 1000's of bacterial types.
- Conserved resources by studying isotopes and bacteria in select wells.

Sampling: The four monitoring well-focused on in this study are shown in Figure 1. They include the upgradient MW-6, the source well MW-5R, and the heavily impacted monitoring well MW-8.

Challenges:

TPH concentrations of 1 mg/l for low range and 0.3 mg/l for mid-range indicated that there was a lot of remediation to be done. Despite this, active operations continued at the site. Minimizing the impact of remedial activities challenged the project team, and it was clear that they needed to develop a plan that relied on very little disturbance of the surface.

The site was covered with asphalt, so oxygenated water had limited opportunity to percolate into the contaminated zone. Still, background sampling showed that some aerobic bacteria were present. Given these potentially conflicting observations, tools needed to be chosen that were going to show how the bacteria responded to the ISCO treatment so that the second treatment could be planned. It would be necessary to measure the population of all bacterial types present rather than a predetermined set.

When utilizing a remediation based upon injections, it is important to show that declining concentrations are due to destruction and not just dilution or "pushing" the contaminants with the large volume of water-based fluid that is injected. The contaminants were TPH, with the only restriction being that they were in the low or mid-range. There are no known, distinct products for oxidation. The product of the oxidation of any hydrocarbon is carbon dioxide (CO_2), which becomes DIC, but there are many other sources of DIC, so increases in the DIC concentration are not a reliable indicator of TPH oxidation.

Approach:

Project managers choose to use ISCO to aggressively treat the contaminant while minimizing the size of the excavation. Since more rapid remediation meant fewer interruptions, it was decided to use base activation with TersOx™ NPS to get a more rapid impact. A combination of sorption and enhanced biodegradation was planned to remediate any TPH that remained after excavation and ISCO. Since ISCO oxidizes the aquifer media but percolation of oxygenated water into the aquifer is limited by the asphalt covering the site, it was decided to use NGS to see what the bacterial response was and to plan the stimulation based on that response. Isotopic analysis of the DIC (as $\delta^{13}\text{C}$) was chosen to monitor the oxidation of the TPH.

Theory of DIC Isotopic Measurement

There are four sources of terrestrial carbon, and they each have a unique carbon isotopic ratio, or $\delta^{13}\text{C}$, as indicated in Table 1.

Table 1. Major carbon sources and their associated DIC $\delta^{13}\text{C}$

Carbon Source	$\delta^{13}\text{C}$ Value (‰, VPDB)
Fossil Fuels	-28
Terrestrial Biosphere	-26
Ocean	-10
Atmosphere	-8

For the purposes of groundwater, the category “terrestrial biosphere” refers to decaying plant life. The major source of DIC in uncontaminated groundwater is the atmosphere, although minor contributions may also come from decaying plant life. In addition, there can be oceanic contributions as well. The sum of all of those DIC sources produces groundwater with a DIC that typically has a $\delta^{13}\text{C}$ of -8 to -11 ‰ VPDB.

As petroleum hydrocarbons are oxidized, they form DIC. The mixing of the light (more negative) $\delta^{13}\text{C}$ DIC produced from the oxidized petroleum with the heavy (more positive) $\delta^{13}\text{C}$ of the background produces groundwater with a DIC $\delta^{13}\text{C}$ value lighter (lower) than the background. Because there are so many sources of DIC, and because the concentration of DIC is very pH sensitive, DIC concentrations are a poor indicator of hydrocarbon oxidation. However, the isotopic signature of the DIC is a much more reliable indicator of hydrocarbon activation. While the preparation of a base-activated persulfate solution creates a lot of heavy DIC with a $\delta^{13}\text{C} = -8$ ‰, the oxidation that solution induces cancels out the effect of that heavy DIC and still make the $\delta^{13}\text{C}(\text{DIC}) > -11$ ‰. The trends in DIC($\delta^{13}\text{C}$) are summarized in Figure 5.

Results:

After the enhanced aerobic stimulants were injected, all wells at the site were sampled for TPH. In both the low and mid ranges, the concentration of TPH was “non-detect.” This fabulous news even surprised the project managers. They expected that the remediation strategy would achieve the project goals, but the rate was even faster than they expected.

Benefits of Approach:

- The DIC($\delta^{13}\text{C}$) in MW-7 was nearly unchanged before and after the second injection, though the TPH concentration was 0.37 mg/l before that injection and non-detect afterward. This may be a sign that the attenuation in that well was more due to TPH sorbing to the Nutribind rather than oxidizing. The combination of sorption and biodegradation allows for a rapid decline of concentration and then a slow release of the contaminants once the bioremediation is established and can readily degrade those contaminants as they are released.
- Combining ISCO with excavation allowed for minimal surface interruption during remedial activities.

Figures:

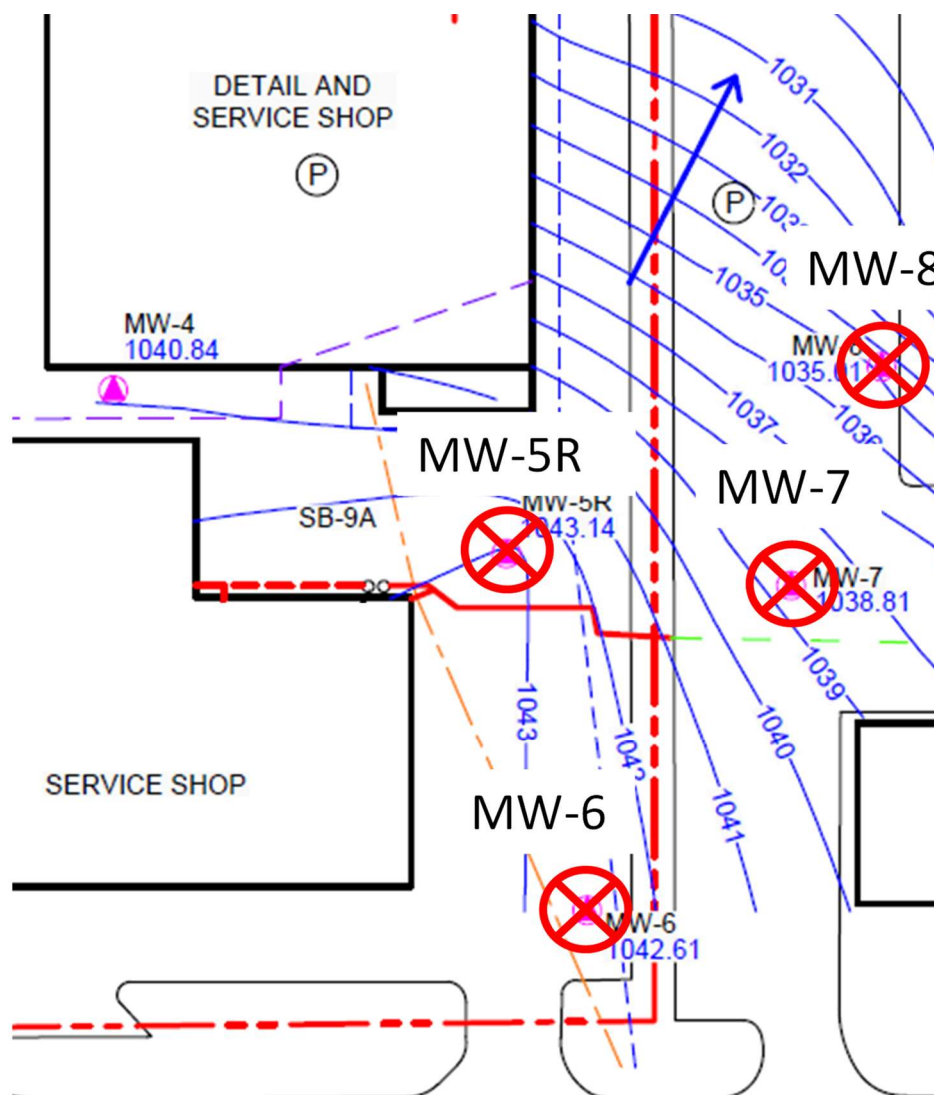


Figure 1. Site map showing groundwater elevations, dominant groundwater flow direction, and the indicator wells

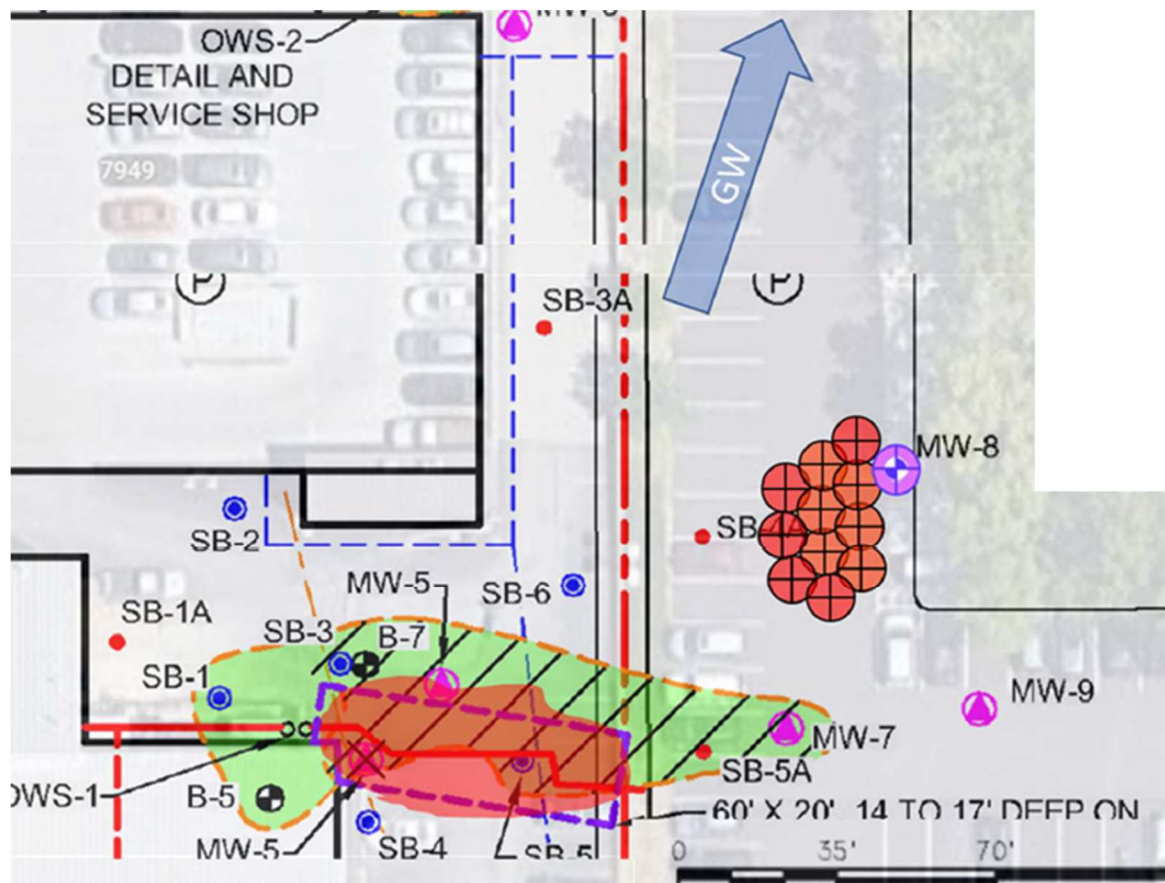


Figure 2. Site map showing TPH contours, DPT injection circles, and box showing infiltration gallery



Figure 3 Timeline for field activities



Figure 4. One of the ISCO injections

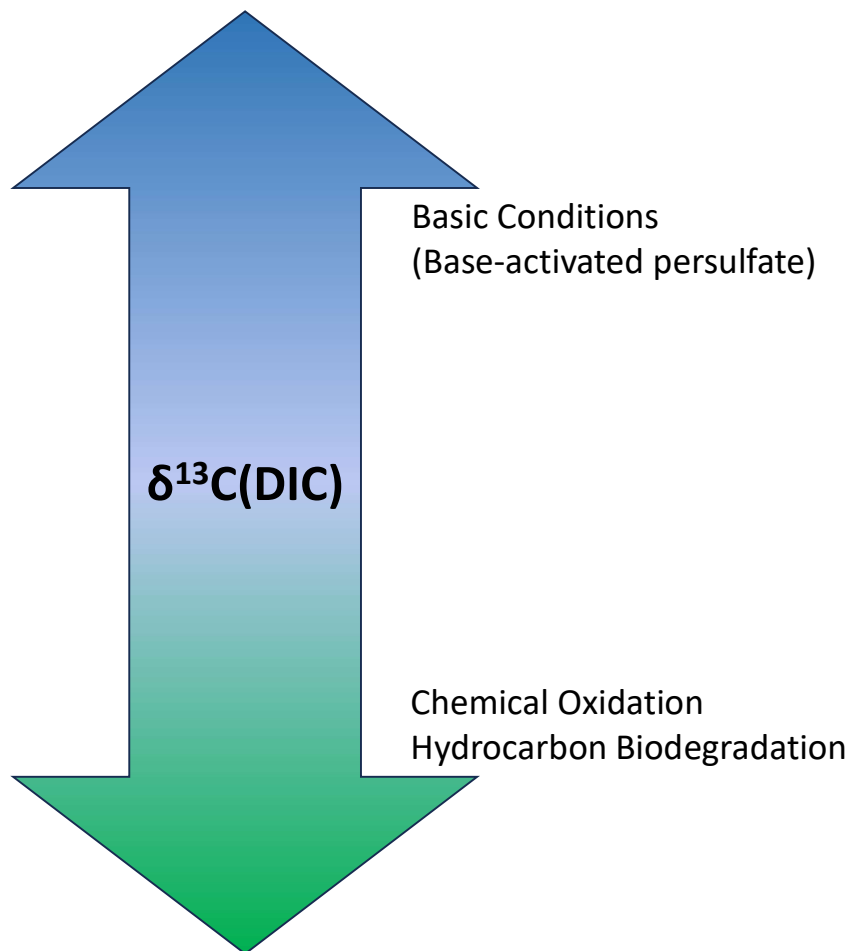


Figure 5. Trends in DIC ($\delta^{13}\text{C}$) changes

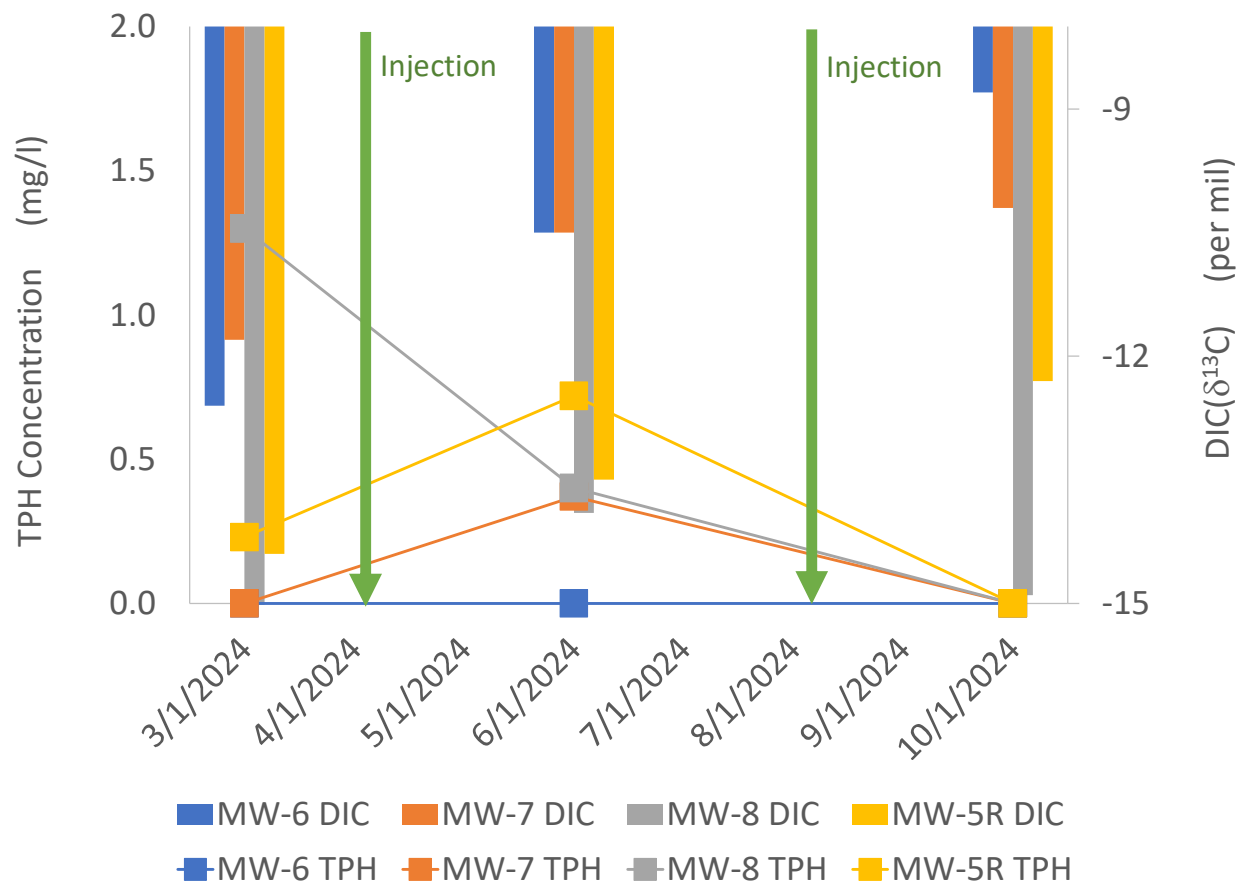


Figure 6. Graph combining TPH concentrations with DIC($\delta^{13}C$) results, showing that low DIC($\delta^{13}C$) were matched with lowering TPH concentrations. Note that natural attenuation was already driving the DIC($\delta^{13}C$) lower in the impacted wells MW-5R and MW-8 at baseline, but the injection sped it up.