SULFATE ENHANCED BIOREMEDIATION OF CUMENE

Case Study and Injection Scoping

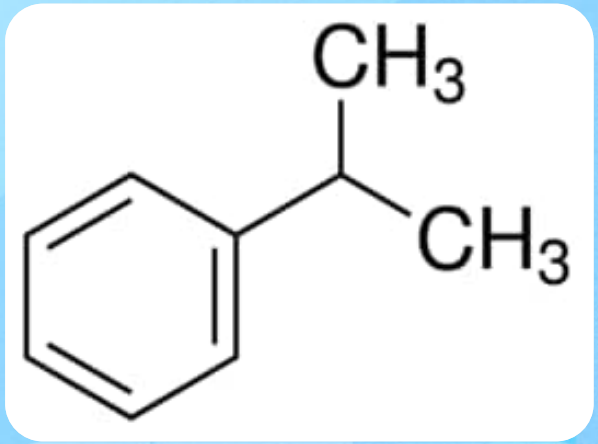
David J. Sheehan, P.E.
Broward County Environmental Permitting Division

Overview

GOALS OF PRESENTATION

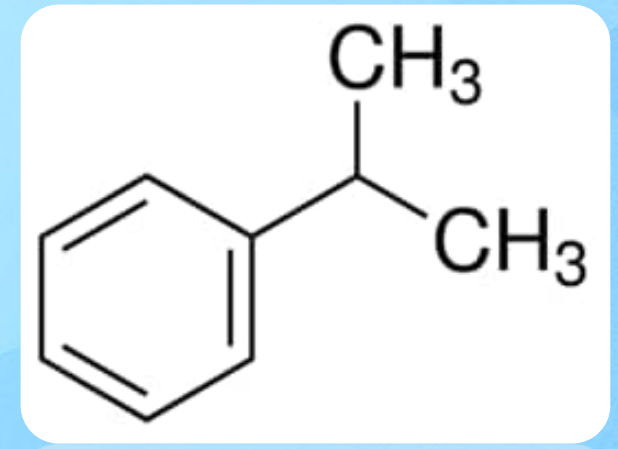
- Brief Discussion on Cumene (Isopropylbenzene)
- Discussion of Sulfate Enhanced Bioremediation (SEB)
- Chevron West Broward Boulevard Case Study
- Scoping tips for pilot testing and remedial injections

Cumene (Isopropylbenzene)



- C_9H_{12}
- A constituent in crude oils
- Also can be used as a fuel additive
- Typically present in low quantities:
  - 0.01% in diesel
  - 0.13% in premium gasoline

Cumene in the Environment



- Strongly adsorbs to soils
- Can be stripped/sparged but less effectively than benzene.
- Low cleanup targets increase the challenge for remediation.
  - GCTL: 0.8 ug/L
  - NADC: 8 ug/L

Sulfate Enhanced Bioremediation

WHAT IS SULFATE ENHANCED BIOREMEDIATION (SEB)

- The injection of a compound containing sulfate where the purpose of the sulfate is to act as an electron acceptor to increase anaerobic degradation.
- Native sulfate-reducing bacteria reduce the added sulfate while oxidizing the hydrocarbons that are present.
- If we can provide more sulfate, more bacteria can reduce it, oxidize the hydrocarbons present and multiply.
- In general if sulfate is being used as an electron acceptor at a site, concentrations of sulfate in the area of the plume will be very low while areas outside of the plume will be higher.

Why Not SEB?

- Air sparge (and biosparge) systems can get a lot of oxygen into the subsurface relatively cheaply and easily, so why not just push the aerobic degradation harder?
- If an active remediation system is an issue for a site, many compounds that increase the dissolved oxygen are available to choose from.
- Aerobic degradation has a proven track record with petroleum hydrocarbons.
- One of the end products of SEB is the production of hydrogen sulfide which is not something we want to be generating at places like service stations.

Why SEB?

- Anaerobic degradation may be slower, but we can get a higher concentration of sulfate into the groundwater than we can get the dissolved oxygen concentration.
- We don't need an active remediation system, if that is a deciding factor, we can simply perform injection events.
- In Epsom salt, there is a cheap source of sulfate to inject instead of some fancy designer remedial additive meant to release oxygen.
- Somebody has to see if this can be an effective technology to address cumene impacts. So if we can find a site where it could be applicable we can see how it performs.

Why SEB?

Why SEB?

- Previous studies have shown that the amount of hydrogen sulfide produced has never been observed to be present in a concentration of concern.
- The main compound we will be monitoring as part of our UIC will be sulfate, which has a relatively high secondary standard.

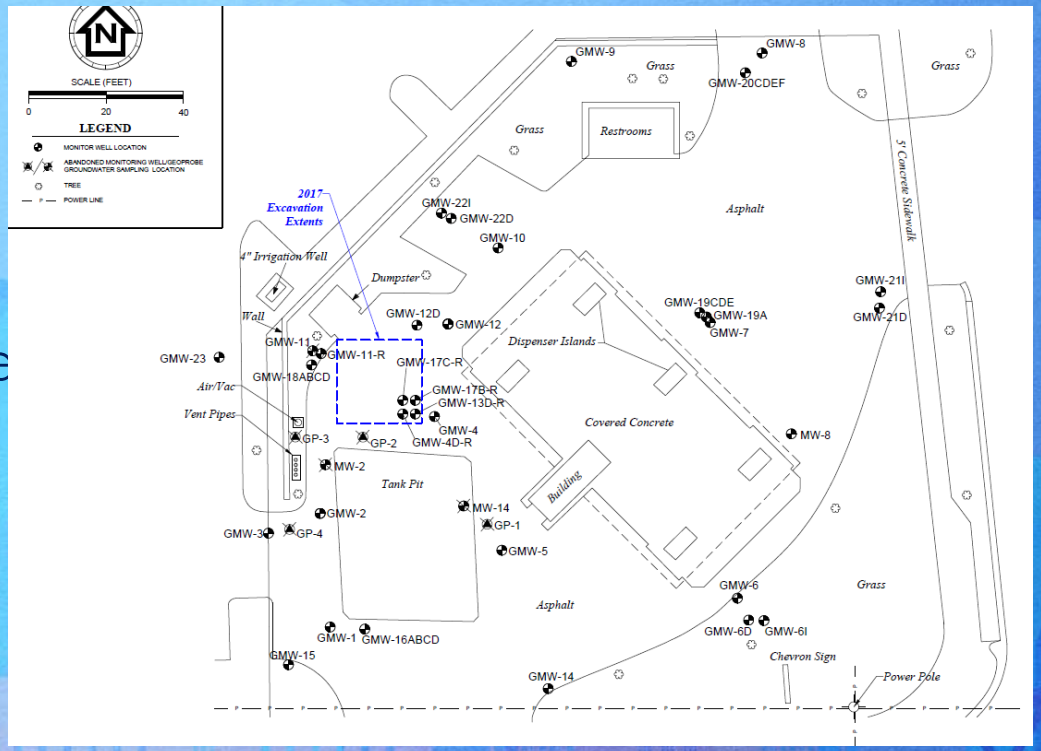
Electron Acceptor (EA)	Maximum Concentration (mg/L)	Mass of benzene degraded per unit mass of EA	Potential Benzene Degraded (mg/L)	Issues
Oxygen (in air)	9 - 10	0.33	3.0 – 3.3	•Limited solubility •Numerous oxygen sinks •Potential aquifer clogging •Biofouling near injection point
Pure Oxygen	60 - 70	0.33	19.8 – 23.1	
Sulfate	100 – 250*	0.22	22.0 – 55.0	•Hydrogen sulfide; never documented as an issue in the field •Secondary MCL for sulfate – 250 mg/L*
Nitrate	80 - 100	0.21	16.8 – 21.0	•DW concern •Primary MCL – 10 mg/L NO_3-N (45 mg/L NO_3)
Iron (III)	0 - 1	0.024	0 – 0.024	•Very low solubility •Aquifer clogging

Townsend et al., Enviro. Sci. Technol., 37, 5213-5218, 2003

The Case Study

The Case Study Site

- Chevron West Broward Boulevard
  6901 W Broward Boulevard, Plantation, FL
  FAC ID # 06/8501703
- EDI Eligible
- Historic GW Impacts
  In shallow (0-15 ft)
  And deep (15-30 ft)
- Baseline sampling
  Sulfate low in source area.



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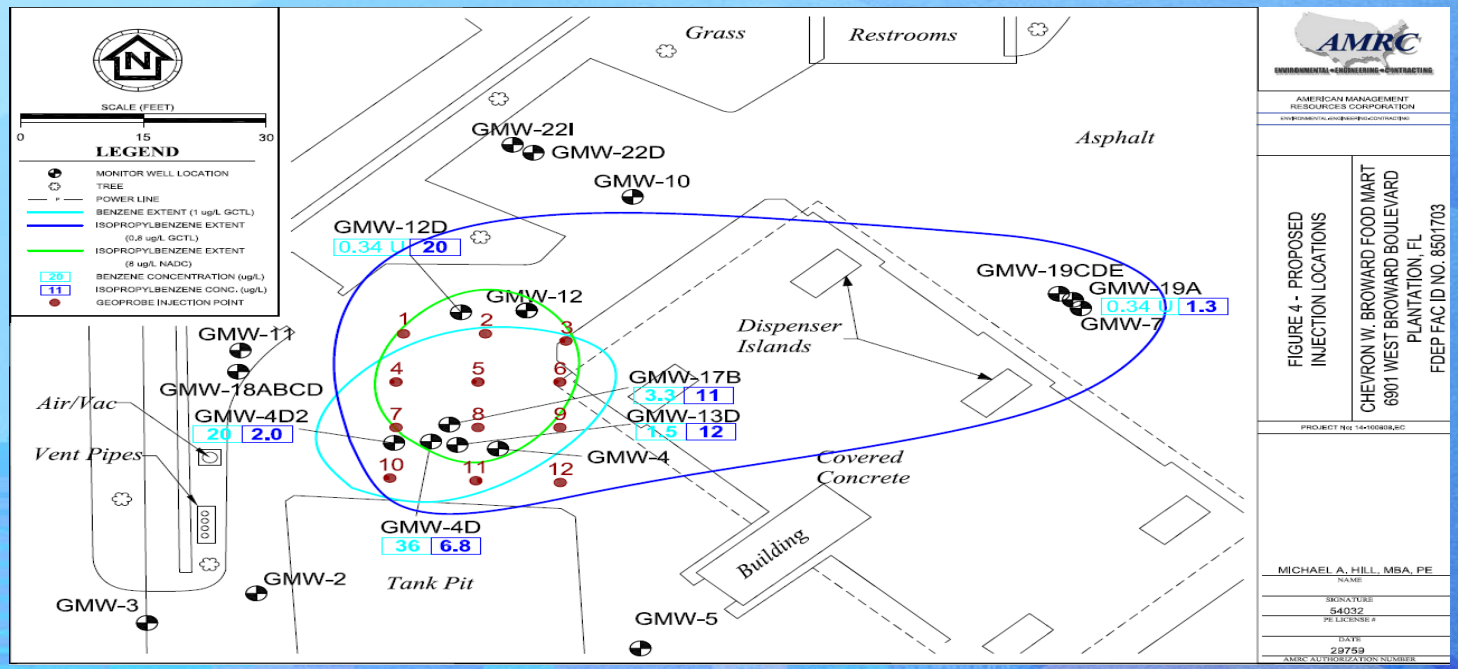
July 17, 2015 – Extent of Hydrocarbon Impacts – Pilot Test Plan

Inject 150 gallons each into 12 points of a 589 mg/L Epsom salt solution.

Monitor nearby wells during injection for field parameters and sample wells at 30 and 60 days post injection.



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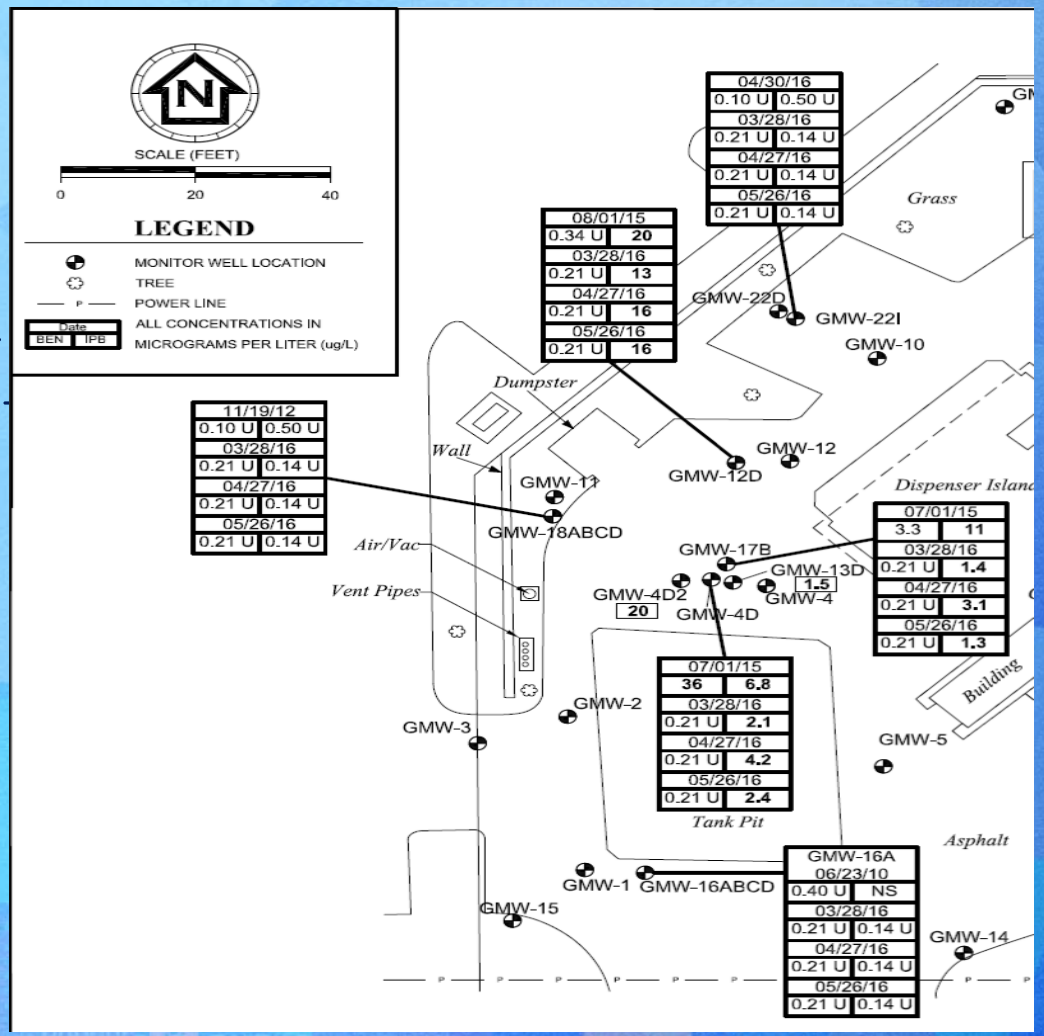
Pilot Test Results

Baseline monitoring was performed prior to the injection and repeated 30-days post injection and 60-days post injection.

Cumene concentrations Increased at the 30-day Sampling, then were reduced at the 60-day sampling



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Pilot Test Results

Baseline monitoring was performed prior to the injection and repeated 30-days post injection and 60-days post injection.

Heterotrophic Plate Counts (HPC) increased at the 30-day sampling event, then decreased at the 60-day event, with the largest increases being observed in wells closest to the injection wells. This was taken as a positive sign that the sulfate injection had resulted in an increase of the number of bacteria colonies.

A decrease in alkalinity, which could be indicative of increased CO2 production which would correspond with increased respiration rates, was also observed.

An effective radius of influence was determined at 5-7 feet and rates of up to 3 gpm were sustained during injection.

Seeing positive results, the development of a RAP was recommended.

The Case Study

RAP

Two injection events were performed, the first in August 2017 and the second in December 2018.

Sulfate concentrations within the plume area were significantly increased (up to 370 mg/L) following the second injection.

Cumene concentrations decreased and the site entered PARM in 2019. After one sampling event with all wells below GCTLs concentrations rebounded at well GMW-11

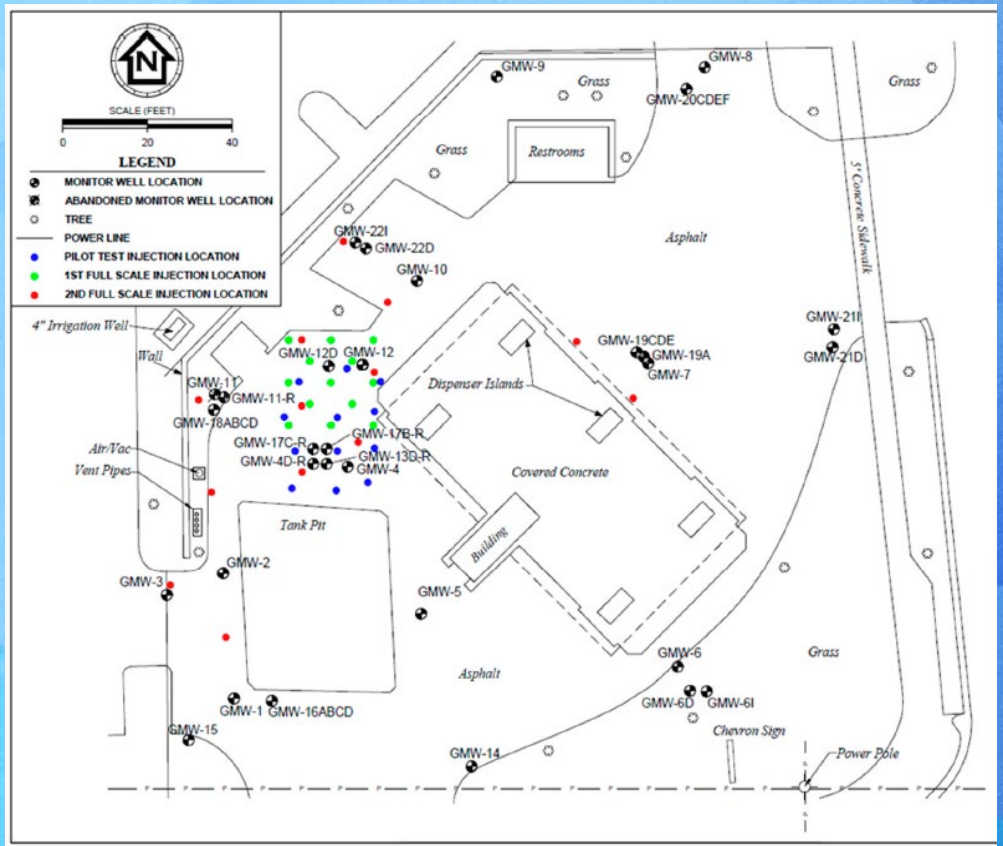

Figure 2. Case study general site plan with injection point locations.

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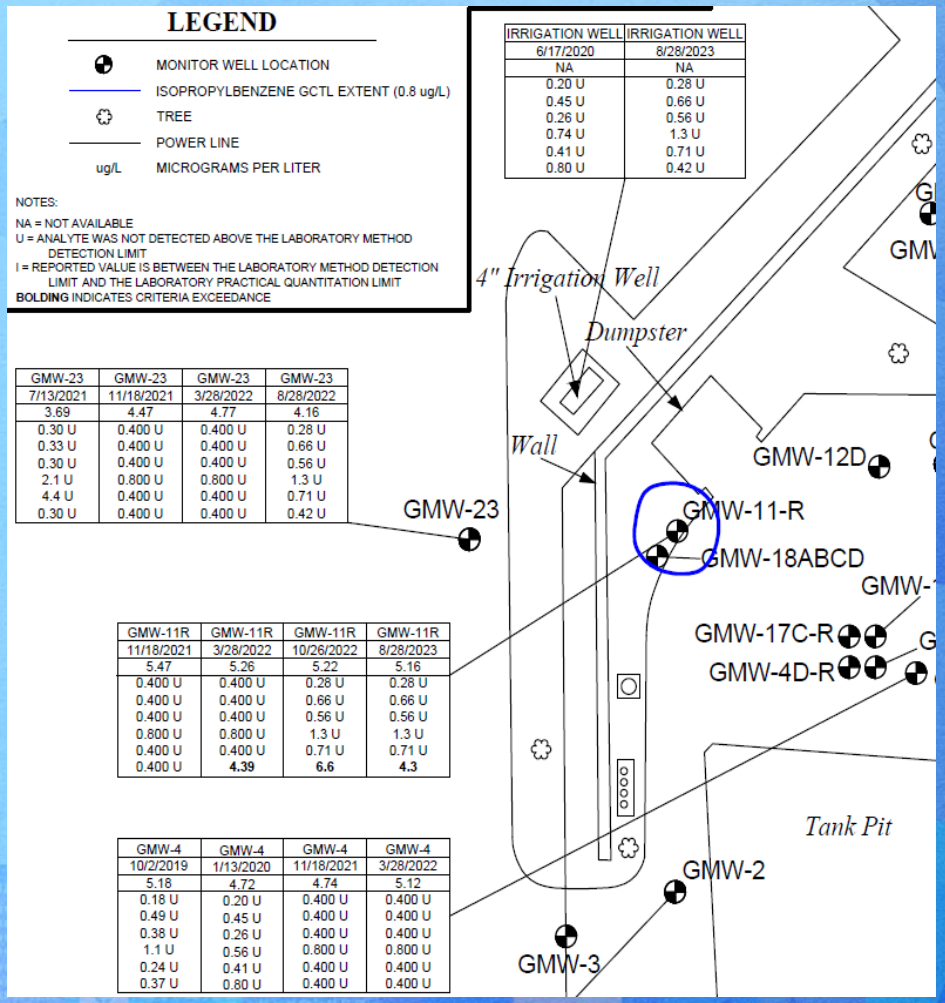
GWM-11

GWM-11 was abandoned and replaced with well GWM-11-R after GWM-11 had been compromised by roots.

Monitoring of GWM-11-R continued to show levels of Cumene above GCTLs.



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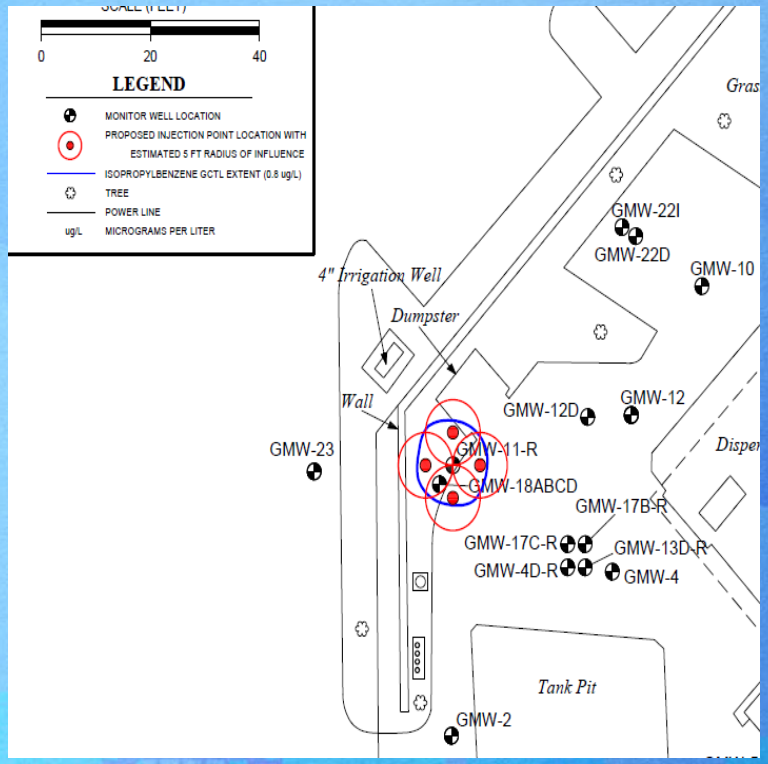
2023 RAPM

A fourth injection, targeted in the area of well GWM-11-R was proposed.

The injection was performed in September 2023, with post-injection sampling performed in December 2023.



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Happy Ending?

Post-injection sampling was performed in December 2023.

The Remedial Action Interim Report has not been submitted as of the date these slides were prepared.

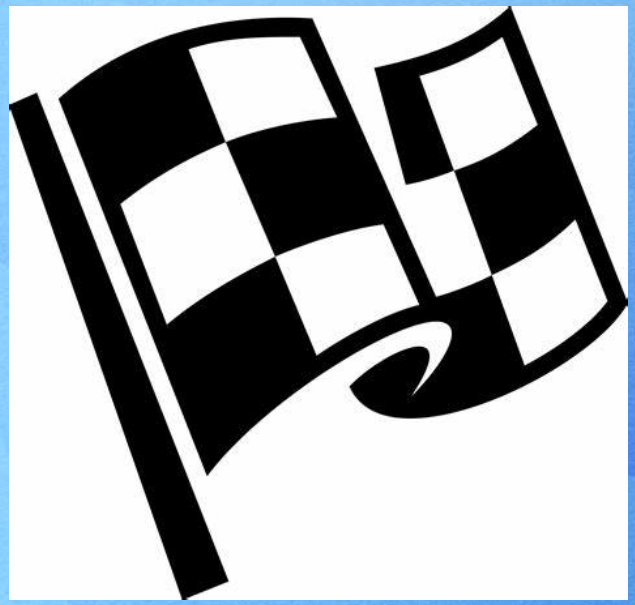
The sampling data was uploaded into the ADaPT system and Cumene levels at GMW-11-R remain above GCTLs.

We will have to see what the ATC recommends as the next step.

The Case Study

What Did We Learn?

That SEB may be an effective way to address Cumene impacts, if site conditions indicate sulfate levels are potentially limiting anaerobic degradation.

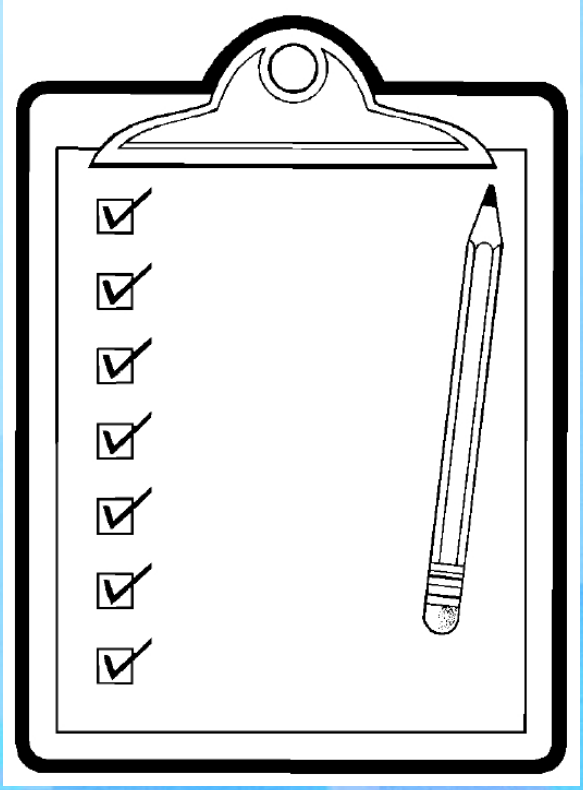


Epsom salt can be injected safely and easily at active retail facilities.

Epsom salt can be significantly less expensive than other remedial additives. The Epsom salt injected in the four events at the case study site amount to less than $200 in materials.

Due to Cumene's affinity for soil, residual Cumene may be bound with site soils that could serve as a residual source

Scoping Tips

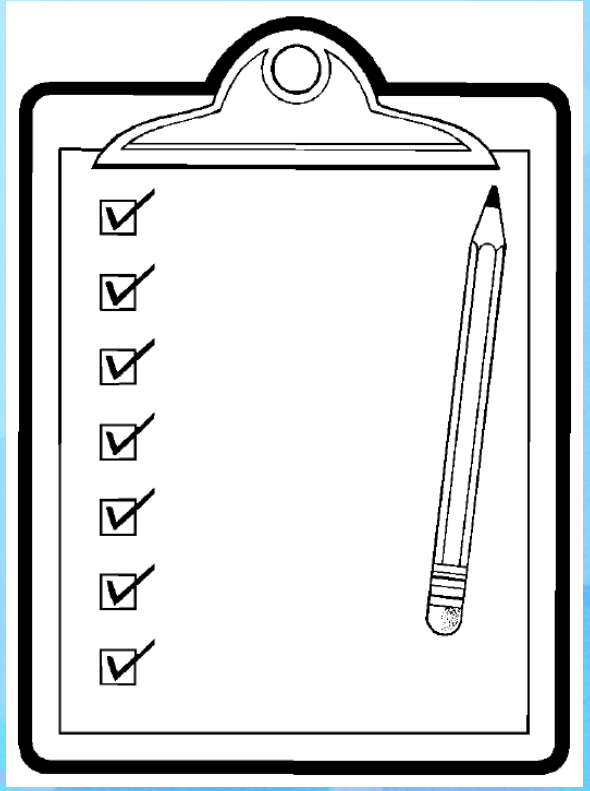


Pilot Test Vs. Remedy Implementation

With a pilot test that involves injection you may need more than one post-injection sampling event to determine the residual effects. Make sure you account for the correct number of events and the time between them in our scope.

Pilot test scopes typically include pilot test packages (from Section 16 of the Pay Items). There isn't a distinction in the equipment used for an injection pilot test and an injection that is part of the remedy implementation.

Scoping Tips



Water, Water Everywhere

The majority of chemical injections that are performed will need make-up water to dilute the remedial additives used to the proper concentration.

Make sure that your ATC understands that using the service station's garden hose is not going to be a realistic option.

Most municipalities will allow you to connect to a nearby fire hydrant for a fee and the cost of the water used. To determine the water used will typically involve renting a flow meter from the municipality. Do not be shocked when your ATC comes back with a quote for several hundred dollars or more for such a service.

Acknowledgement

In addition to the deliverables prepared for the Chevron Broward Boulevard Food Mart site this presentation utilized materials from the paper:

"Cumene Contamination in Groundwater: Observed Concentrations, Evaluation of Remediation by Sulfate Enhanced Bioremediation (SEB), and Public Health Issues" by John P. Herman, Lauren Redfern, Christopher Teaf, Douglas Covert, Peter R. Michael, and Thomas M. Missimer; Int J Environ Res Public Health. 2020 Nov; 17(22): 8380.

Which can be found at:

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7696069/

Questions?

DAVID J. SHEEHAN P.E., LICENSED ENGINEER
Resilient Environment Department
ENVIRONMENTAL PERMITTING DIVISION
1 N University Dr, Mailbox 201 | Plantation, Florida 33324
Office: 954.519.1439
www.broward.org