The Use of Nitrate as a Supplied Electron Acceptor to Sequentially Transition to Sulfate Reducing Conditions for Petroleum Hydrocarbon Degradation

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One Team. Infinite Solutions

Contributors and Project Team

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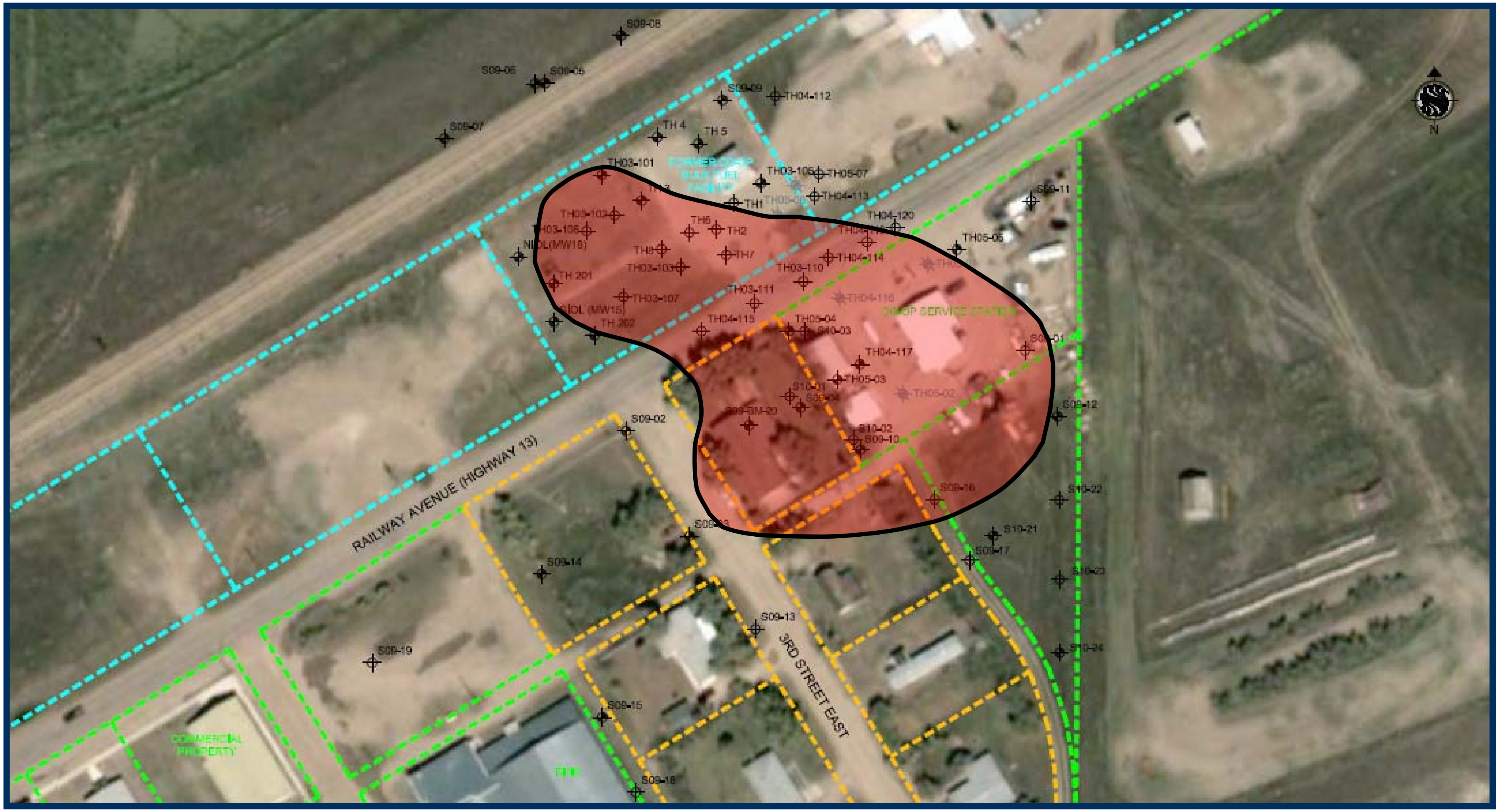
Outline

- Site Description and Conceptual Site Model
- Development of Remediation Concepts
- Implementation of Remediation System
- Results and Interpretations
- Future Concepts
- Questions

Background Information

- Active Service Station and Former Bulk Fuel Facility in SW Saskatchewan.
- The site is bordered by a residential property.
- Former assessments identified the presence of petroleum hydrocarbon impacts.
- Site characterization activities were completed in 2009 to delineate the impacts and collect data to support remedial planning.

Site Plan and Extent of Impacts



Challenges and Objectives

- The assessment activities concluded that impacts were present across a significant area, which included client-owned properties, a residence and municipal properties.
- The remediation program needed to effectively reduce the primary concerns associated with potential exposure pathways on the residential property.
- The challenge was to develop a cost effective remediation program, since the site is located in a small town where property values are not supportive of high-cost remedial efforts.

Remediation Concepts

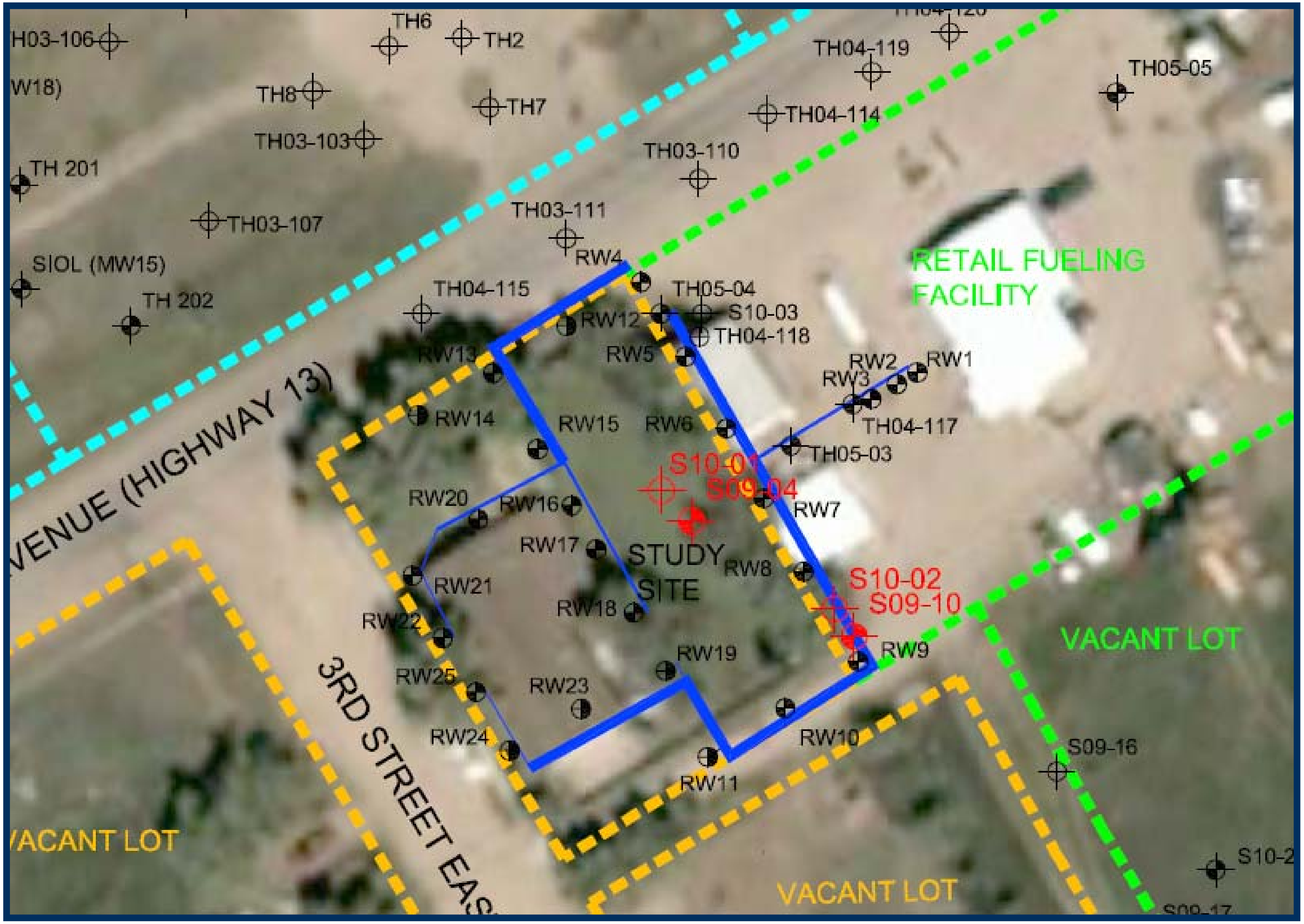
- The data collected that impacted zone contains significant levels of sulfate (average groundwater concentration of 18,500 mg/L), which could be utilized as an electron acceptor.
- The available data suggested that sulfate reducing conditions were present at select locations; however, the rate of degradation appeared to be relatively low.
- The low degradation rates were attributed to limited nutrients, such as phosphorus.
- The project team concluded that a combination of physical removal and enhanced biological methods would provide the best solution, considering the various stakeholders and the associated challenges.

Remediation Concepts

The following remediation plan was developed:

1. A multi-phase vacuum extraction (MPVE) system would be installed and connected to the 25 recovery wells located on and surrounding the residential property.
2. The MPVE system would operate for approximately 45 days to aggressively reduce the hydrocarbon mass.
3. Potassium nitrate and triethly phosphate (TEP) would be injected to optimize electron acceptor and nutrient conditions for enhanced biodegradation. The injection solution would be amended with a surfactant to assist with the desorption of hydrocarbons and increase the bioavailable hydrocarbon mass.
4. The nitrate would act as a supplied electron acceptor and a macronutrient with the TEP breaking down into inorganic orthophosphate (macronutrient). Hydrocarbon degradation would occur under nitrate reducing conditions.
5. Biodegradation processes would transition towards sulfate-reducing conditions, once the nitrate was preferentially consumed. At this point, naturally occurring sulfate would be used as the terminal electron acceptor and hydrocarbon degradation would continue.

Remediation Concepts



Implementation

- The MPVE system operated for approximately 45 days and recovered approximately 10,000 L of hydrocarbons, which was primarily in the vapour phase.
- Recovery rates declined from approximately 65 L/hr to 3 L/hr, at which time the physical recovery methods were discontinued.

Implementation

The following amendments were injected once the physical recovery methods were discontinued:

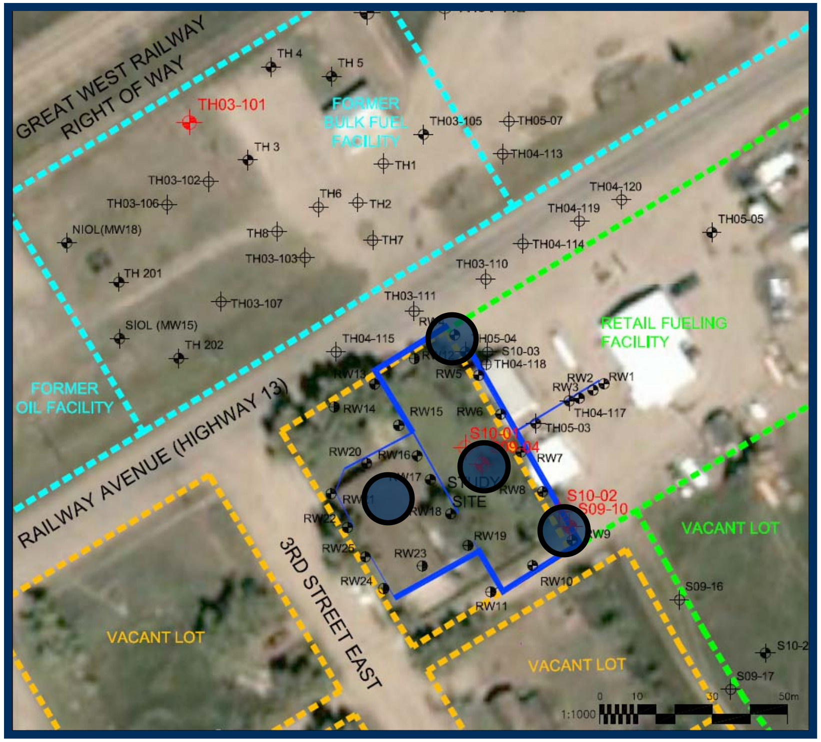
1. 1,150 kg of Potassium Nitrate (KNO_3)
2. 205 kg of Triethyl Phosphate ($(C_2H_5)_3PO_4$)
3. 1,000 L of Surfactant Solution.

Preliminary Results

- Groundwater monitoring and sampling was conducted in April 2010 to evaluate the progress of the remediation. The key indicators are summarized as follows:
  - Total dissolved BTEX removal efficiency was approximately 60%
  - Benzene removal efficiency ranged between approximately 20% and 50%
  - Theoretical dissolved nitrate concentrations were initially 1,000 mg/L, but were reduced to non-detectable levels by April 2010
  - Sulfate concentrations had decreased by 30 to 40% by April 2010.
  - Oxidation-reduction potential (ORP) values reduced from an average of -60 mV (prior to injections) to -135 mV in April 2010.
  - Orthophosphate concentrations were non-detectable.
- The data concluded that the nitrate had been preferentially consumed, ORP values had declined and become more suitable for sulfate-reducing conditions, and sulfate was being utilized as an electron acceptor.
- The decision was made allow the biodegradation processes to continue during the summer of 2010.

Results and Interpretation

Additional soil and groundwater investigations were conducted in late July 2010 to evaluate the remediation progress.



Results and Interpretation

- Borehole S10-01 was drilled approximately 1 m away from S09-04.
- Soil samples were collected from the direct push core which exhibited the most significant impacts.
- Significant removal efficiencies were identified.

Removal Efficiencies

B – 97%

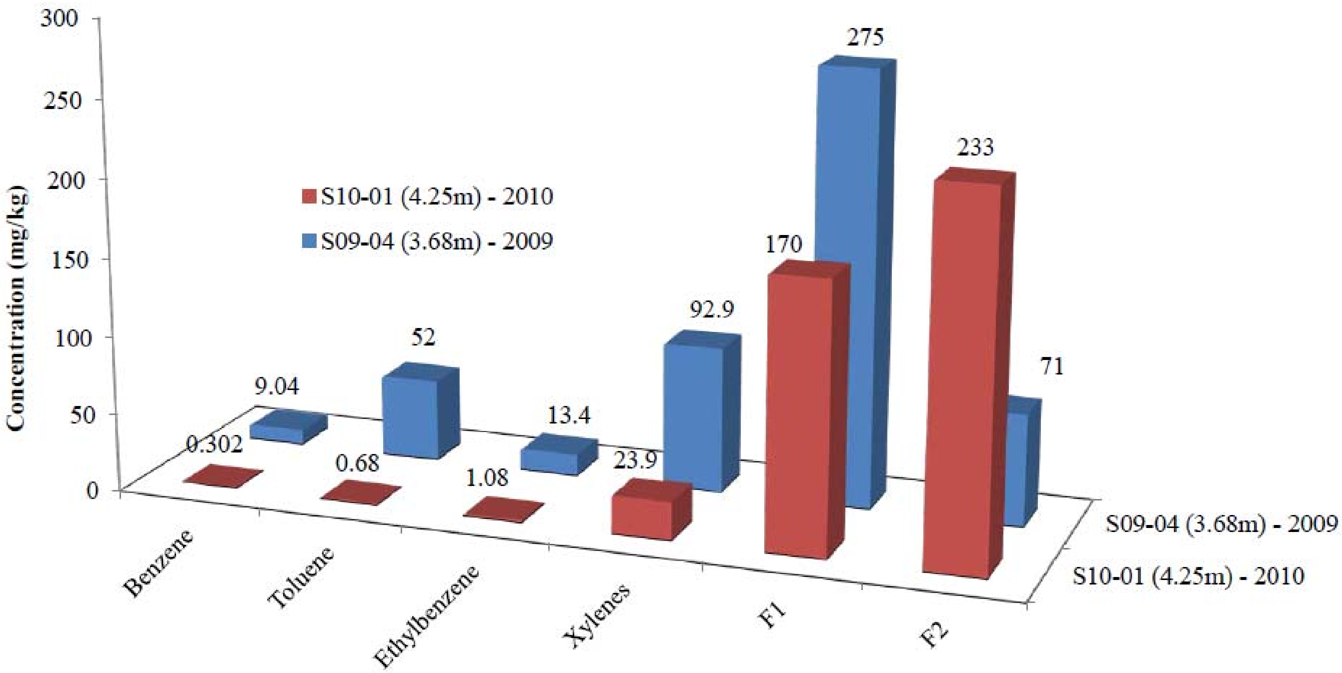
T – 99%

E – 92%

X – 74%

F1 – 38%

F2 - Increased



Results and Interpretation

Second set of soil samples collected from S09-04 and S10-01 at depths of approximately 4.5 m below grade level.

Removal Efficiencies

B – 93%

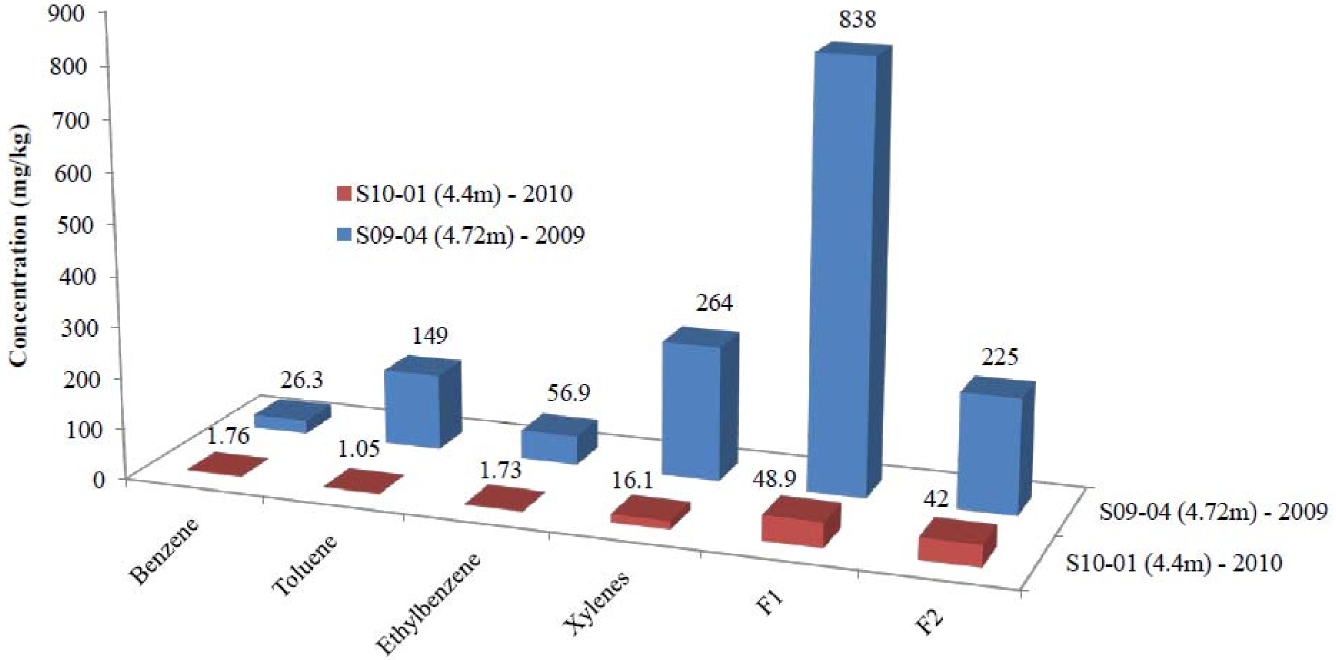
T – 99%

E – 97%

X – 94%

F1 – 94%

F2 – 81%



Results and Interpretation

- Borehole S10-02 was drilled approximately 1 m away from S09-10.
- Results were similar to S09-04, with significant removal efficiencies identified.

Removal Efficiencies

B – 76%

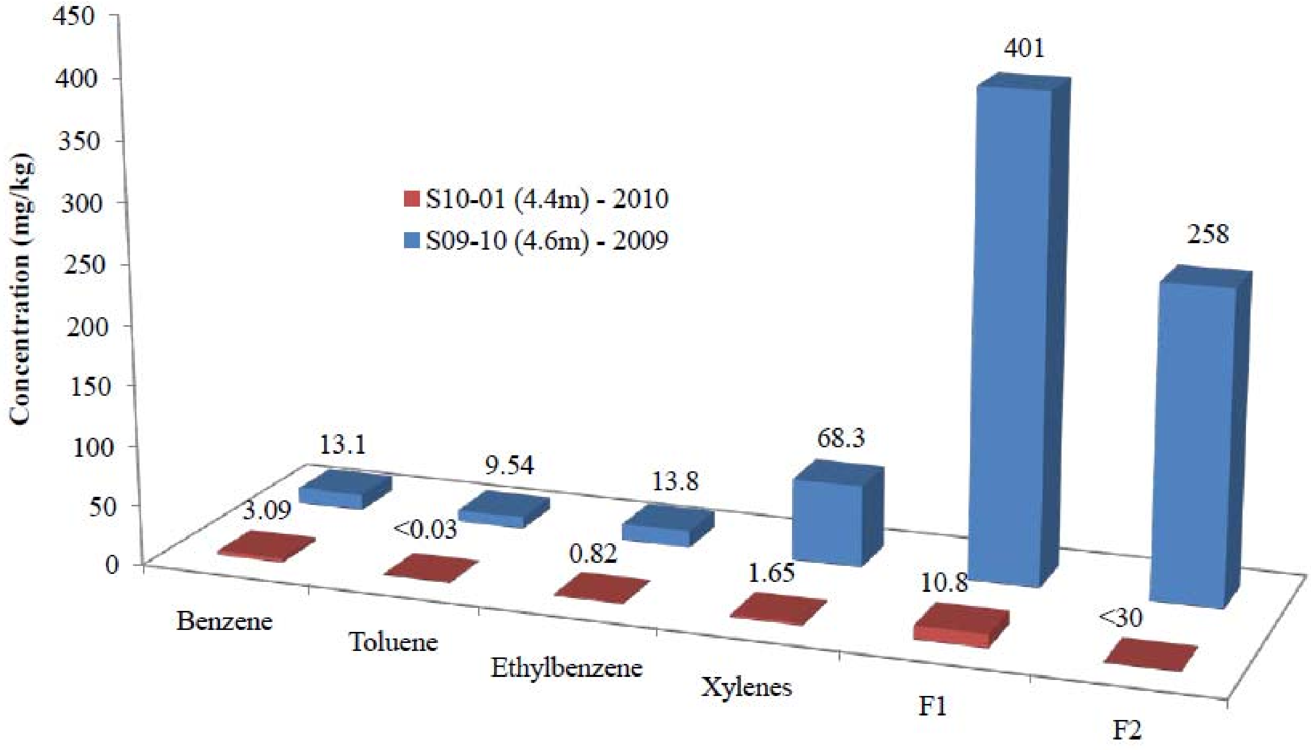
T – 99%

E – 94%

X – 98%

F1 – 97%

F2 – >88%



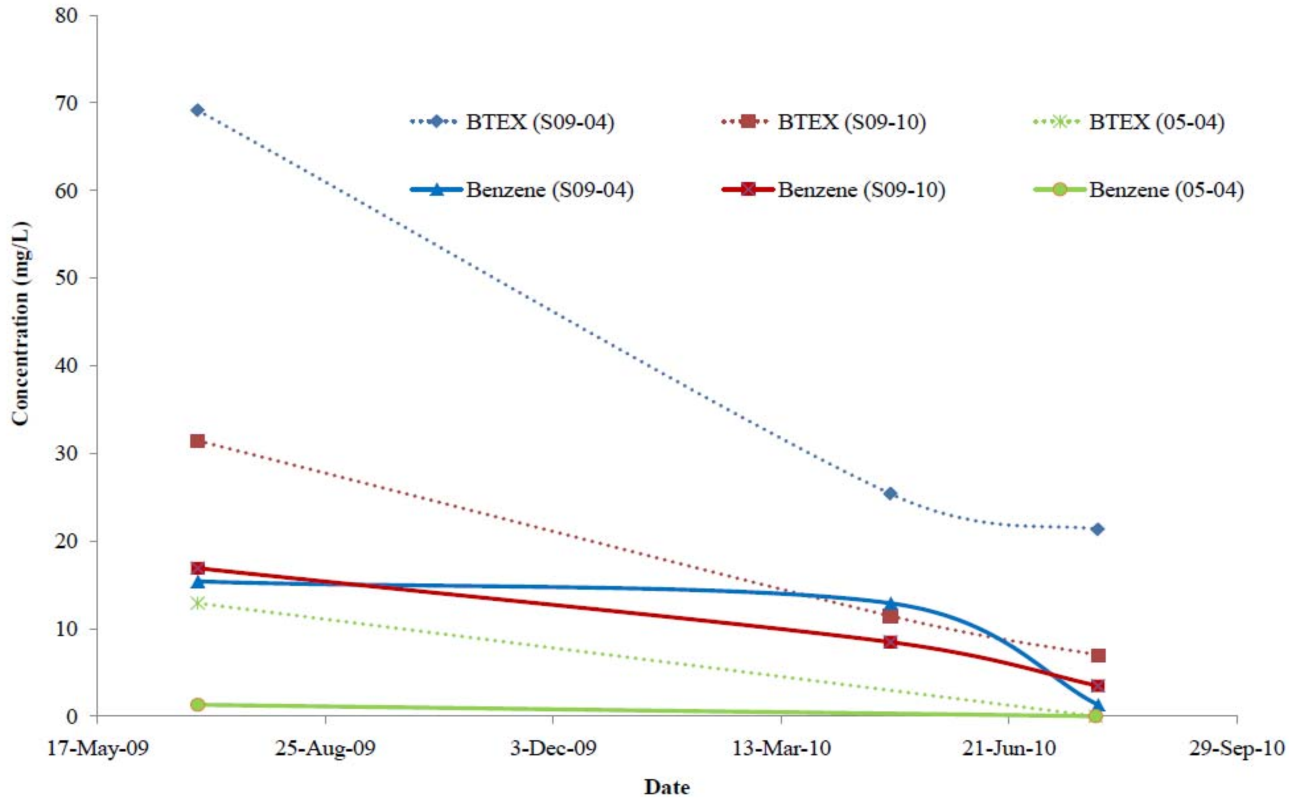
Results and Interpretation

- Groundwater samples were collected from three monitoring wells.
- A groundwater samples was also collected from a monitoring well installed in the basement of the residential house, which confirmed BTEX concentrations were low. Benzene was detected at 0.07 mg/L.

Removal Efficiencies

BTEX – 69% to 99%

Benzene – 80% to 99%



Results and Interpretation

Other key performance indicators are as follows:

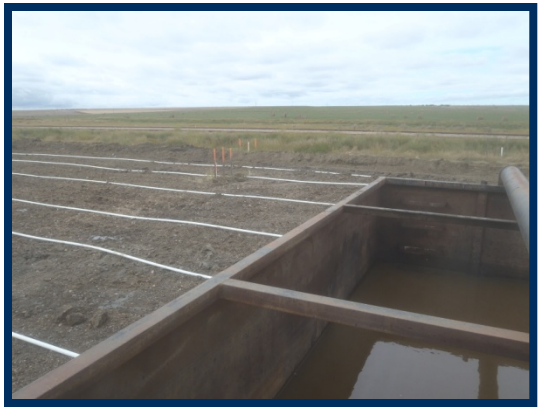
- ORP values in the treatment area decreased from an average of -60 mV (prior to remediation) to -135 mV in July 2010, suggesting sulfate reducing conditions are occurring.
- ORP values at adjacent locations (outside treatment area) remained relatively consistent.
- Orthophosphate concentrations remain non-detectable or at low concentrations. It is hypothesized that organic phosphorus is being converted to inorganic phosphorus, which is immediately consumed as a macronutrient under nitrate and sulfate reducing conditions.
- Phosphate is considered one of the primary limitations in optimizing the biodegradation rates.

The most important outcome is that the majority of the soil and groundwater hydrocarbon results from within the residential property are below the applicable Saskatchewan Tier 2B Guidelines.

Future Concepts

The remediation program has been expanded to build off the recent successes and optimize other aspects.

- A MPVE system is currently operating on the Service Station property to reduce the hydrocarbon mass.
- Recovered water is treated throughout the MPVE system (approximately 500 L to 1,000 L per hour) and is transferred to the Bulk Fuel Facility and surface applied across a cultivated plot area.
- The irrigated water is supplemented with phosphorus (triethly phosphate and phosphoric acid) to provide the required macronutrient.
- Potassium nitrate is being surface applied to act as a supplied electron acceptor, in addition to the naturally existing sulfate which will be used as a terminal electron acceptor.
- The irrigated water and existing groundwater contains elevated sulfate to be used as a terminal electron acceptor.



Conclusions

- The remediation concepts have proven to be very successful at this site.
- Soil and groundwater results demonstrate that significant hydrocarbon reductions have been achieved and the majority of the results are now below the applicable guidelines.
- Combination of nitrate and sulfate appear to be more successful than only nitrate, based on these results and data from other sites.
- Orthophosphate is considered to be one of the limiting factors in optimizing both nitrate and sulfate reducing conditions. It is hypothesized that organic phosphorus is being transformed to inorganic orthophosphate. One hypotheses is that orthophosphate is utilized at the rate of production; therefore, is not detected by standard laboratory methods.
- Additional research may be pursued to determine if nitrate and sulfate reduction are occurring simultaneously or sequentially. Some of the collected information suggests that the nitrate can be used as a macronutrient under sulfate reducing conditions, which creates a synergistic effect.

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Responsible • Responsive • Ready

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QUESTIONS