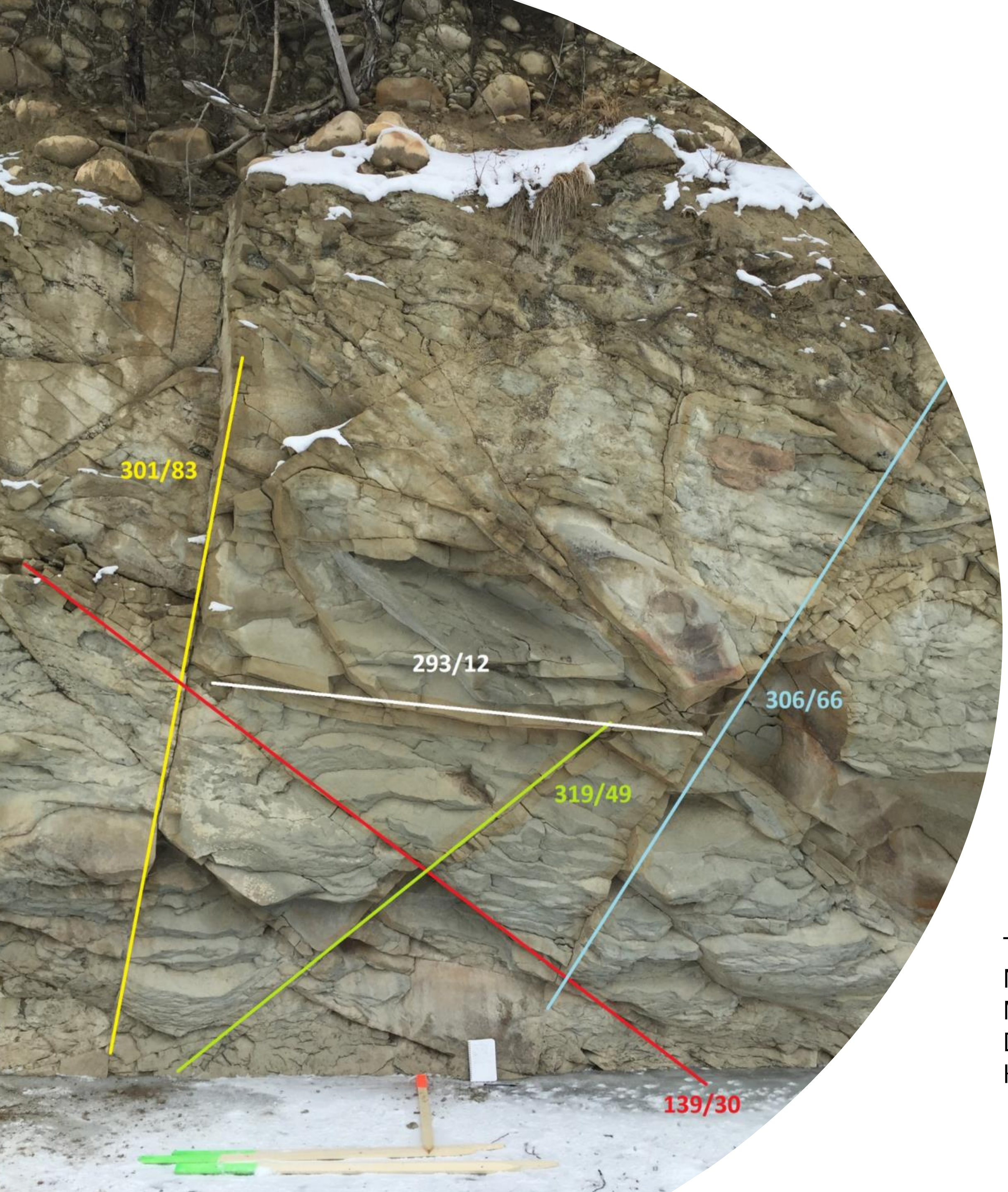


Application of Natural Source Zone Depletion in Fractured Aquifer Remediation & Liability Management

Vincent Stein, M.Sc., P.Eng.

Team:
Neil Krystopowicz, Advisian
Mike Brown, Advisian
David Gibson, Advisian
Kerri Gilders, Keyera

Advisian
Worley Group

KEYERA

I want to acknowledge

I work, live, and play on the traditional gathering place, travelling route and home for many Indigenous Peoples.

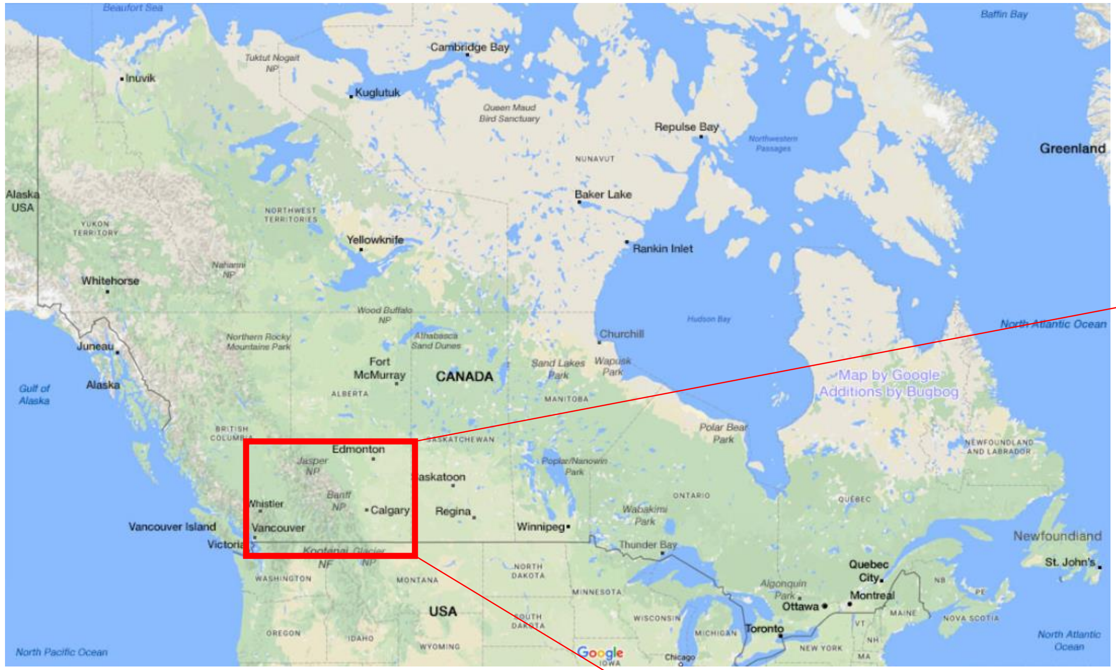
Progressive Aboriginal RELATIONS COMMITTED

Canadian Council for Aboriginal Business

Presentation Outline

- Why I'm giving this talk
- Project Background
  - Contaminant situation
  - Remediation history
  - Original conceptual site model
- NSZD – "The biggest new idea in contaminated site management to emerge in the last decade"
  - The NSZD conceptual model
  - Quantification approaches
  - How it is being applied to this site
- Conclusions and Caveats

Project Background



Download from https://www.bugbog.com/maps/north_america/canada_map/

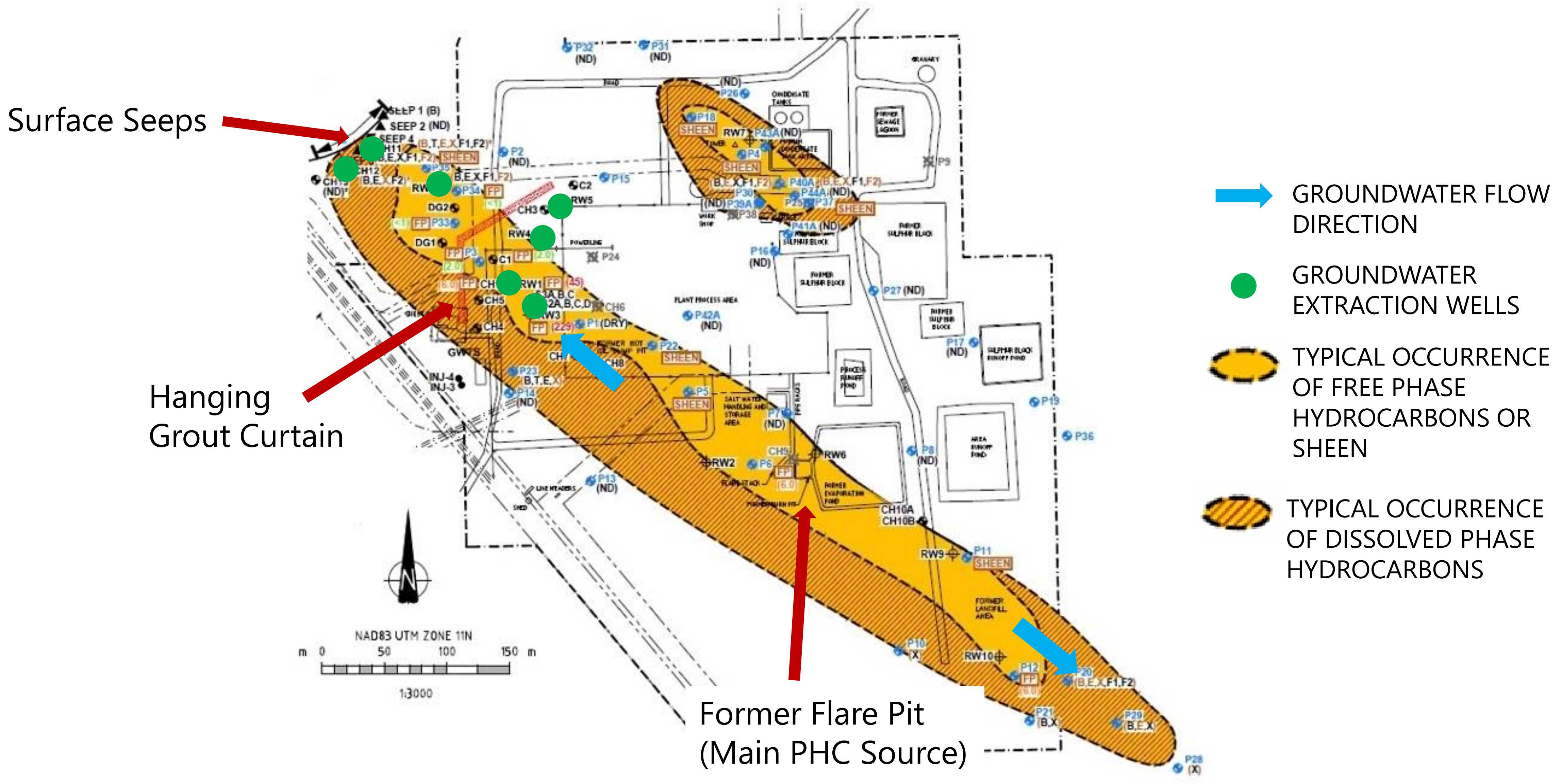
Site is located in the foothills of Alberta.

Project Background

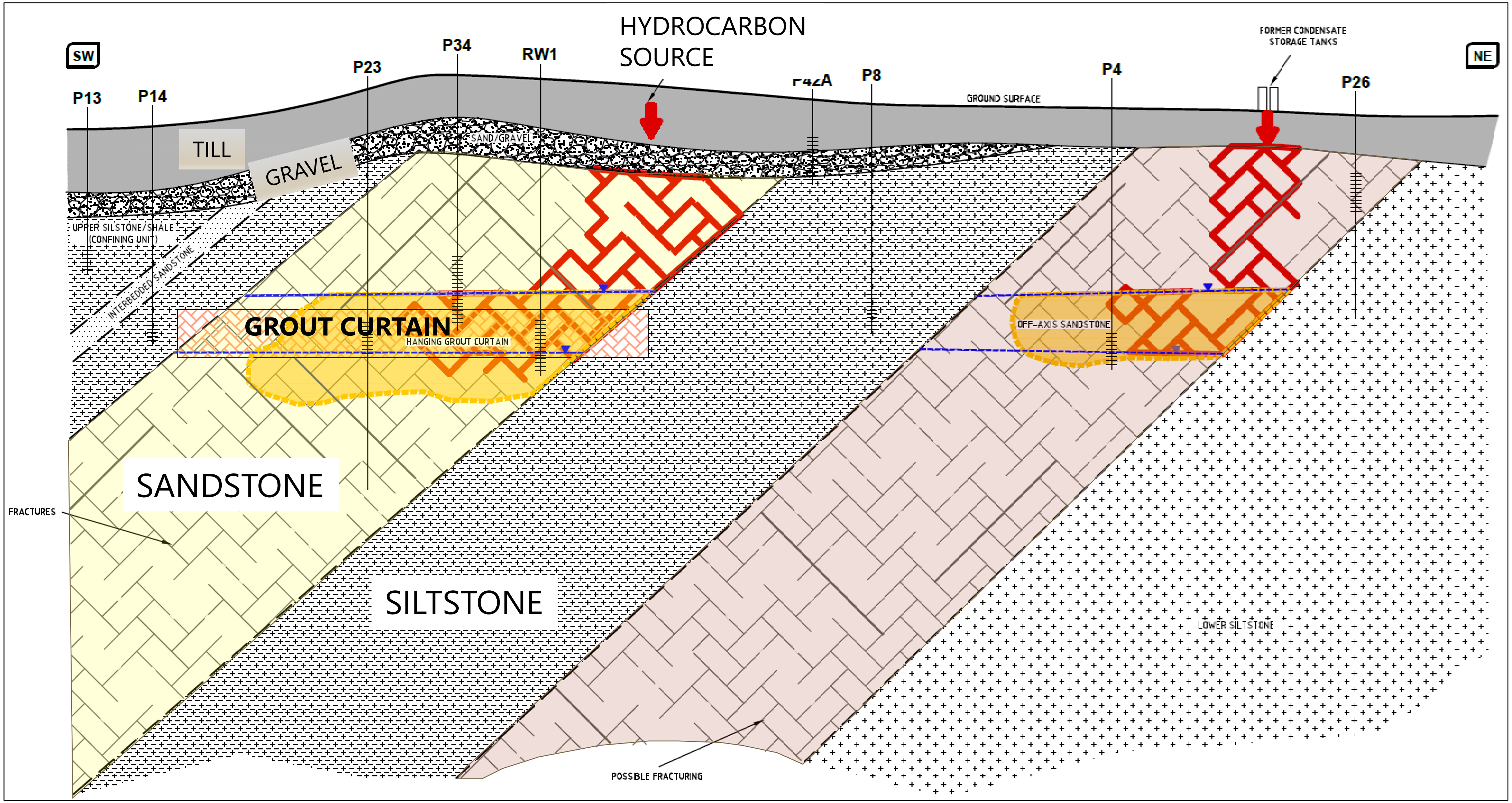
Gas Plant

- Constructed in the 1960s to process raw sour gas
- Currently, processes natural gas from an extensive network of gathering systems
- A number of historical events and operational practices at the site resulted in groundwater contamination with light non-aqueous phase liquid (LNAPL) hydrocarbons

Contaminant Situation



Conceptual Site Model



Groundwater Remediation History

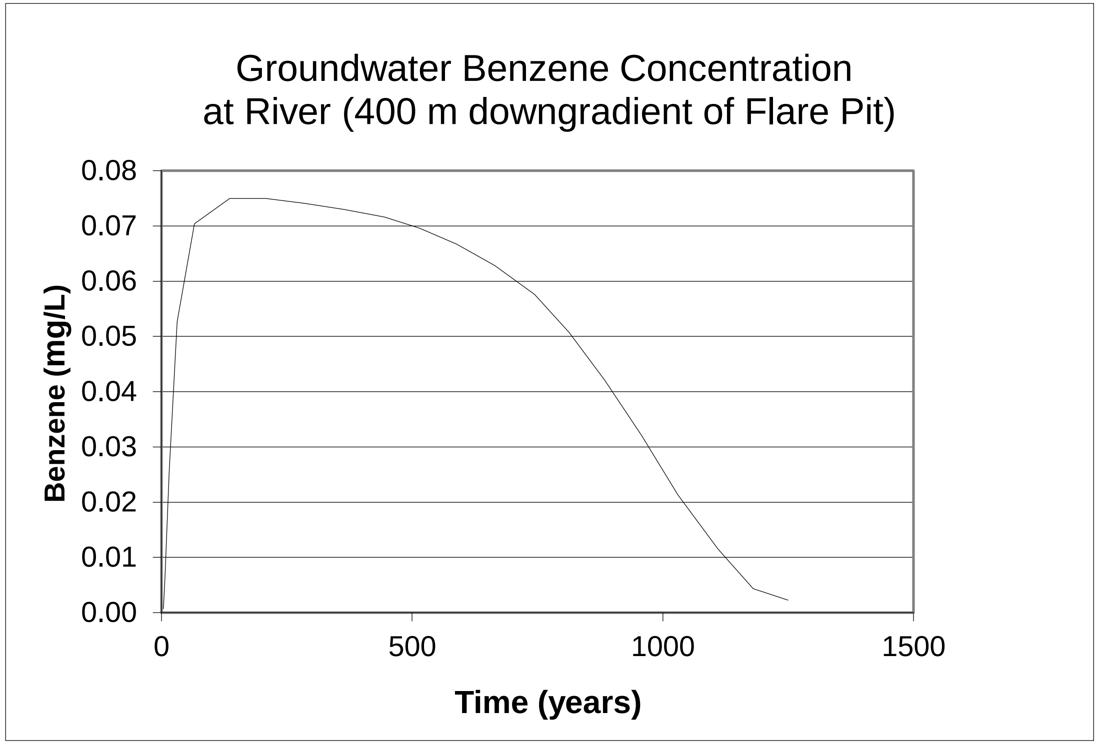
1993-present	• Plume containment system installed in 1993 / 1994
	  • Grout Barrier to halt flow of NAPL
	  • Groundwater extraction and NAPL skimming system
	• Groundwater extraction is ongoing (>71,000,000 litres extracted and treated to date; 307 kg dissolved phase PHCs removed)
	• NAPL accumulating in wells removed with portable NAPL skimmer

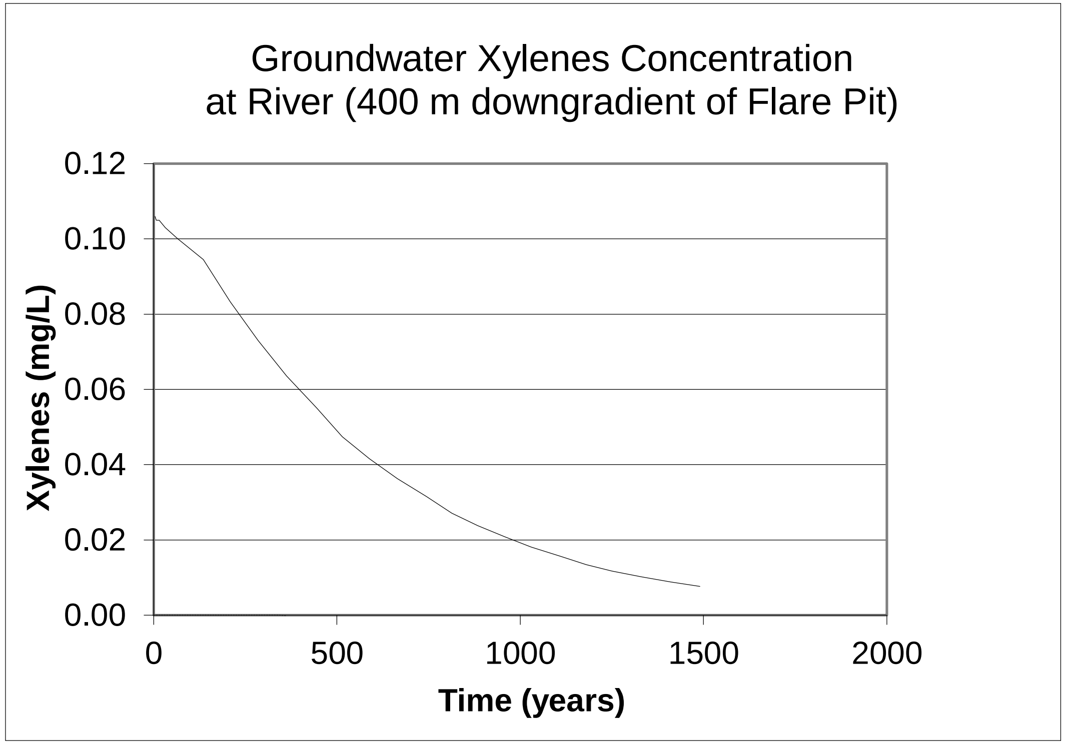
2000-2008	Soil vapour extraction 25,229 kg VOCs removed from angled coreholes upgradient of grout curtain and near Former Flare Pit

2012-2013	Soil vapour extraction
	  • Negligible quantities of VOCs removed due to NAPL composition having shifted to compounds with lower volatility (F2)
	  • Large quantities of methane and carbon dioxide present in extracted vapour

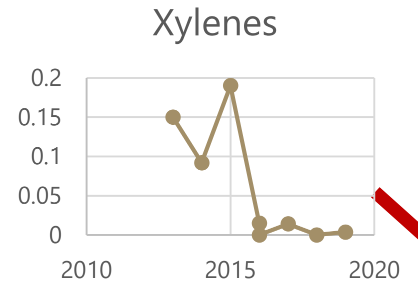
2014-2021	• Fracture network characterization program • Installation of additional extraction wells and groundwater extraction pilot testing near seepage face • NSZD program

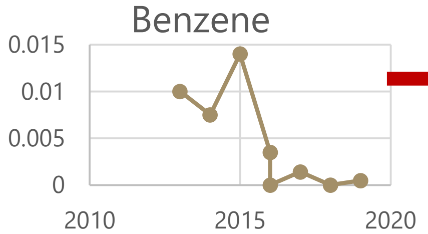
MNA Prognosis (Developed in 2010)

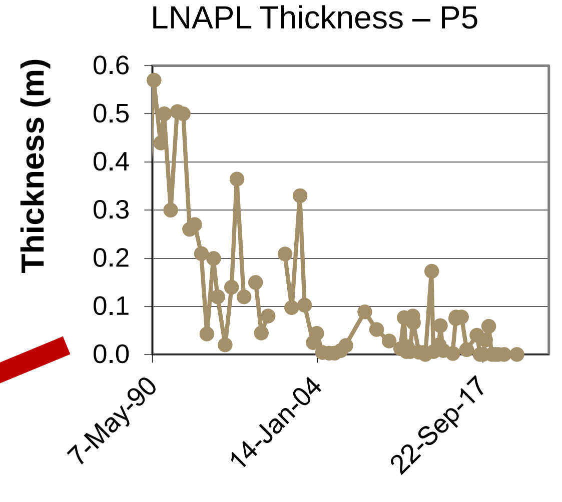


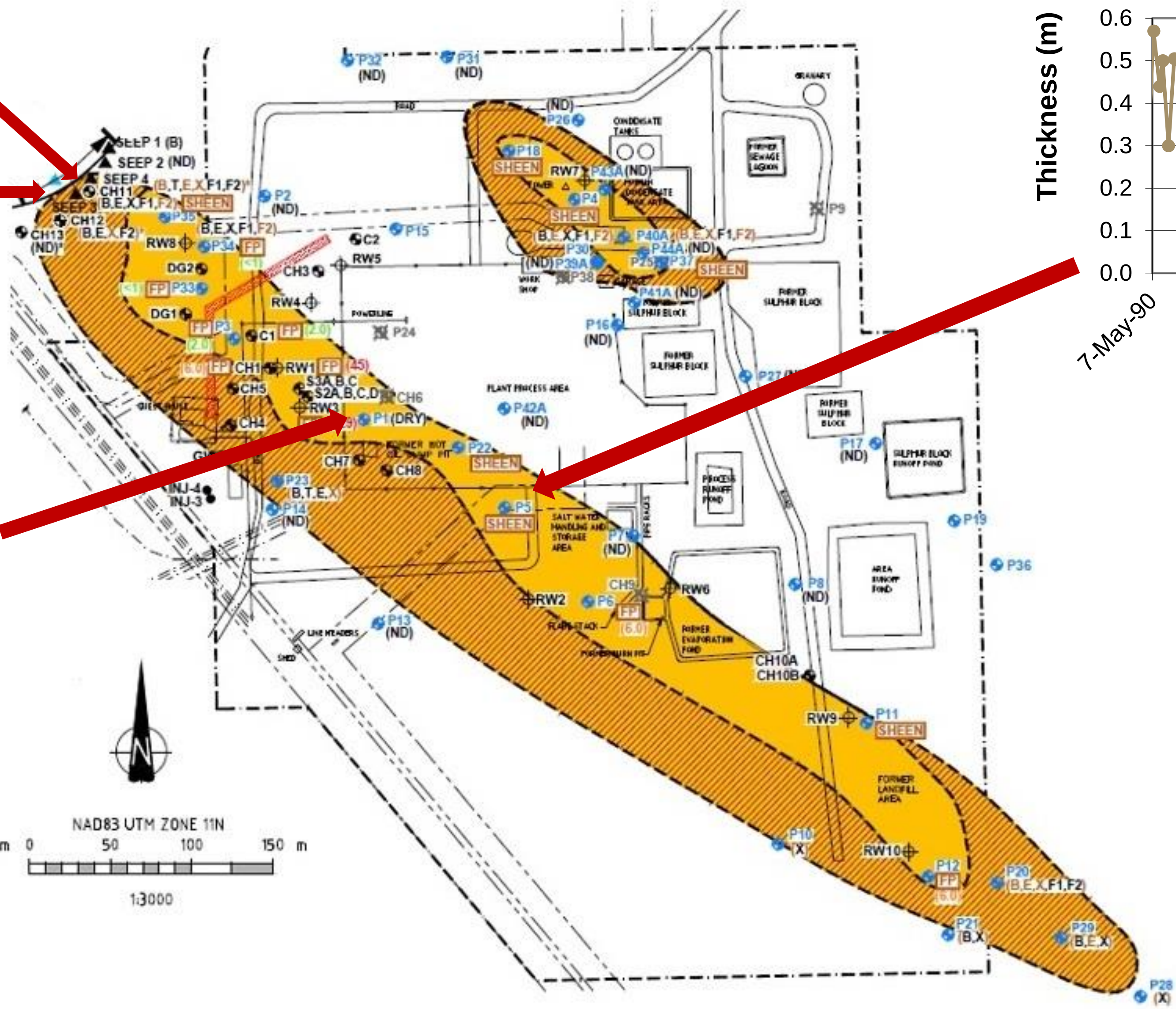


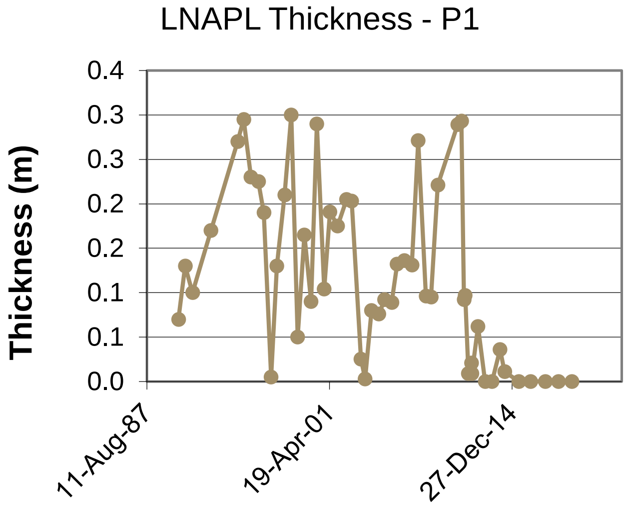
Hydrocarbon Trends











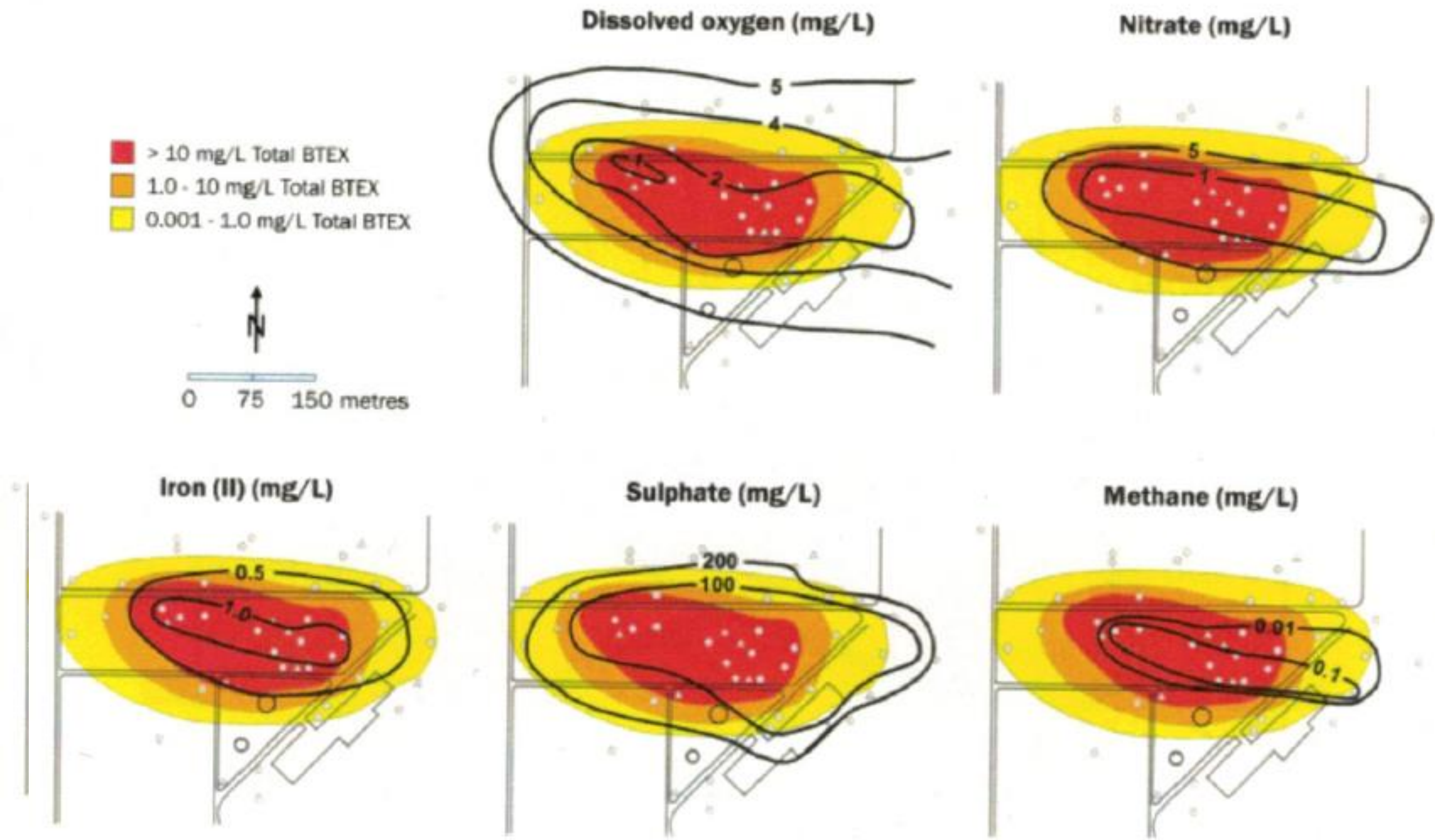
Contaminant Situation as of 2020

All BTEX constituents and PHC F1 met Tier 1 Guidelines at the only seep where hydrocarbons have been continually present

PHC F2 = 0.12 mg/L (slightly above AEP surface Water Guideline of 0.11 mg/L)

MNA model appears to have overestimated natural attenuation timeframe

Monitored Natural Attenuation (MNA)



Source: Sale, T. and Newell, C., 2019

MNA Reactions

US EPA, 1998

$$3.75\ NO_3^- + C_6H_6 + 7.5\ H^+ + 0.75\ H_2O \rightarrow 6\ CO_{2(g)} + 3.75\ NH_4^+$$

benzene oxidation/nitrate reduction

$$60\ H^+ + 30\ Fe(OH)_{3(aq)} + C_6H_6 \rightarrow 6\ CO_{2(g)} + 30\ Fe^{2+} + 78\ H_2O$$

benzene oxidation/iron reduction

$$7.5\ H^+ + 3.75\ SO_4^{2-} + C_6H_6 \rightarrow 6\ CO_{2(g)} + 3.75\ H_2S + 3\ H_2O$$

benzene oxidation/sulfate reduction

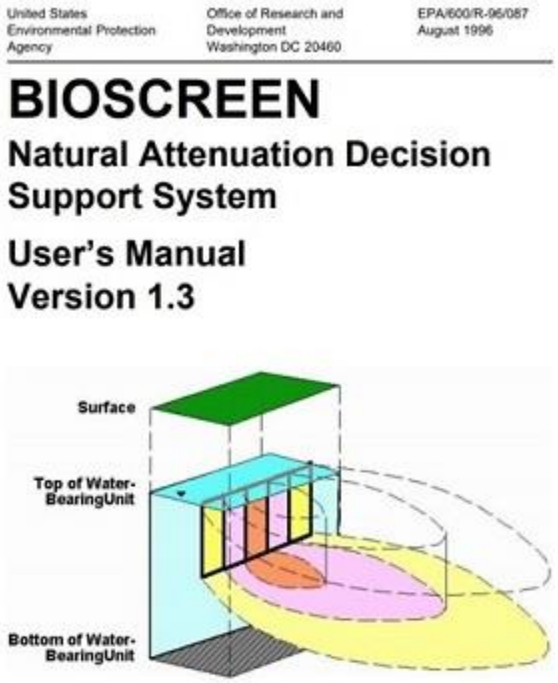
$$6\ NO_3^- + 6\ H^+ + C_6H_6 \rightarrow 6\ CO_{2(g)} + 6\ H_2O + 3\ N_{2(g)}$$

benzene oxidation/denitrification

$$4.5\ H_2O + C_6H_6 \rightarrow 2.25\ CO_{2(g)} + 3.75\ CH_4$$

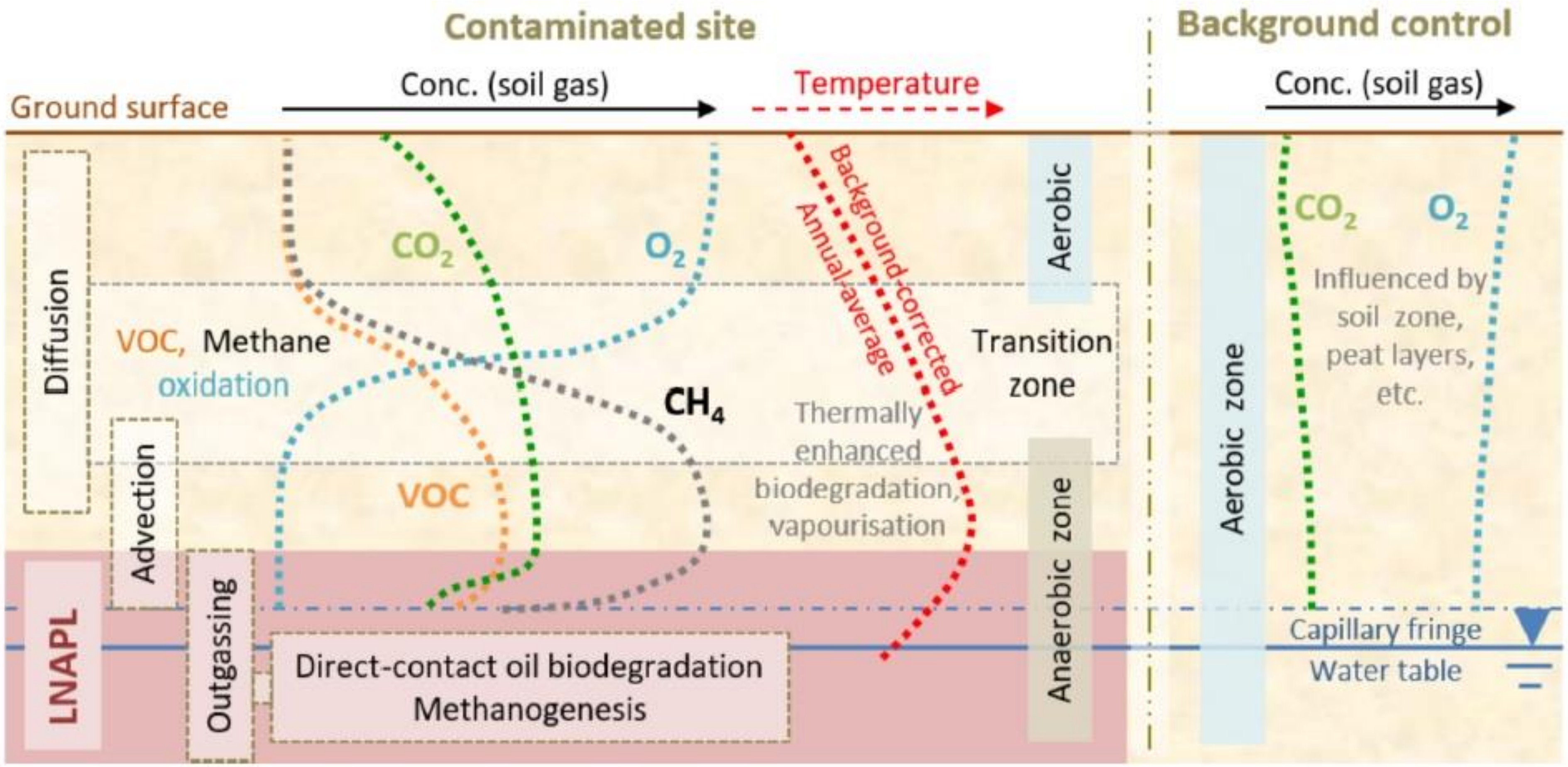
benzene oxidation/methanogenesis

Electron Acceptor Utilization



Electron Acceptor or By-Product	Utilization Factor for benzene (mass e^- acceptor or by-product consumed per mass of dissolved hydrocarbon degraded)
Oxygen	3.1 g/g
Nitrate	4.9 g/g
Ferrous iron	21.8 g/g
Sulphate	4.6 g/g
Methane	0.78 g/g

Natural Source Zone Depletion (NSZD)



Source: CL:AIRE Technical Bulletin TB20, June 2019

A Good Introduction to NSZD

Overview of Natural Source Zone Depletion: Processes, Controlling Factors, and Composition Change

by Sanjay Garg, Charles J. Newell, Poonam R. Kulkarni, David C. King, David T. Adamson, Maria Irianni Renno, and Tom Sale

Abstract

Natural source zone depletion (NSZD) has emerged as a practical alternative for restoration of light non-aqueous phase liquid (LNAPL) sites that are in the later stages of their remediation lifecycle. Due to significant research, the NSZD conceptual model has evolved dramatically in recent years, and methanogenesis is now accepted as a dominant attenuation process (e.g., Lundegard and Johnson 2006; Ng et al. 2015). Most of the methane is generated within the pore space adjacent to LNAPL (Ng et al. 2015) from where it migrates through the unsaturated zone (e.g., Amos and Mayer 2006), where it is oxidized. While great progress has been made, there are still some important gaps in our understanding of NSZD. NSZD measurements provide little insight on which constituents are actually degrading; it is unclear which rate-limiting factors that can be manipulated to increase NSZD rates; and how longevity of the bulk LNAPL and its key constituents can be predicted. Various threads of literature were pursued to shed light on some of the questions listed above. Several processes that may influence NSZD or its measurement were identified: temperature, inhibition from acetate buildup, protozoa predation, presence of electron acceptors, inhibition from volatile hydrocarbons, alkalinity/pH, and the availability of nutrients can all affect methanogenesis rates, while factors such as moisture content and soil type can influence its measurement. The methanogenic process appears to have a sequenced utilization of the constituents or chemical classes present in the LNAPL due to varying thermodynamic feasibility, biodegradability, and effects of inhibition, but the bulk NSZD rate appears to remain quasi-zero order. A simplified version of the reactive transport model presented by Ng et al. 2015 has the potential to be a useful tool for predicting the longevity of key LNAPL constituents or chemical fractions, and of bulk LNAPL, but more work is needed to obtain key input parameters such as chemical classes and their biodegradation rates and any potential inhibitions.

Introduction

Natural source zone depletion (NSZD) is emerging as an

First, we present the origins of the NSZD conceptual model and the emergence of methanogenesis and vertical

NSZD Rates

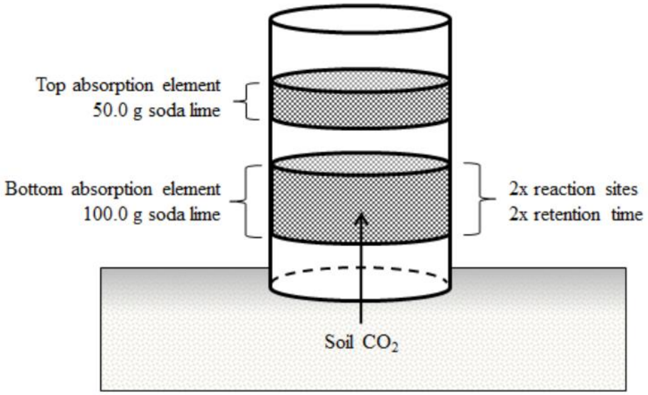
Examples of Site-Wide Average NSZD Rate Measurements at Field Sites

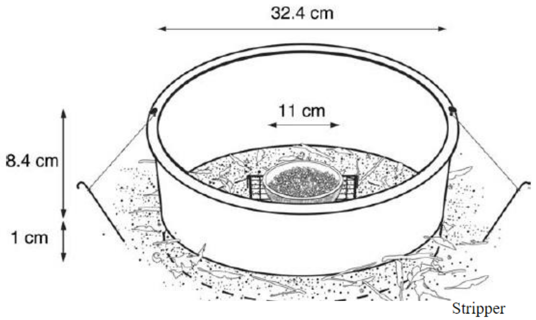
NSZD Study	Number of Sites	Site-Wide NSZD Rate (All Sites) (Gallons/Acre/Year)	Site-Wide NSZD Rate (Middle 50%) (Gallons/Acre/Year)	Reference
Refinery terminal sites	6	2100–7700	2400–3700	McCoy 2012
1979 crude oil spill	1	1600	—	Sihota et al. 2011
Seasonal range		310–1100	—	Sihota et al. 2016
Refinery/terminal sites	2	1100–1700	1250–1550	Workgroup, L.A. LNAPL 2015
Fuel/diesel/gasoline	5	300–3100	1050–2700	Piontek et al. 2014
Diverse petroleum sites	11	300–5600	600–800	Palaia 2016
All studies	25	300–7700	700–2800	
Saturated zone electron acceptor biodegradation capacity	**9**	**0.4–53**	**1.7–19**	This paper (see Appendix S1)

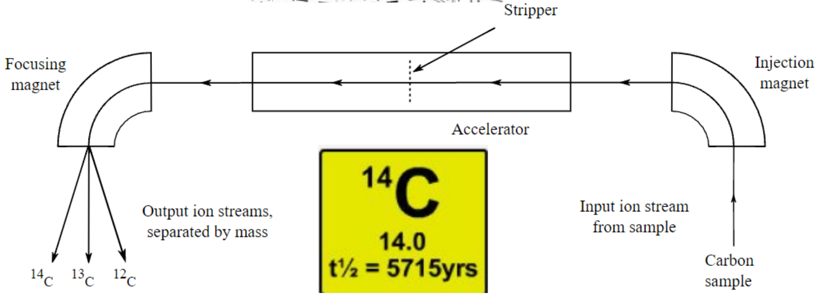
Notes: Middle 50% column shows the 25th and 75th percentile values. To demonstrate the significance of methanogenesis, NSZD rates calculated from the biodegradation capacity of electron acceptors in the saturated zone, ignoring methanogenesis, are shown in the last row.

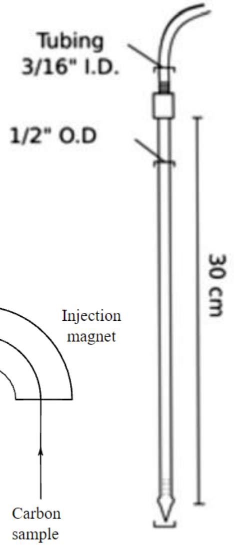
Source: Garg et al., 2017

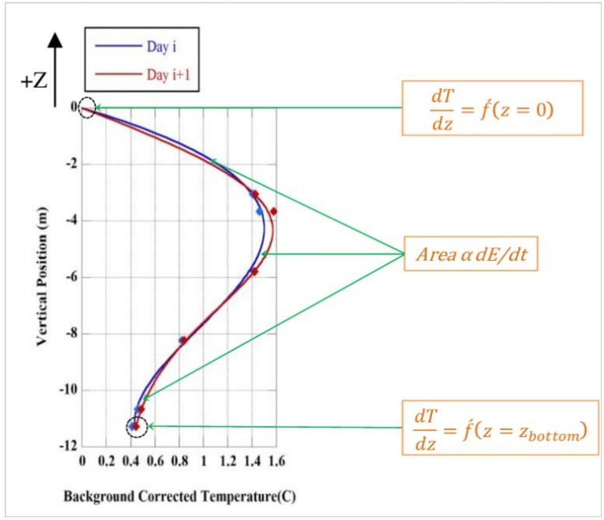
NSZD Quantification Methods



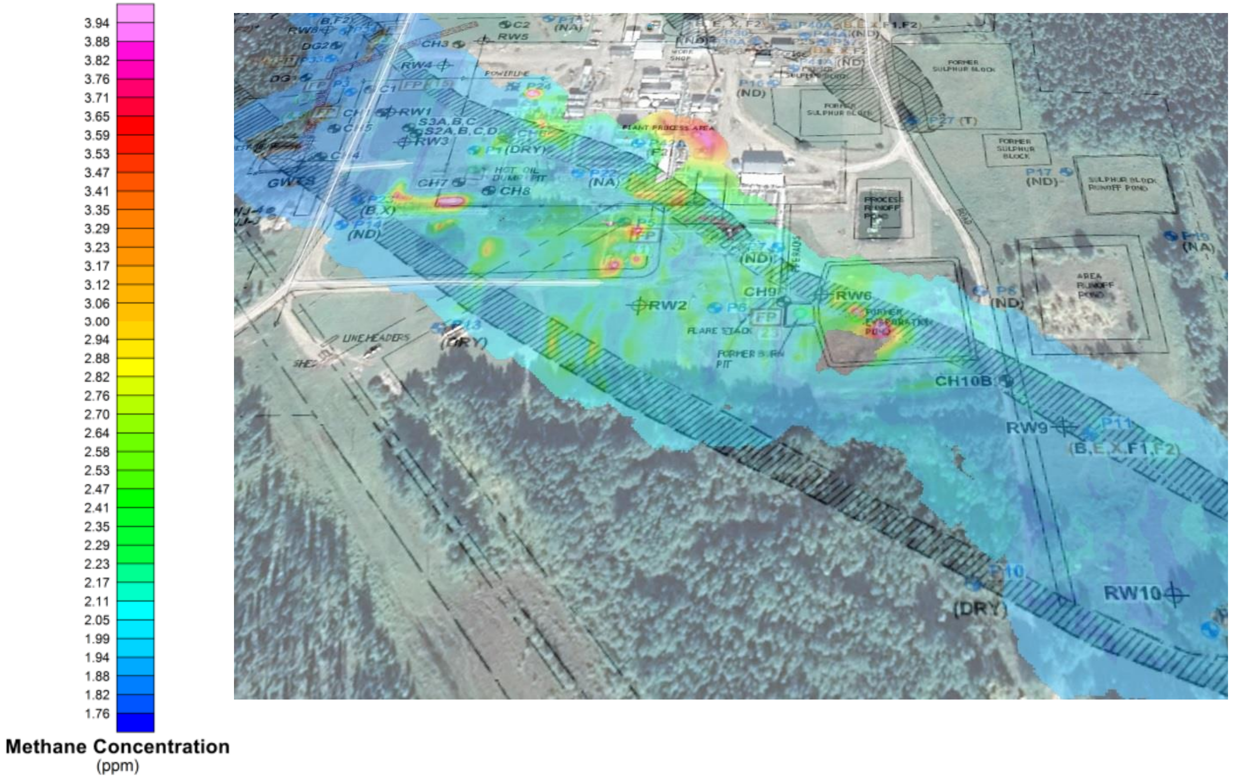


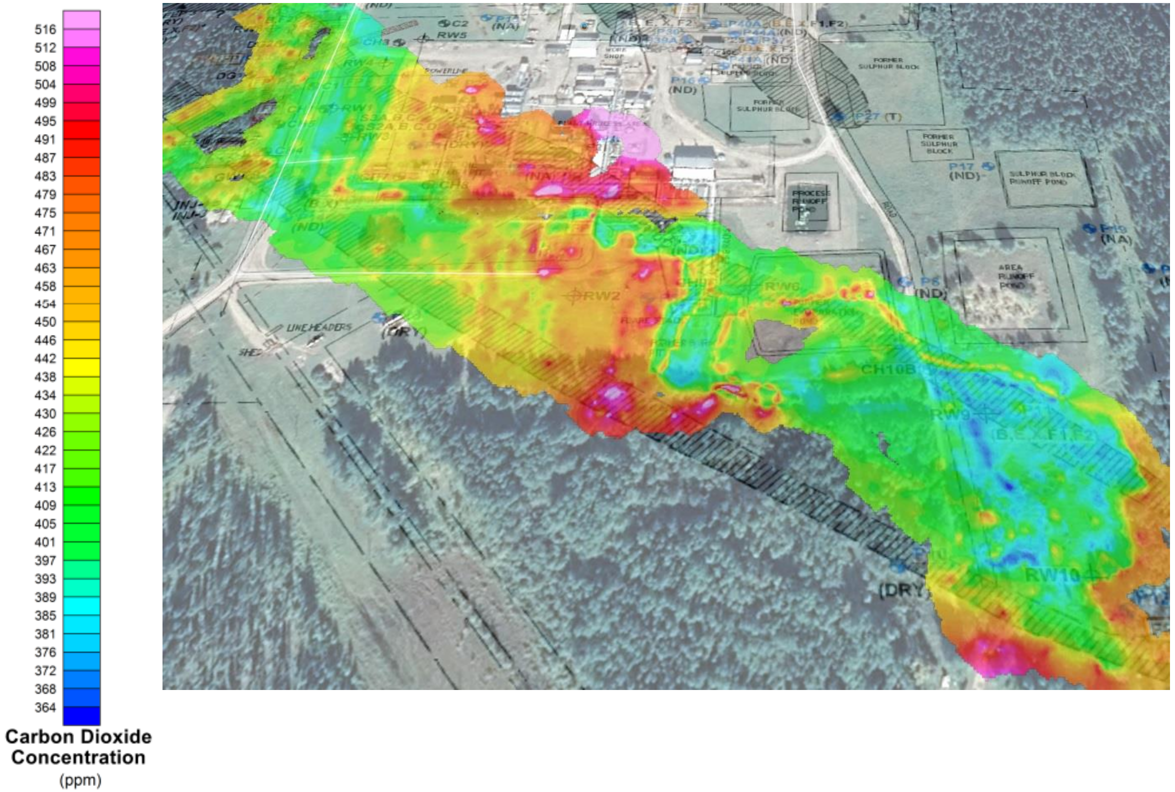






Surface CH_4 and CO_2 Distribution





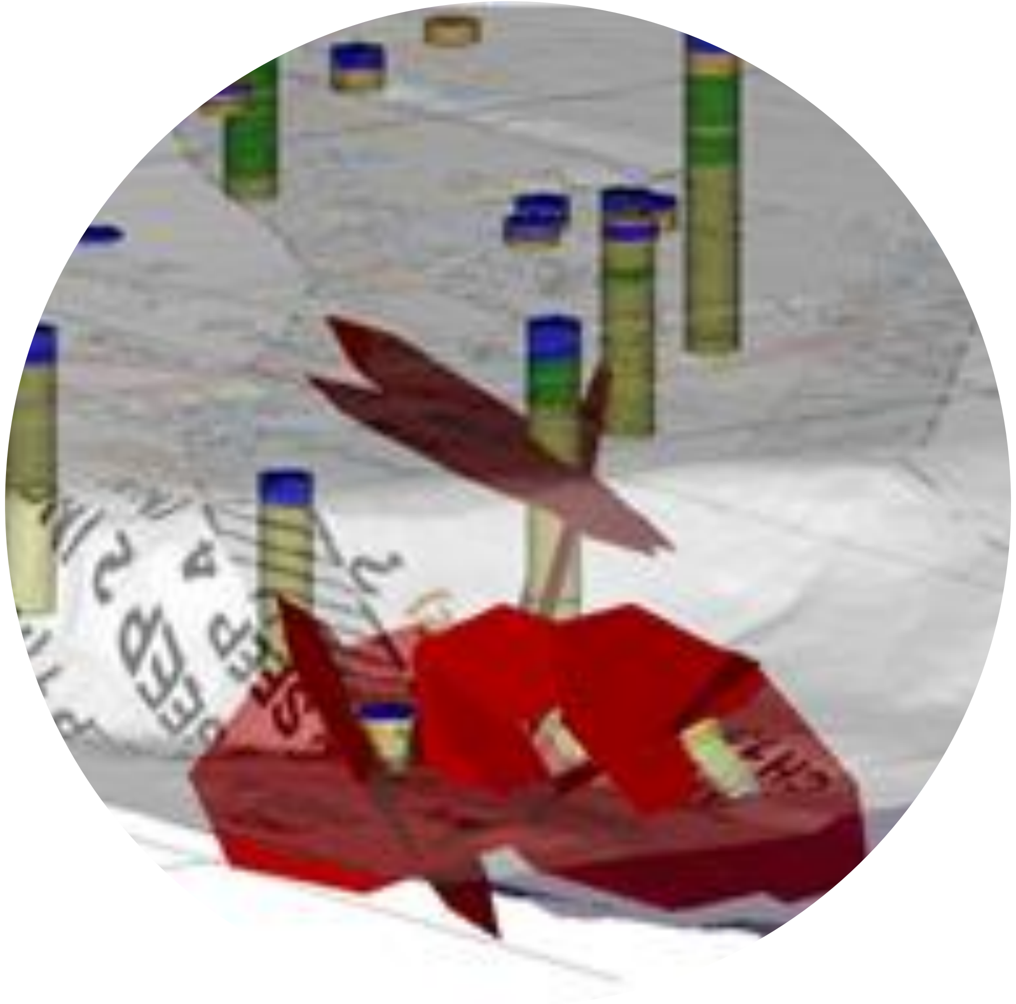
Fracture Network Characterization Program

The objective of the program was to identify a solution for preventing all impacted groundwater from reaching receptors and provide a timeline for remediating hydrocarbon impacts within a "reasonable period of time".

Our Approach:

Improve understanding of the fracture network to allow us to:

1. Develop effective strategies for minimizing seepage of hydrocarbons, including evaluation for effectiveness of a second grout curtain.
2. Remediate hydrocarbon impacts downgradient and upgradient of the grout curtain using methods such as surfactant flushing.



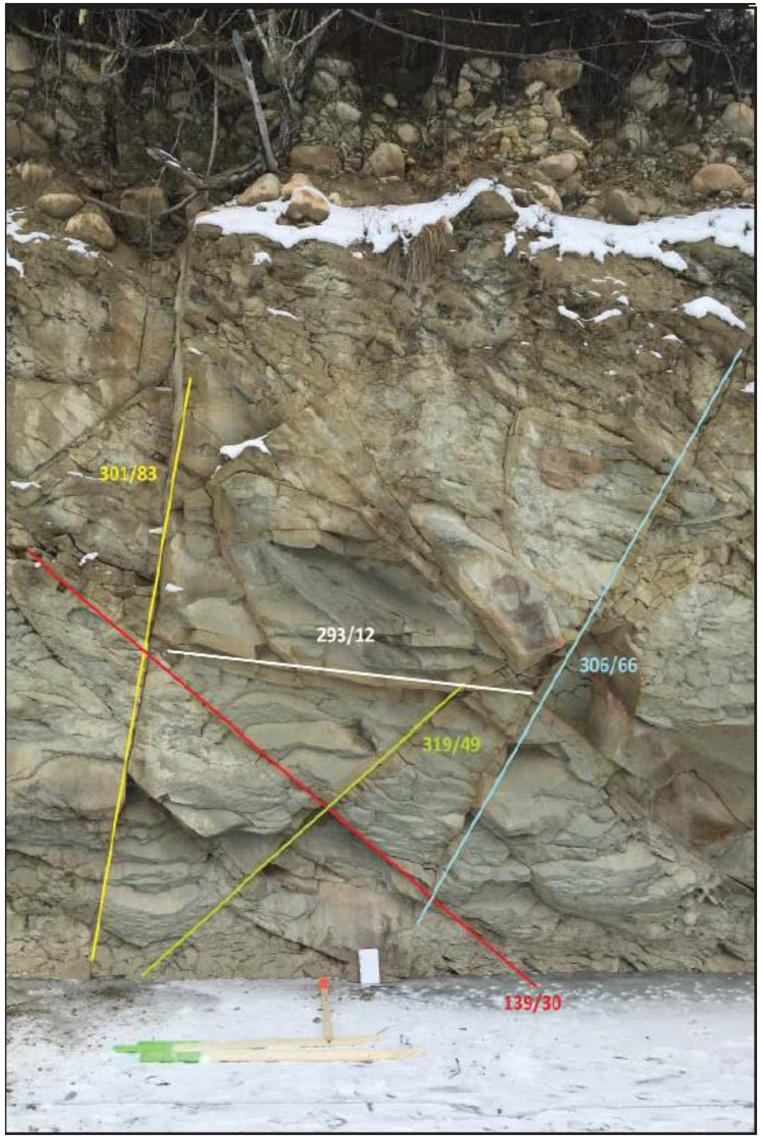
Methodology & Approach

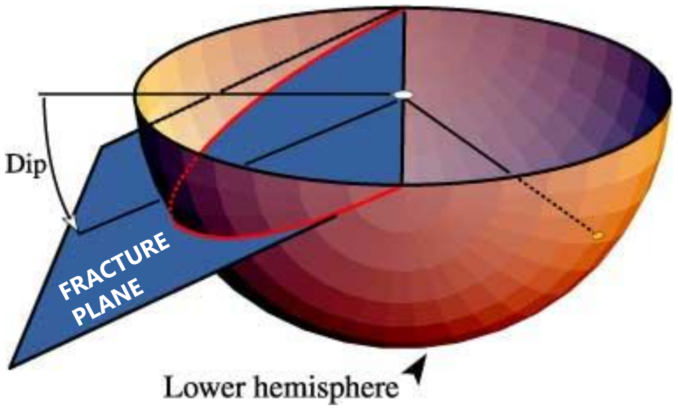
The fracture network characterization included the following:

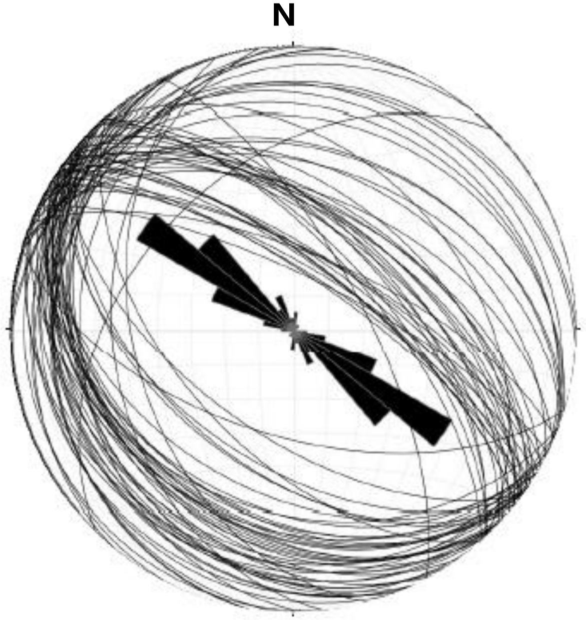
- Data Review & Processing
- Field-based Data Collection & Fracture Mapping
- Borehole Investigation
- Geophysical Investigation
- Leapfrog Modelling & Visualization

Fracture Mapping

- Characterize potential trends and patterns within the fracture network.
- Identify key contaminant pathways within the fracture network.
- Measure fracture apertures.
- Perform statistical analysis on dataset.
- Use data input for a discrete fracture network model (fluid injection and/or transport).





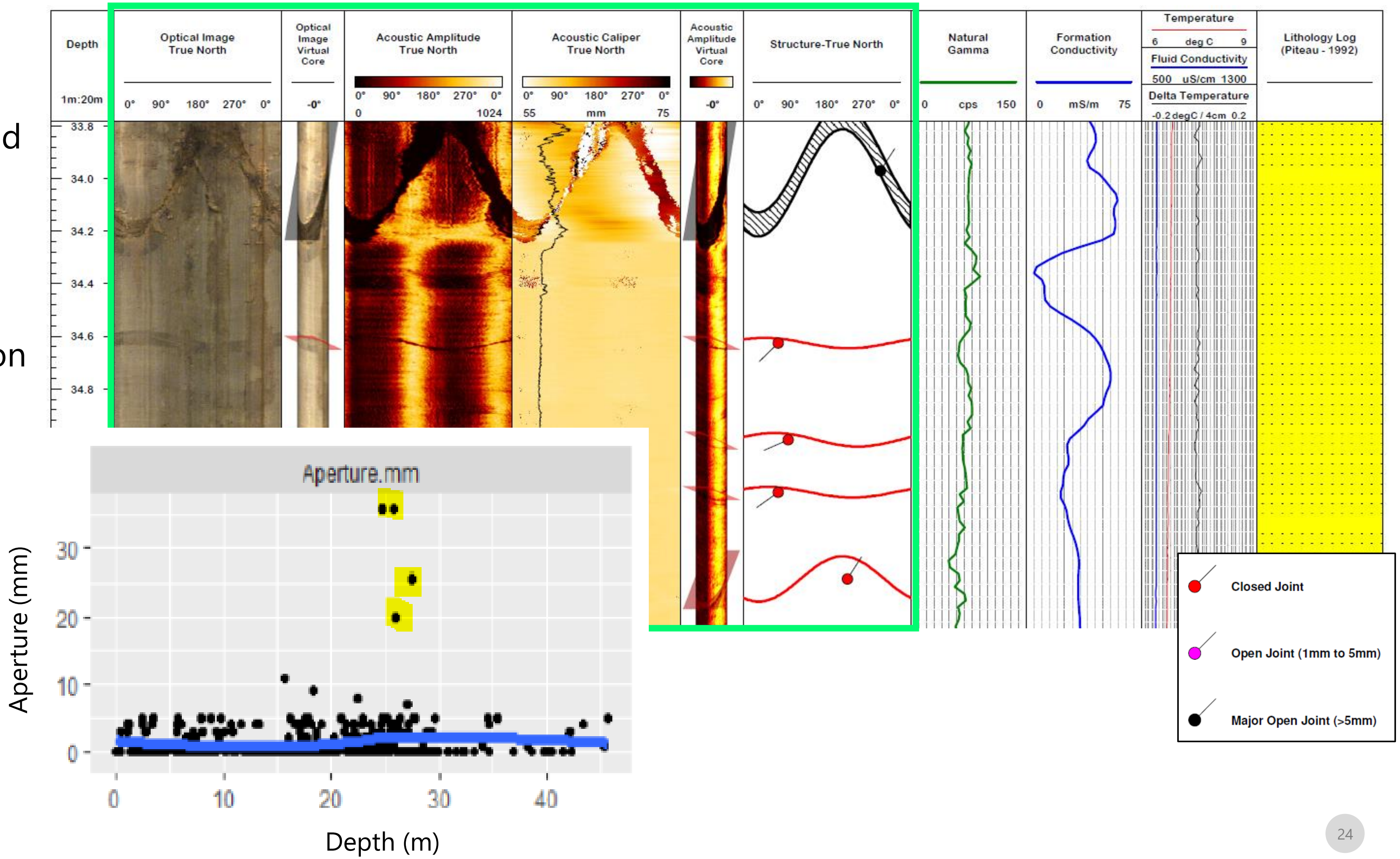


Borehole Investigation

- Refine our understanding of the site geology and contaminant distribution, and identify major fractures.
- Characterize impacts downgradient of the grout curtain.
- Utilize these holes for groundwater sampling and/or extraction/pumping.

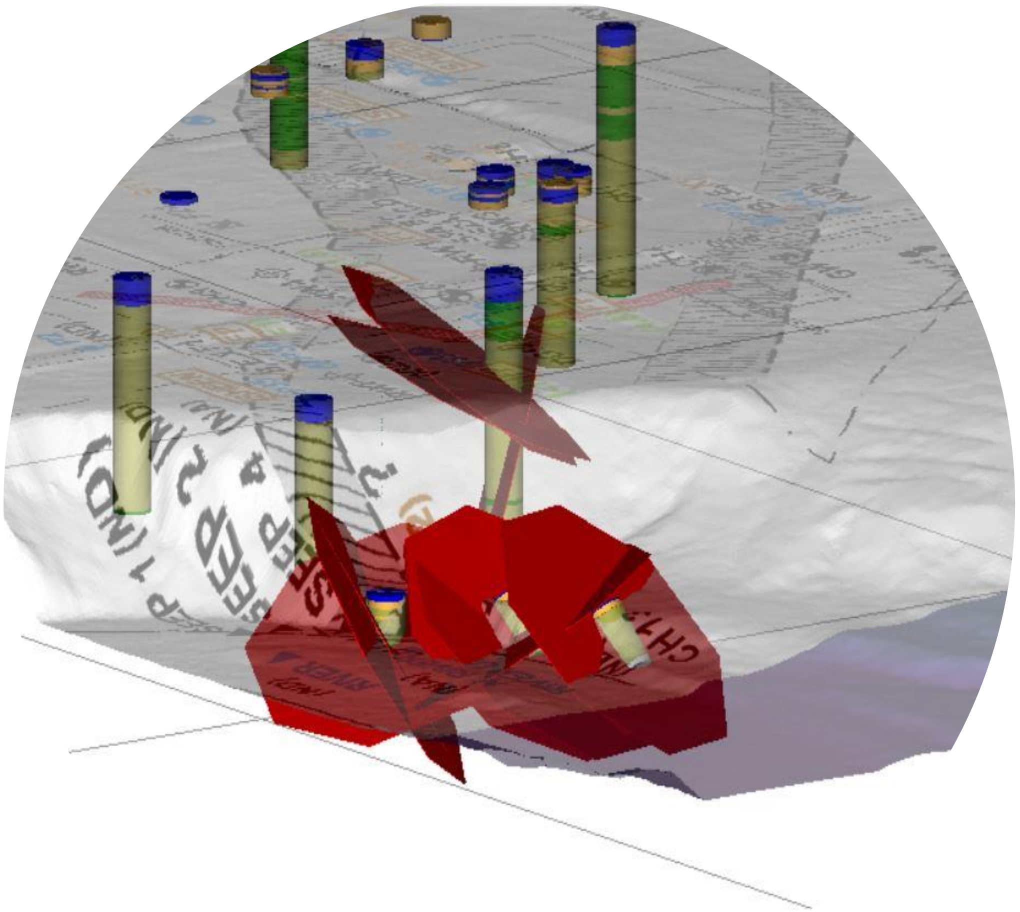
Geophysical Investigations

- Optical/Acoustic Televiewer
  - Identify fractures and estimate the orientation and aperture of the fractures.
  - Use this information to estimate fracture porosity.
- Temperature Delta & Formation Conductivity
  - Identify fractures that are acting as key conduits for groundwater and/or contaminant transport.
- Perform statistical analysis on the dataset.



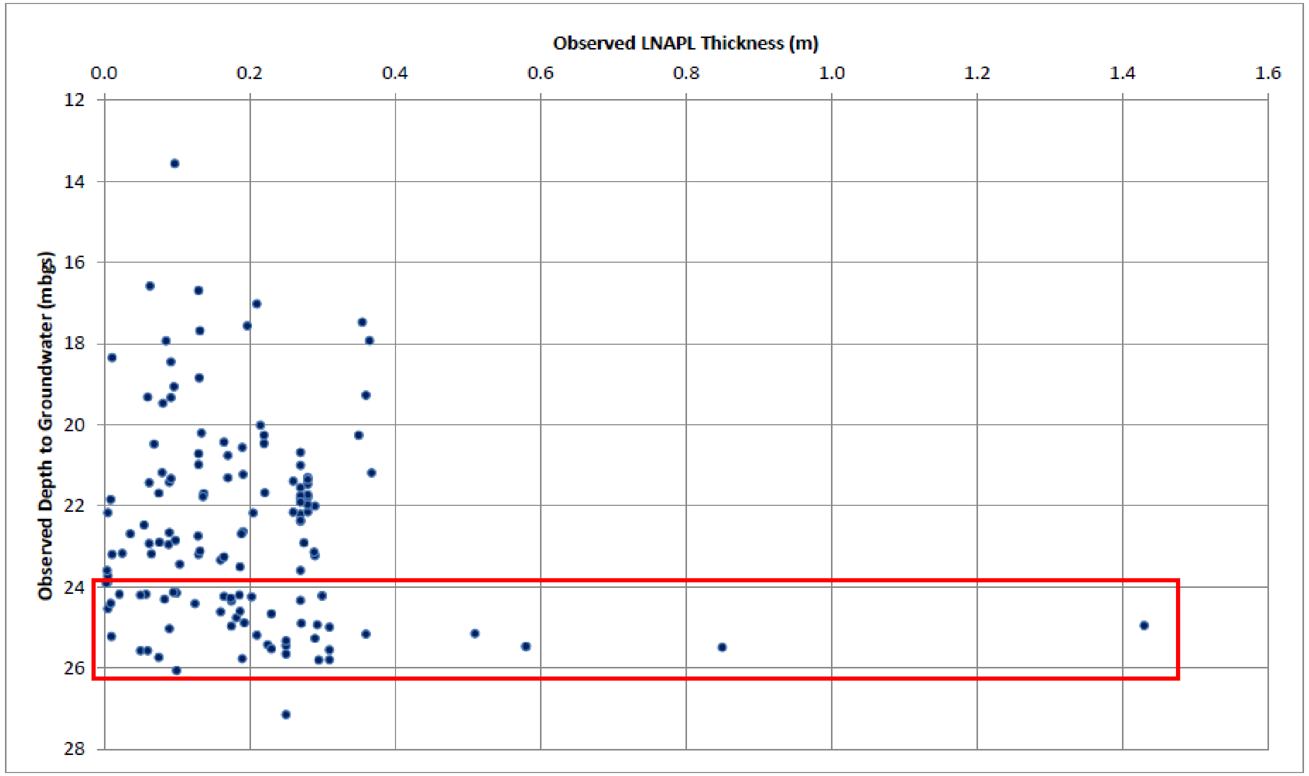
Leapfrog Modelling & Visualization

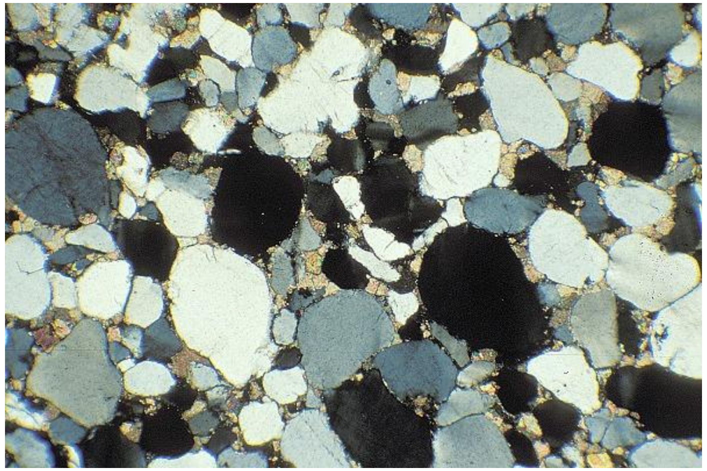
- Tool to visualize the fracture network in 3-dimensions.
- Project key fractures to determine intersection with certain boreholes.
- Screen wells that intersect specific fractures.



Historical Data Review & Processing

- Thin-section analysis
- Borehole tracer test
- Groundwater data:
  - Pumping tests & hydraulic analysis.
  - Trends in dissolved hydrocarbon concentrations.
- LNAPL thickness correlation
- Hydrocarbon fluorescence, sponge coring, LNAPL entry pressure calculations





Estimated NSZD Rates Using Historical Soil Vapour Extraction Data

- Soil vapour extraction conducted during 2012/2013 produced little VOCs but significant quantities of CH_4 and CO_2.
- Vacuum response was reported in monitoring wells on both sides of the grout curtain, extending 40 m downgradient and 240 m upgradient.
- Estimated capture zone area = 2 Ha
- Flow rate = 60 scfm
- “Steady-state” CH_4 ranged from 0.002-0.0051 mol/mol and CO_2 0.007 mol/mol

Estimated Time Required to Remediate LNAPL by NSZD

- Based on the fracture network characterization work described above, the estimated volume of LNAPL remaining in the main sandstone unit is 94 m^3 per hectare.
- This would correspond to an additional three decades required for remediation of the remaining LNAPL.
- Although there is considerable uncertainty in the LNAPL volume estimates, as well as the NSZD rate estimate, the above estimated rate of decrease is consistent with decreases in LNAPL thicknesses that have been observed in most monitoring wells over the last two decades.
- Long-term NSZD rates (i.e., over decades) have been shown by others to be generally zero order. Therefore a constant depletion rate can be assumed for much of the life of the LNAPL until a low saturation of LNAPL remains.

Conclusions

- Nature is amazing; it can help us.
- If subsequent NSZD assessments at the Site continue to confirm the above findings then NSZD could be considered for use as the primary remediation technique for residual LNAPL removal at the Site, instead of surfactant flushing combined with installation of a second grout curtain, as was previously being considered.
- Traditional electron acceptor-driven mass balance approaches to modeling NSZD have been greatly underestimating the rate of LNAPL depletion, as these models were not based on a complete understanding of role of methanogenesis. Methanogenic biodegradation of LNAPL is occurring at much greater rates than thought a few years ago – tens to hundreds of times greater.
- Clean-up times using NSZD as the primary remedy for thousands of contaminated sites in Alberta may not take centuries or millennia as previously thought.

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