

## Occurrence of Polar Organic Compounds in Groundwater Resulting from Biodegradation – Implications for Petroleum Site Investigations and Remediation

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# Presentation Outline

- Introduction and Definitions
- Polar Organic Compounds 101
- Case Study
  - Background
  - Key Issues Assessed
  - Investigation Program
  - Results
  - Conclusions
- Implications to Investigation Work and Remediation Programs



# Definitions

- **Petroleum Hydrocarbons (PHCs)** – organic compounds that consist only of C and H in their chemical structure
- **Polar Organic Compounds** – organic compounds that include O, S, or N in their chemical structure. Polar compounds resulting from petroleum biodegradation contain O (e.g. alcohols, aldehydes, ketones, carboxylic acids, and phenols)
- **Hyporheic Zone** – the zone of groundwater and surface water mixing in the pore waters of sediments beneath a river bed
- **EPH** – Extractable Petroleum Hydrocarbons of the carbon range C10-C19. This CSR analytical procedure quantifies the concentration of extractable organics in the sample, which can include both petroleum hydrocarbon and polar (non-hydrocarbon) organic compounds.
- **Silica Gel Cleanup Procedure** – Contaminated Sites Regulation (CSR) Analytical Method 7: *Aliphatic/Aromatic Separation of Extractable Petroleum Hydrocarbons in Solids or Water by Silica gel Fractionation*. The method uses silica gel to physically separate the components of Extractable Petroleum Hydrocarbons (EPH) based on their polarities. Generally, polar compounds are retained within the silica gel column due to their relatively high polarity.

# Polar Organic Compounds 101

## General:

- Polar compounds are not hydrocarbons; they have different chemical properties, fate and transport in the environment, and toxicity

## Common Sources:

- Naturally occurring (e.g. organic matter, humic and fulvic acids)
- Generated through biodegradation of PHCs (primarily alcohols and organic acids, with possible phenols, aldehydes and ketones)

## Properties of polar biodegradation byproducts:

- High solubility in groundwater relative to PHCs
- Can be majority of organics in groundwater at sites with biodegrading petroleum
- Biodegrade rapidly in aerobic environments
- Relatively less toxic compared to PHC

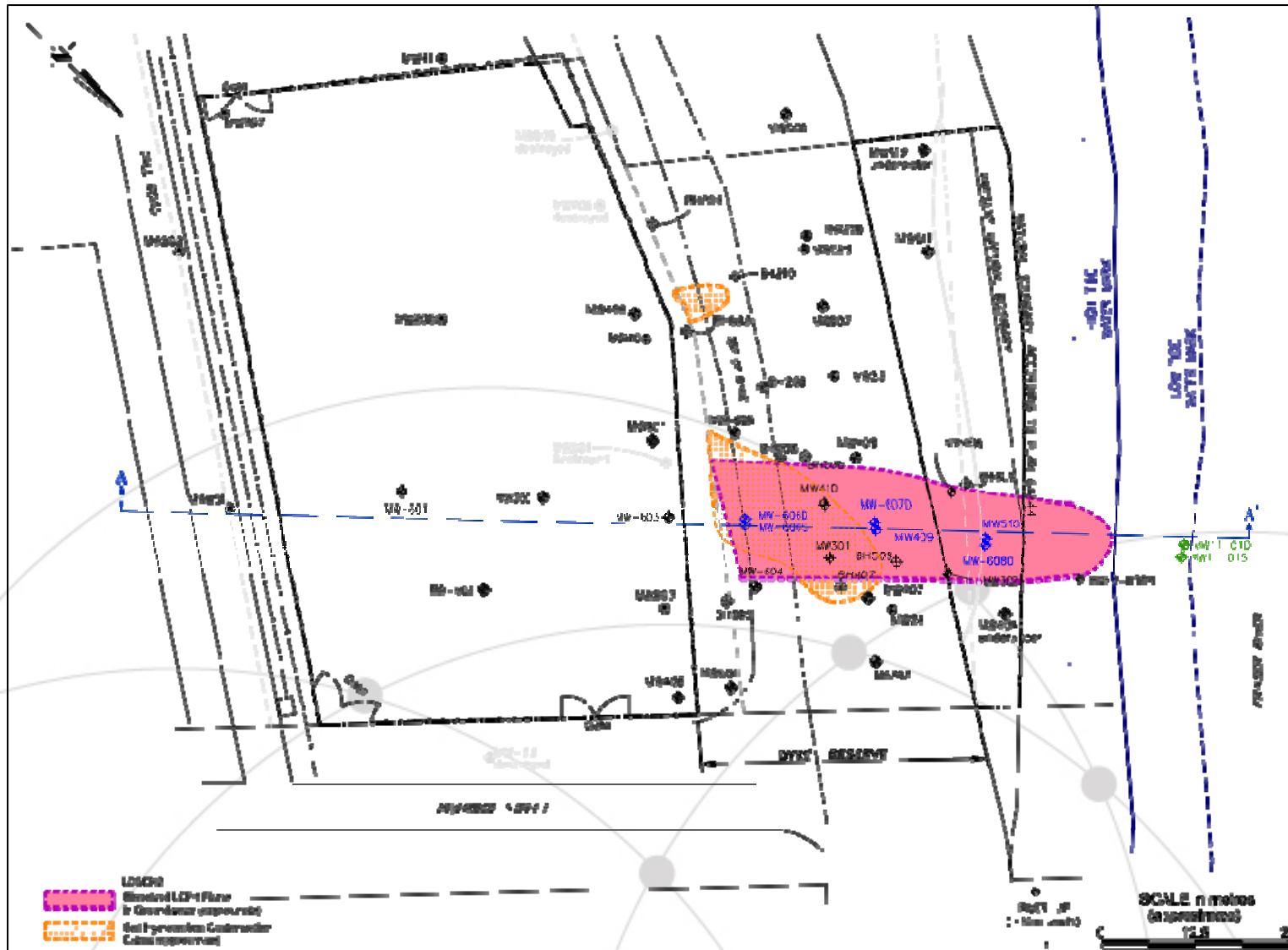
## Regulatory:

- Currently no standards for polar compounds
- CSR allows silica gel cleanup to be used, if soils contain (>30%) organics

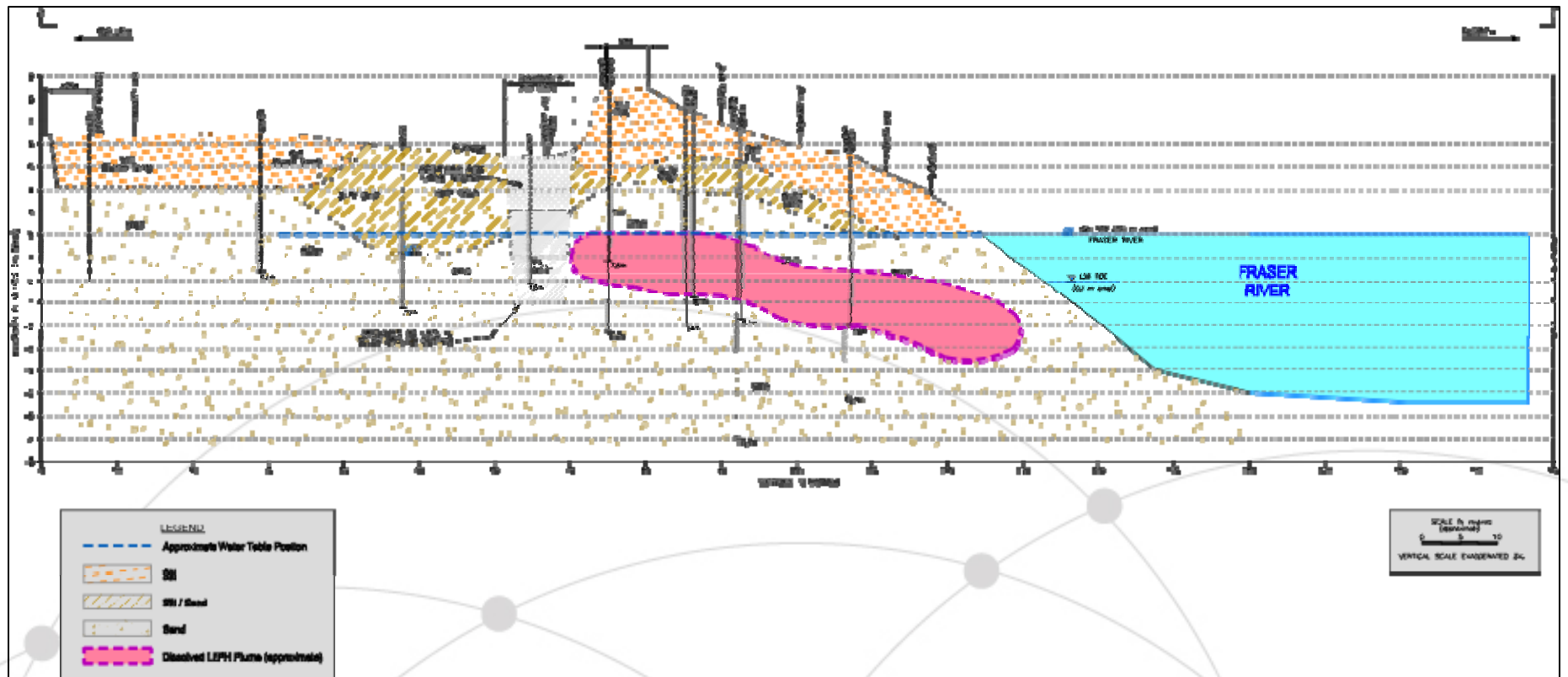
# Case Study Background

- Fuel bulk plant 1949 to 1991 (decommissioned); close to river
- Fuel (diesel, gasoline, & heating oil) pumped via pipeline from river through a dyke
- Multiple site investigation and remediation events (1992 to 2007)
- Small sliver of residual soil contamination remaining beneath dyke reserve (EPH and naphthalene)
- Groundwater exceeded CSR AW only for EPH
- The EPH plume was modeled to not reach the river in the future (Risk Assessment)
- In 2008 a risk based instrument was issued for the site with contingent 2 year monitoring program
- Exceedances of EPH during 2 year monitoring program at sentinel wells
- Applied silica gel cleanup and [EPH] reduced to non-detect in most wells
  - **confirmed presence of polar compounds, and not dissolved hydrocarbons**

# Residual Soil Contamination and Dissolved EPH Plume



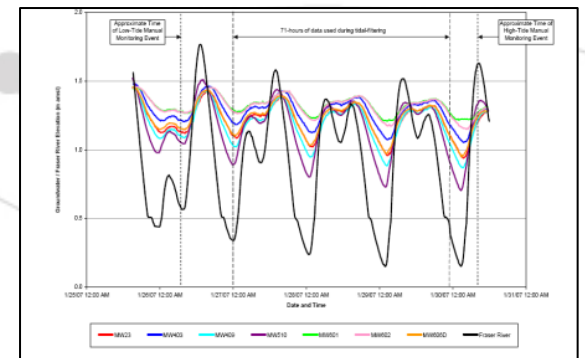
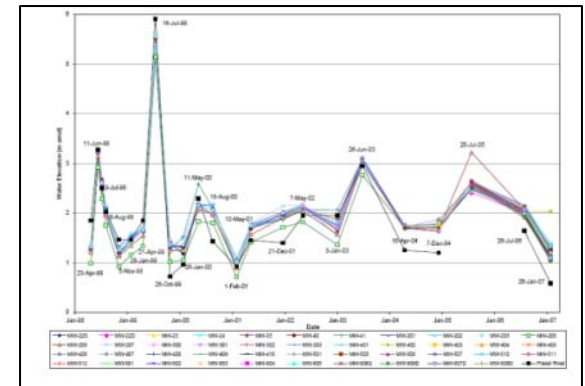
# Residual Soil Contamination and Dissolved EPH Plume





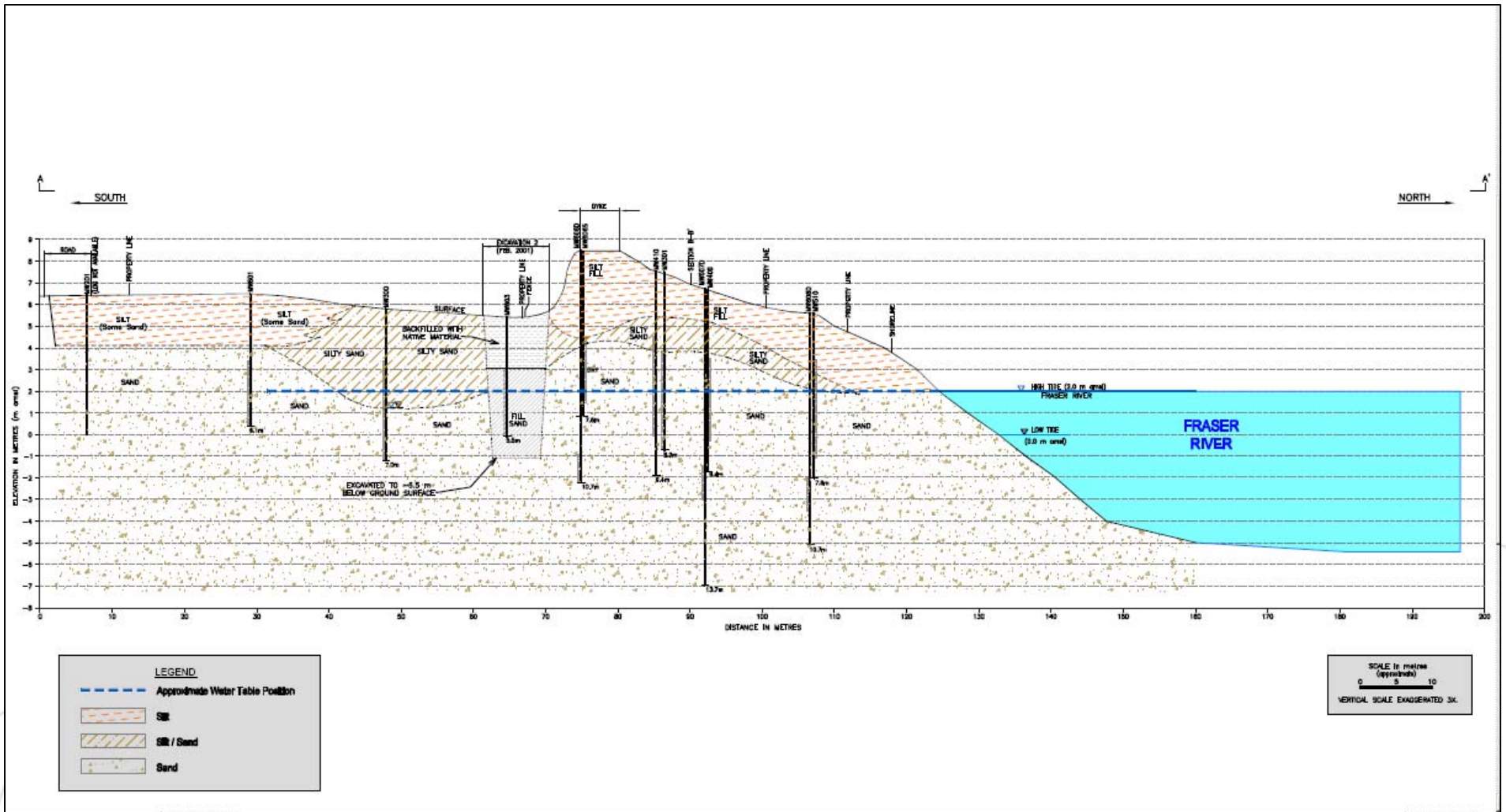
# Site Geology and Hydrogeology

- Fine to medium grained sands (fluvial deposits)
- Unconfined sand aquifer
- Groundwater levels strongly seasonally influenced by fluctuating river levels (up to 6 m fluctuations)
- Groundwater levels fluctuate up to 1 m daily due to tidal influence of the river



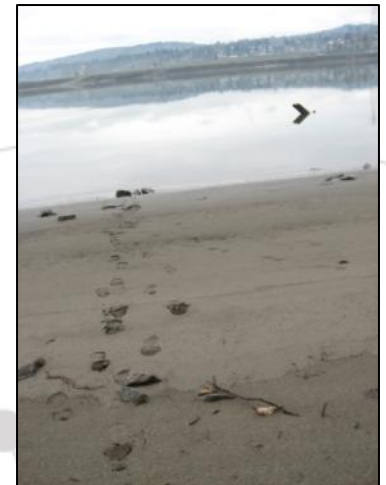


# Geology Cross-Section



# Key Issues Assessed

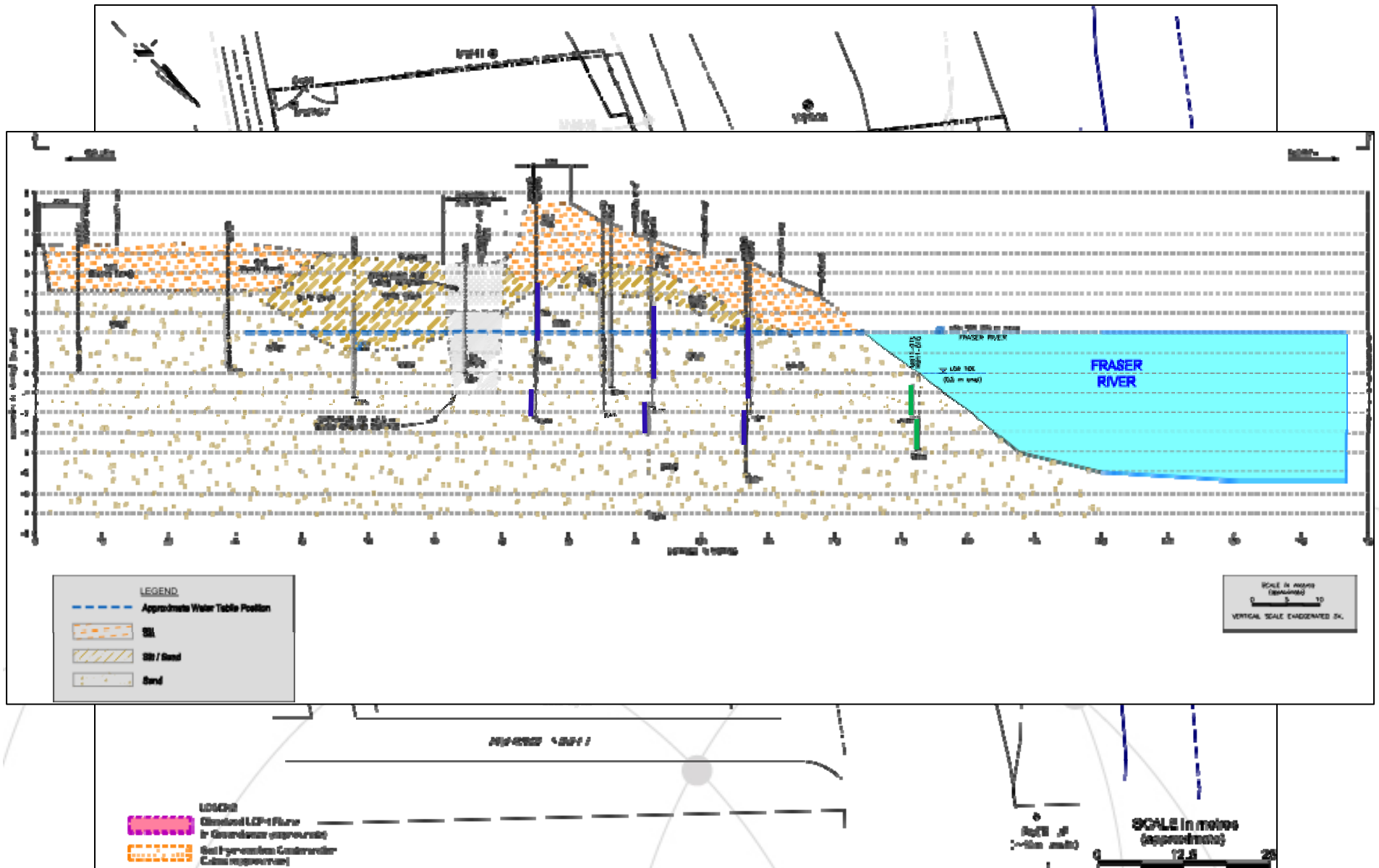
1. Are there polar compounds in groundwater natural background or related to the site (i.e. PHCs)?
2. Are the polar compounds reaching the river (i.e.  $>250 \mu\text{g/L}$  EPH)?



# Investigation Program

- Groundwater sampling of key existing wells in residual source area and downgradient
- Analysis of groundwater samples for EPH with and without SGC
- GCMS analysis (library search) on selected samples
- Literature review of hyporheic studies regarding conditions conducive to attenuation
- Installation of new downgradient monitoring wells at river and groundwater sampling

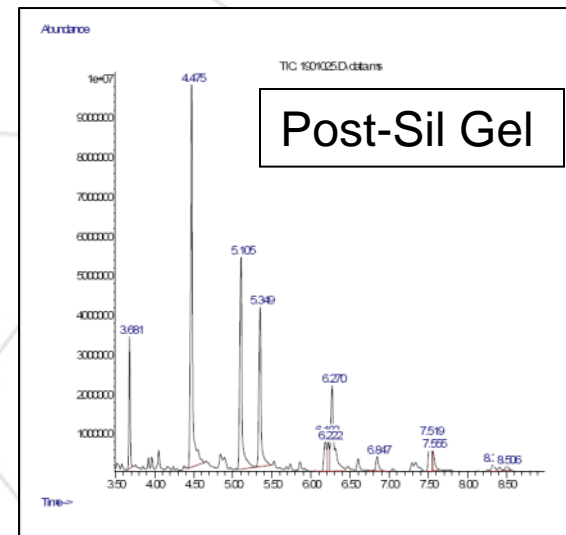
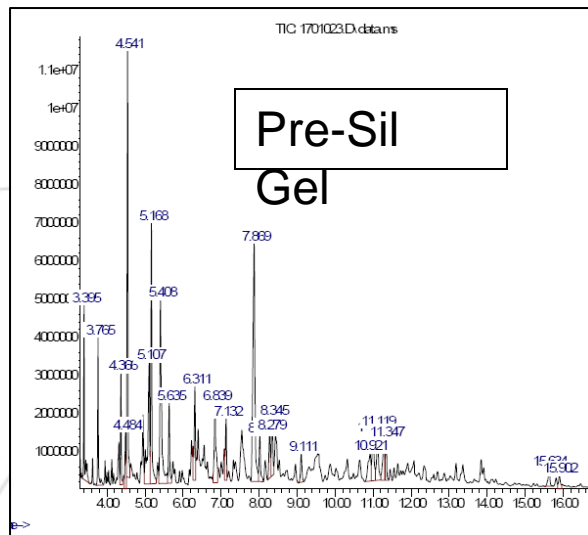
# Investigation Locations



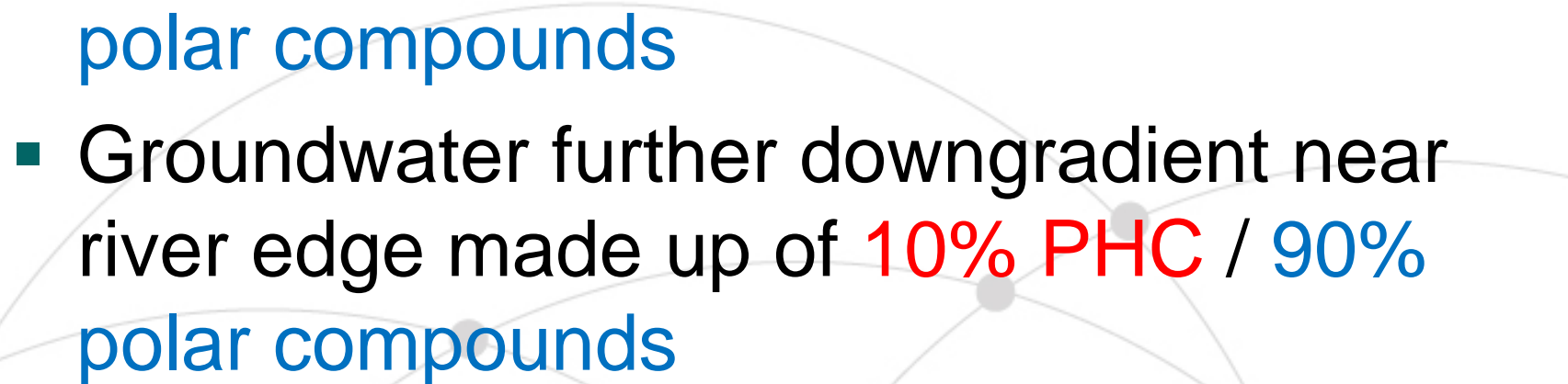
# Results: Issue No.1

Are the polar compounds in groundwater natural or related to the site (i.e. PHCs)?

- Polar compounds were interpreted as biodegradation byproducts using GCMS
- Polar compounds identified mainly ketones



# Results: Issue No.1 (cont.)

- Groundwater in source zone is made up of **44% PHC** / **56% polar compounds**
  - Groundwater immediately downgradient of source zone made up of **16% PHC** / **84% polar compounds**
  - Groundwater further downgradient near river edge made up of **10% PHC** / **90% polar compounds**
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# Results: Issue No.1 (cont.)



Monitoring Well:	MW606S	MW606D	MW409	MW607D	MW510	MW608D	MW11-01S	MW11-01D
EPH C10-19 (µg/L)	1840	<250	1720	<250	320	3080	<250	<250
EPH C10-19 Sil-gel (µg/L)	810	<250	270	<250	<250	380	<250	<250
% PHC Composition	44.0	N/A	15.7	N/A	0.0	12.3	N/A	N/A
% Polar Composition	56.0	N/A	84.3	N/A	N/A	87.7	N/A	N/A





# Results: Issue No. 2

Are the polar compounds reaching the river (i.e. >250  $\mu\text{g/L}$  EPH)?

- **PHCs and polar compounds not reaching the river**
  - EPH results (with no SGC): <250  $\mu\text{g/L}$  at MW11-01
- Polar compounds present only within redox shadow caused by biodegradation
- Redox conditions more aerobic at MW11-01, supporting that under more aerobic conditions, polar compounds rapidly biodegrade
- Study results consistent with findings from literature regarding attenuation of polars

# Conclusions

## Key Findings:

- Majority of EPH (10-19) / LEPH fraction made up of polar compounds rather than PHCs
- Polar compounds generated through biodegradation of PHCs are common on all sites – more prevalent on aged plumes
- Polar compounds not very persistent beyond redox shadow of bioactivity (i.e. in aerobic environments)
- There is no CSR standard for polar compounds in the C10-19 range – not appropriate to compare polars to EPH / LEPH standards

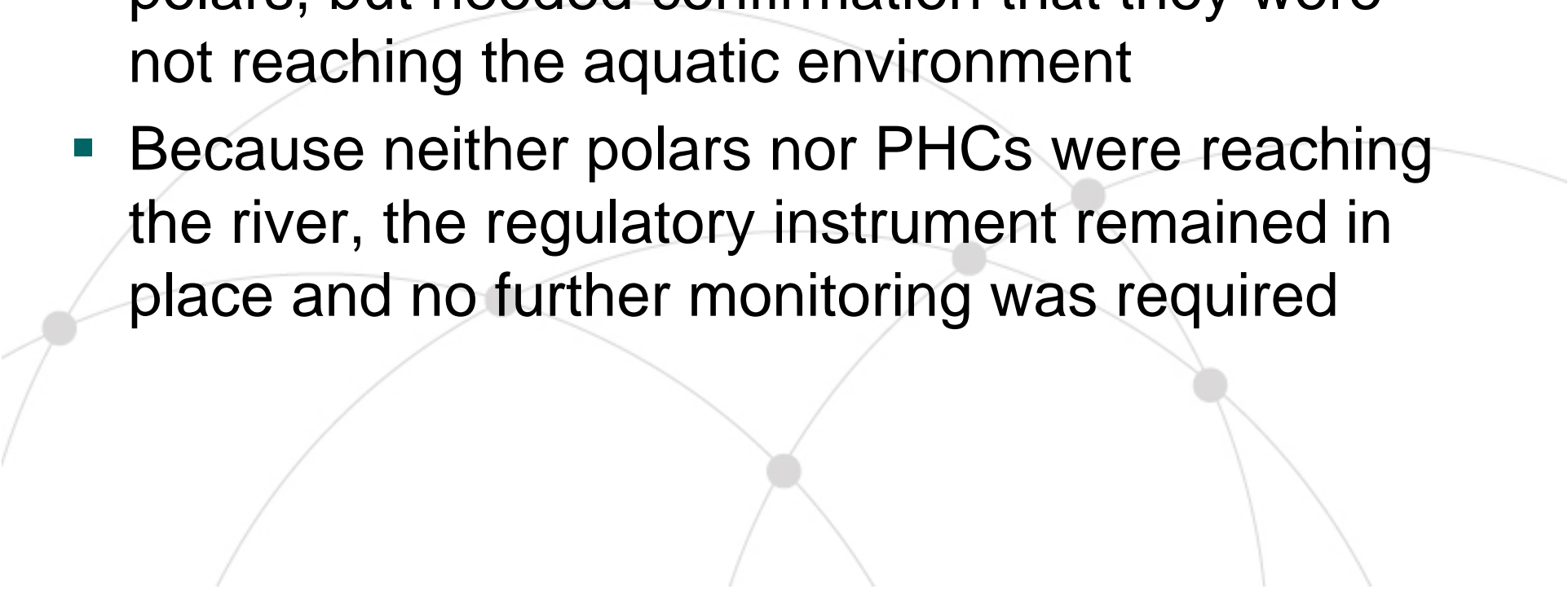
# Conclusions (Cont'd)

## Potential Solutions:

- Run SGC routinely to remove the polars and allow for appropriate comparison to EPH standards, OR
- Analyze PHCs on a compound specific basis and compare directly to the appropriate standard (i.e. eliminate EPH standards)

*But* – what about the polars?

# PROJECT PROGRESS

- Results of this assessment were presented to the ministry of environment (MoE) and were well received
  - MoE appreciated the technical issues with the polars, but needed confirmation that they were not reaching the aquatic environment
  - Because neither polars nor PHCs were reaching the river, the regulatory instrument remained in place and no further monitoring was required
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# Implications for Investigation/Remediation Programs

## ■ Investigation:

- Delineation of polars plumes rather than PHC plumes
- Delineation of polars plume may not be needed
- Potential greater investigation costs incurred than required

## ■ Remediation:

- Potential unnecessary remediation of polar compounds in groundwater rather than PHCs
- Monitored natural attenuation programs will need to distinguish between polars and PHCs
- Risk assessment work may erroneously assume toxicity associated with PHCs rather than the less toxic polar compounds

# THANK YOU!

# QUESTIONS?

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