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False Positive Detection of Naphthenic Acids in Groundwater Samples at a SAGD Facility near Ft McMurray

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Site Overview

SAGD Facility located near Ft McMurray, AB.

- 2009-2011:
  - Baseline Data Collection
  - Development of the **Groundwater Monitoring Program**
- 2011:
  - Development of **Targets and Threshold** (T&T)
  - Site construction.
- 2012:
  - Start of operations (incl. steaming)

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Groundwater Monitoring Program

- Requirement under the EPEA Approval.
- Main aspects include:
  - Frequency of sampling
  - Geological units to monitored
  - Parameters to be analyzed
  - Development of **targets and thresholds** (T&T)
  - Groundwater Response Plan
  - Reporting requirements

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Targets and Thresholds

- Target:
  - 95th percentile calculated from background concentrations
- Threshold:
  - AB Tier 1 Guidelines; or
  - Lower Athabasca Regional Plan (LARP) value; or
  - Highest background value.

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Targets and Thresholds

Typically, bi-annual sampling values are compared to targets and thresholds:

- Value above Target triggers:
  - Lab check
  - Resampling/ confirmation
  - Flagging (for trend)
- Value above Thresholds triggers:
  - Lab check
  - Resampling/ confirmation
  - Review for Trend:
    - No trend: flagging (extreme not captured during baseline)
    - Rising trend: source investigation and plume delineation

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Parameters above Threshold at the Site

- 2012 and spring 2013 sampling events: first detection of parameters above target and thresholds :
  - Toluene, xylenes, hydrocarbons F1 and F2;
  - Phenols; and
  - Naphthenic Acids.
- Naphthenic Acids: indicator of spill/ groundwater contamination during SAGD Operations under the LARP (2 mg/L).

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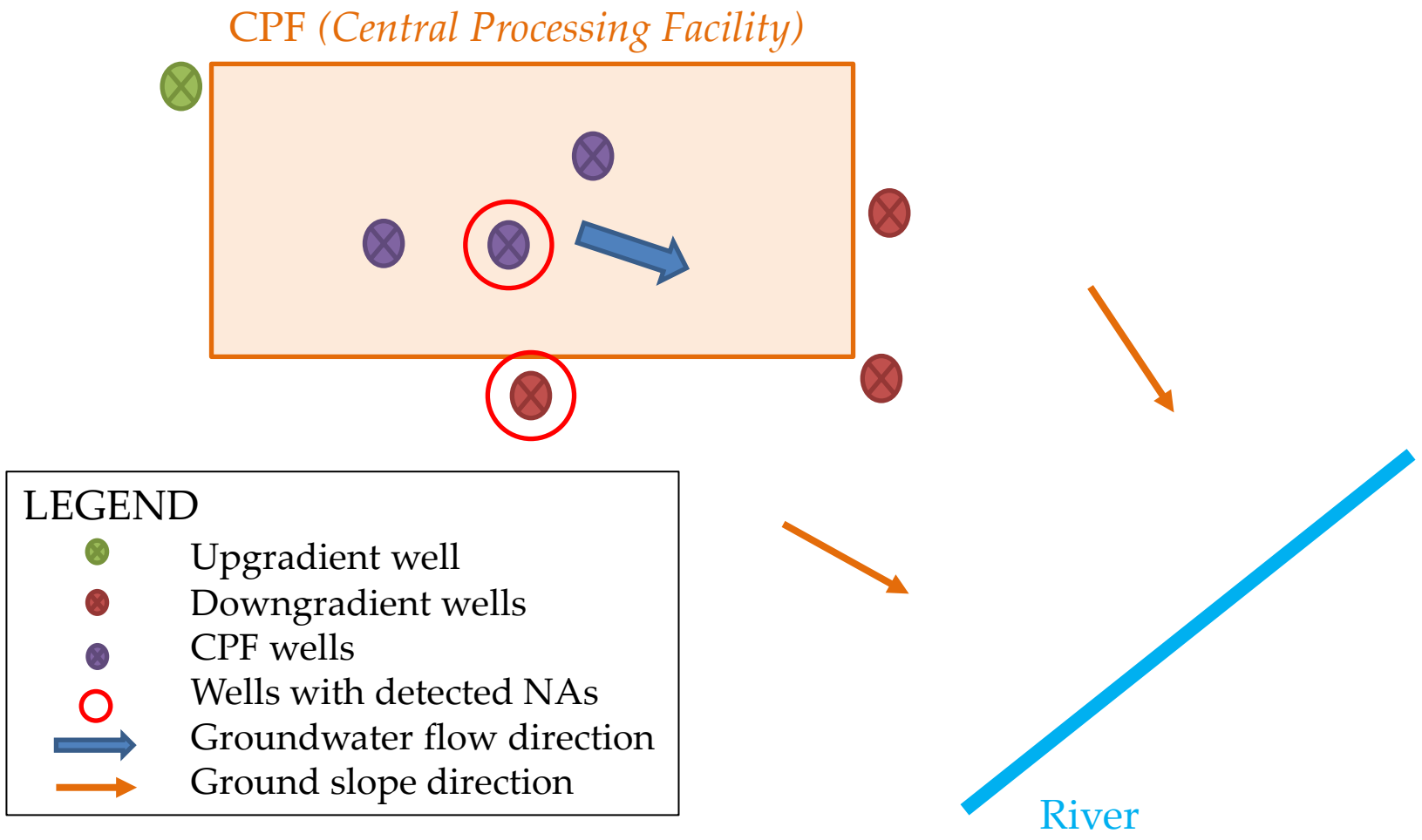
Plant Site Map



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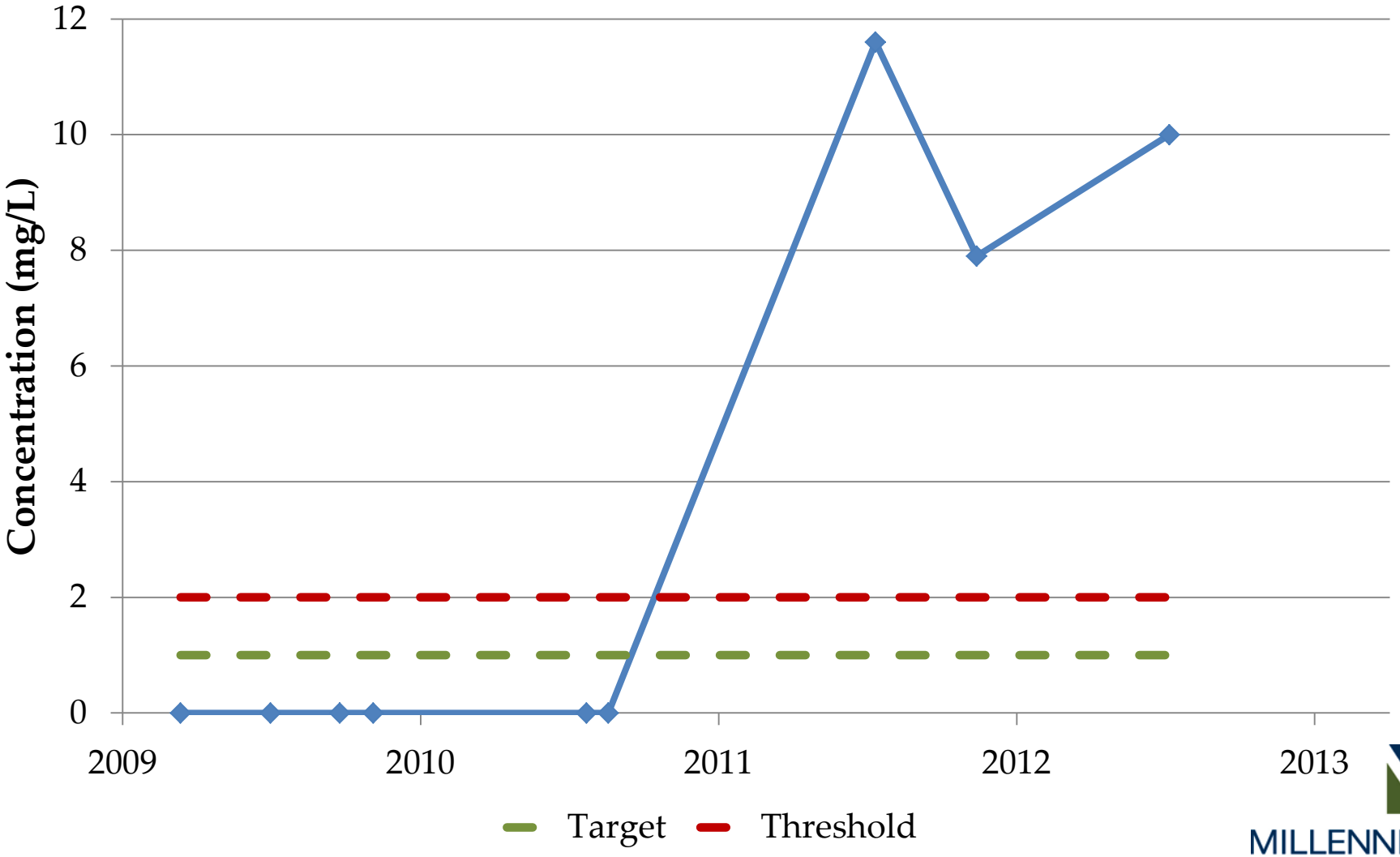
Concentrations of Naphthenic Acids



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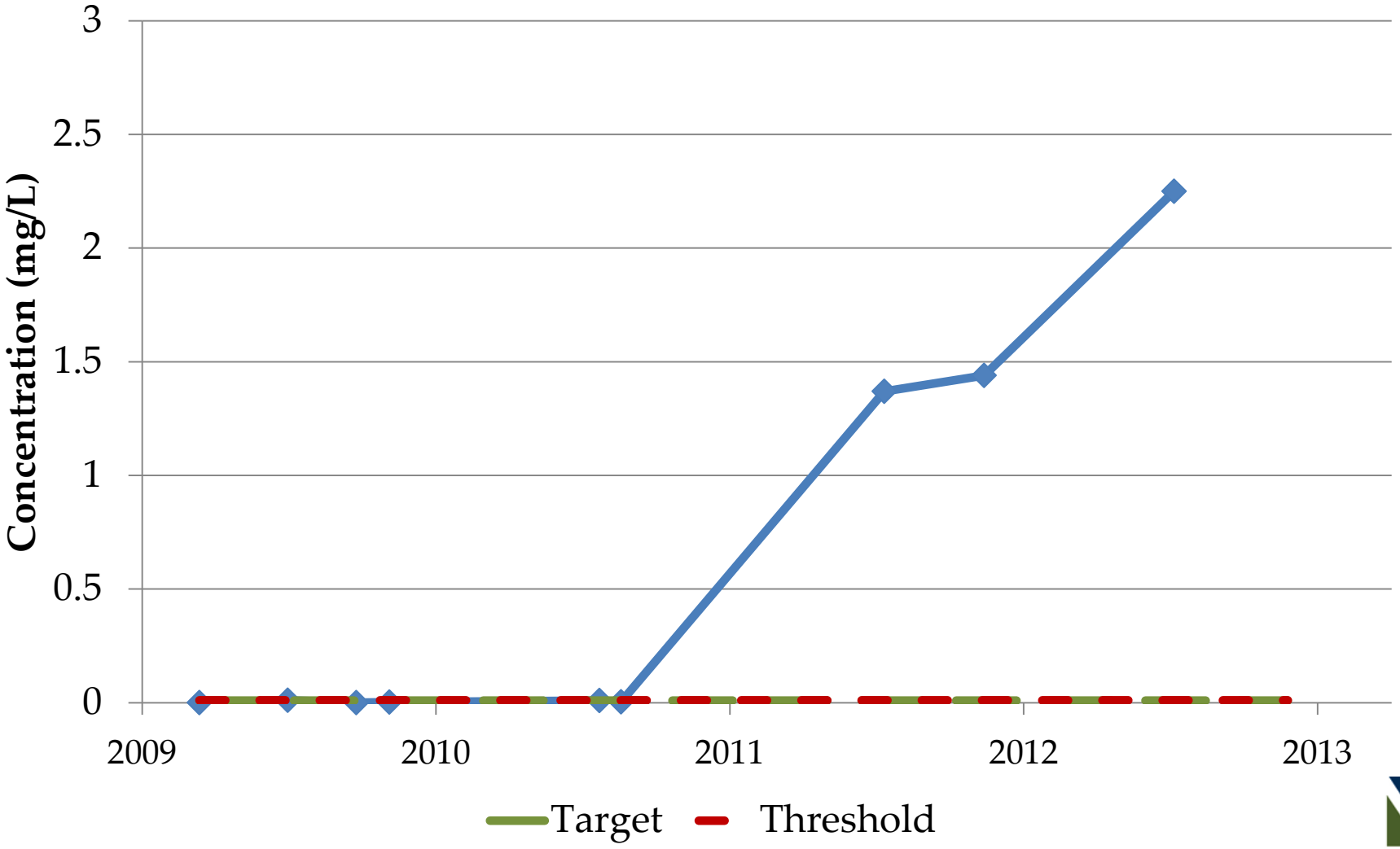
Concentrations of Phenols



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Groundwater Response Plan

- Groundwater Response Plan was initiated:
  - Confirm results with the lab.
  - Resample and confirm Threshold exceedance
- Parameter(s) confirmed above threshold
- Source investigation and impact delineation initiated:
  - Review/ spill event record (if available)
  - Conduct soil sampling (if applicable)
  - Drill additional wells

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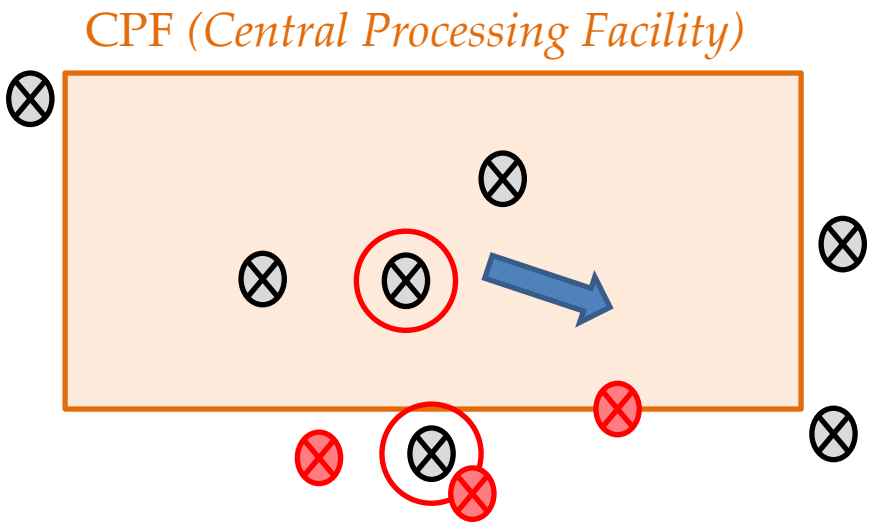
Plume Delineation

- 2013: drilling of additional monitoring wells
  - Locations constrained to existing lease boundaries



LEGEND

- Existing wells
- Wells with detected NAs
- Additional wells
- Groundwater flow direction

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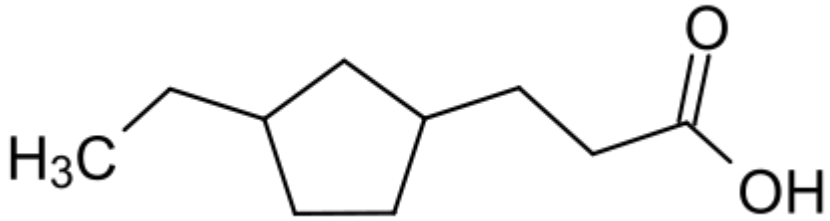
Objective of Investigation

- Determine the source of the impact.
- Focus on the naphthenic acids.

So what are naphthenic acids?

- Carboxylic acid functional group; and
- 1 to 6+ cyclopentyl and/or cyclohexyl rings; and
- 9 to 50+ carbon atoms.



Example of a Naphthenic acid

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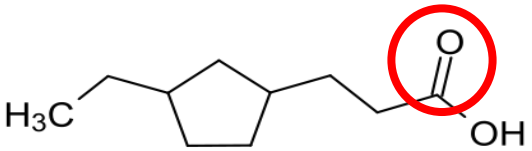
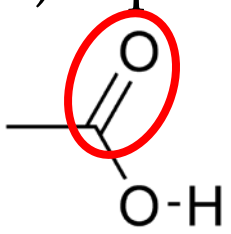
Naphthenic Acids Characterization

- The typical method used by labs to detect naphthenic acids is the Fourier Transform Infra-Red (FTIR).
  - Detects resonance in the vibrations of particular bond, in this case the C=O bond in the carboxylic group.



Naphthenic acid

  - Can also detect other carboxylic acids (such as acetic, propionic and butyric acids) if present in the sample, creating false positive.



Acetic acid

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Naphthenic Acids Characterization

- FTIR indicated naphthenic acids in groundwater: unexpected and unlikely result

- Conducted further laboratory analysis to investigate the positive detection of naphthenic acids by FTIR in groundwater
  - Thank you to Dr. Igor Volochtchik and AGAT Laboratories

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Naphthenic Acids Characterization

- Lab analysis investigation:
  - Groundwater sample
    - Run open-scan GC-MS
    - Analyze sample for volatile fatty acids to confirm presence and concentration.
  - Spike deionized water with similar concentrations of volatile fatty acids as groundwater sample and analyze for naphthenic acids by FTIR.

- These two techniques together can show whether volatile fatty acids could account for the naphthenic acid measured.

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Naphthenic Acids Characterization

- LC-MS/MS would be required to definitively exclude any possibility of naphthenic acid presence.
  - One lab in B.C. offering the analysis
  - Any Alberta based laboratories options?
  - Other options for detecting naphthenic acids only?

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Results

Chemical	Groundwater Sample (mg/L)	Spiked DI water (mg/L)
Volatile Fatty Acids		
Acetic acid	**192**	**200**
Propionic acid	**20**	**20**
Butyric acid	**27**	**20**
Naphthenic Acids *(by FTIR)*	**2.6**	**1.6**

- Open scan analysis detected the presence of a range of plant-related chemicals:
  - *phenylpropanoic acid, benzoic acid, 3-ethyl-phenol, hexanoic, acid, camphor, cyclohexanecarboxylic acid, an unknown terpene, an unknown siloxane, and pinocamphone*

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Conclusion

- Naphthenic acids detected, among other parameters, above T&T during compliance monitoring.
  - Triggered the GW Response Plan:
    - Resampling;
    - Delineation; and
    - Confirmation of Concentrations.
- Presence of volatile fatty acids in significant quantity.
- Volatile fatty acids likely creating a false positive detection of naphthenic acids.
- Likely no likely no naphthenic acids present in the groundwater sample, but naphthenic acids can only be ruled out by performing a LC-MS analysis.

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Conclusion

- Chemical signature of the groundwater impact is not consistent with a release of hydrocarbon fuel or crude oil (no benzene).
- Based on the phenols and other biogenic compounds concentrations, it is however consistent with the decay of coniferous and other plant-based organic matter.
- CPF pad was built by adding fill on top of the native material (peat, moss and brushed coniferous material) without stripping.
- We are likely seeing the degradation of the organic matter trapped below the pad fill.

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Questions?

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