

Toluene in Peatlands and Wetlands

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Overview



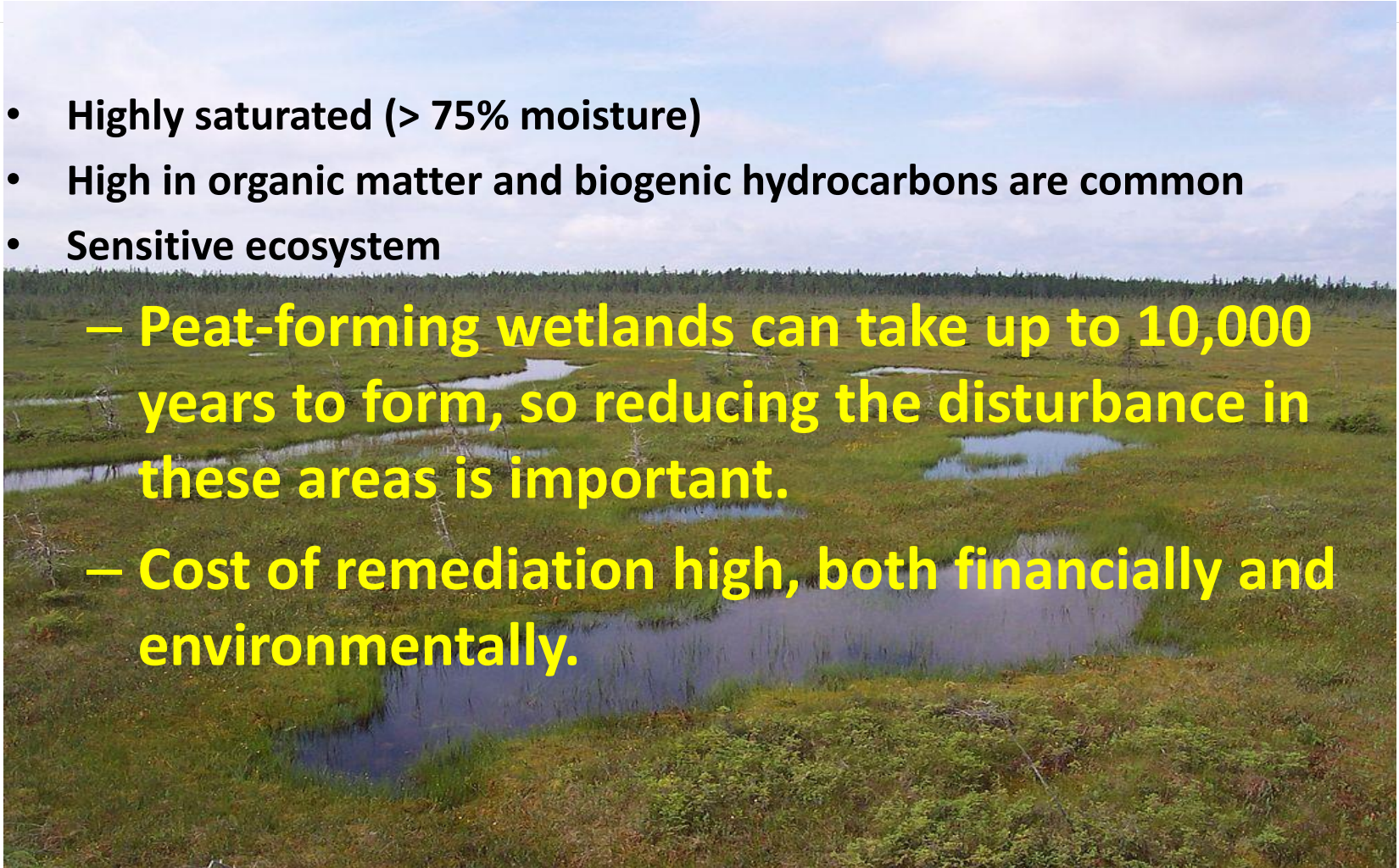
- Peatland and wetland characteristics
- Reason for studies
- Sources of petrogenic and biogenic toluene in the environment
- Proposed forensic approach
- Case studies
- Next steps and conclusions



Peatlands and Wetlands

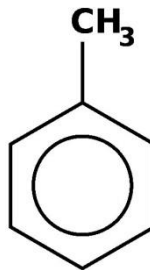


- Highly saturated (> 75% moisture)
- High in organic matter and biogenic hydrocarbons are common
- Sensitive ecosystem
 - Peat-forming wetlands can take up to 10,000 years to form, so reducing the disturbance in these areas is important.
 - Cost of remediation high, both financially and environmentally.



Why did Matrix do these studies?

- Toluene measured at concentrations greater than guidelines in soil and water from peatlands and wetlands
- Areas of potential impact extended off-lease into undisturbed areas



Literature Search - Sources of Toluene



Petrogenic

- Deep subsurface
 - Petroleum generation



Biogenic

- Surface and near-surface
 - Plant growth (atmosphere)
 - Microbial metabolism (hydrosphere)



Pyrogenic

- Thermal
 - Combustion of organic matter
- Ambient
 - Combustion of fuels from urban areas



Literature Search - Sources of Biogenic Toluene

Plant Growth

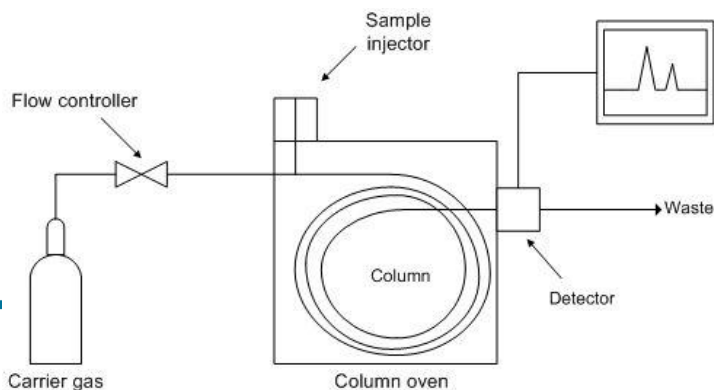
- Toluene emitted to atmosphere by plants under stress
- New England study demonstrates that summer pattern of atmospheric toluene does not follow benzene
 - Biogenic toluene up to 7% of total toluene measured in air

Microbial Metabolism

- A bacterium isolated from anoxic lake waters produces toluene from phenyl precursor
- Biogenic toluene documented in sludge bioreactor

Routine Analytical Approach

- Analysis of BTEX, F1 using GC/MS in selective ion mode
- Analysis of F2 to F4 PHCs using GC/FID
 - Method also extracts biogenic organic compounds (BOCs)
 - Soil extract subjected to silica gel clean-up to remove contribution from biogenic hydrocarbons present in organic soils



New Approach Needed



- Contacted lab:
 - Was there a way to determine if the toluene measured in samples is biogenic or petrogenic?
 - Could they come up with an analytical approach to solve the problem?

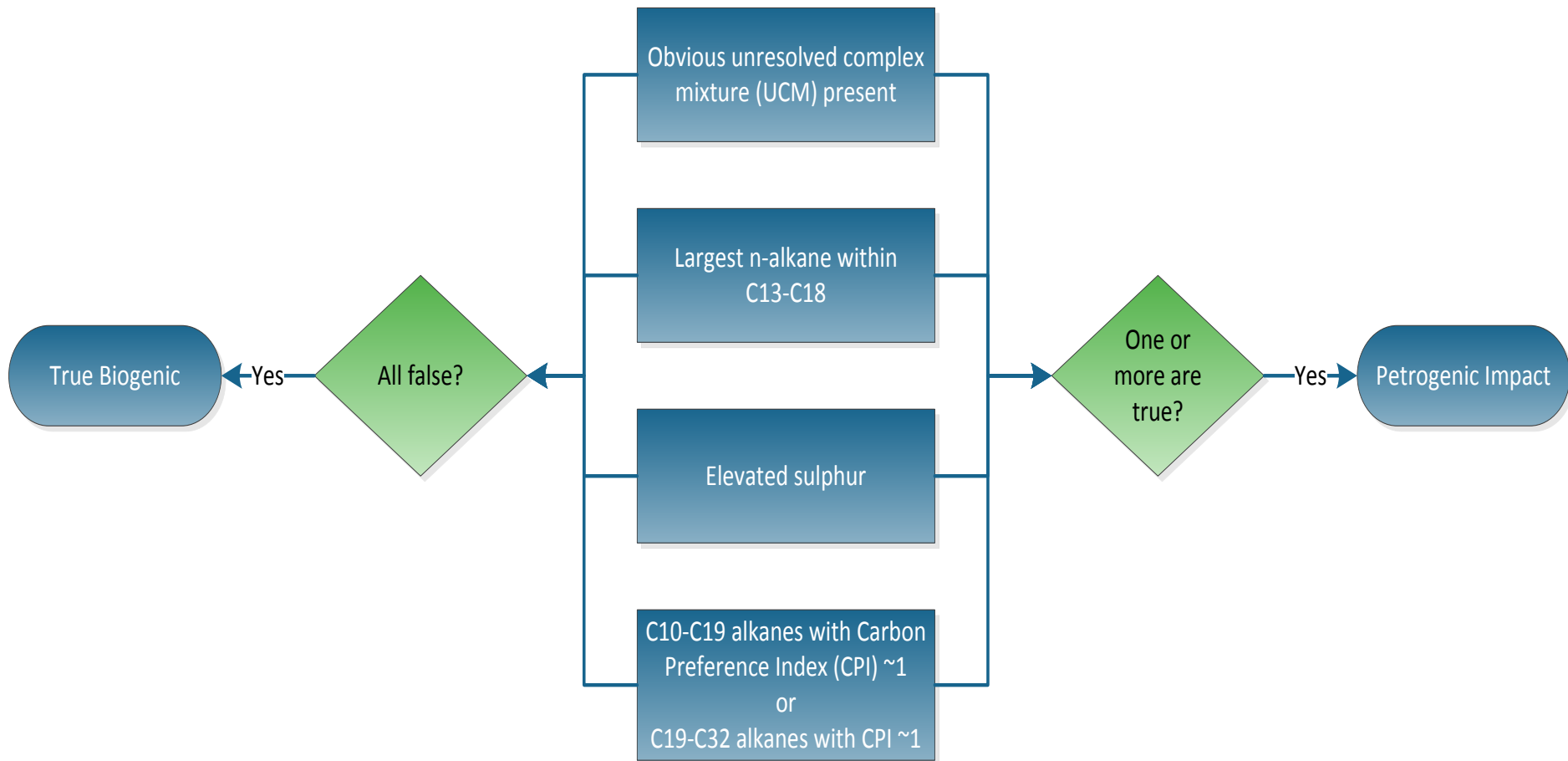


Forensic Approaches



- Forensic approaches to date
 - most forensic approaches look only at extractable hydrocarbons
- Forensic approach taken for this work
 - In conjunction with an extractable hydrocarbon evaluation, applied a forensic approach looking at the volatile organic carbon (VOC) fraction
 - C13:C12 isotope characterization

Determination of “True Biogenic” Samples - F3 Fraction





Pre-screening

Pre-screening requires chromatogram interpretation expertise

Does the contamination source have an F2:F3b ratio of ≥ 0.10 ?

No

Do not proceed with evaluation

Yes

Does the GC-FID pattern in the peat sample match the GC-FID pattern(s) in the contamination source and/or background soil?

No

Exclude sample from evaluation

Yes

Tier 1 Evaluation

Do the F2 and/or F4 concentrations in the soil sample exceed soil standards?

No

Management required

Yes

Does the F3 concentration in the soil sample exceed the soil standard?

No

Management not required

Yes

Tier 2 Evaluation

Is the F2:F3b ratio in the soil sample ≥ 0.10 ?

No

Management not required

Yes

Does the soil sample biomarker and/or PAH analysis indicate PHC presence?

No

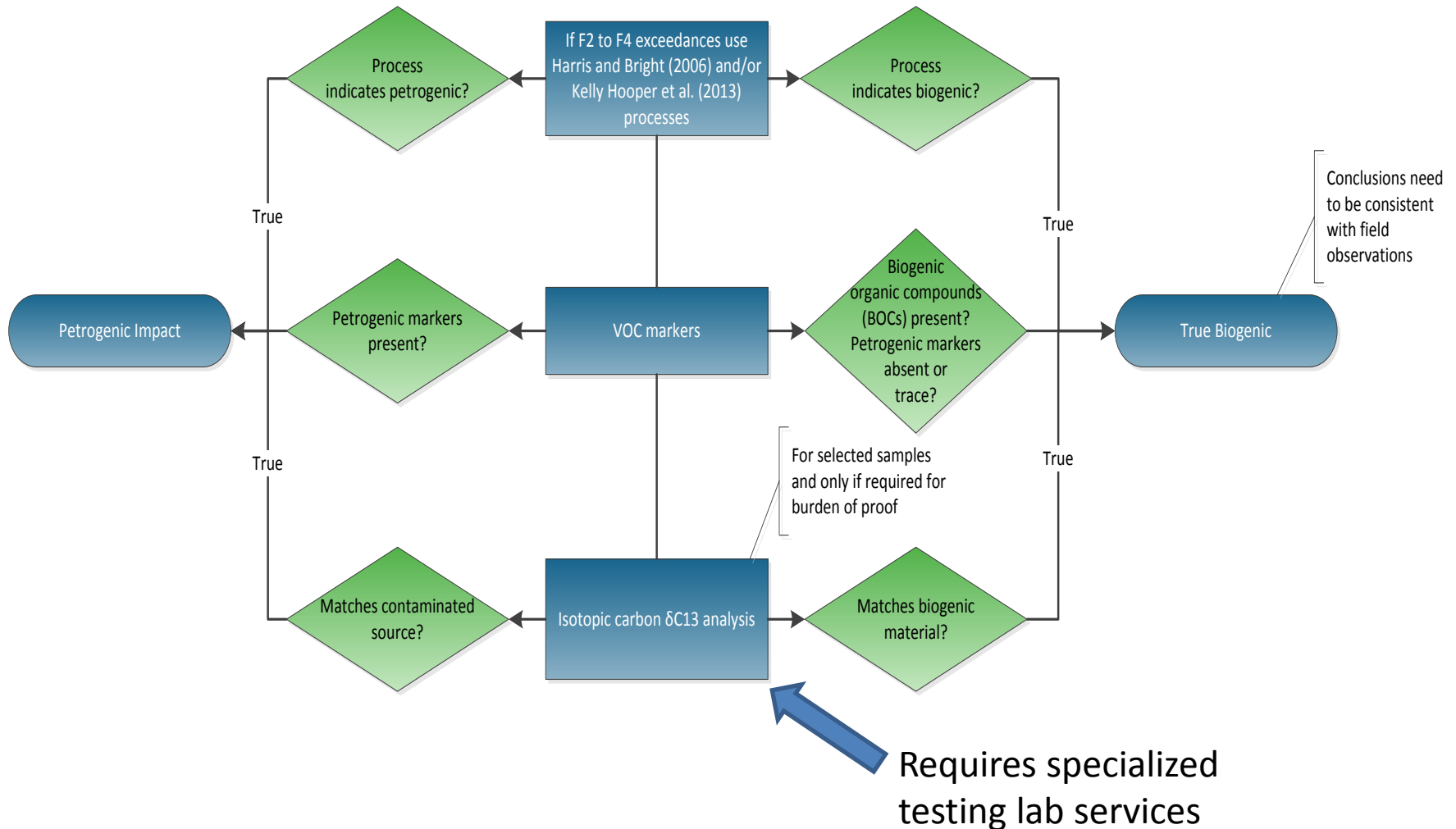
Management not required

Yes

Management required

Decision Process for Biogenic F3 Encountered in Organic Soil

Proposed Decision Process for Biogenic Toluene



Carbon Isotopes



- Isotopes: atoms of the same element with different amount of neutrons, but equal number of protons in their nuclei
- Carbon isotopes include:
 - C12 – stable and predominant
 - C13 – stable
 - C14 – radioisotope
- The approximate ratio of C13 to C12 is 1:99

Carbon Isotope Analysis



- Analysis of stable isotopes *for specific compounds* is done by Isotope Ratio, Mass Spectrometer (IRMS)– known as Compound Specific Isotope Analysis (CSIA)
- Results expressed relative to a benchmark standard of C13

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 \text{ expressed as } \text{‰}$$

or per mil, and

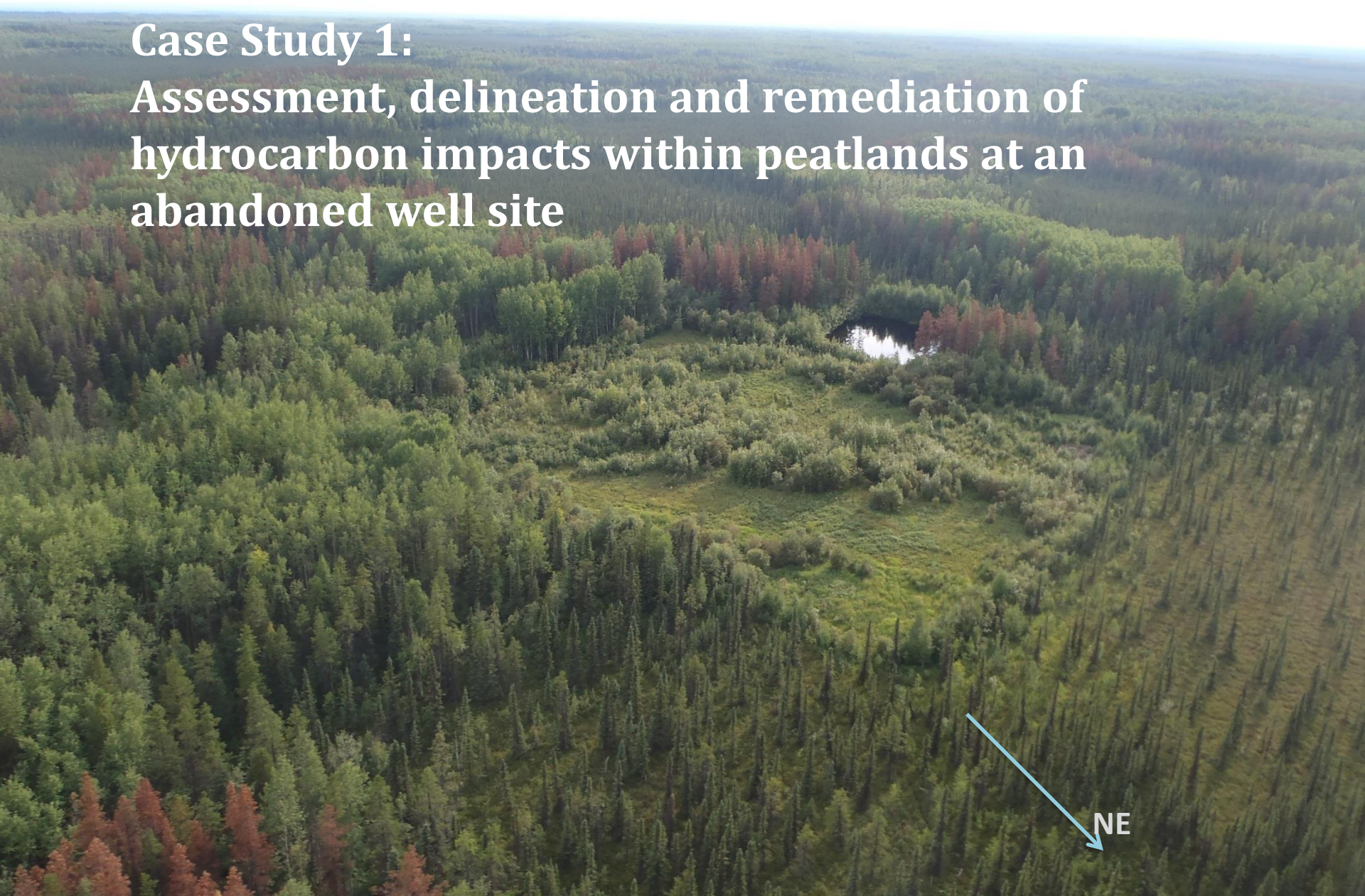
$$R = {}^{13}\text{C}/{}^{12}\text{C}$$

Case Study Applications



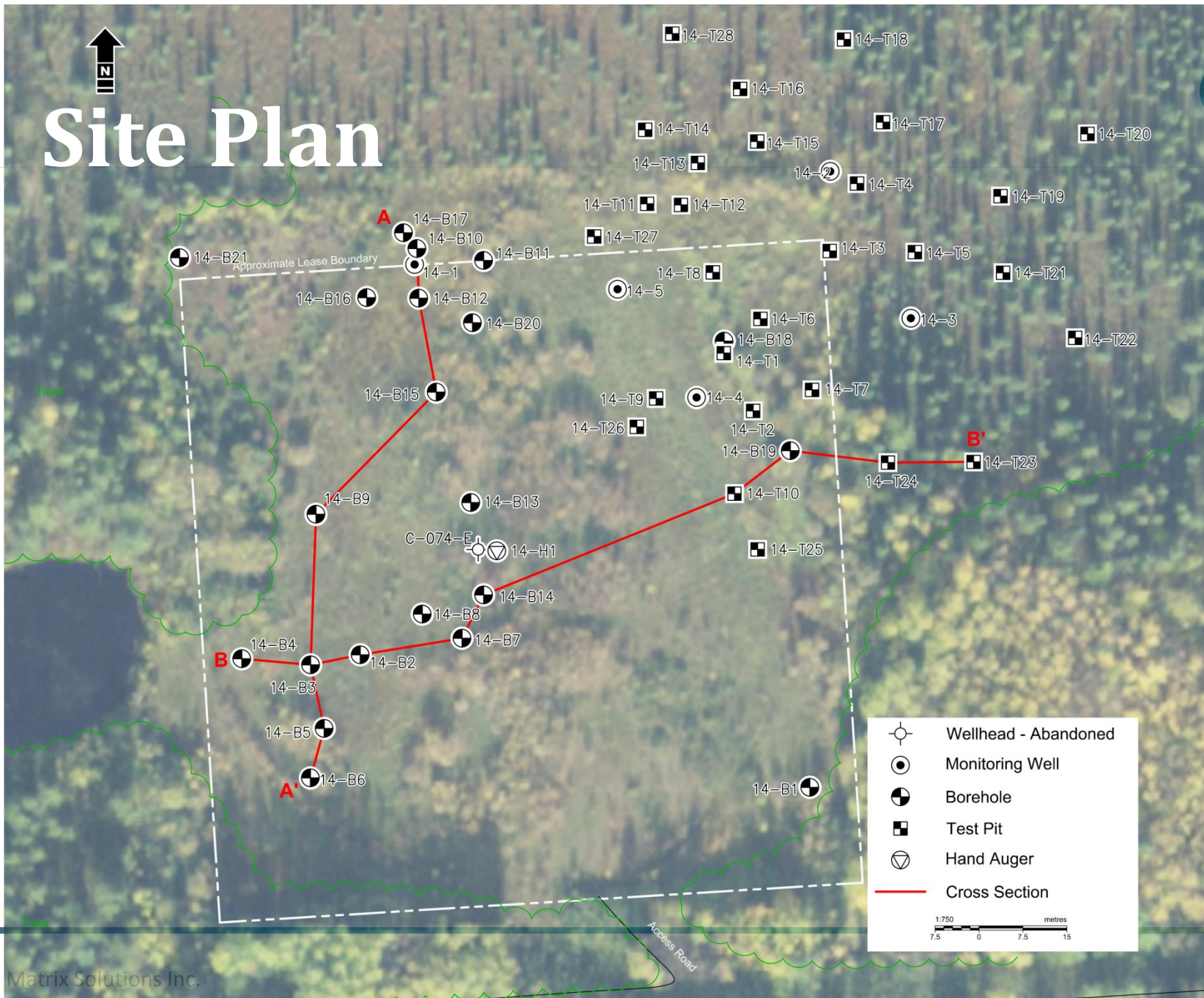
- Selected sites that had the following:
 - Toluene in organic soils from remedial excavations
 - Toluene measured in soil and surface water from peatlands and wetlands from undisturbed areas
- In collaboration with local laboratories, tested analytical process to distinguish between petrogenic and biogenic toluene
 - Case Study 1 – Peatland
 - Case Study 2 – Boreal Forest Wetlands

**Case Study 1:
Assessment, delineation and remediation of
hydrocarbon impacts within peatlands at an
abandoned well site**

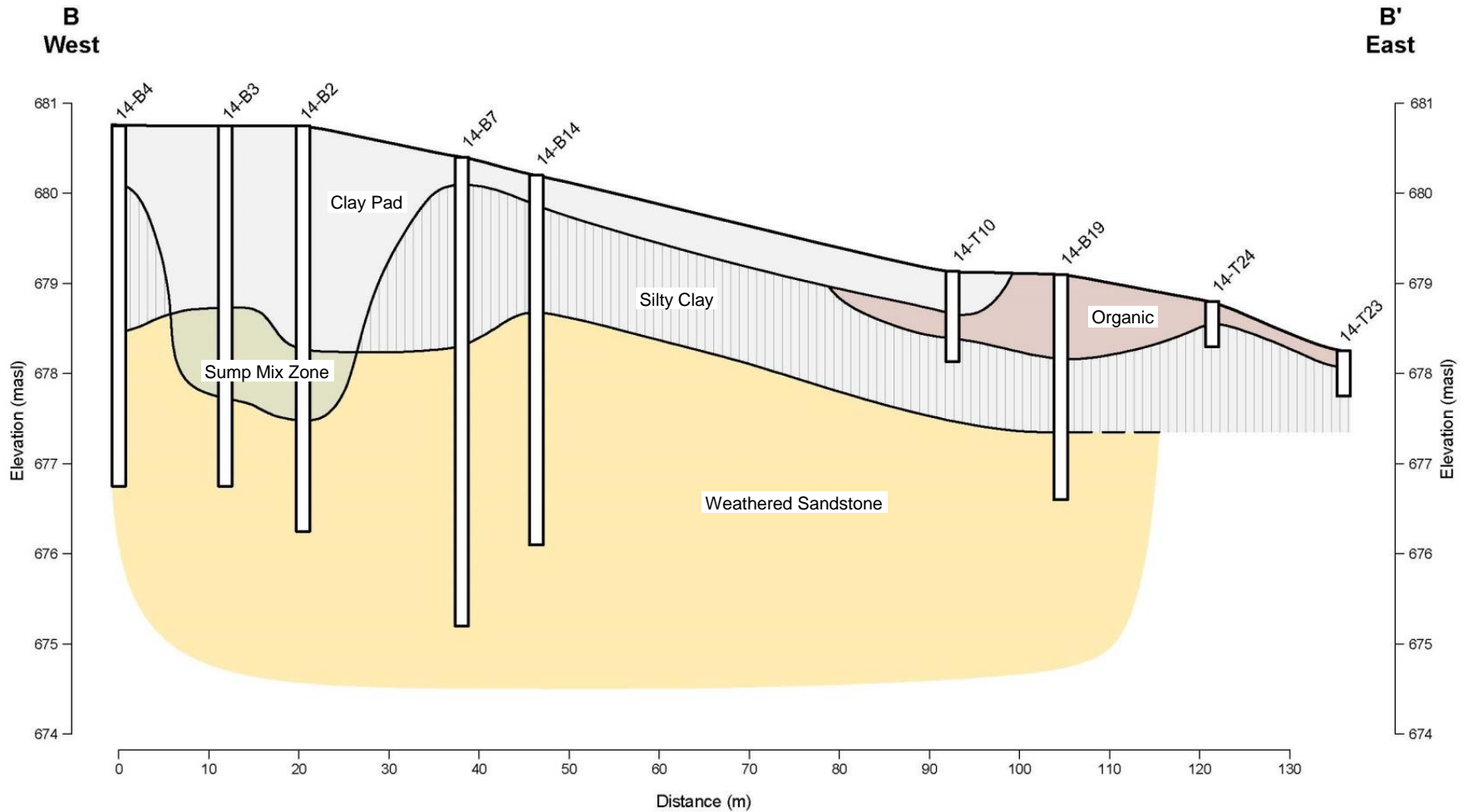




Site Plan



West – East Cross Section





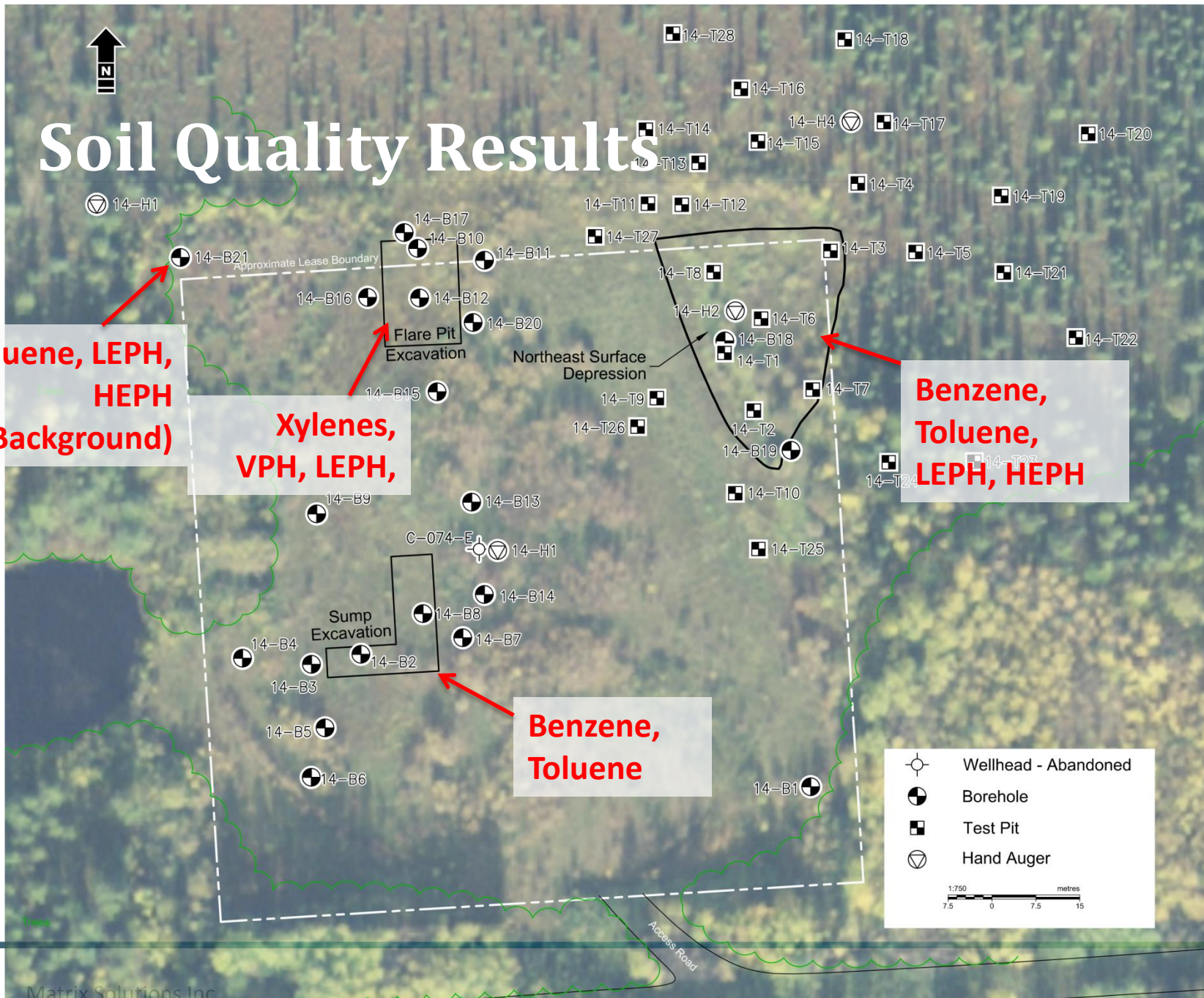
Soil Quality Results

**Toluene, LEPH,
HEPH
(Background)**

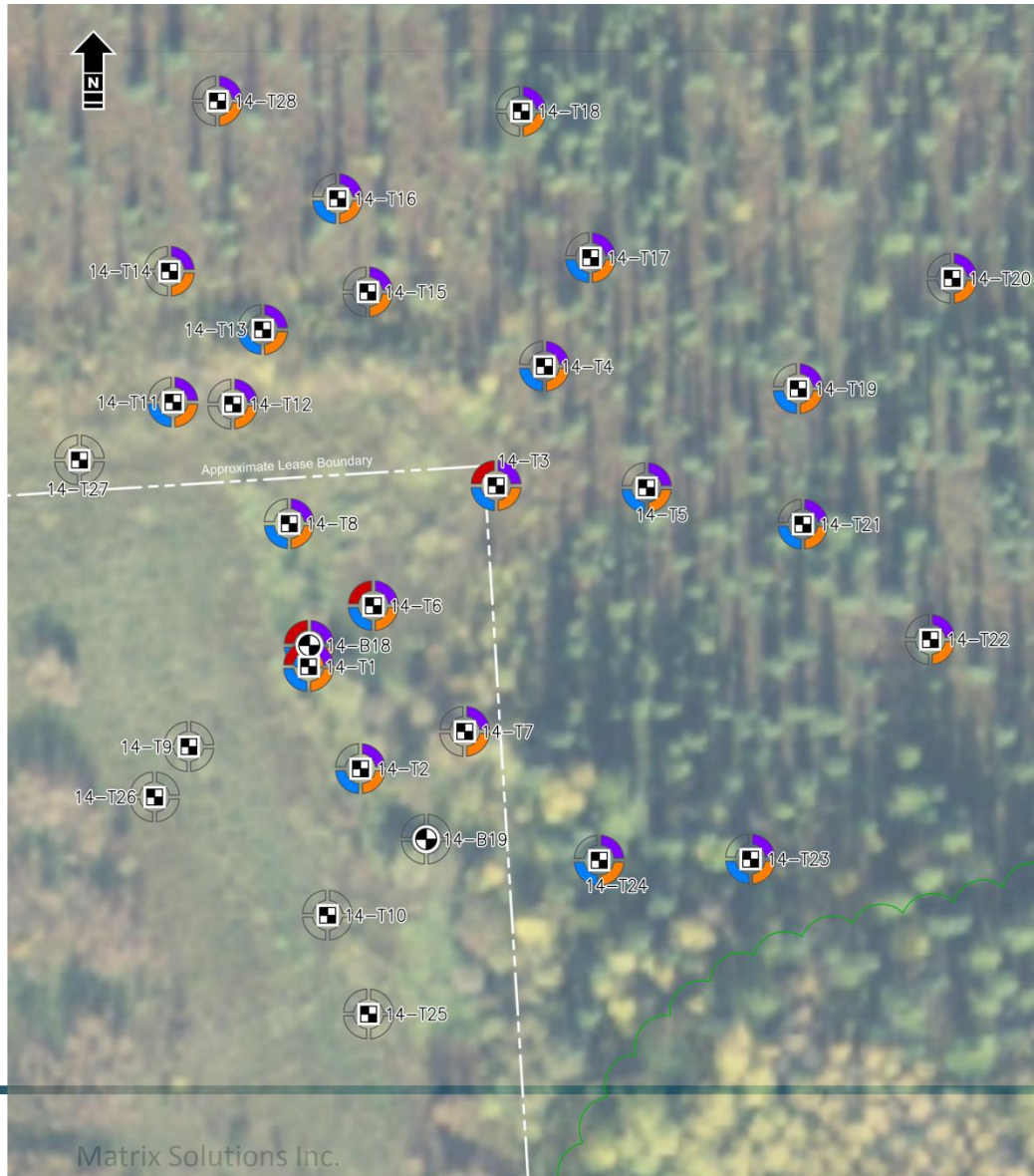
**Xylenes,
VPH, LEPH,**

**Benzene,
Toluene,
LEPH, HEPH**

**Benzene,
Toluene**



Soil Quality Results



Contaminants of concern

- benzene
- toluene
- LEPH (C_{10} - C_{19})
- HEPH (C_{19} - C_{32+})

- Toluene concentration range **1 to 22.8 mg/kg**

Extent of impact large if lab results were used as received (no interpretation)

Parameters Exceeding Regulatory Standards

Benzene



HEPH (C_{19} - C_{32})

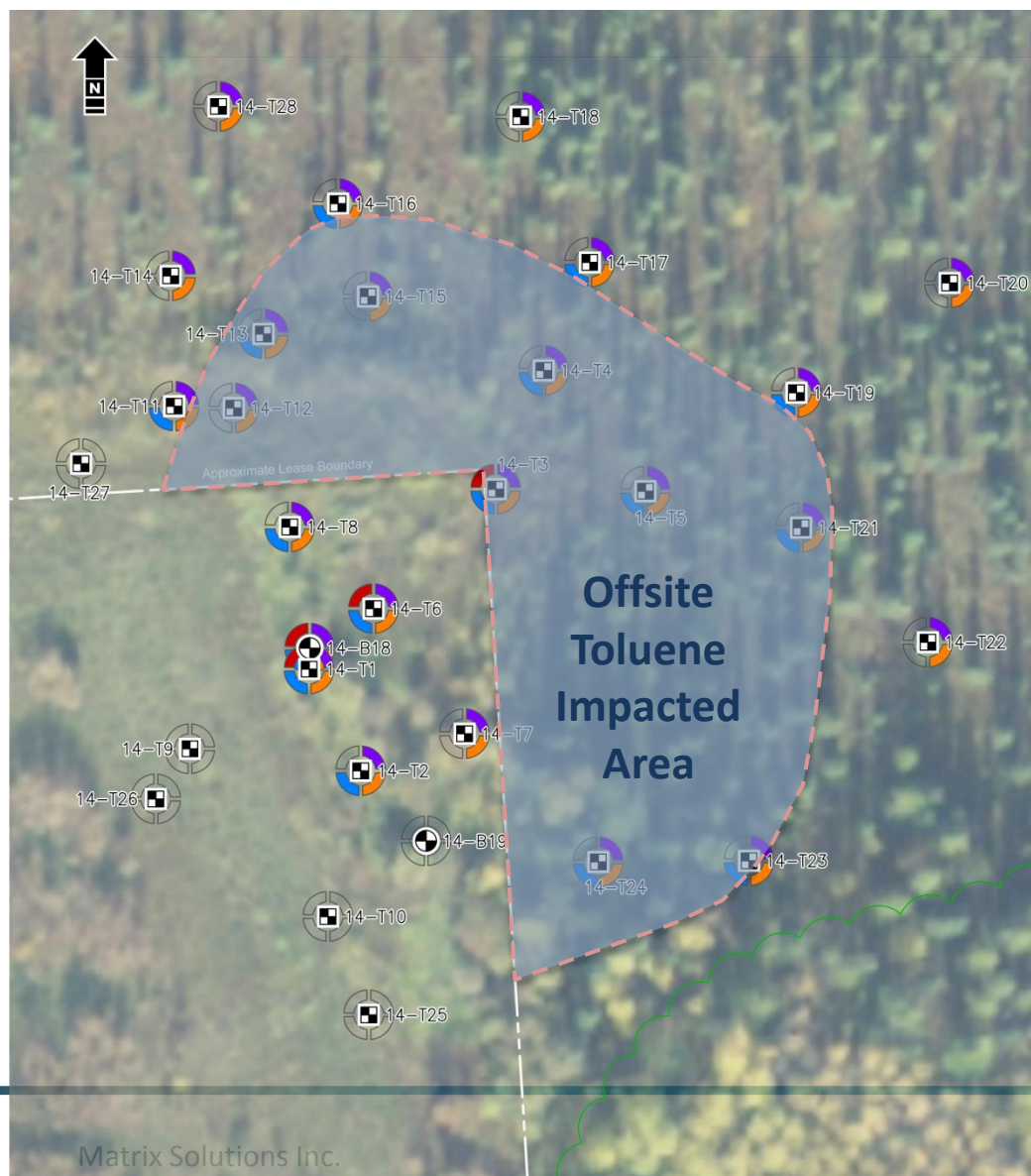
Toluene

LEPH (C_{10} - C_{19})



Analyzed - No Exceedance

Soil Quality Results



Contaminants of concern

- benzene
- toluene
- LEPH (C_{10} - C_{19})
- HEPH (C_{19} - C_{32+})

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Parameters Exceeding Regulatory Standards

Benzene

Toluene

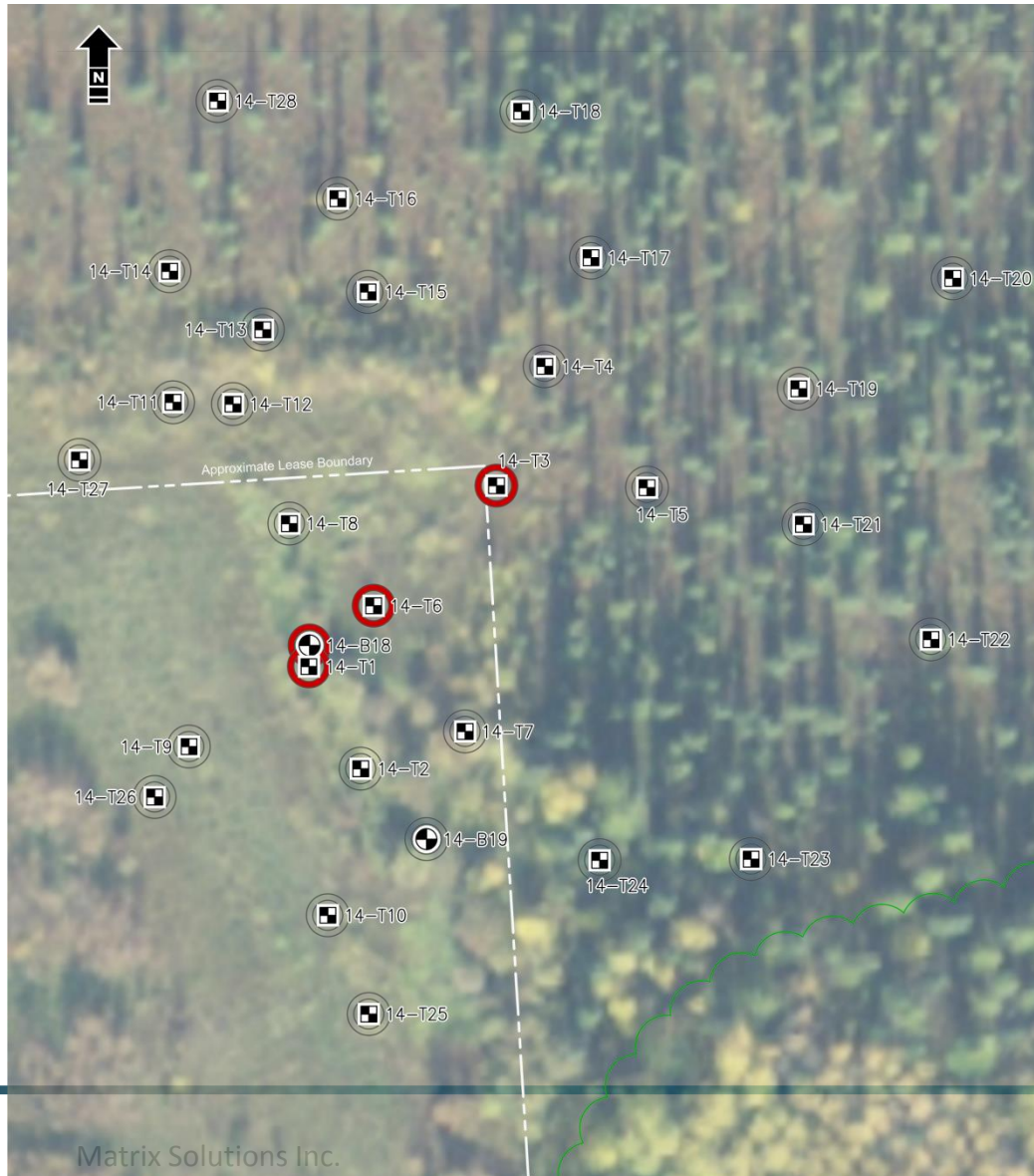
HEPH (C_{19} - C_{32})

LEPH (C_{10} - C_{19})



Analyzed - No Exceedance

Soil Quality Results



Contaminant of concern

- benzene

Extent of impact much smaller

- Minimizes disturbance to sensitive undisturbed peat land

Parameters Exceeding Regulatory Standards

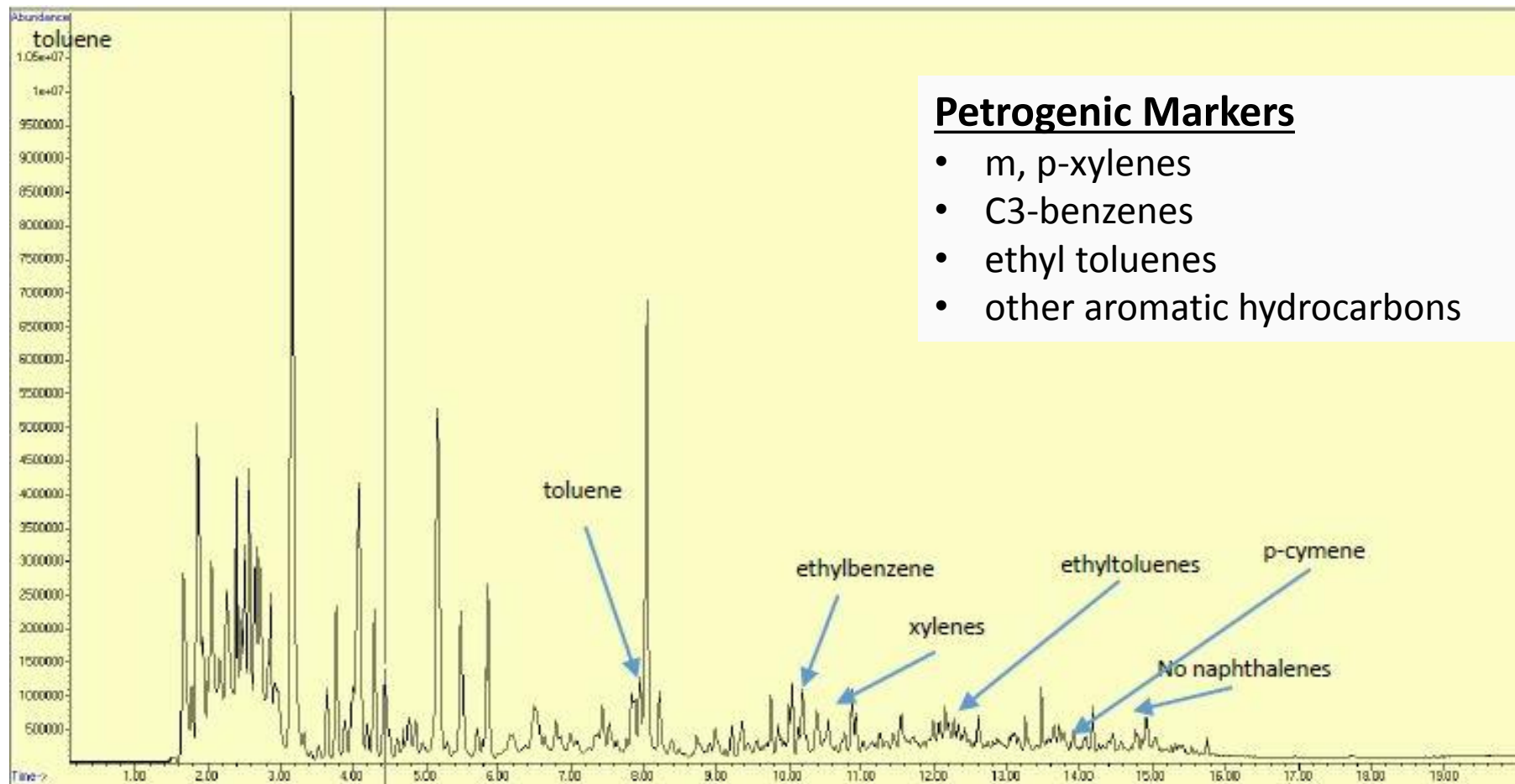


Benzene

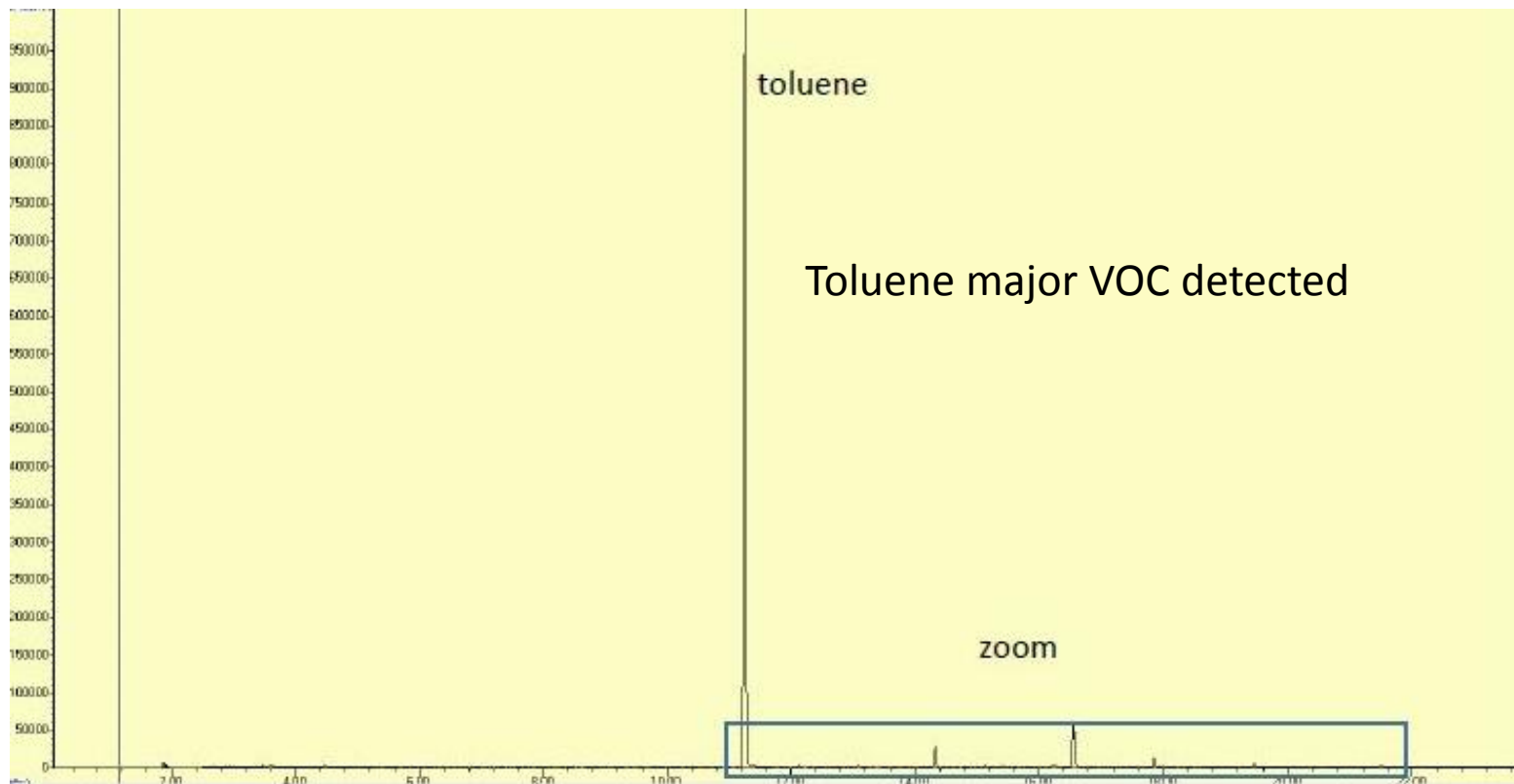


Analyzed - No Exceedance

VOC scan – Petrogenic Markers



VOC Biogenic Markers

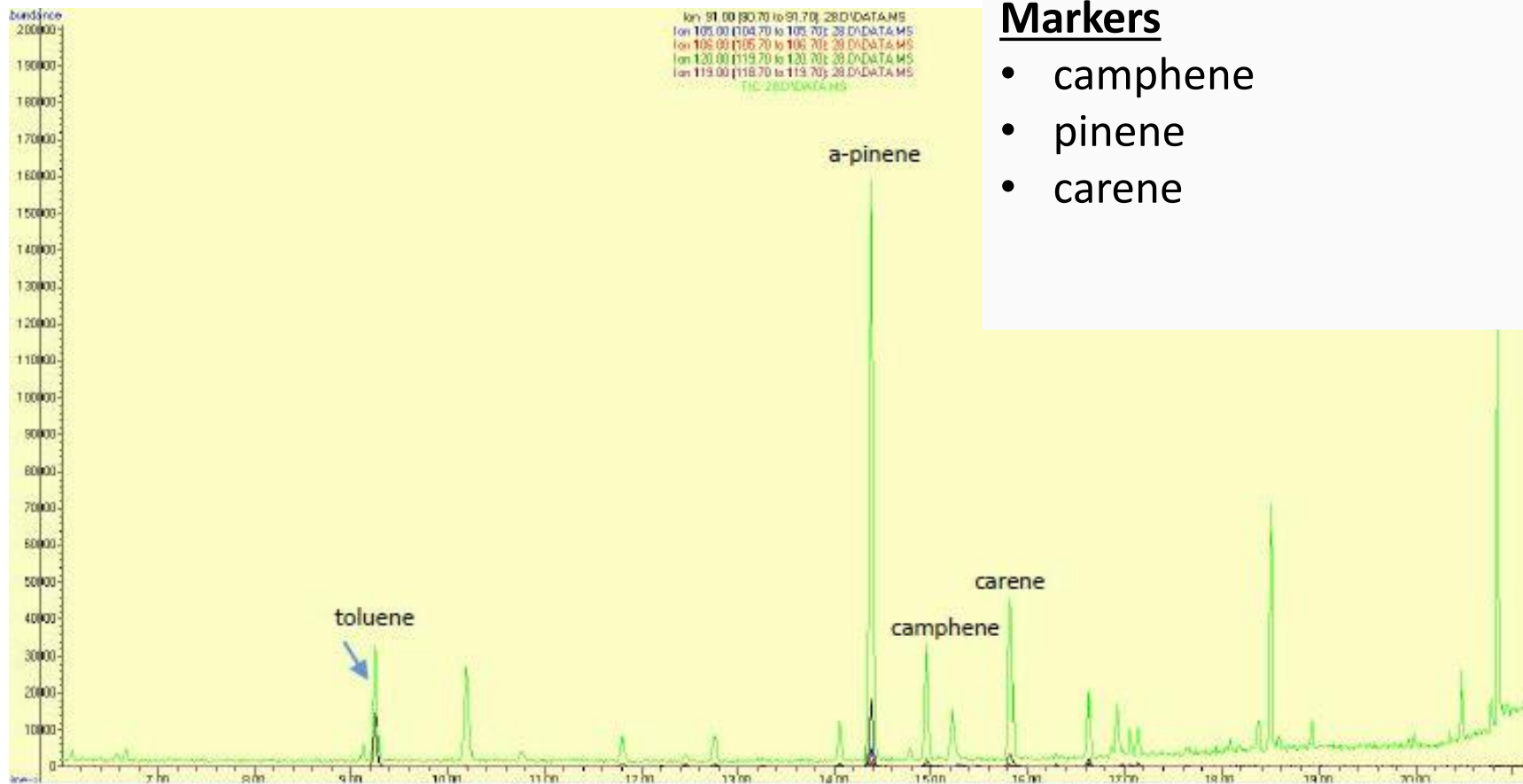


VOC Biogenic Markers

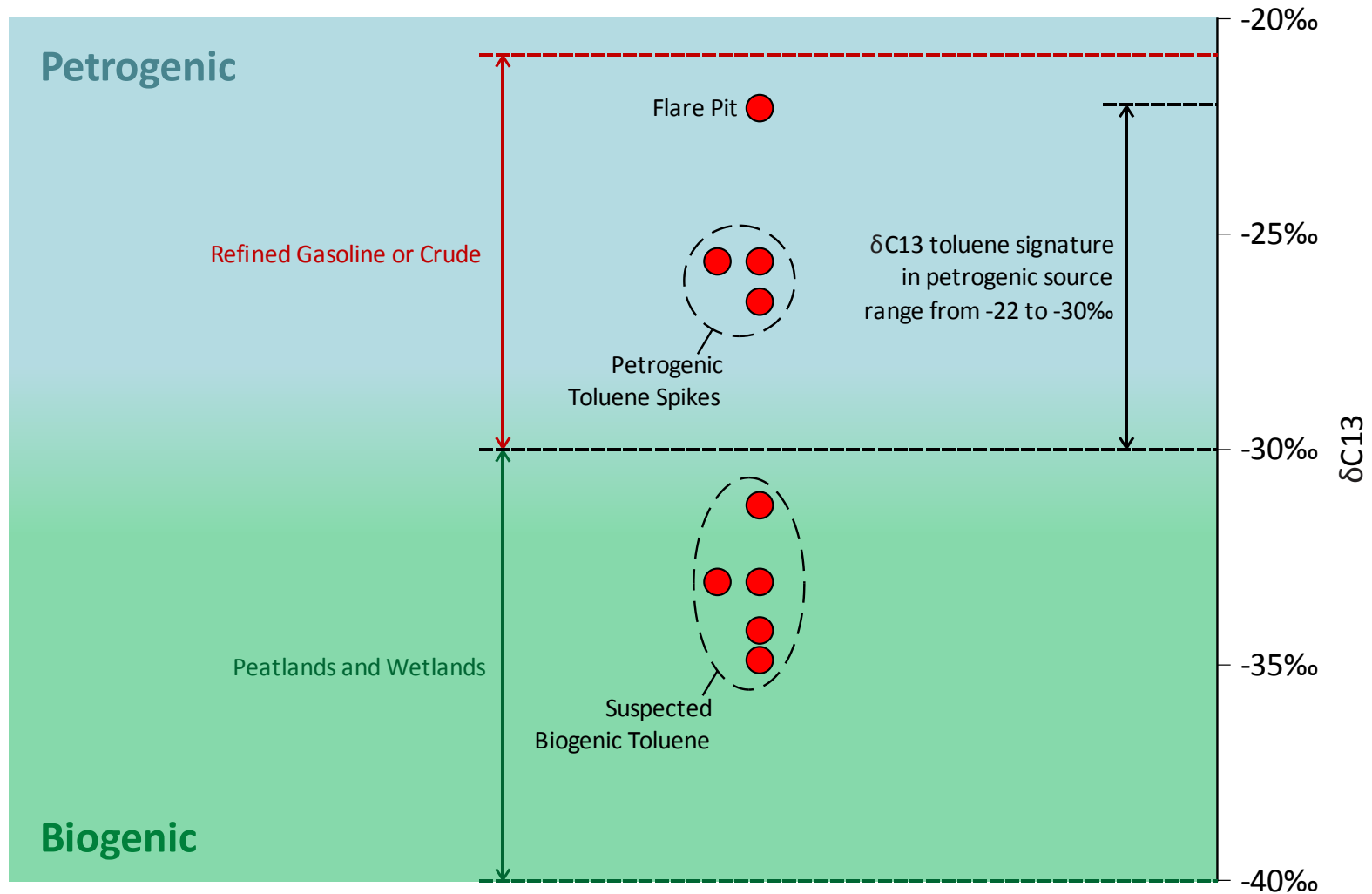


VOC Scans – Example Biogenic Markers

- camphene
- pinene
- carene



Case Study 1 – Carbon Isotopes



Case Study 2:

Background Wetlands Study

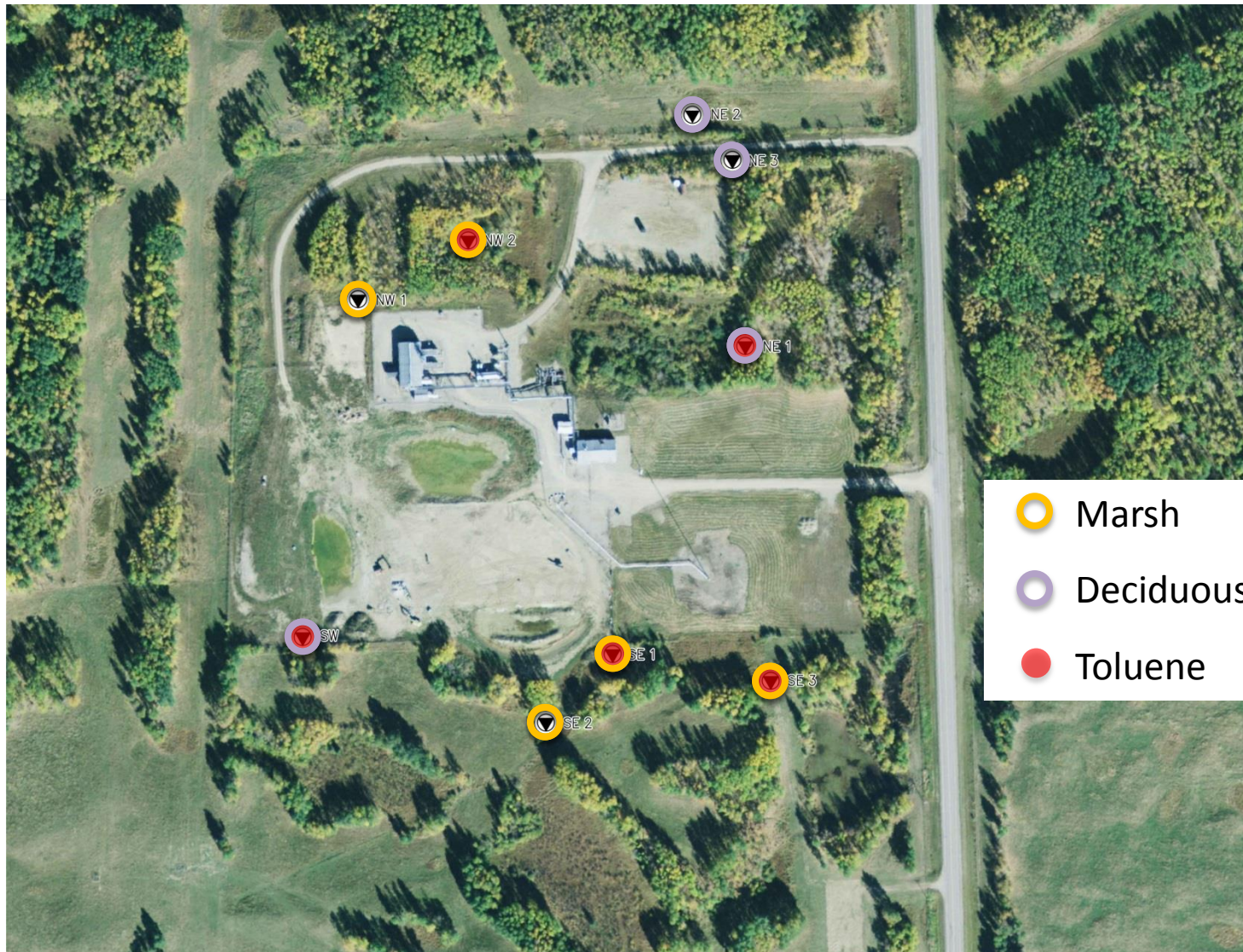


- Former Gas Plant and Active Compressor Station in green zone, west Alberta
- Gas Plant (south part of site) is part of a regulatory decommissioning project as per the EPEA Approval requirements
- Decade-long soil remedial program nearly complete
- Surface water monitoring program at site (9 locations)

Site Wetlands Monitoring



- Applied *Environmental Quality Guidelines for Alberta Surface Waters* (ESRD 2014)
- Regulatory exceedances encountered:
 - Acidic pH (one location)
 - Toluene (five locations)
 - Total metals – As, Cd, Cr, Co, Cu, Pb, Ag, Zn
 - Dissolved metals – Al, Fe
- Question: Are exceedances natural or introduced?



Site Surface Water Monitoring

Background Wetland Study



- 15 sites from area sampled
- Sites classified by Alberta Wetland Inventory classification system



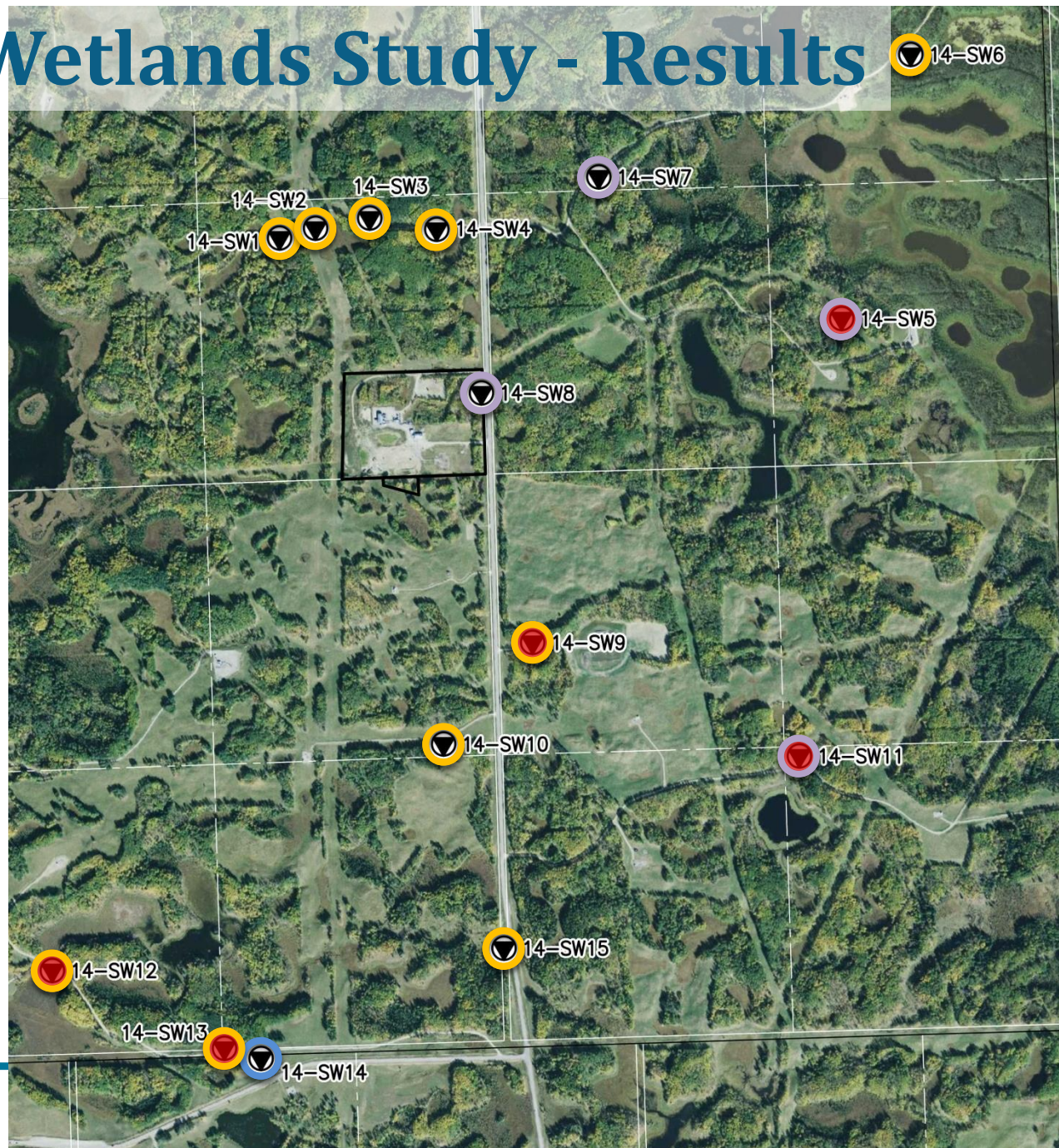
Background Wetland Study - Methods



- Field
 - Wetland descriptions and classification
 - In situ water chemistry (temperature, dissolved oxygen, pH, conductivity and turbidity)
- Lab Analysis
 - Routine chemistry
 - Dissolved hydrocarbons by headspace analysis
 - 5 of 15 samples had detectable toluene
 - These 5 samples - open scan purge and trap dissolved hydrocarbon analysis including full VOC scan
 - 1 of the 5 samples submitted for toluene carbon isotope analysis

Background Wetlands Study - Results

- Marsh
- Deciduous Swamp
- Shallow Open Water
- Toluene



Toluene Concentrations at Site and Background Surface Water



Results (cont.)



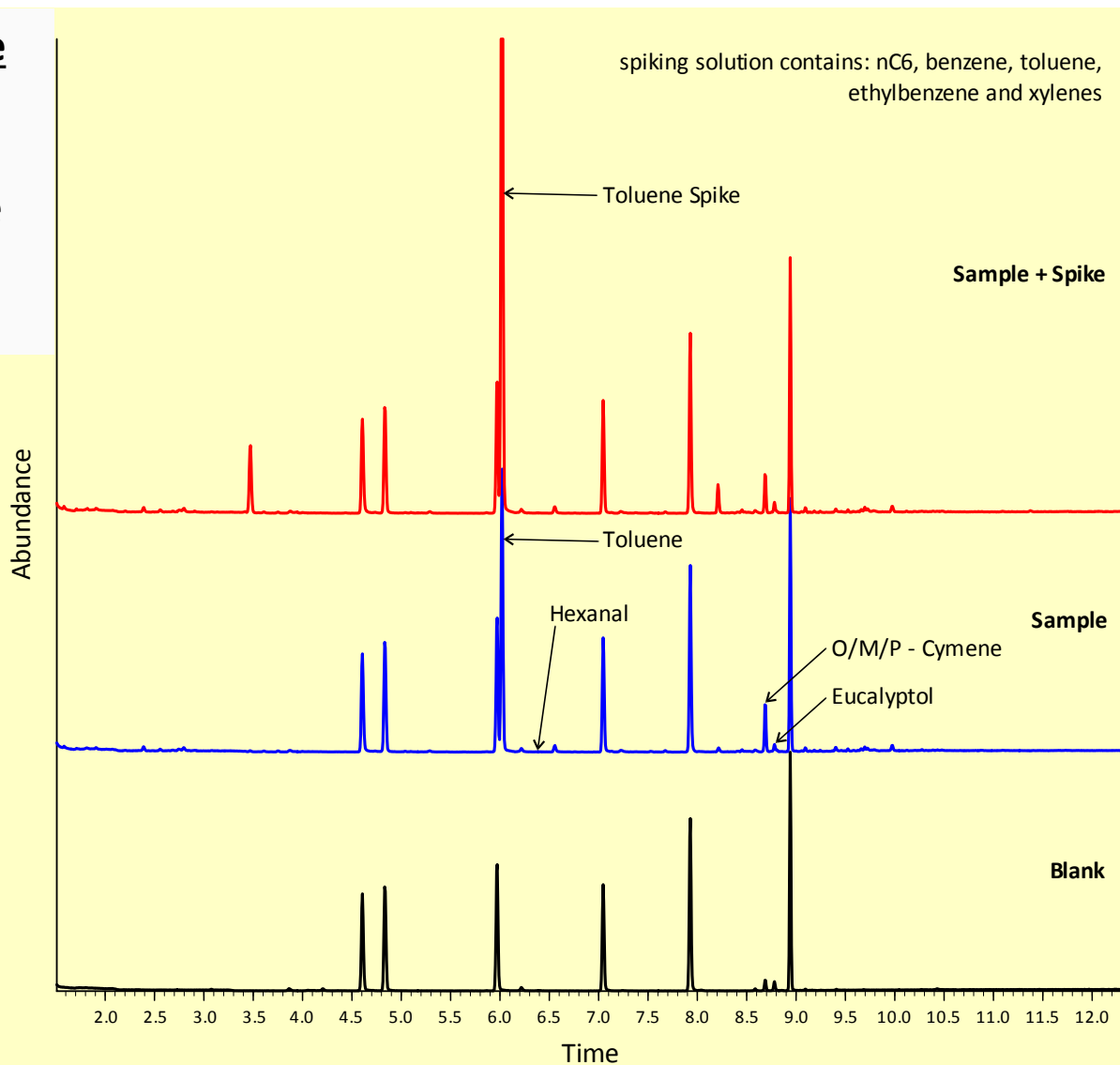
- VOC chromatograms indicated both compounds understood to be biogenic (BOCs) and those potentially anthropogenic (?)
 - toluene (?)
 - hexanal (BOC)
 - heptanal (BOC)
 - trimethylbenzene (?)
 - 3-octanone (BOC)
 - o/m/p-cymene (BOC)
 - eucalyptol (BOC)

VOCs Biogenic Markers

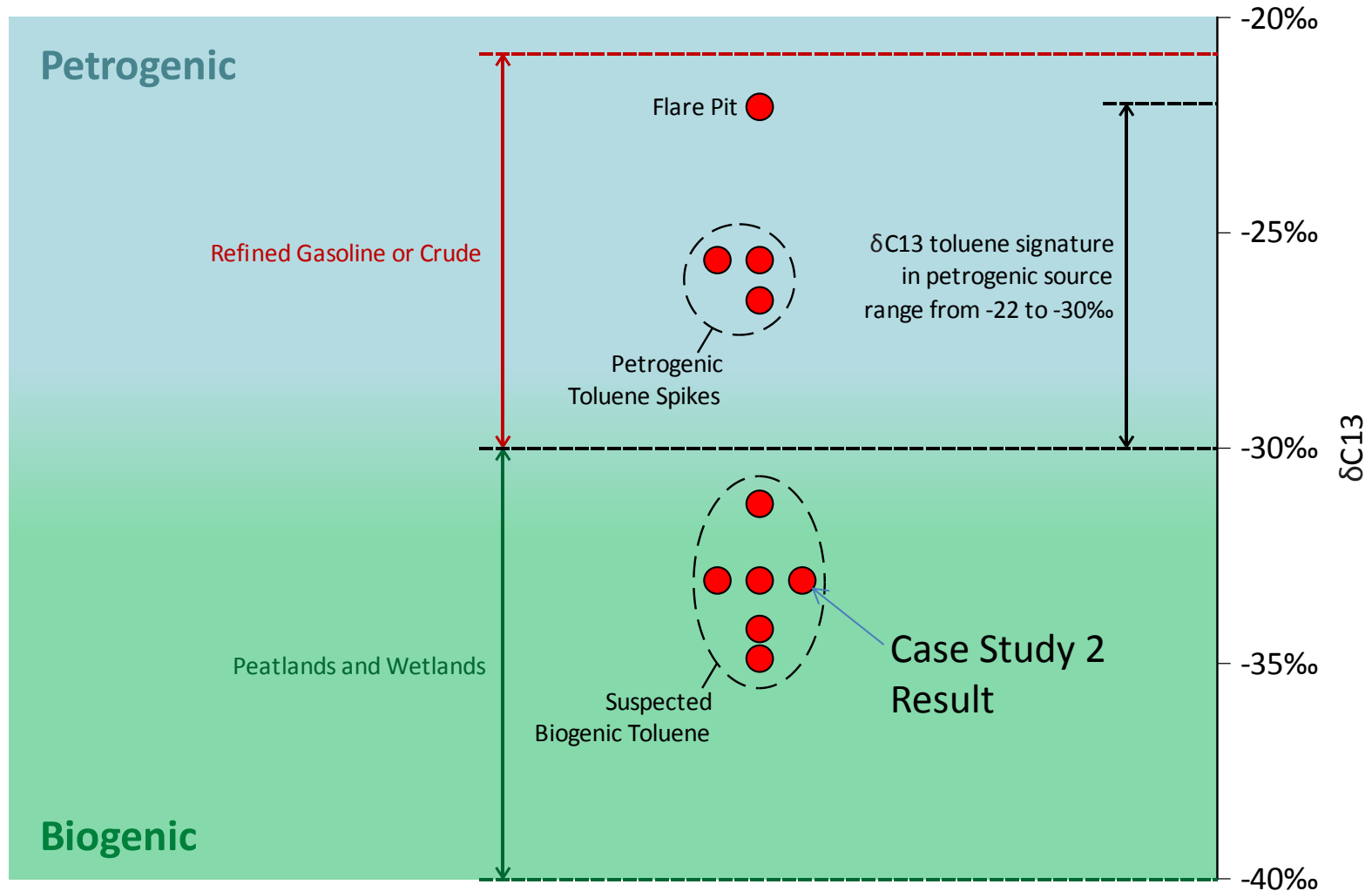


VOC Scan – Example Biogenic Markers

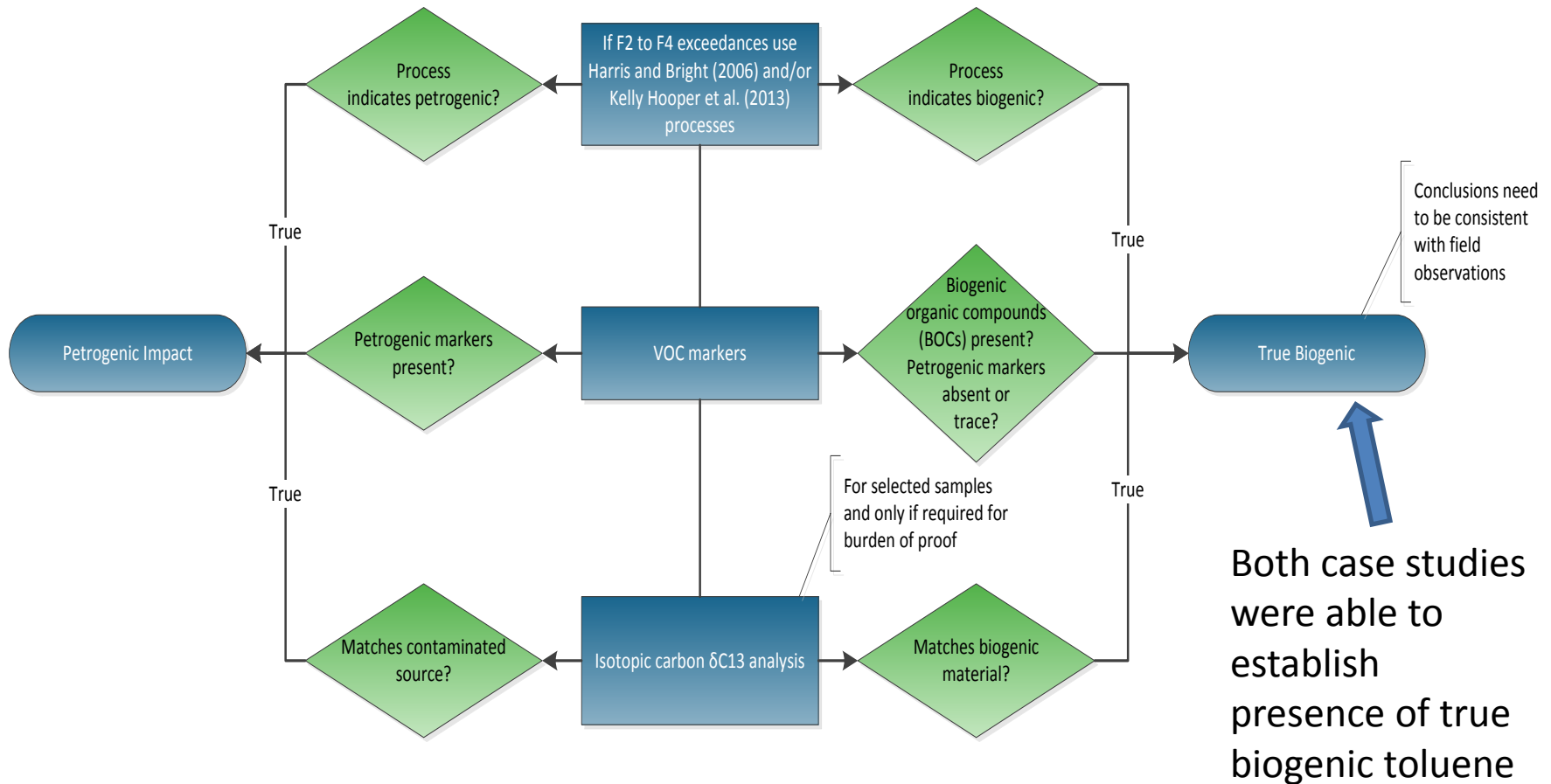
- Hexanal
- O/M/P – Cymene
- Eucalyptol

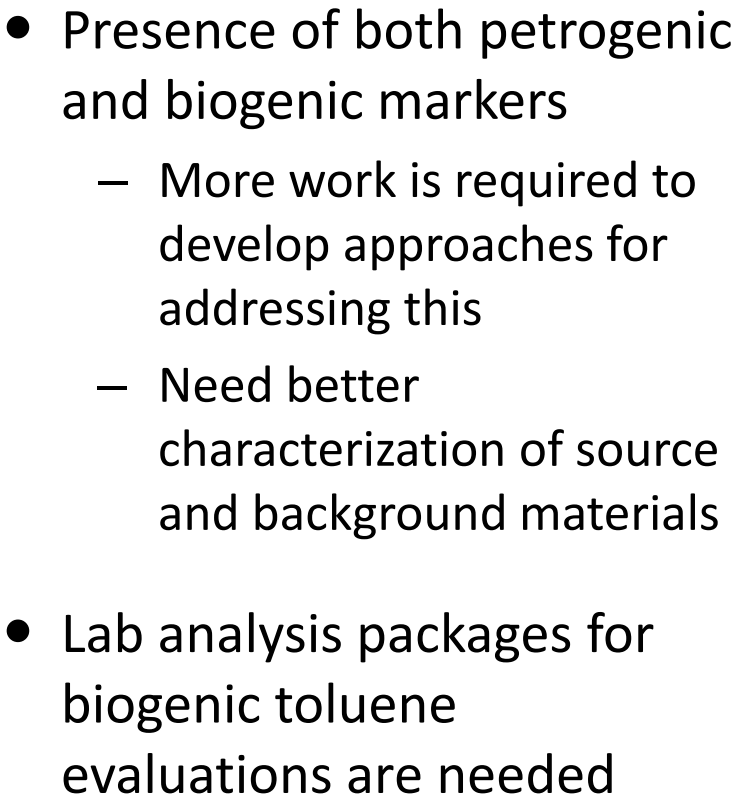


Case Study 2 Carbon Isotope Result



Proposed Decision Process for Biogenic Toluene





Conclusions



- If you are doing work in peatlands and wetlands, and suspect that you need to do these evaluations:
 - Need extra sample bottles
 - Always run two or more background samples in open scan mode to determine biomarkers for your site
 - In BC, you should also do silica gel clean up for extractable hydrocarbons (done automatically in Alberta)
 - If you anticipate needing additional evidence (i.e. biomarkers, carbon isotopes) – plan in advance
- Use targeted analyses for characterization - no need to analyze all samples
- Talk to the lab in advance



Thank You



**Exova
Maxxam
Apache**



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