# Light and Middle Distillate Environmental Forensics

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# Outline

1 Introduction

2 Site Characterization and Sample Collection

3 Gasoline Impact Source Identification

4 Diesel Impact Source Identification

5 Conclusions

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# 1 Introduction

- Most oils spilled into the environment are 48% fuels and 29% crude oils
  - Of annual Canadian oil spill accidents, 11% are gasoline and 25% diesel spills
- Large environmental consequences and clean up costs can result from even small gasoline and diesel spill accidents
  - These result in legal problems or environmental liabilities
- Environmental forensics may be required
  - To distinguish sources of petroleum hydrocarbons entering the environment
  - To distinguish legal liability
  - To evaluate relevant ecological and human health risks
  - To select appropriate spill response measures

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# 1 Introduction

- Currently, environmental forensics is mostly focused on fingerprinting crude oil spills
  - Crude oil contains a wide selection of biomarkers and other compounds
  - Biomarkers are resistant to weathering and biodegradation
- However, gasoline and diesel are a challenge to fingerprint because refinery processes remove most of the higher molecular weight biomarkers including pentacyclic triterpanes and steranes

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# 1 Introduction

- A tiered environmental forensics strategy is recommended
  - Site operational history investigation
  - Site characterization including geology/hydrogeology study
  - Gas chromatography (GC) using flame ionization detection (FID) pre-screening
  - Gasoline GC/mass spectrometric detection (GC/MS) full scan and GC/MS selected ion monitoring (SIM) chromatograms

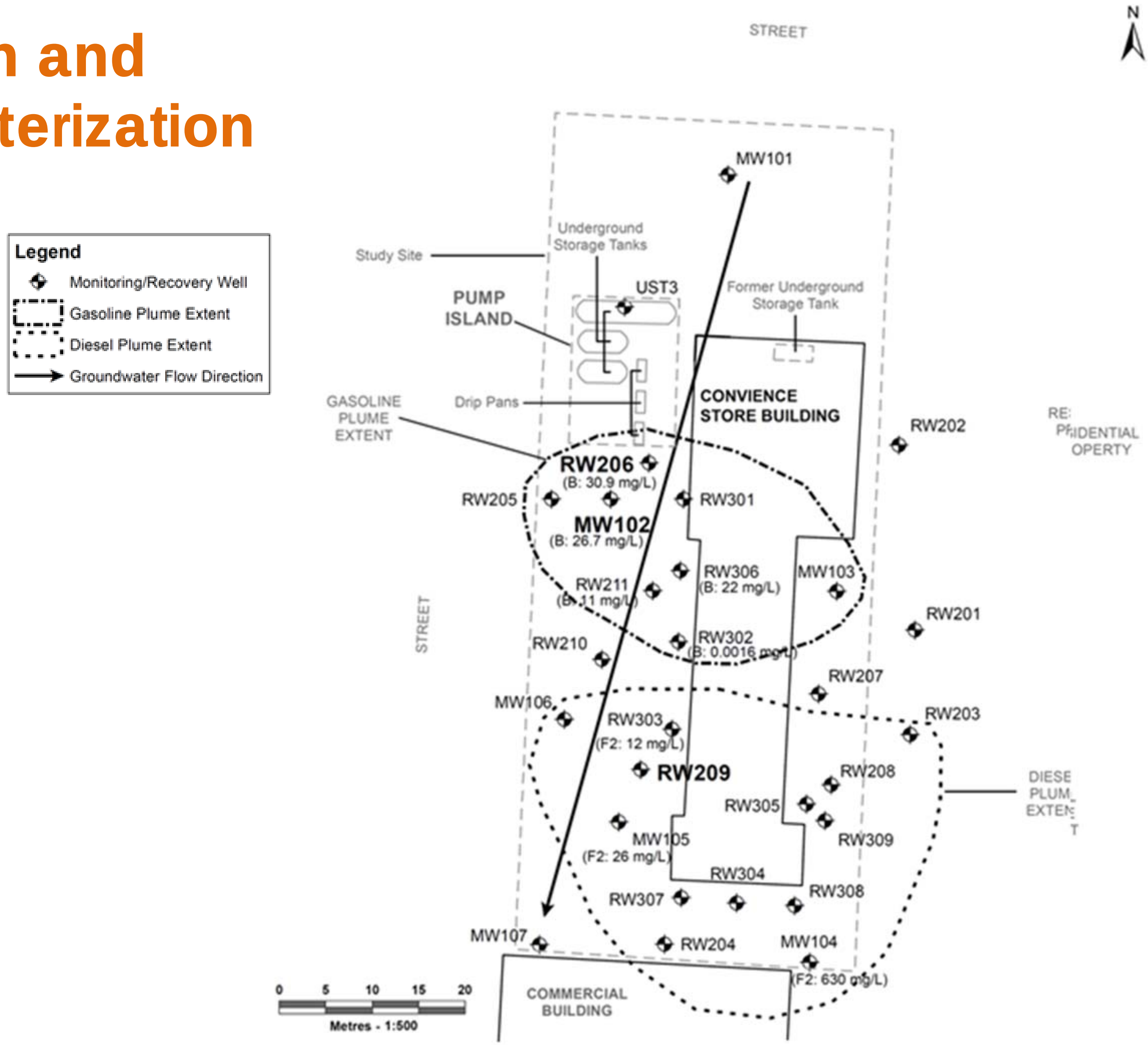
# 1 Introduction

- GC/MS full scan & SIM analysis on gasoline source identification
  - C3-alkylbenzenes distribution
  - C4-alkylbenzenes distribution
  - Diamondoids
  - Diagnostic ratios of specific compounds that have a comparable aqueous solubility

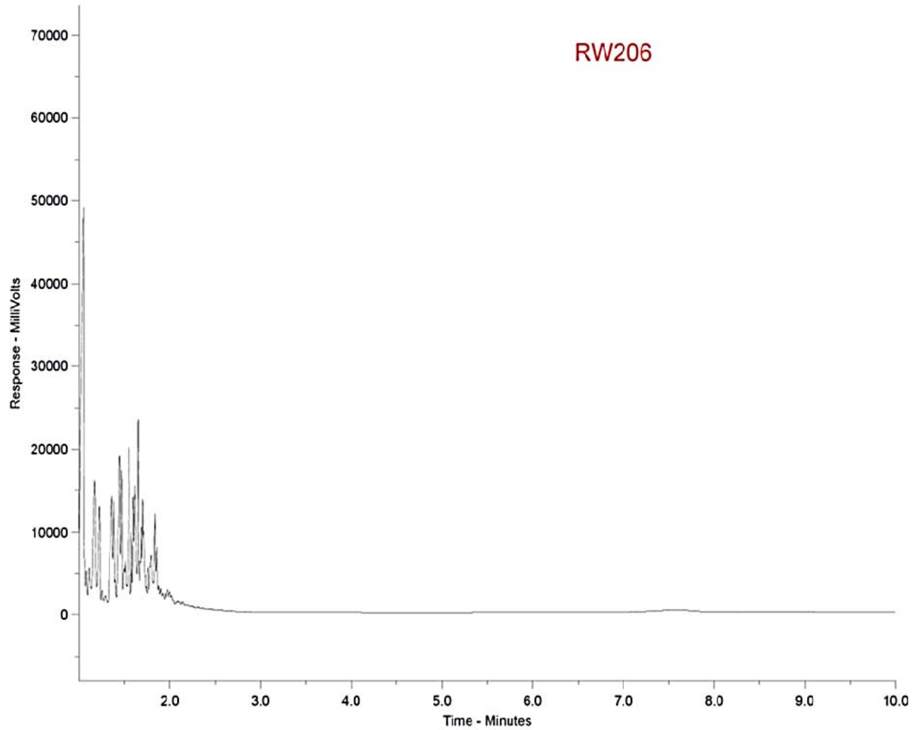
# 1 Introduction

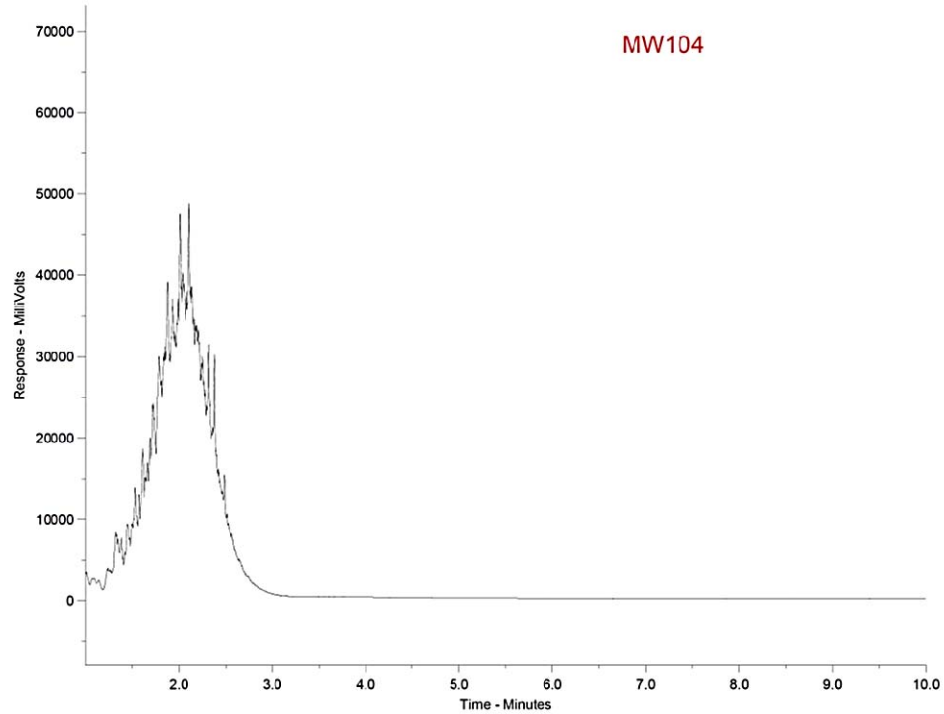
- GC/MS full scan & SIM analysis on diesel source identification
  - Sesquiterpanes
  - Alkylated polycyclic aromatic hydrocarbons (PAH)
  - Diamondoids

# Site Plan and Characterization



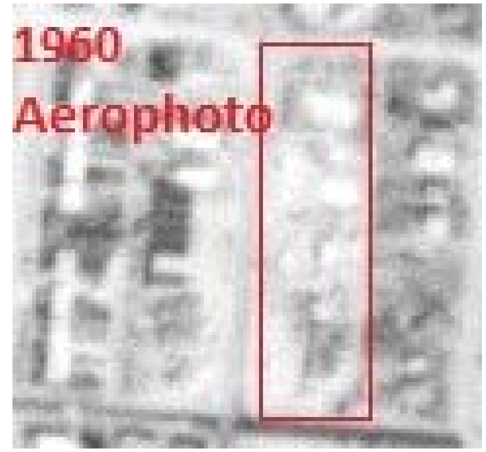
# GC/FID Pre-screening



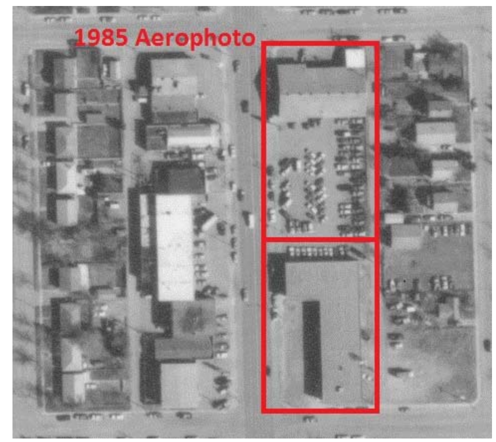



# Operational History

- In 1950s, a fuel retailing facility occupied land immediately south of the Site.
- A northern facility expansion occurred in August of 1959.
- The Site was retained by an investment company in 1968.
- A car dealership owned south of the Site in January 1970 and a furniture store started owning south of the Site in June 1984.
- An underground storage tank (UST) was removed in June 1984.
- In August 1989, our client gained possession of the investment company.
- A 1,000 gallon UST was removed on June 1, 1989.
- On August 17, 1990 three new USTs were installed.






# Sample Collection and Preparation

- Gasoline-impacted samples
  - Fresh gasoline sample was collected directly from the pump island
  - Two groundwater samples were collected from gasoline-impacted monitoring wells RW206 and MW102
- Diesel-impacted samples
  - Fresh diesel sample was collected directly from the pump island
  - Light non-aqueous phase liquid (LNAPL) was collected from diesel-impacted monitoring well RW209
- Sample preparation
  - Fresh gasoline sample was shaken with deionized water for five minutes and the mixture was allowed to settle for two hours
  - Samples were extracted with 5 mL of hexane by tumbling the bottle for 1 hour

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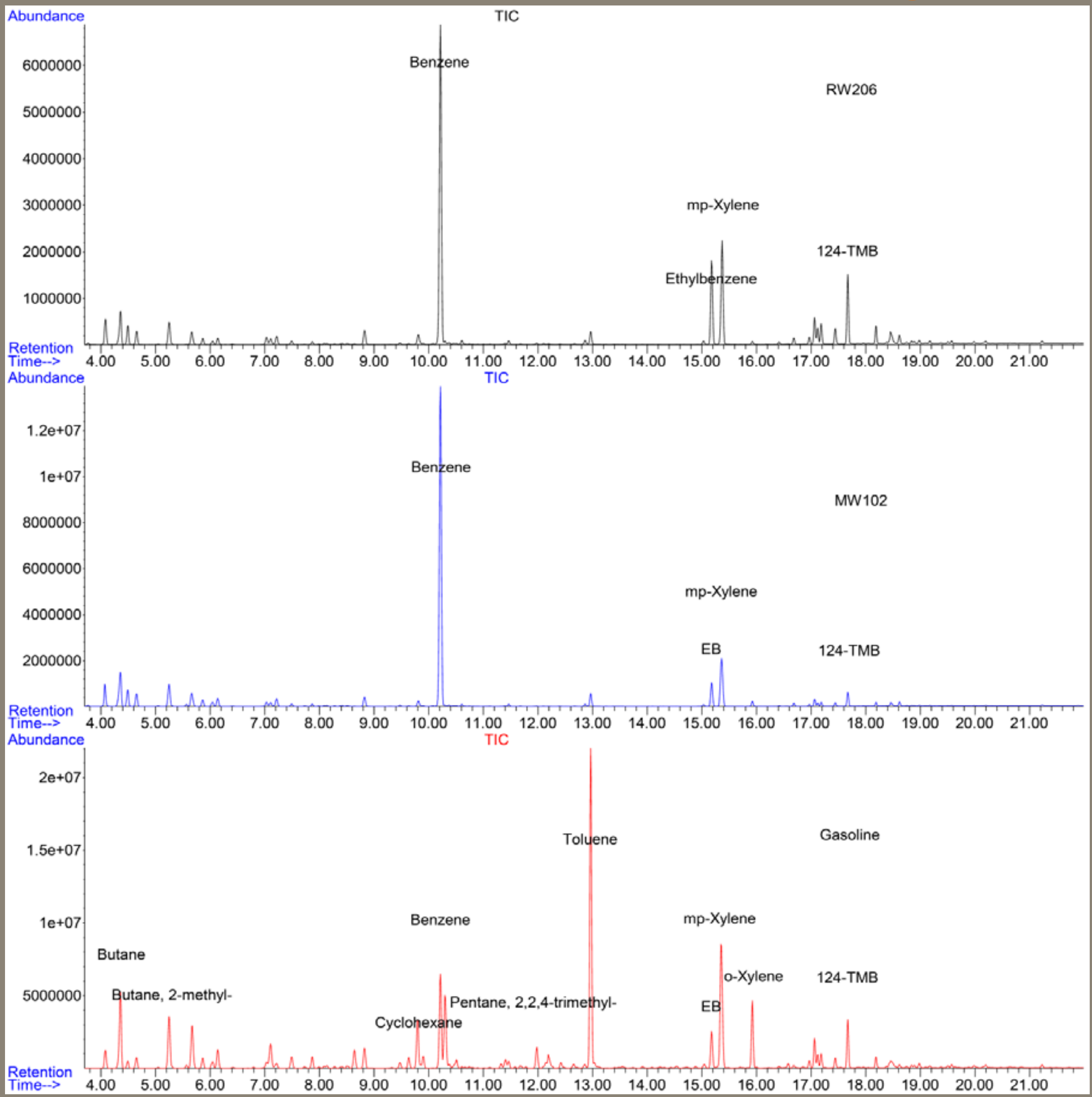
# 3 Gasoline Source Identification

## GC/MS Total Ion Chromatograms




- Contamination of RW206 and MW102 groundwater resulted from a gasoline spill, confirming the GC/FID classification
- Hydrocarbon weathering occurred in the RW206 and MW102 groundwater

# 3 Gasoline Source Identification

## Gasoline SIM and C3-alkylated Benzene

- Gasoline subjects to rapid evaporation and biodegradation due to its low boiling range
- Chemical fingerprinting of the highest boiling fractions of any gasoline residues, e.g. in the C9+ range may still yield useful results
  - major hydrocarbon compounds of gasoline: BTEX, C3-alkylbenzenes and naphthalene
- Distribution of C3-alkylbenzenes can be used to fingerprint gasoline impacts in soil and groundwater.

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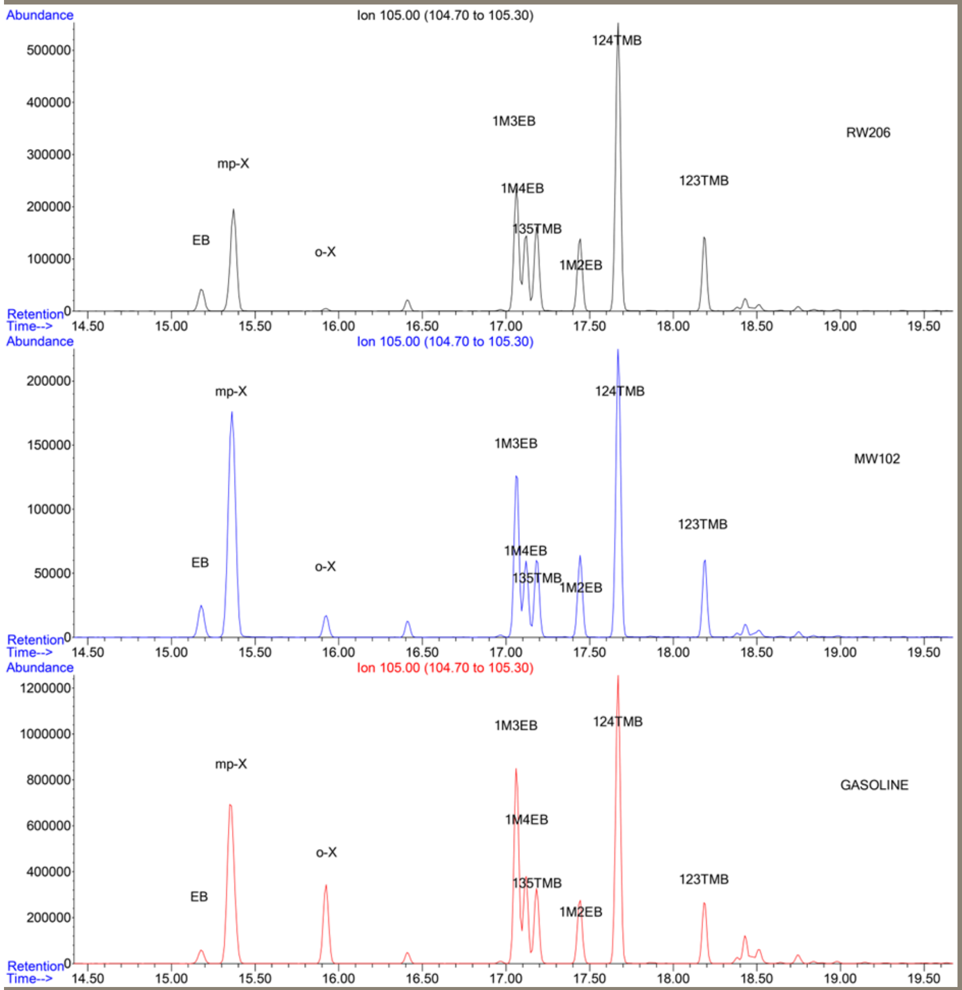
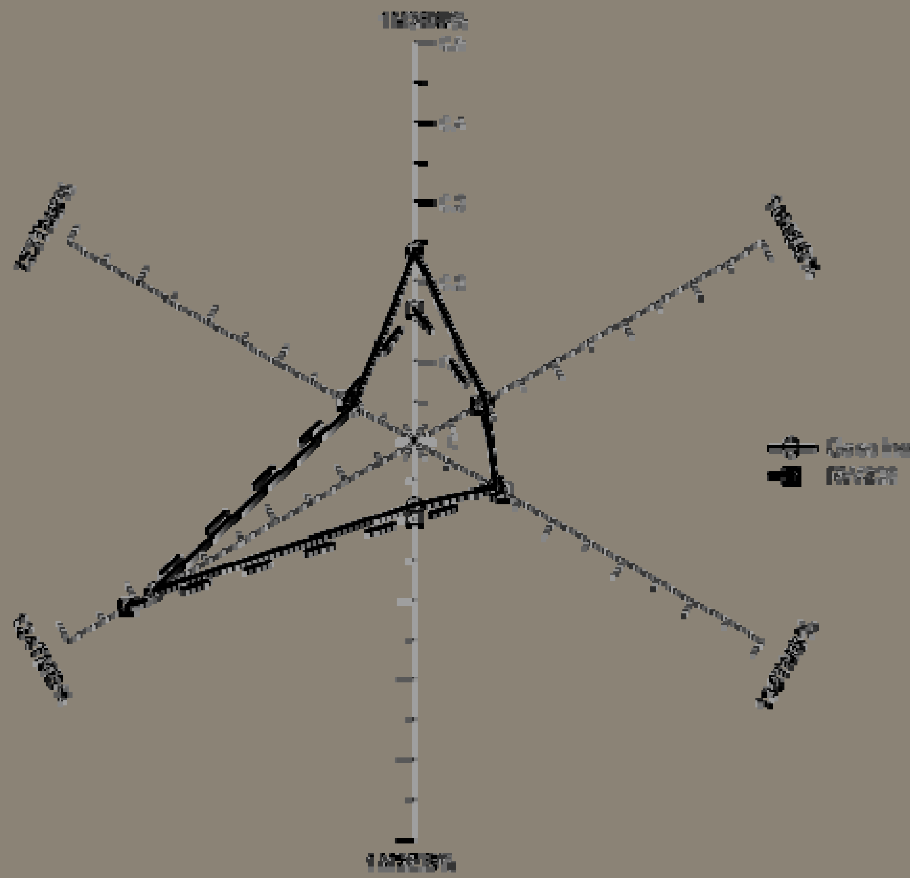
# 3 Gasoline Source Identification

## Gasoline SIM and C3-alkylated Benzene



- The C3-alkylbenzene distributions of the two samples are almost the same

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# 3 Gasoline Source Identification

## Diagnostic Ratios for Gasoline Fingerprinting

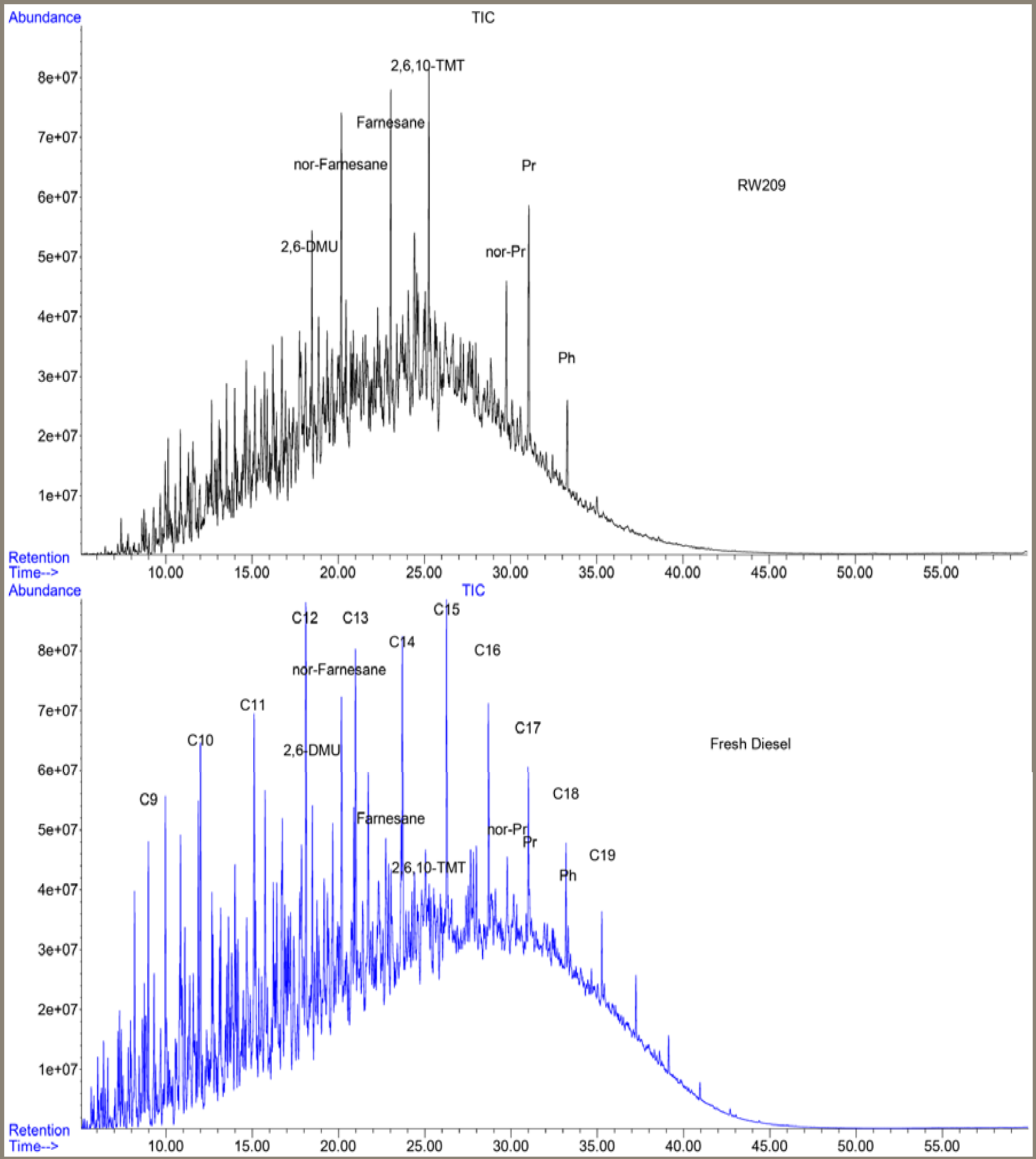
- Diagnostic ratios were calculated using peak areas of specific compounds that have a comparable aqueous solubility
  - Similar physicochemical properties → similar behaviors and fates in the environment

| Diagnostic ratios | Ion m/z | Fresh Gasoline | RW206 | MW102 |
|---|---|---|---|---|
| 135-TMB/124-TMB | 105 | 0.27 | 0.30 | 0.28 |
| 123-TMB/124-TMB | 105 | 0.21 | 0.25 | 0.26 |
| 1M3EB/1M4EB | 105 | 2.26 | 1.63 | 2.25 |
| 1M2EB/124TMB | 105 | 0.23 | 0.26 | 0.28 |
| 1M2EB/123-TMB | 105 | 1.10 | 1.05 | 1.10 |
| 135-TMB/124-TMB | 119 | 0.29 | 0.30 | 0.30 |
| 123-TMB/124-TMB | 119 | 0.16 | 0.20 | 0.22 |
| 1245-TMB/1235-TMB | 119 | 0.66 | 0.66 | 0.71 |
| 1234-TMB/1235-TMB | 119 | 0.41 | 0.41 | 0.38 |
| 1234-TMB/1245-TMB | 119 | 0.61 | 0.62 | 0.54 |

- This similarity further confirms that dissolved PHCs in RW206 and MW102 groundwater likely originated from the gasoline UST

# 4 Diesel Source Identification

## GC/MS Total Ion Chromatograms




- RW209 LNAPL originated from a diesel fuel spill or leak, confirming the GC/FID classification
- Absence of n-alkanes indicates LNAPL collected in RW209 has been weathered

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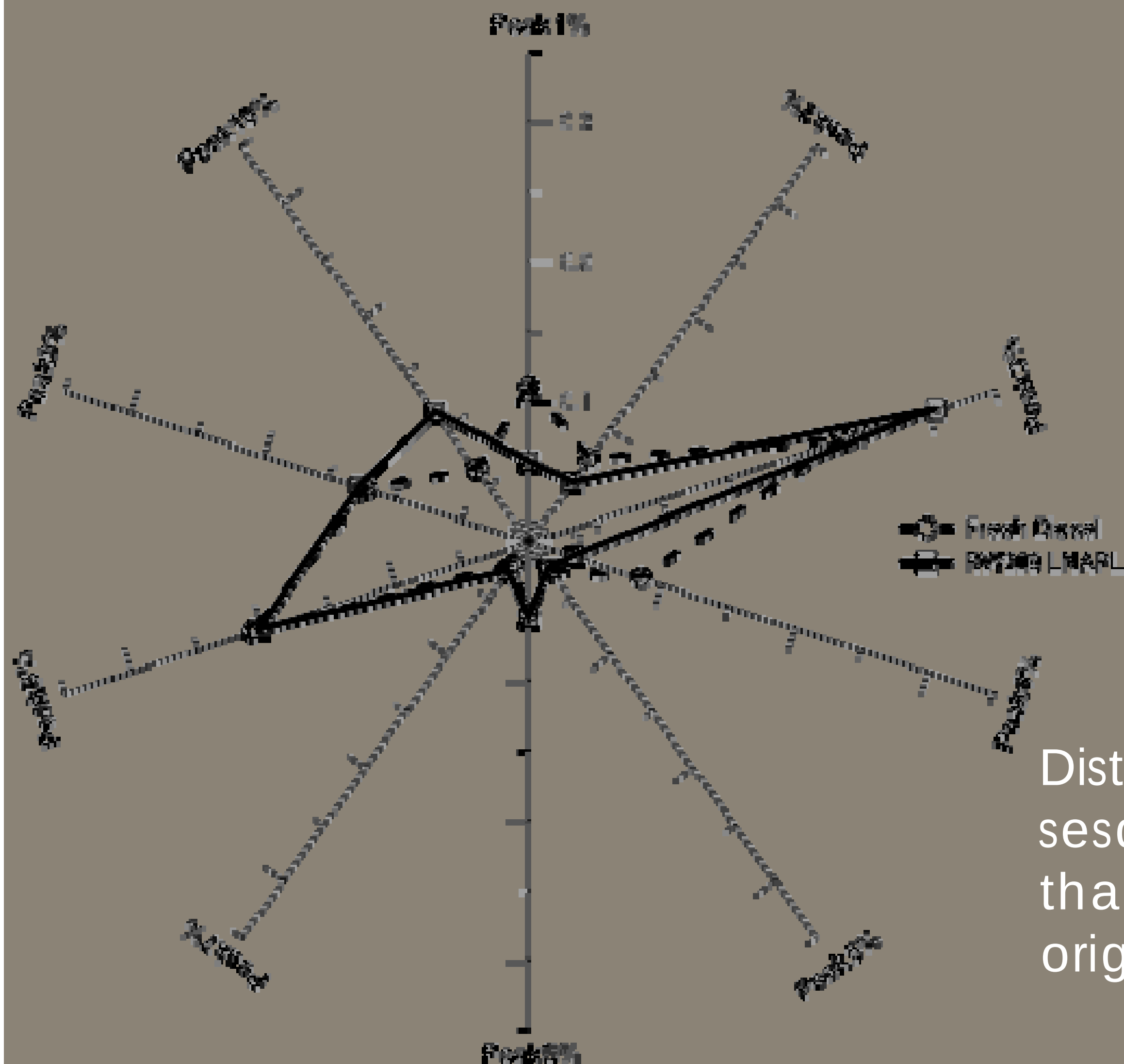
# 4 Diesel Source Identification

## GC/MS Sesquiterpanes Analysis




- Peaks 9 and 10: C14 ($C_{14}H_{26}$)
- Peaks 1 to 4: C15 ($C_{15}H_{28}$)
- Peaks 5 to 8: C16 ($C_{16}H_{30}$)

Distinct distribution pattern of sesquiterpane isomers suggests that RW209 LNAPL might originate from a different source

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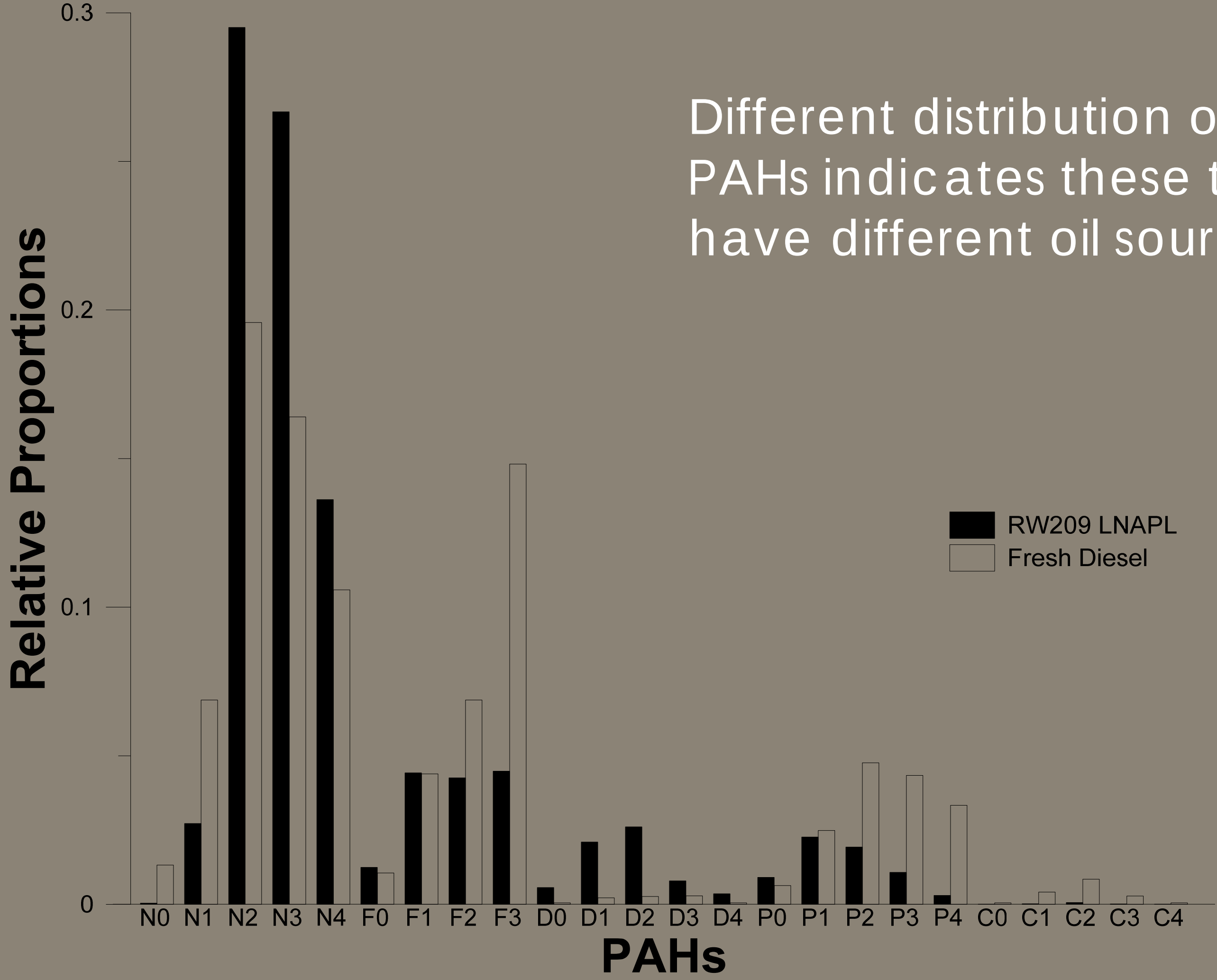
# 4 Diesel Source Identification

## Alkylated PAH Distribution




Different distribution of alkylated PAHs indicates these two samples have different oil sources

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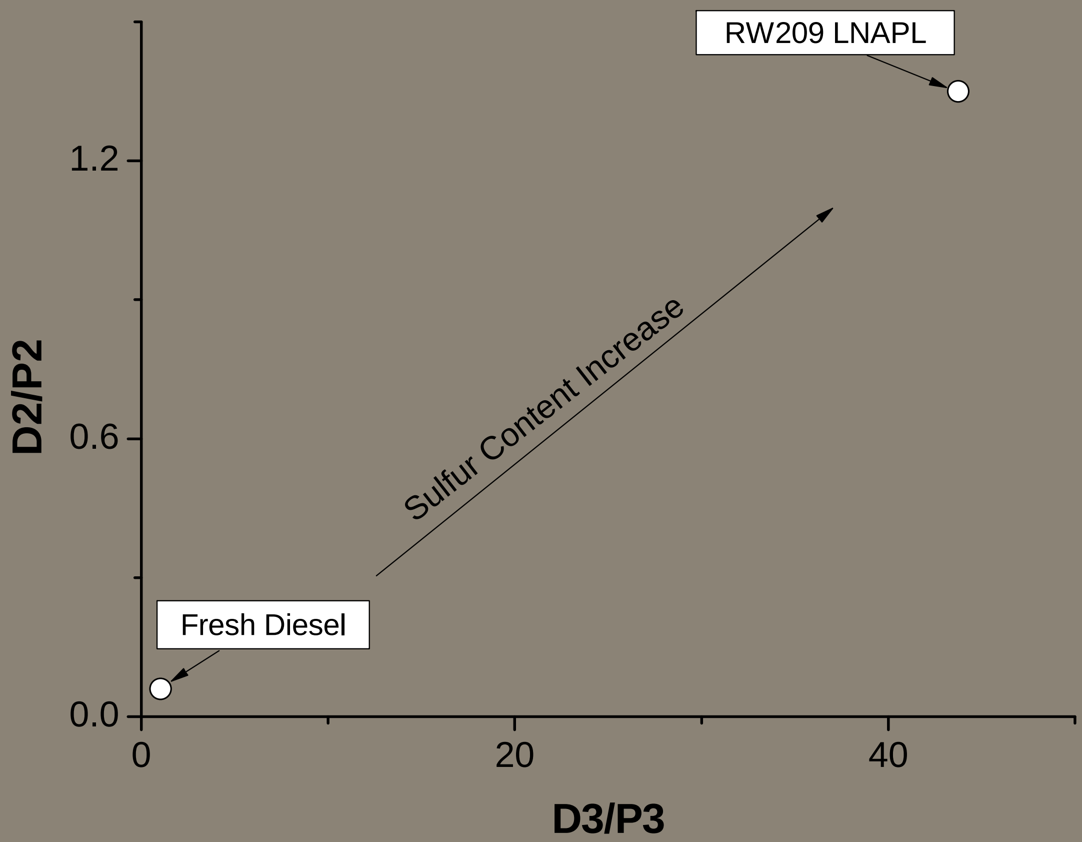
# 4 Diesel Source Identification

## Ratios of D2/P2 and D3/P3




- C2- and C3-phenanthrenes (P2 and P3) and C2- and C3-dibenzothiophenes (D2 and D3)
- Ratios of D2/P2 and D3/P3 remain relatively stable as weathering proceeds

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# 5 Conclusions

- GC/FID chromatograms of groundwater samples demonstrated that two gasoline and diesel plumes are separately present at the Site.
- Hydrogeology and Site investigations indicated that the diesel impacts to groundwater may not be caused by the current fuel service station operation.
- The similar distribution of C3-alkylbenzenes (most stable chemicals in gasoline) and the consistent diagnostic ratios of the analyte pairs with similar solubility indicate that the source for the gasoline impacts to groundwater in monitoring wells RW206 and MW102 likely originated from gasoline leakage from the currently existing USTs.
- The distinct distribution of sesquiterpanes (biomarkers for diesel) and alkylated PAHs confirm that the RW209 LNAPL sample is a nonmatch to the fresh diesel and they originated from different crude oil sources

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# Thank you

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