



CHALLENGES WITH PETROLEUM SPILL CHARACTERIZATION

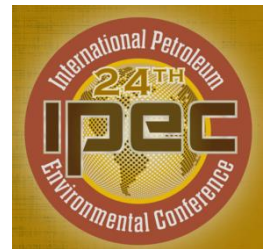
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M9P 3V6



Ministry of the Environment and Climate Change

Laboratory Services Branch

- Created in 1972 with a current staff complement of just over 2000 staff
 - Laboratory Services Branch has 140 staff (Full service laboratory 160,000 square feet)
- The Branch provides analytical laboratory services for the needs of the Ministry of the Environment and Climate Change to ensure:
 - a province-wide full service analytical laboratory that delivers readily available and high quality analytical testing
 - Organic, Inorganic, General Chemistry, Microscopy, Microbiology and Toxicology testing
 - Provide support of compliance, abatement, enforcement, litigation, audit of drinking water quality, environmental monitoring programs and standard setting initiatives
 - Emergency analytical response on a 24/7 basis as needed
 - Participate on international analytical committees
- Provide expert consultation and reference centre services for environmental analysis

Topics Covered

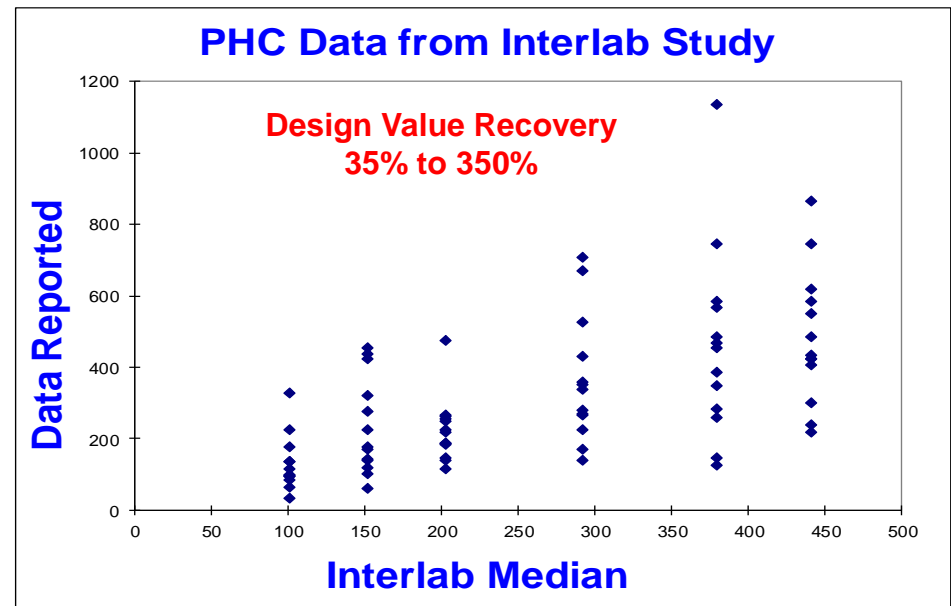
- Background on petroleum hydrocarbon analysis
 - Canadian perspective
- Conventional analytical approach
- Environmental Case Studies
 - Look at some advanced methodologies
 - Additional forensic indicators/techniques
- Challenges to consider

Why Standardize Petroleum Methods?

- **Prior to 2004 in ONTARIO**
- No uniform analytical methodology
- No defined reporting
- No standardized calibration

Thus:

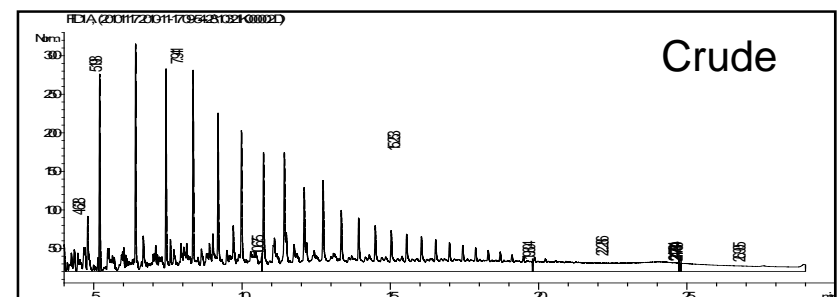
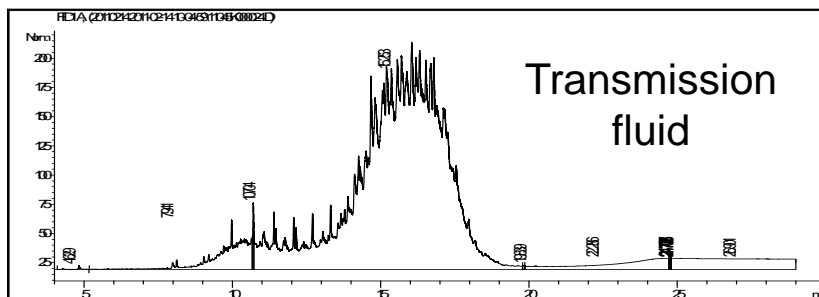
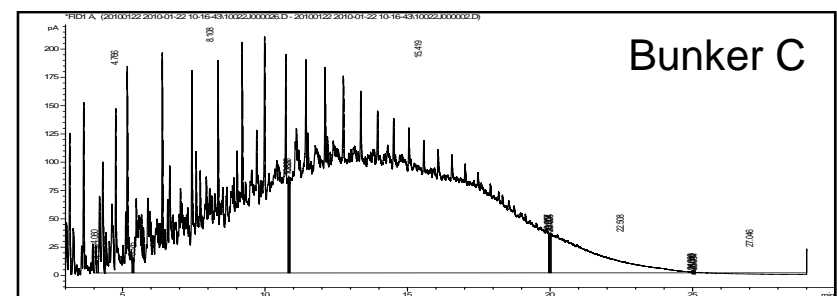
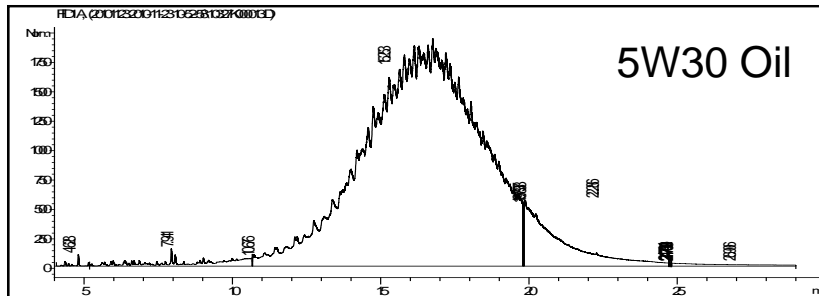
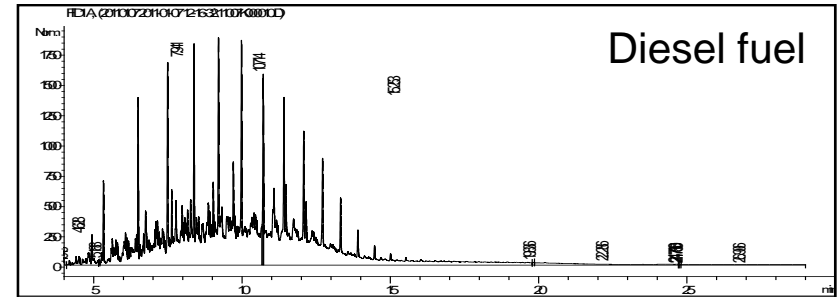
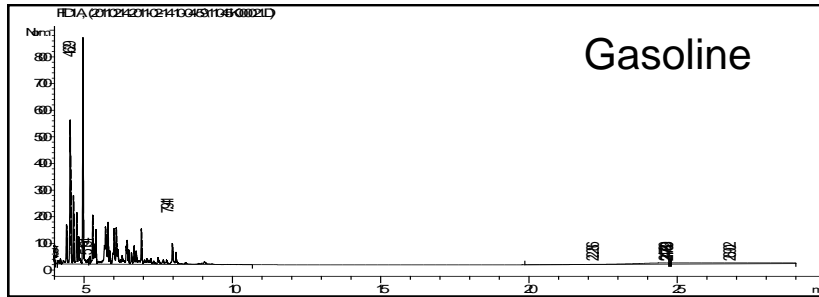
- Between laboratory results were incomparable
- Considered a new approach
- **METHOD STANDARIZATION**



“Reference Method for the Canada-Wide Standard Petroleum Hydrocarbons in Soils – Tier 1”
Canadian Council Ministers of the Environment

Petroleum Product Profiles by GC/FID

nC₁₀ to nC₅₀ Range



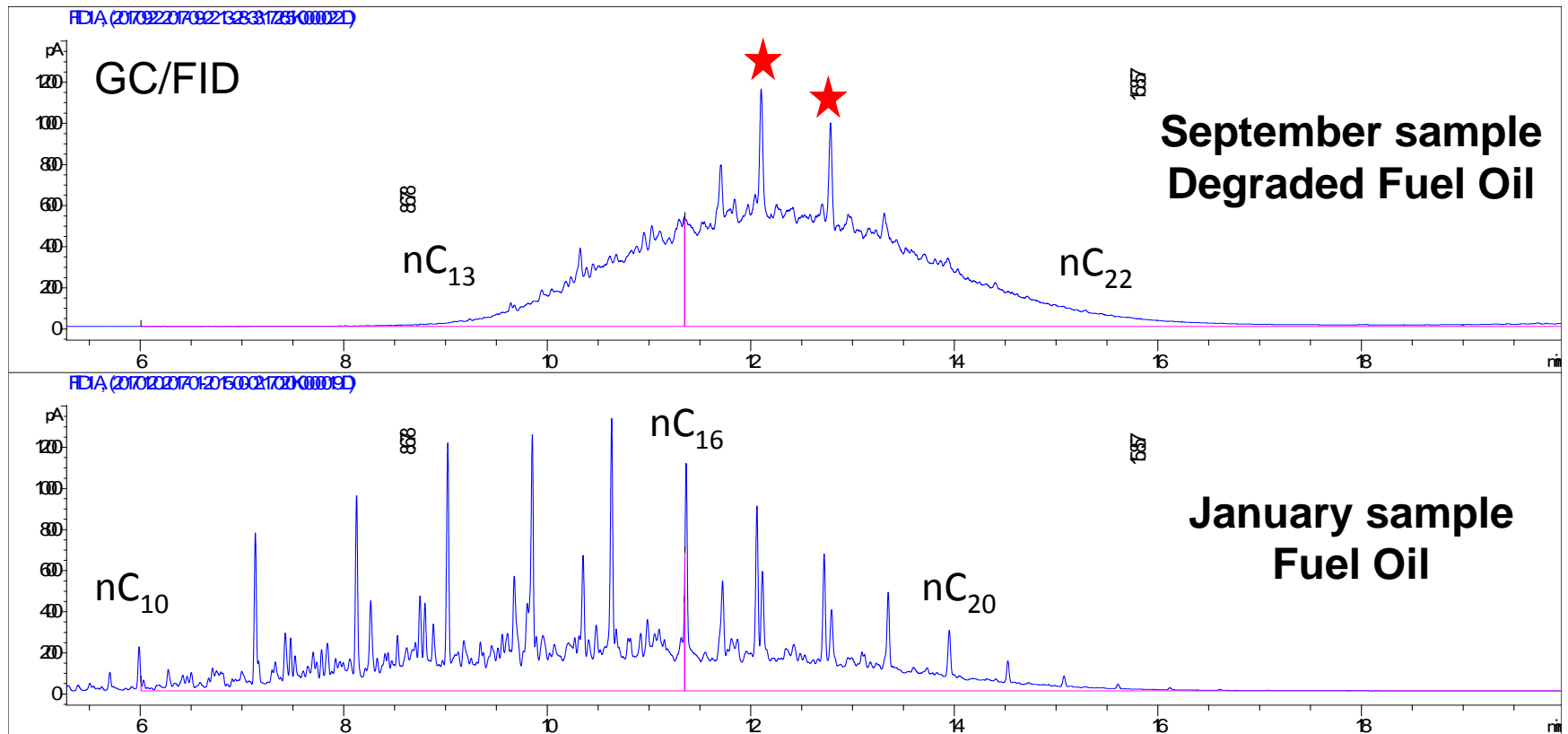
Useful in distinguishing petroleum products

Case 1: Product Found in an Open Pit

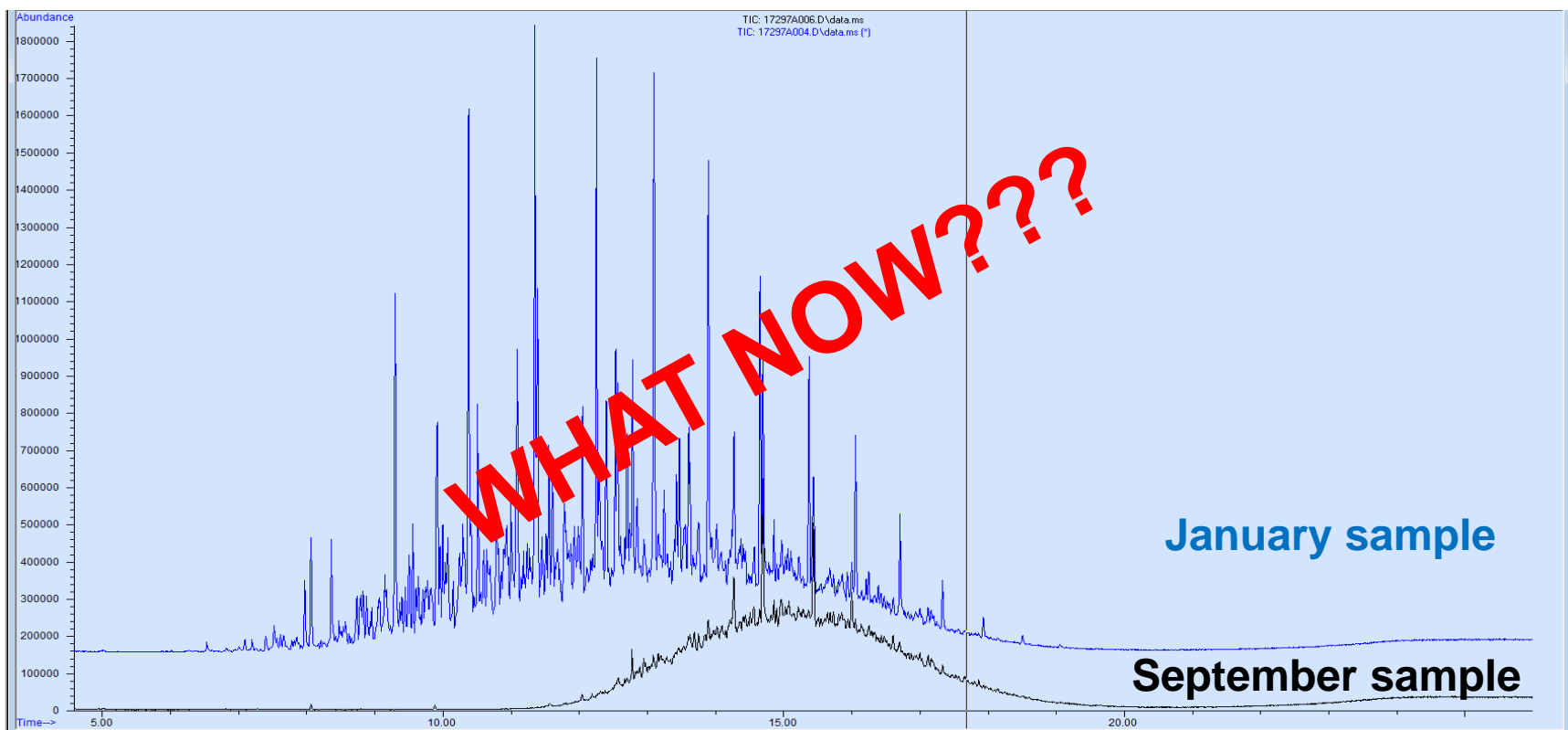


- Remediation activity were being conducted from a fuel oil UST removal (under Officers Order)
- Neighbouring property detected some strong odour which lead to finding pure product in an open pit.
- Two samples were analyzed one from January and a second from September

Samples Collected from Open Pit in January and September

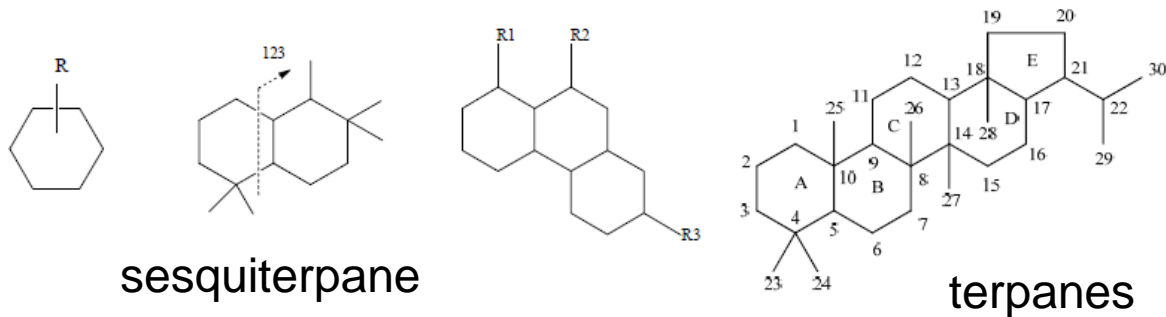


Samples Collected from Open Pit



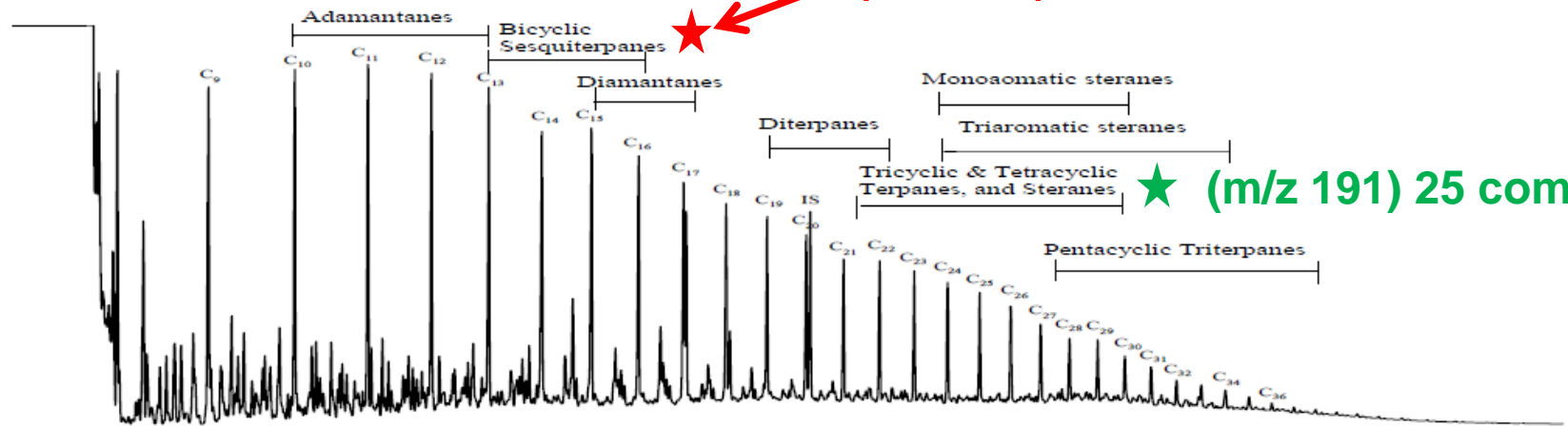
Biomarker Analysis

- Biomarkers are more resilient and less prone to weathering
- Biomarkers signatures are related back to the original crude oil
- Fingerprinting analysis by Mass Spectrometry
 - Typical n-Alkanes distribution (n-C₁₀ to n-C₄₀)
 - Branched alkanes (pristane and phytane)
 - **Bicyclic sesquiterpanes (C₁₄ to C₁₆) at m/z 123**
 - **Biomarker terpanes/hopanes at m/z 191**
 - Biomarker steranes at m/z 217 and 218



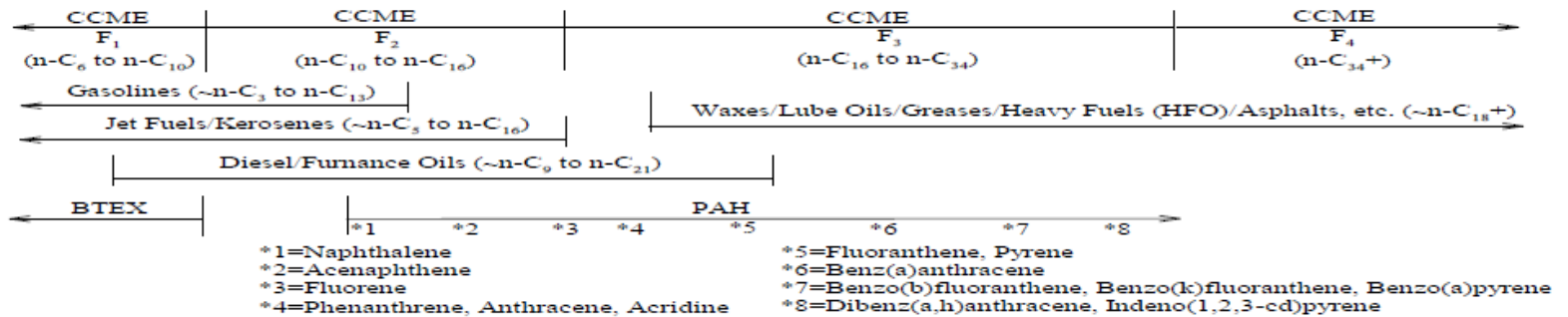
Petrogenic Hydrocarbons

(m/z 123) 10 common



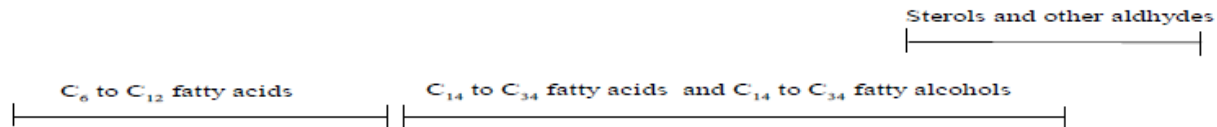
(m/z 191) 25 common

Carbon Number of n-Alkane	10	15	20	25	30	35	40	
Boiling Point	174	271	343	406	449	501	539	°C
Boiling Point of n-Alkane at 1 atm.	345	520	649	763	840	934	1002	°F



Note: The carbon ranges of the four fractions, F1 to F4, are defined in the Tier 1 TPH analytical method by the Canadian Council of Ministers of the Environment (CCME).

Biogenic Organic Matter (BOM)



Instrumentation



GC/FID

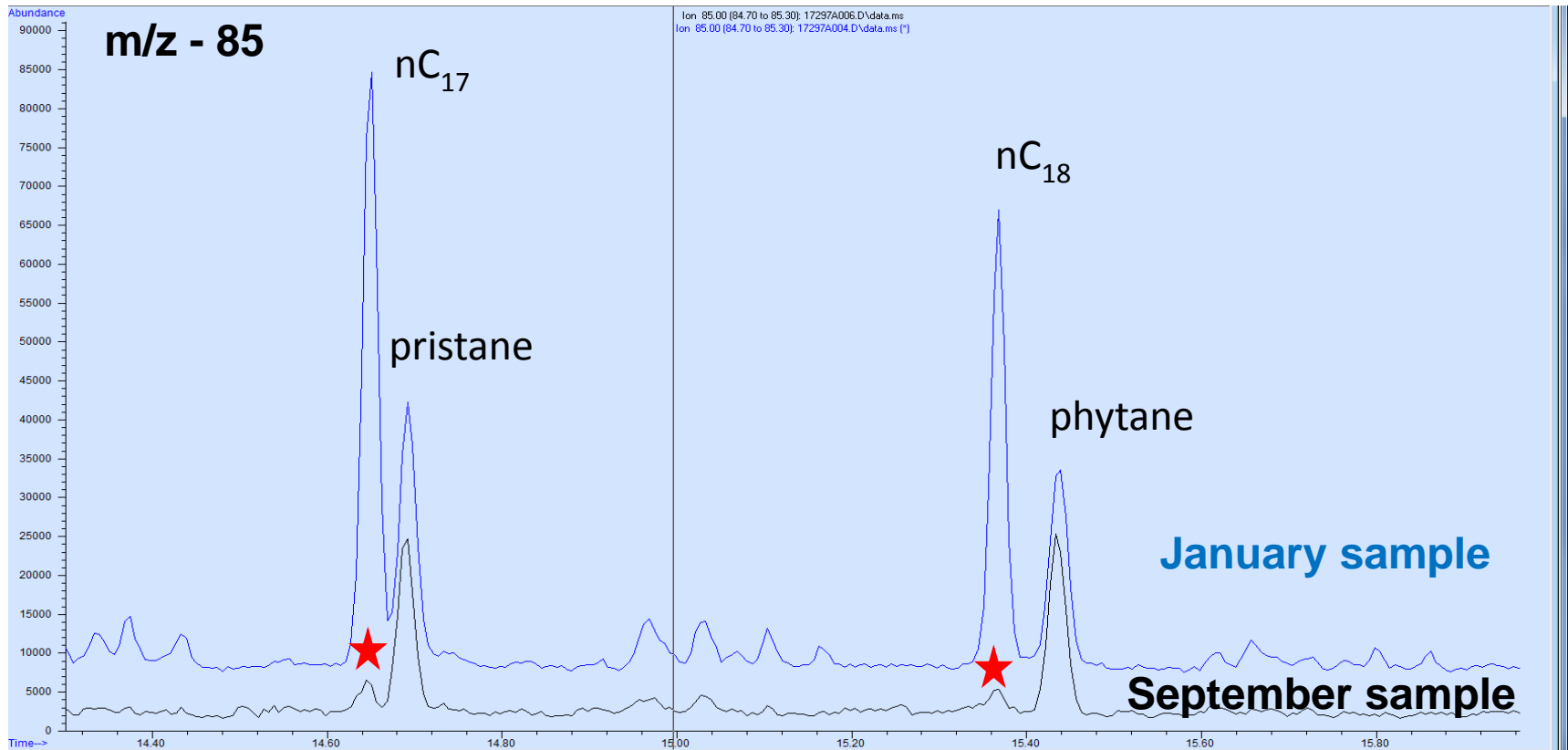
- Gives response if compound burn/combust
- Gives equal response independent of molecular weight
- Inexpensive (excellent candidate for petroleum)



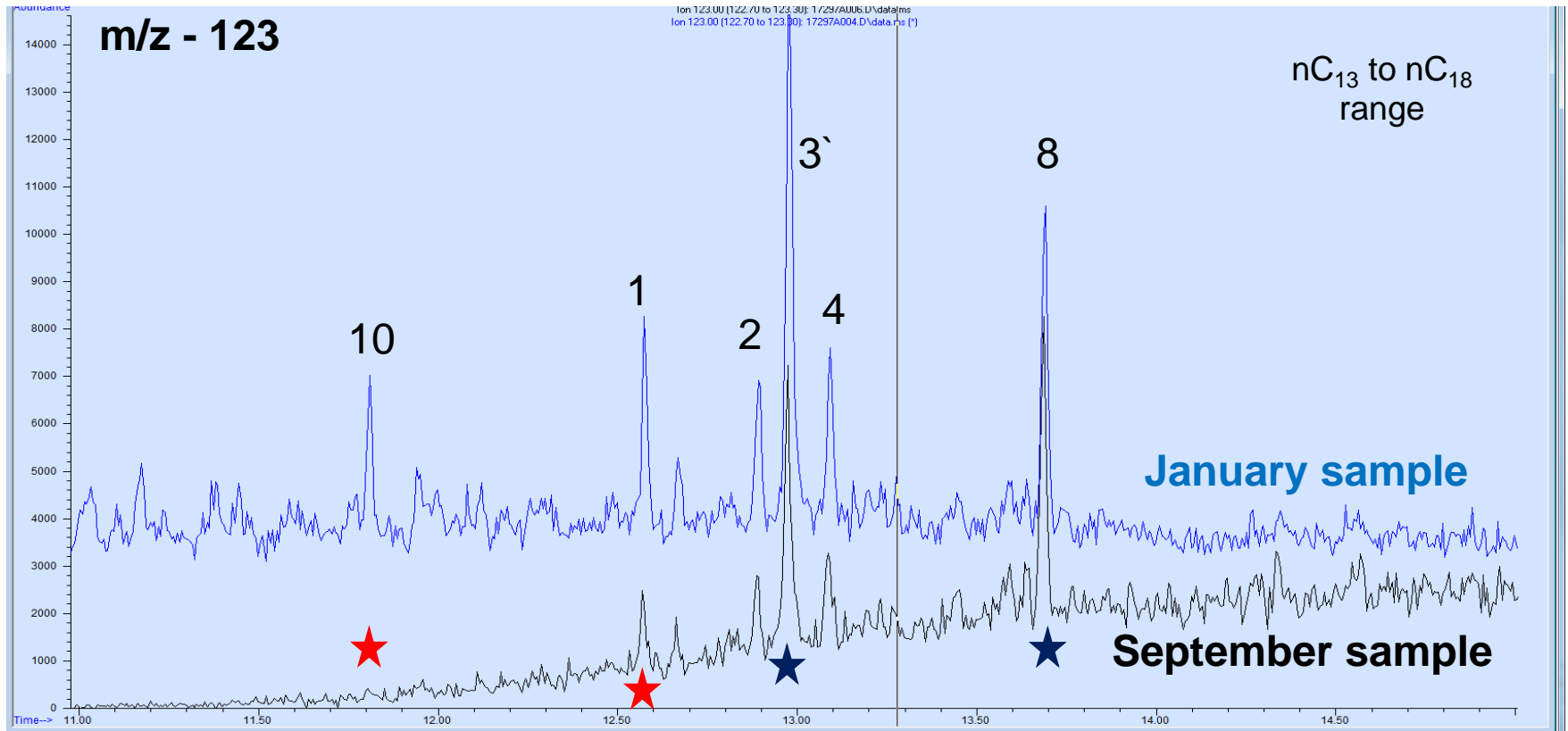
GC/MSD

- Yields structural information based on the fragmentation pattern of ionized molecules (biomarkers)
- However, can get significant mass discrimination
- MSD can operate in Full Scan or Selected Ion Monitoring (SIM)

Alkanes and Isoprenoids



Sesquiterpane Biomarkers



These appears to be two different sources and are not related

CASE 2: Mysterious Ooze Leaking from Two Potential Sources into a Tributary

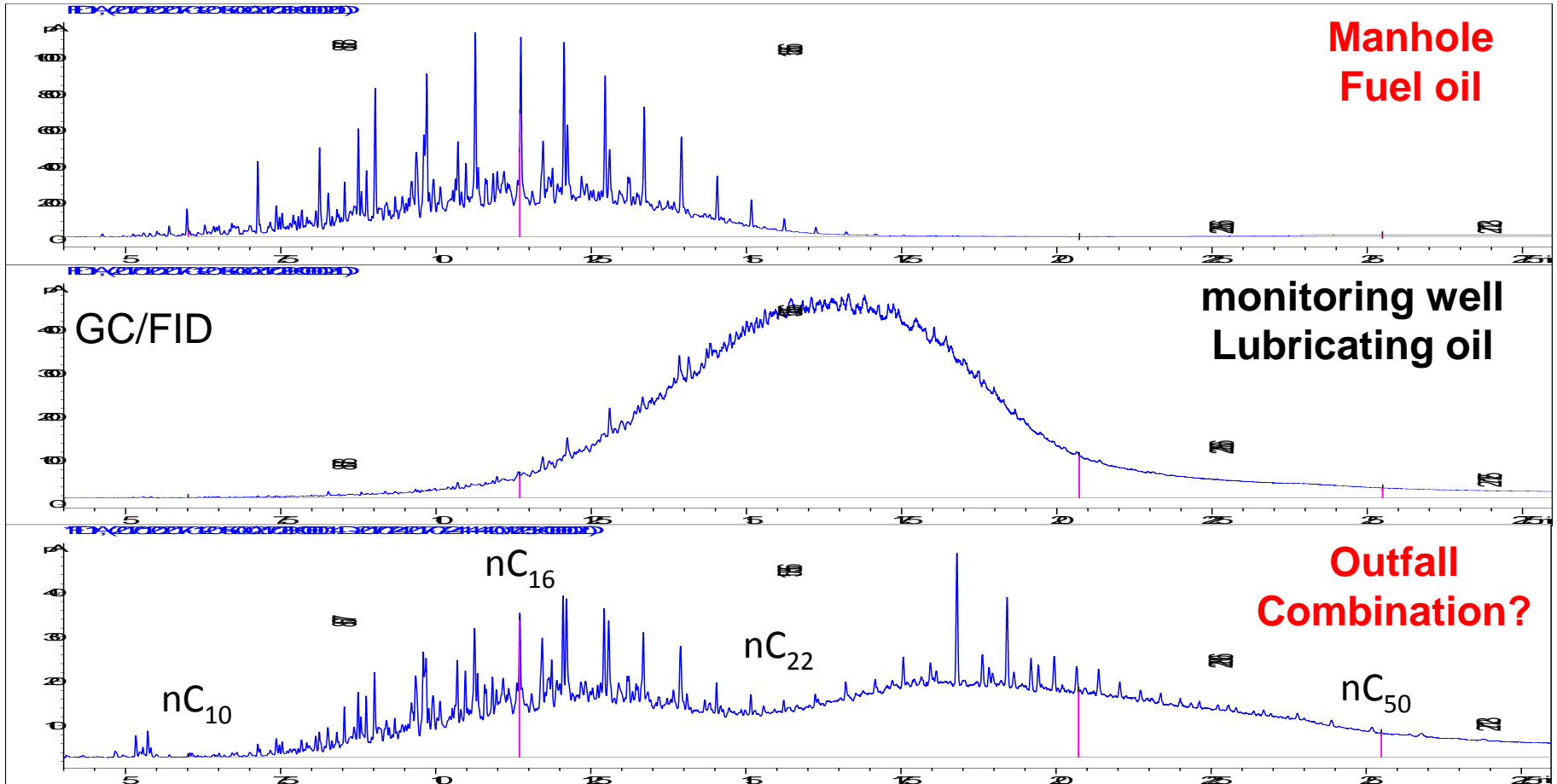


Two potential inputs

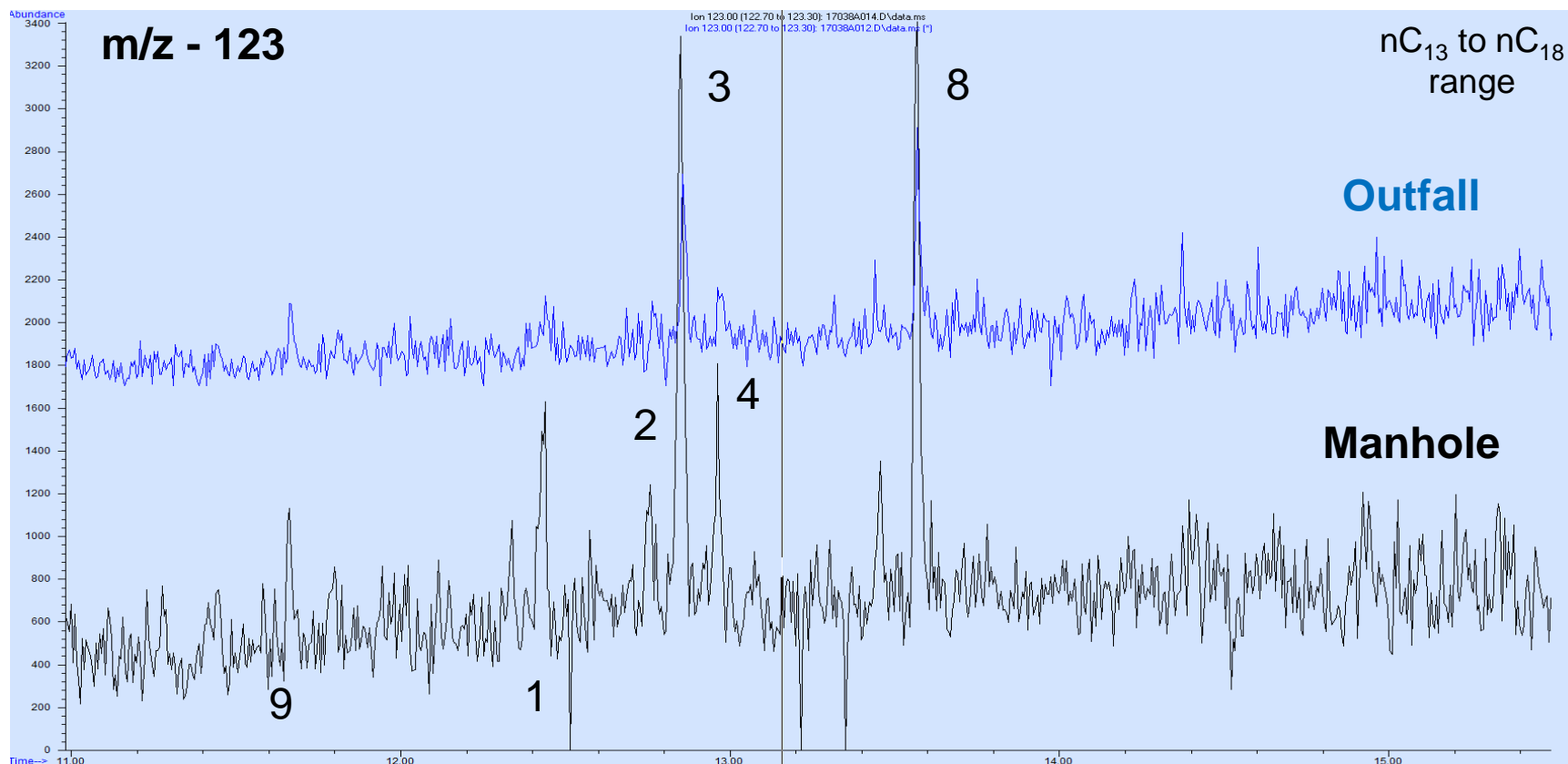
1. Municipal service manhole
2. Storm water input from adjacent apartment complex



Sampling of Outfall and 2 Potential Sources

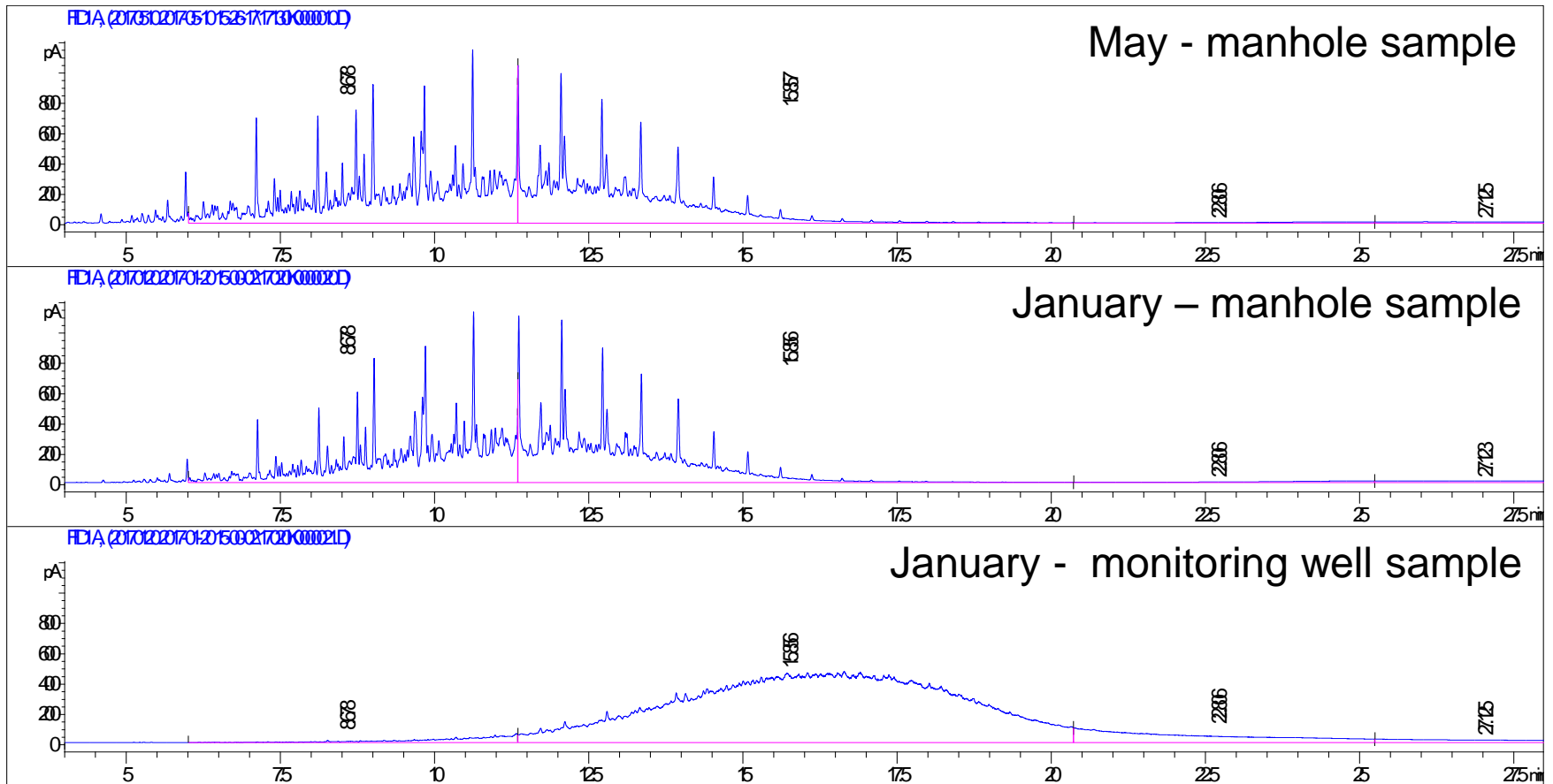


Sesquiterpane SIM Experiments

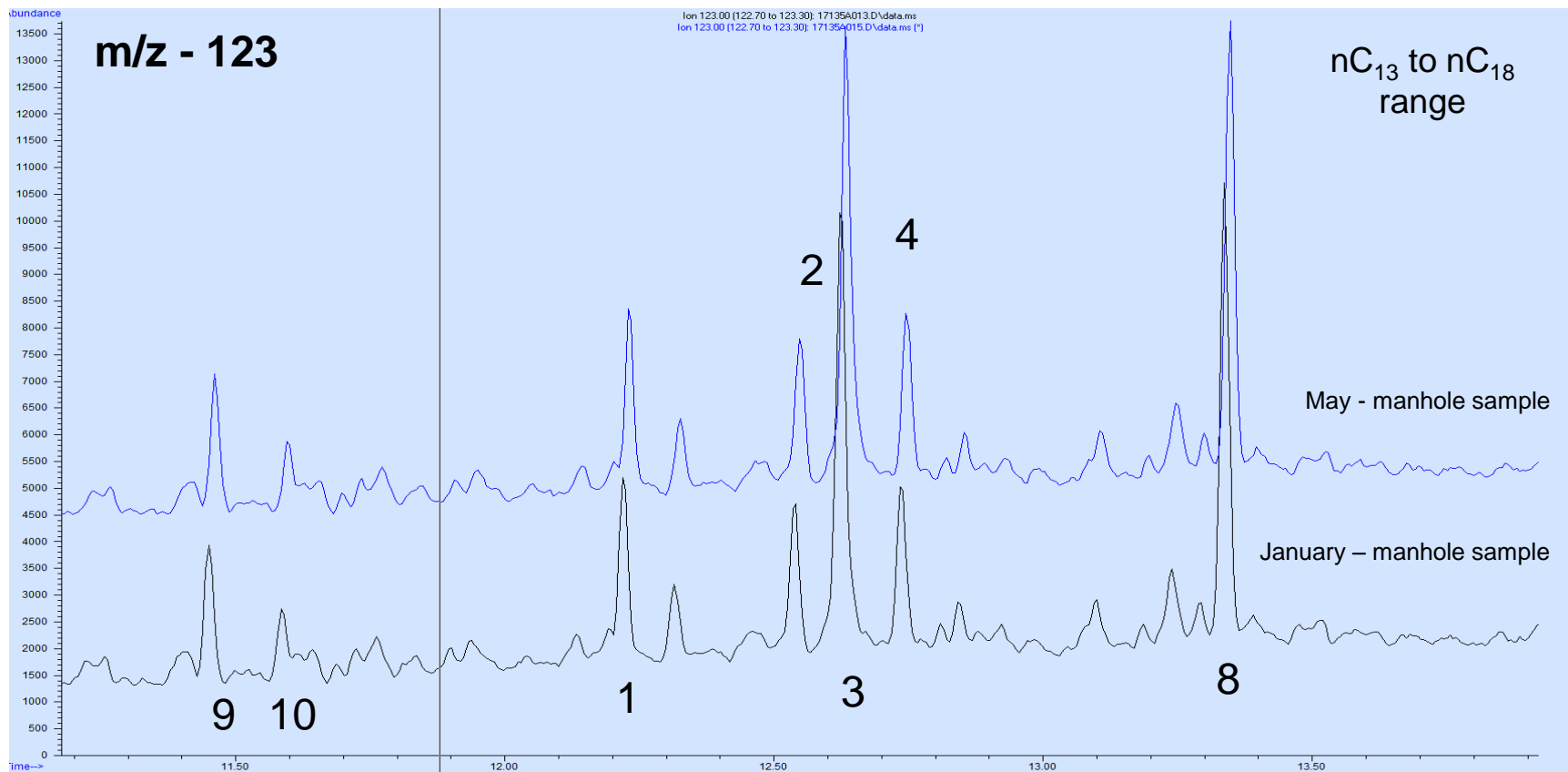


MSD not sensitive enough even in SIM mode

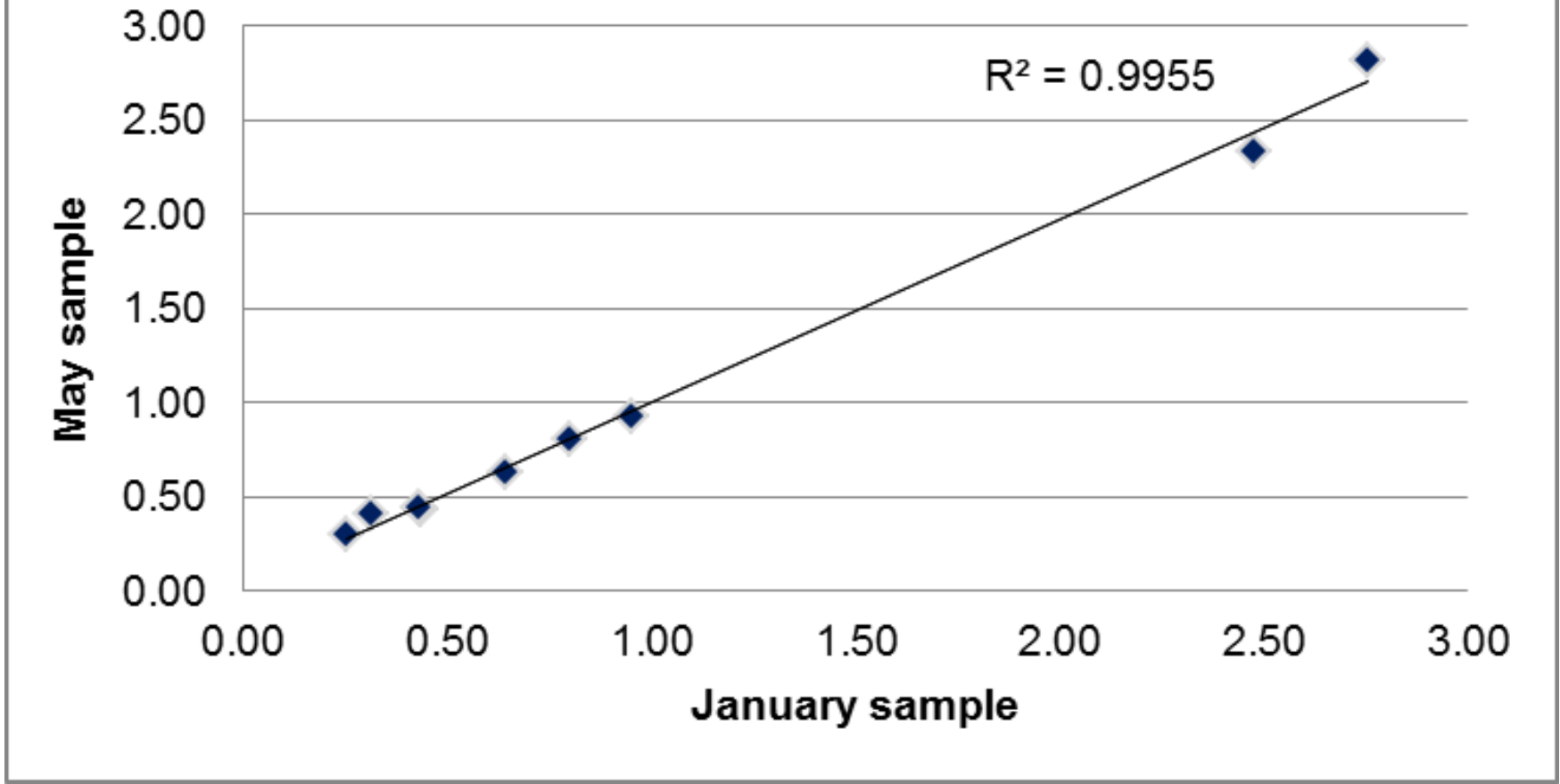
An Additional Sample was Collected Serval Months Later



Are Manhole Product Samples From May and January the Same?

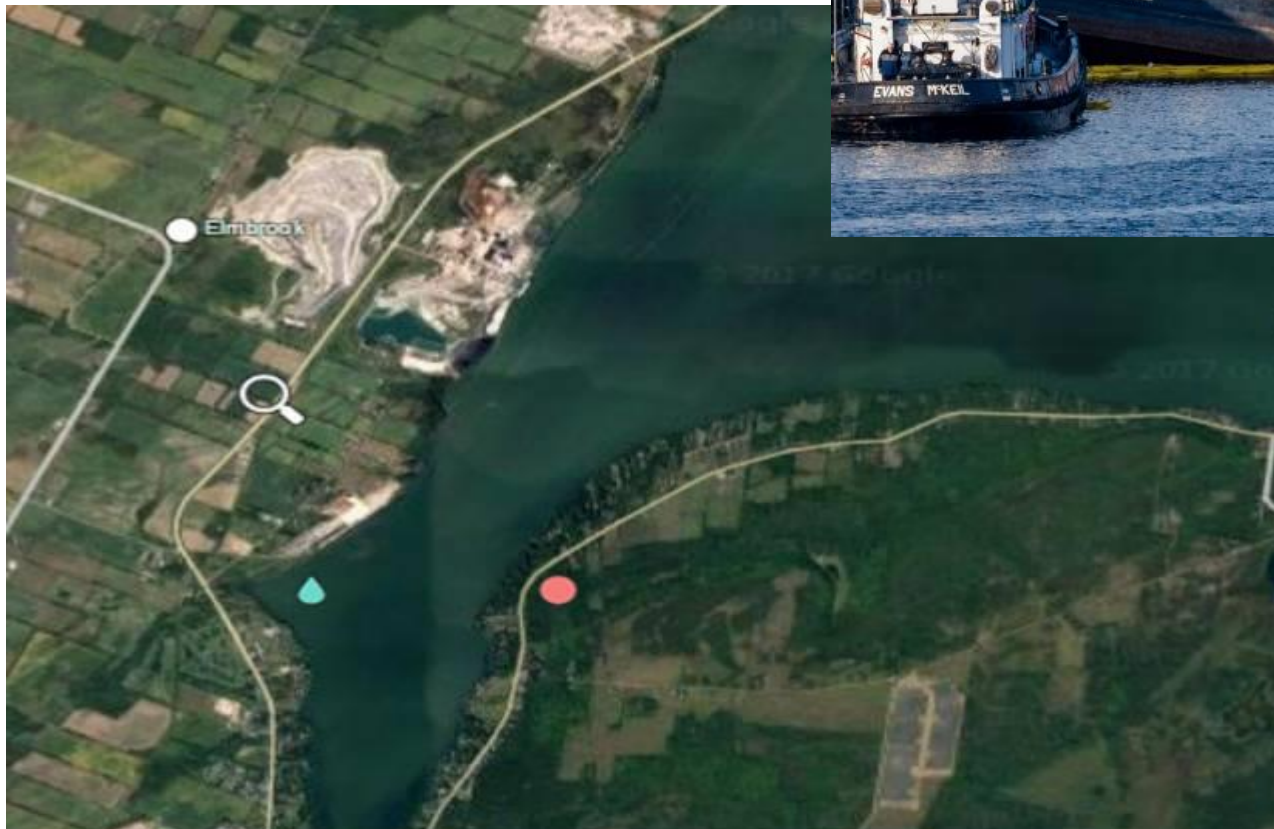


Biomarker Ratio Plot



8 Biomarker Ratios : good agreement indicating these samples are same source

Case 3: Barge Sinks in Harbour



Late Winter : EMERGENCY RESONSE (10 days)

partially submerged
barge reported about
1,200 litres (320gal) of
diesel fuel and 100 litres
(27gal) of hydraulic fluid.

WTP shut down.

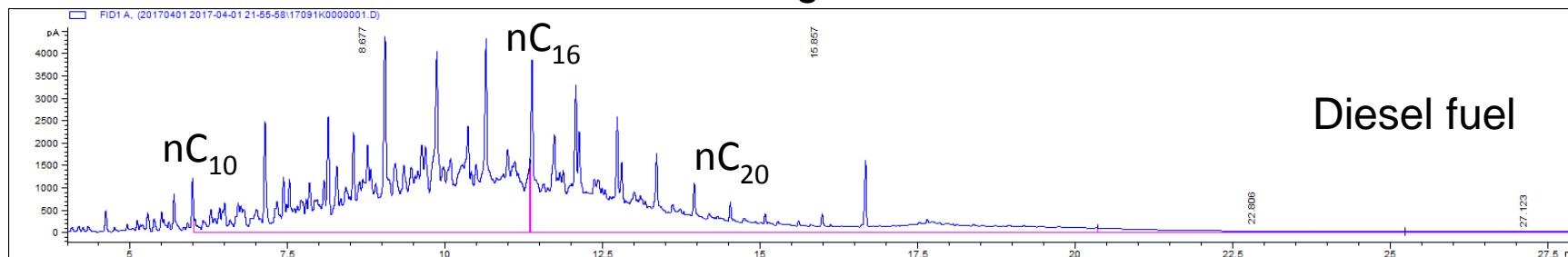
About 10,000 peoples'
drinking water affected.

Boil water advisory in
place for about 10 days.

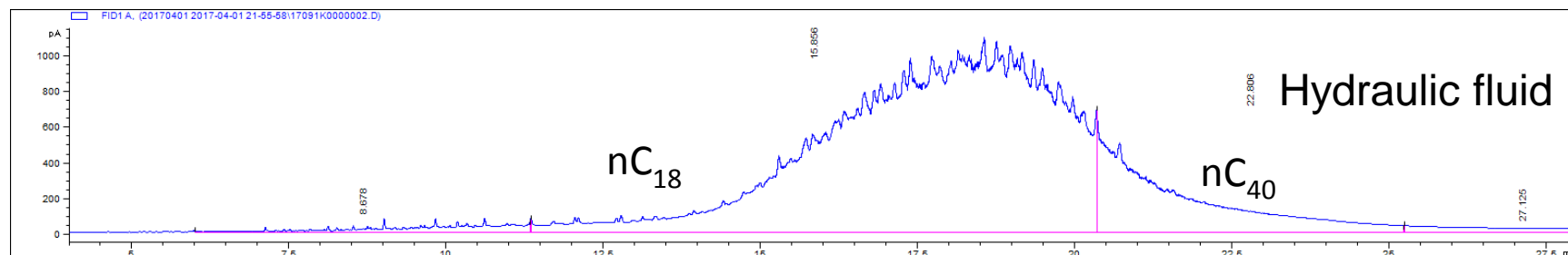
Samples obtained during barge recovery along with a surface water sample from Bay



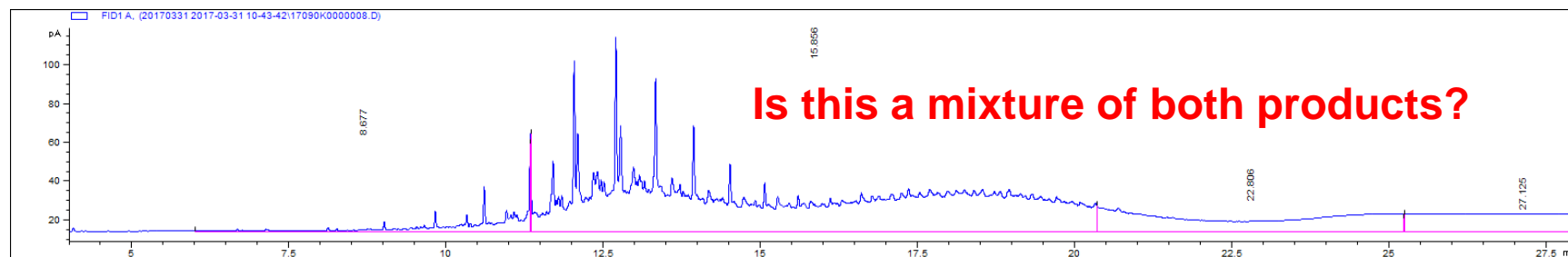
Product 1: brown sludge from boomed area



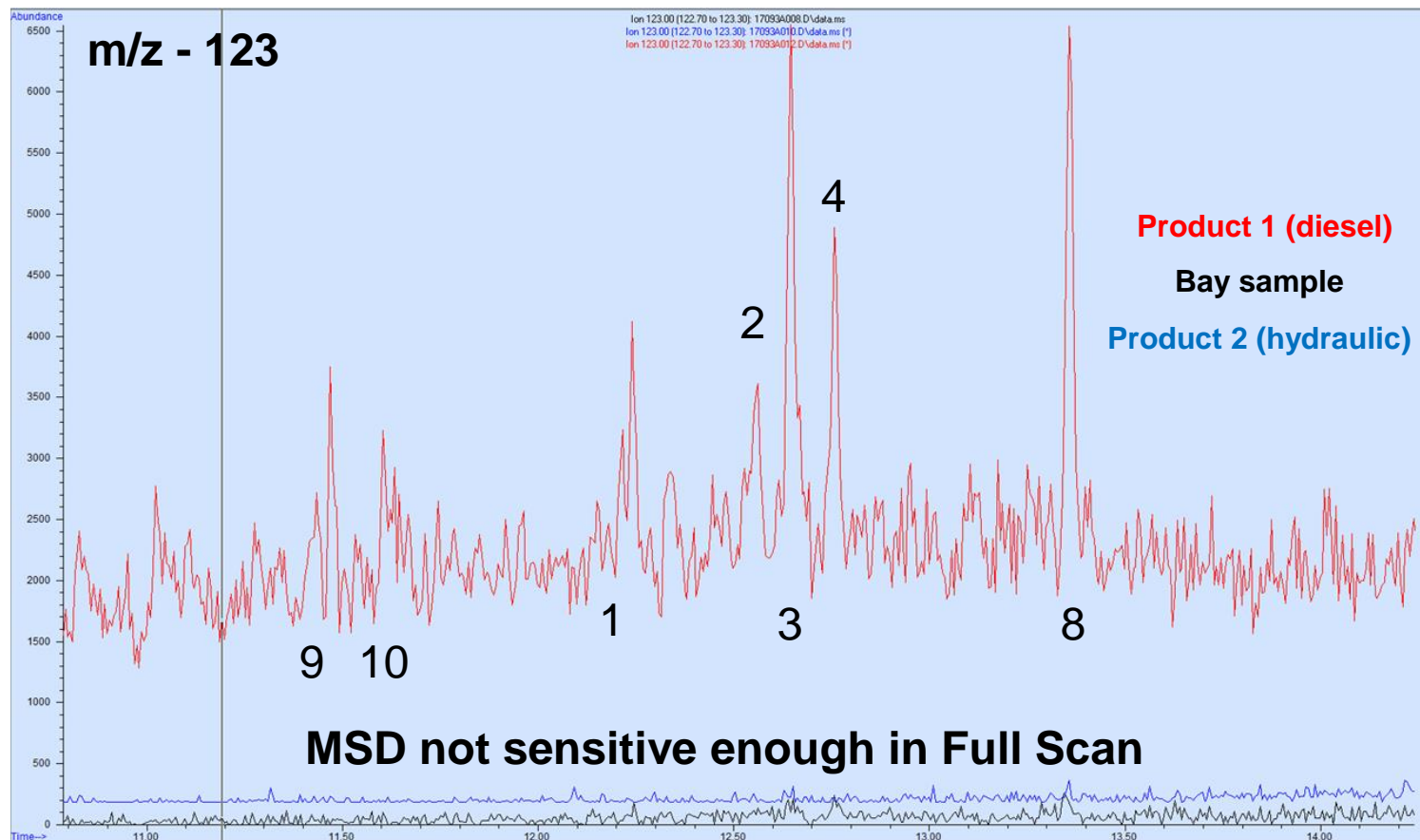
Product 2: collected from surface of water in boomed area



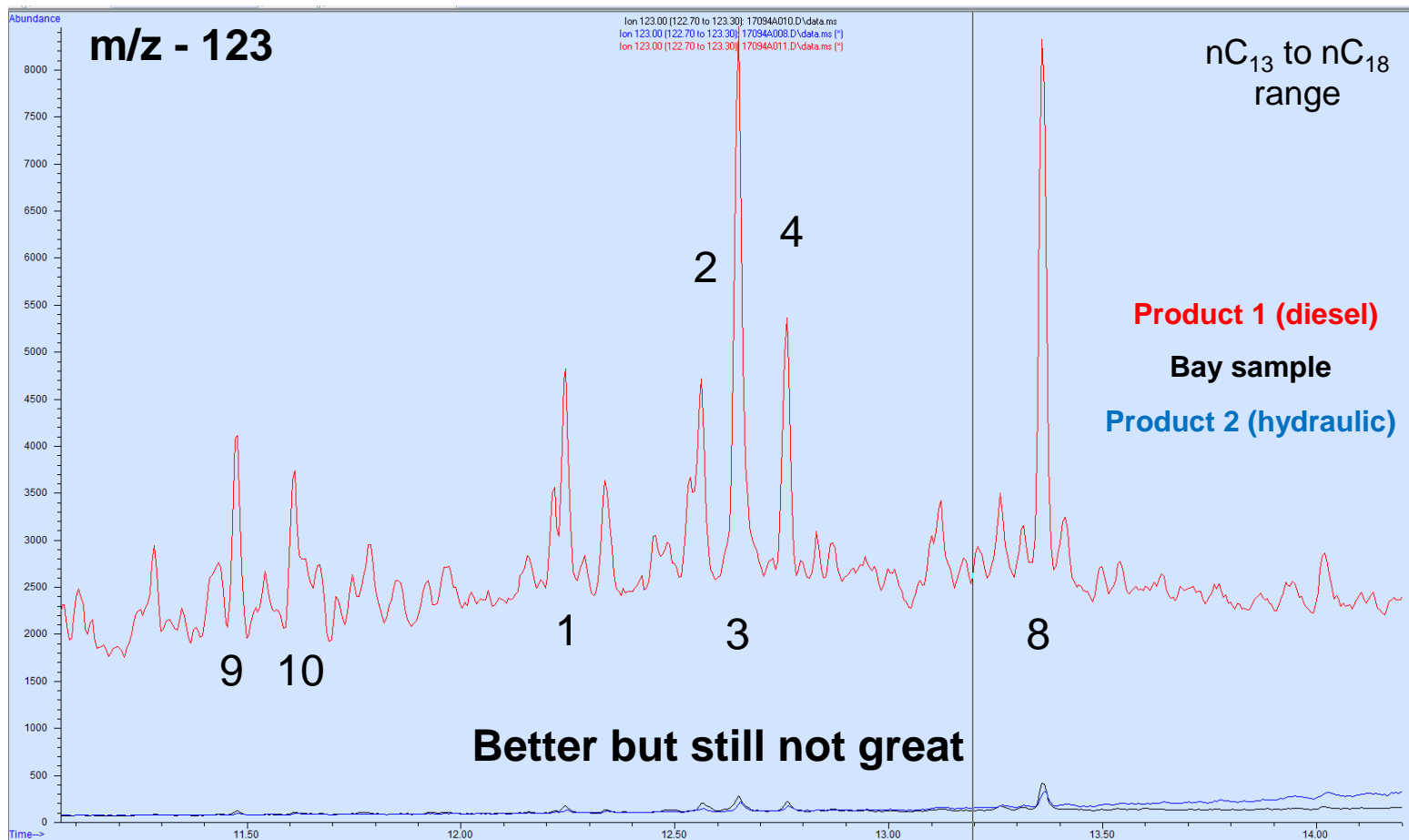
Sample collected from surface of water in Bay near water intake



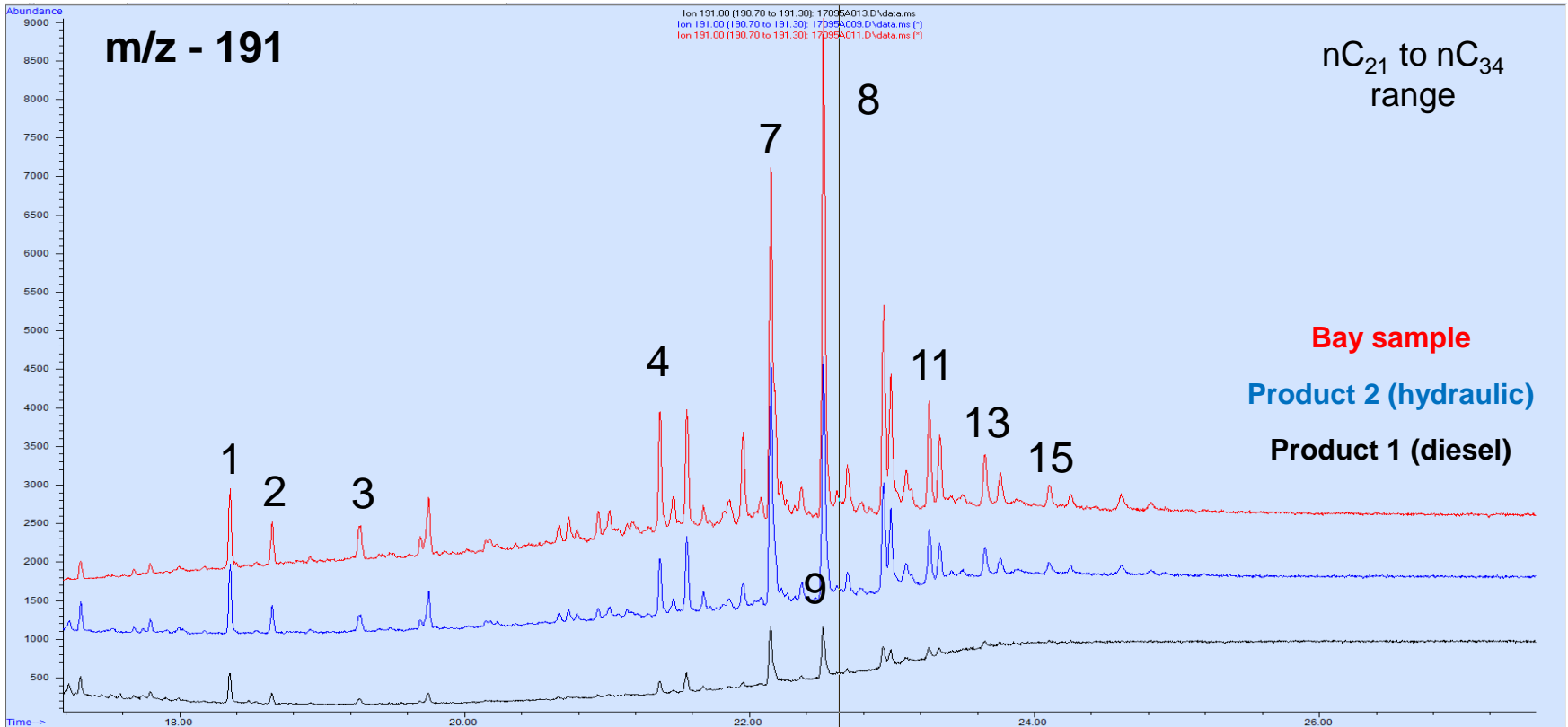
Sesquiterpane Biomarker : Full Scan



Sesquiterpane SIM experiments



Sterane/Hopane Biomarker SIM experiment



	1/8	2/8	7/8	9/8	5/6	9/8	10/8	11/8	13/8	15/8	correlation coefficient
Bay sample	0.23	0.10	0.21	0.25	0.84	0.41	0.31	0.18	0.12	0.11	1.000
Product 1	0.46	0.18	0.22	0.31	0.71	0.23	0.34	0.41	0.41	0.28	0.713
Product 2	0.13	0.08	0.23	0.23	1.02	0.40	0.30	0.20	0.13	0.12	0.984

Closing Comments

- GC/FID data can be extremely useful in identification of product type
 - Standardized petroleum methods facilitate data comparison between laboratories
- Biomarker data can often provide an additional line of evidence for source tracking

THANK YOU