Analytical tools for renewable fuel spill response and a discussion on toxicity

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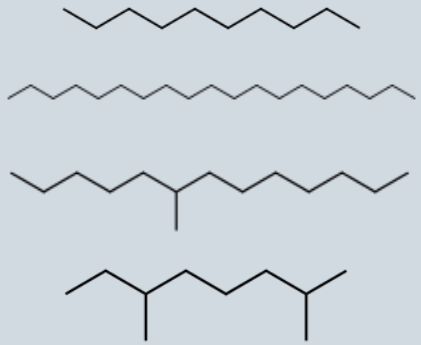
OSPR LABORATORY PROGRAM

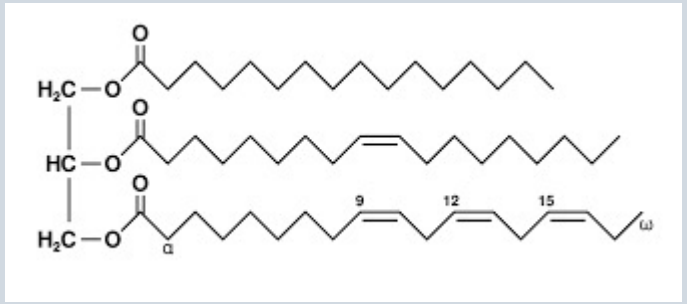
Outline

- Highlight chemical differences between renewable diesel and biodiesel
- Traditional tools and approaches for fingerprinting petroleum and renewables
- Work being done at OSPR Petroleum Chemistry Laboratory on renewable diesel
- General information on toxicity of renewables

Renewable diesel



Vegetable and Animal Fats: Triglycerides



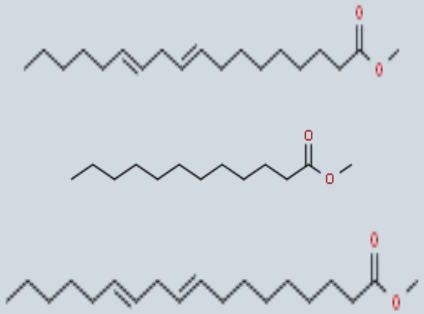
Hydrotreatment
Isomerization

Linear and branched chain hydrocarbons

+

Renewable Propane

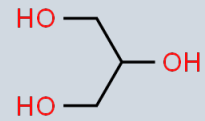
Biodiesel



Transesterification

Fatty Acid Methyl Ester (FAME)

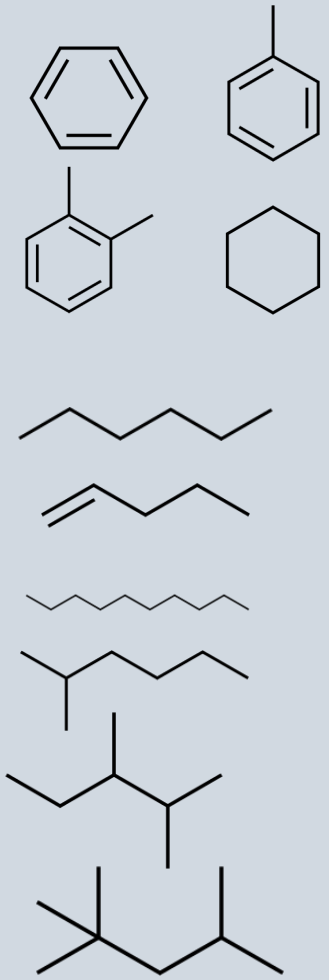
+



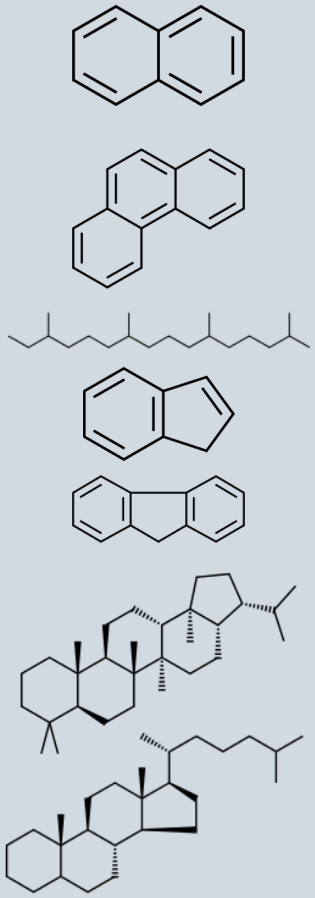
Glycerol

Tools for Analysis and Fingerprinting – GC/FID, GC/MS

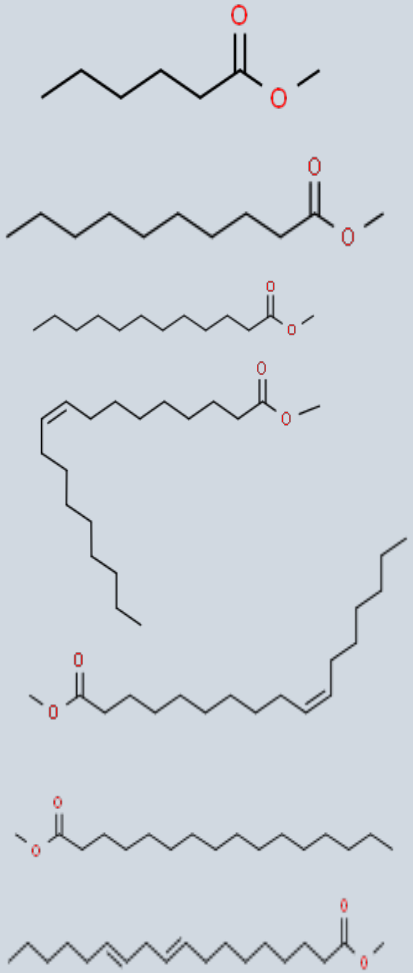
Gasoline (C6-C12)



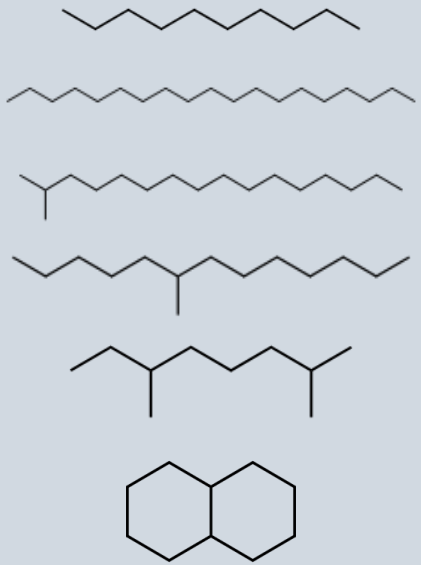
Petroleum Diesel(C10-28) and Oil



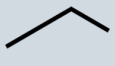
Biodiesel (FAME)*



Renewable Diesel (C10-C20)



No documented approach for fingerprinting renewable diesel

Ethanol 

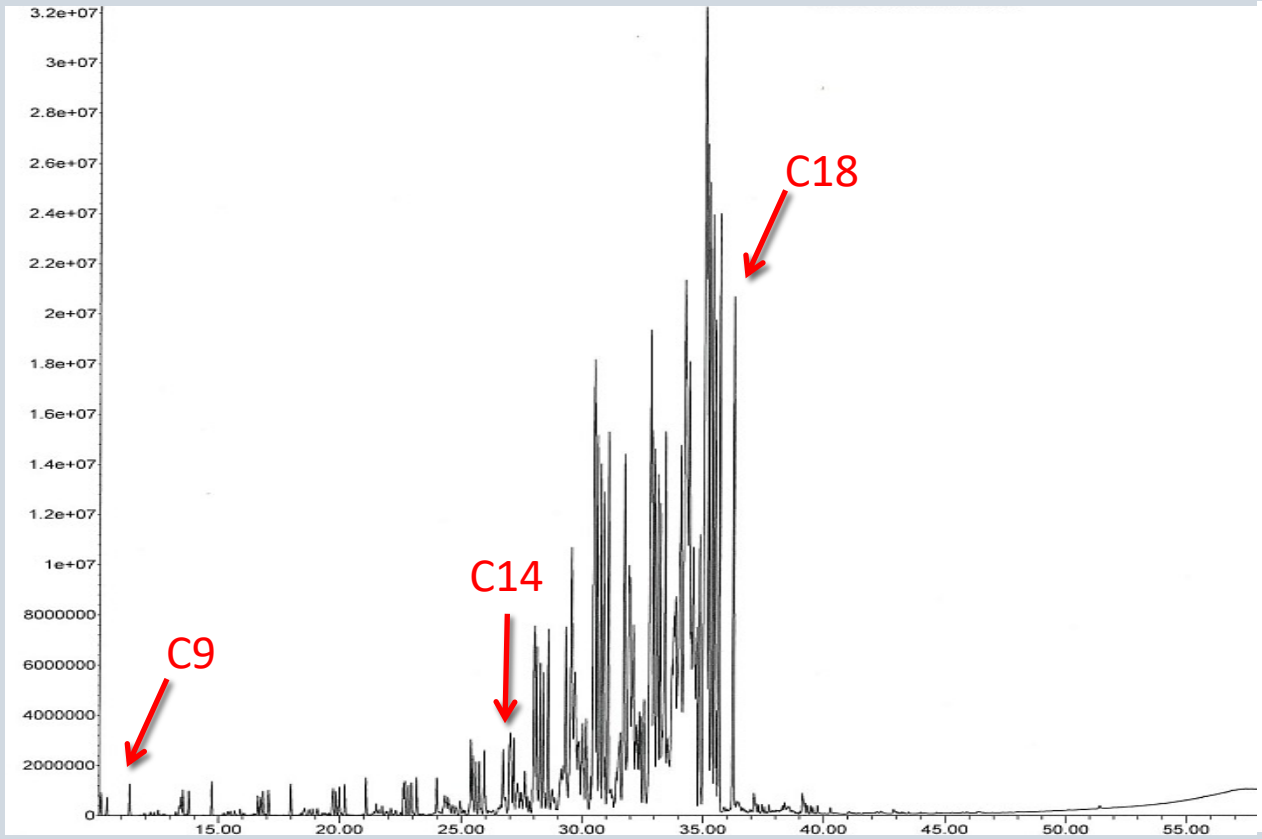
*Infrared Spectroscopy

Main Project Objectives

1. Evaluate the applicability of current petroleum spill analytical methodologies for characterization and fingerprinting of renewable diesel spills.
    a. Can we differentiate renewable diesel from petroleum diesel? Renewable diesel from Biodiesel?
    b. Can we fingerprint renewable diesel?
    c. What about mixtures?

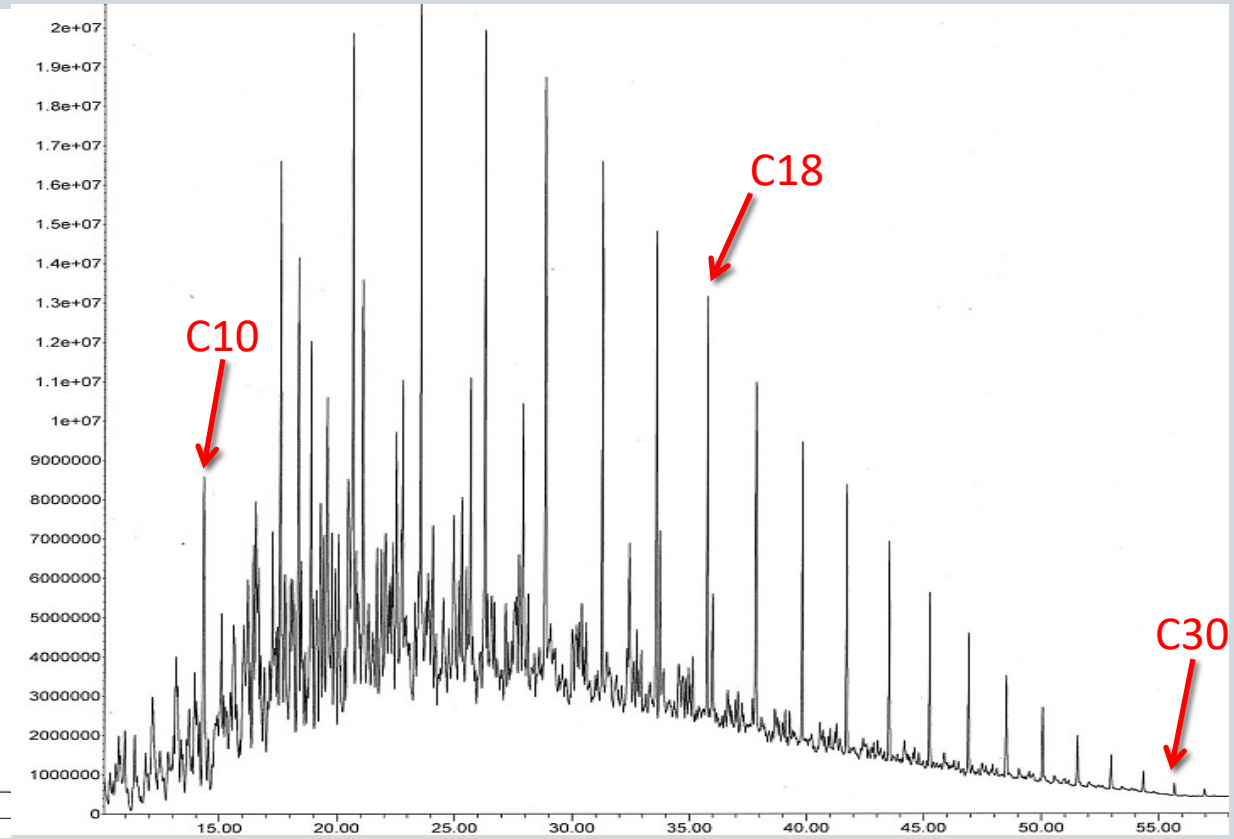
Can we tell the difference between renewable diesel and petroleum diesel using our traditional full scan GCMS screening?

Traditional GC can be used to confirm and characterize renewable diesel



100% Renewable Diesel

- Carbon range C9 – C18, majority of signal C15–C18
- Extreme abundance C17 – C18, easily overloading detector

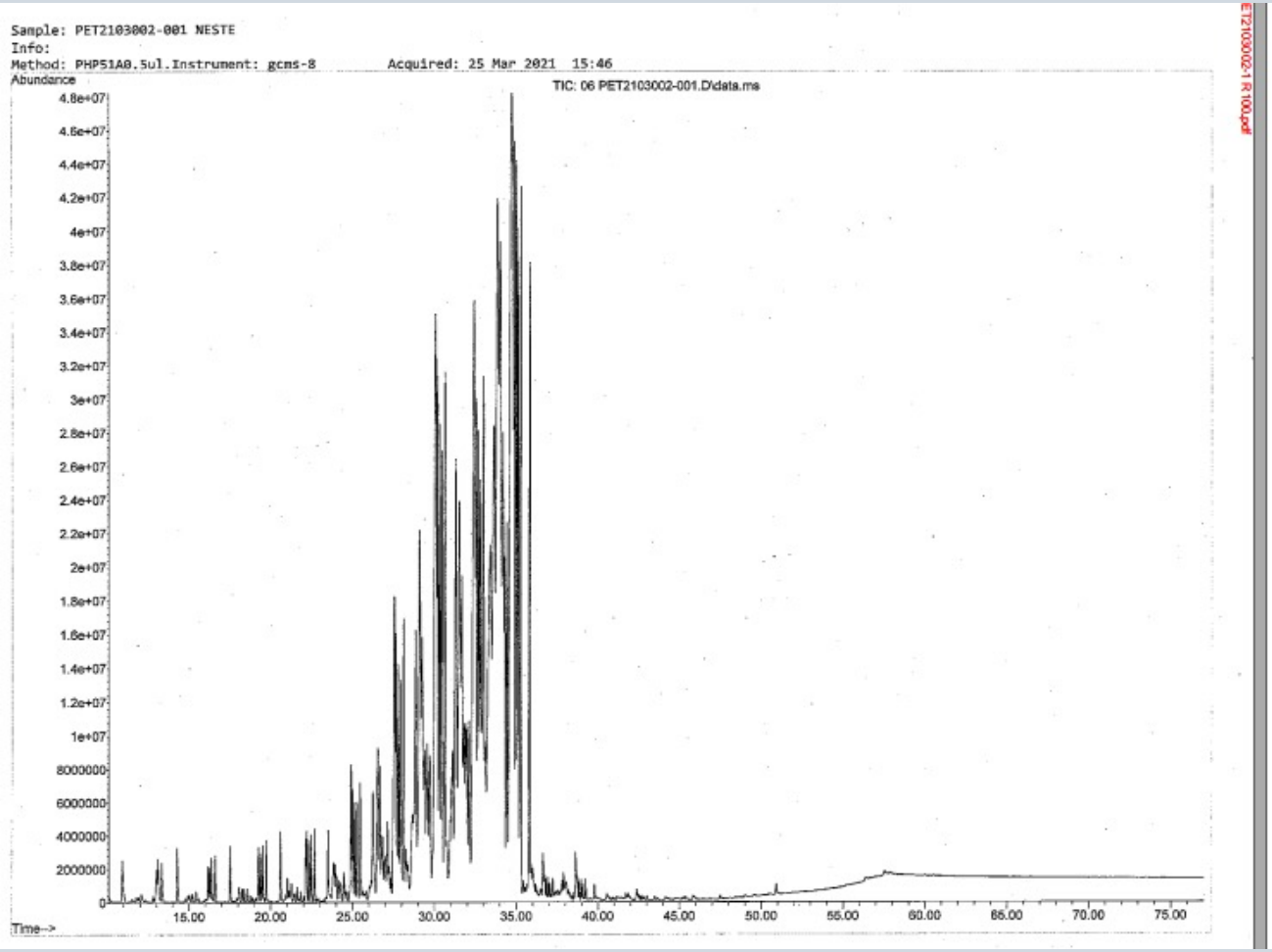


100% Petroleum Diesel

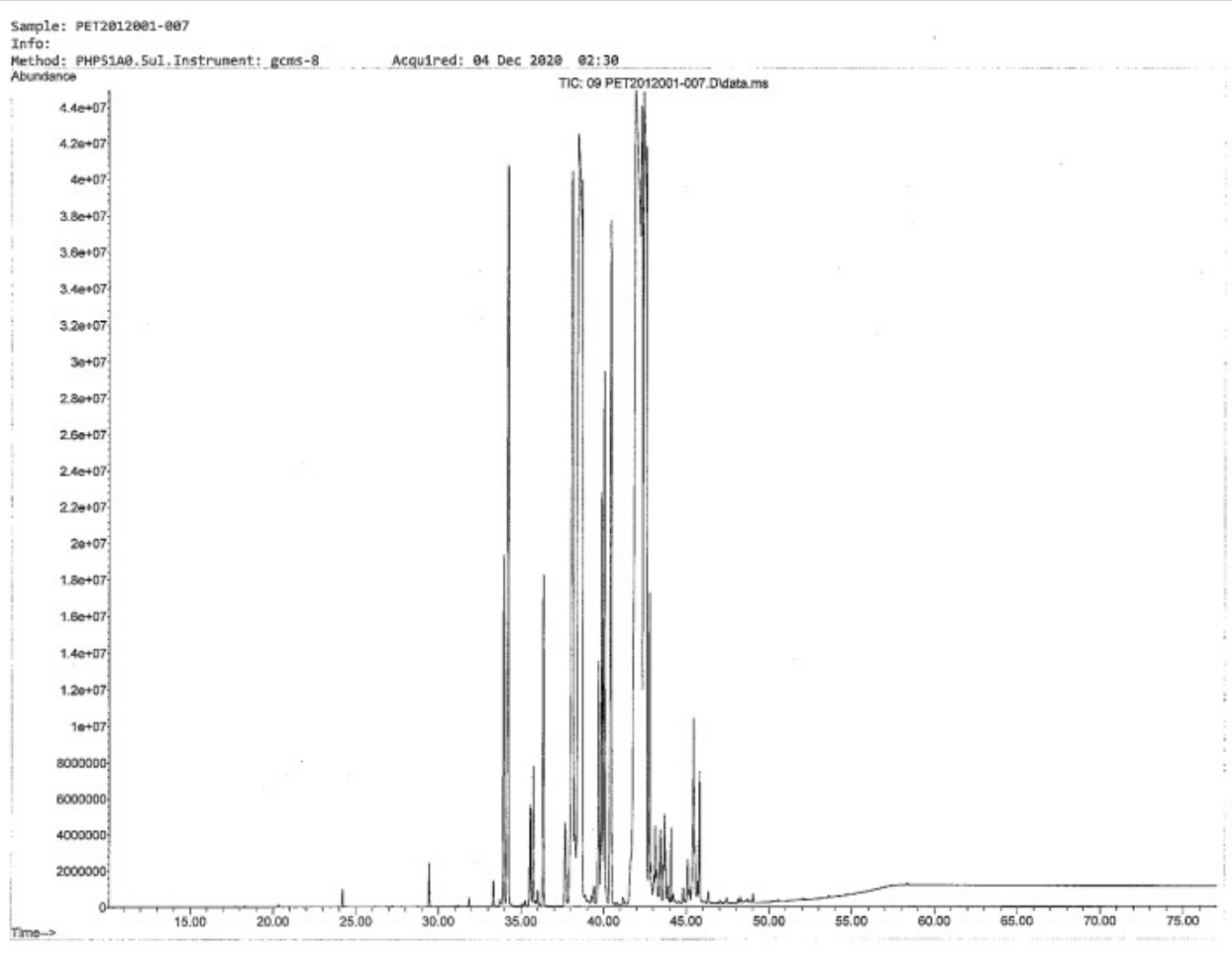
- Carbon range: ~C9 – C28
- UCM is present for the majority of carbon range

Can we tell the difference between renewable diesel and biodiesel using our traditional full scan GCMS screening?

Traditional gas chromatography can be used to confirm and characterize RD samples



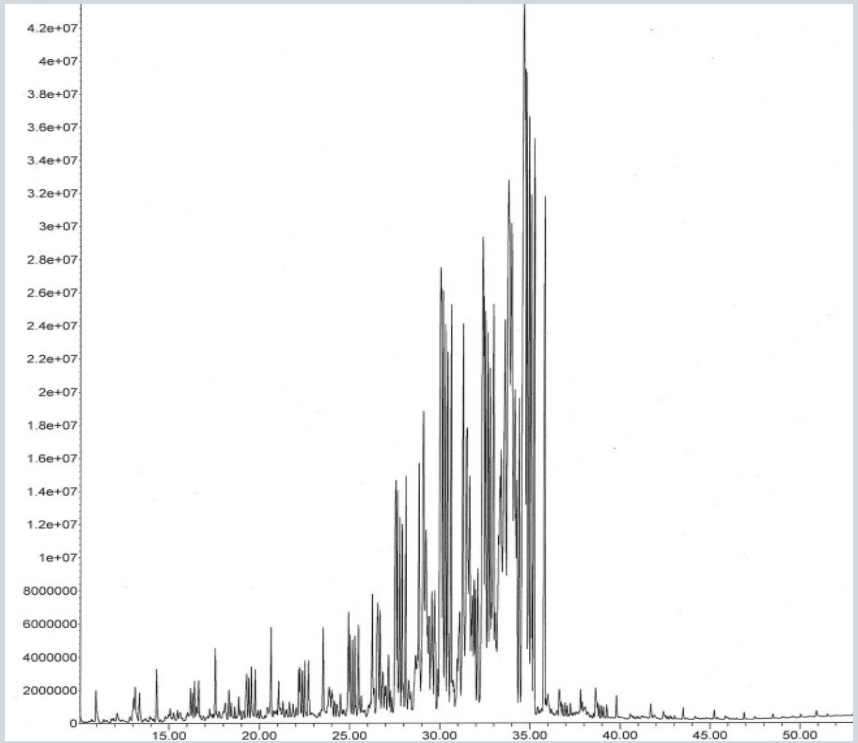
100% Renewable Diesel



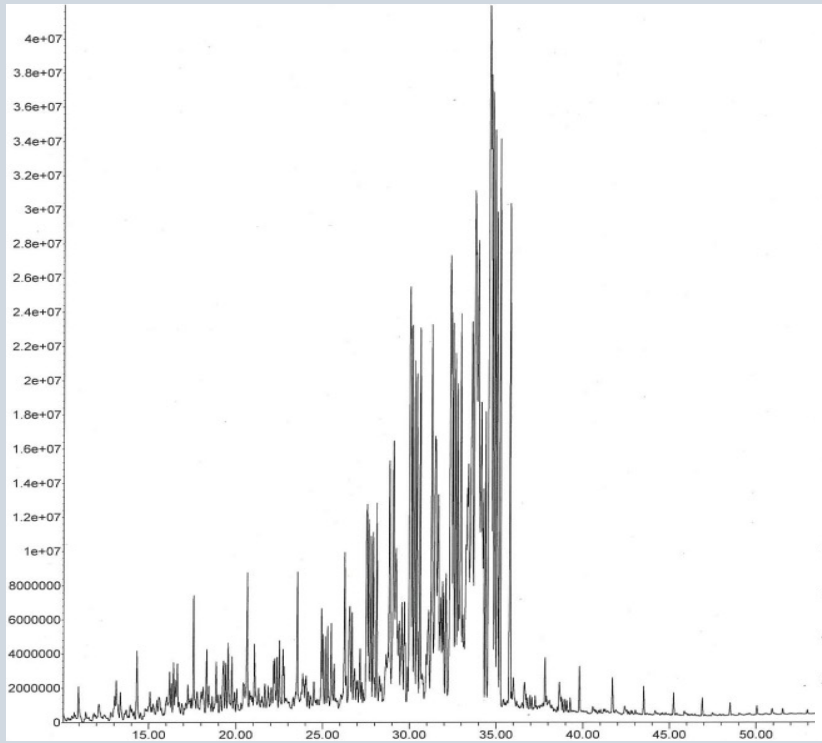
100% Biodiesel

What about mixtures of renewable diesel and petroleum diesel?

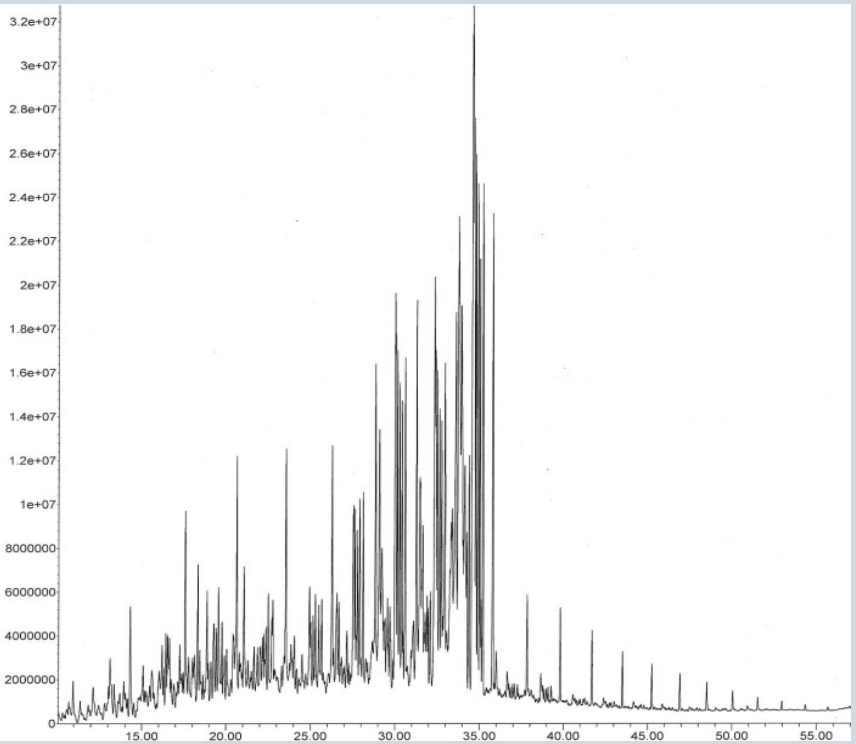
We can tell if there is a mixture between the two qualitatively but can not say what percentage the mixture is petroleum diesel vs renewable diesel



90% Renewable Diesel; 10 % Diesel



75% Renewable Diesel; 25 % Diesel



50% Renewable Diesel; 50 % Diesel

We can not distinguish between “old” and “new” carbon using GCMS

- ^{14}C Isotopic analysis is required to quantitate percentages in a mixture of renewable and petroleum diesel.
- When organisms stops growing, the 14C begins to decline (t1/2 = 5730 years)
- Fossil diesel no longer contains 14C isotope and the portion of new organic material can be detected.
- Accelerator Mass Spectrometry (AMS) or Liquid Scintillation Counting (LCS)

Can we fingerprint renewable diesel?

Fingerprinting Renewable Diesel?

- RD lacks biomarkers and PAHs used for petroleum fingerprinting
- Linear and branched chain alkanes dominate signal
- Mining full scan GCMS data for relevant compound class signatures
  - m/z 85 (alkanes)
  - m/z 83 (alkylcyclohexanes)
  - m/z 123(bicyclanes)
  - m/z 113 (isoparaffins)
  - m/z 98 (common fragment of cyclic alkane)

Next Steps - Fingerprinting Renewable Diesel

- Working to improve chromatographic resolution
- Identify compounds and define diagnostic ratios for sample comparison
- So far, no differences in various samples of RD but need to look at more samples and different manufacturers
- Continue weathering and mixing studies

What about toxicity of renewables?

Acute Aquatic Toxicity of Biodiesel vs Petroleum Diesel

24-HOUR LC50, D. MAGNA (JUVENILE)

FUEL	LC50 (ppm)
Diesel	1.78
B100	4.65
B50	3.29
B20	4.54
B5	1.98

Khan et al 2007

24 – 96 HOUR LC 50, O. MYKISS (FRY)

Table 10. The LC50 values for diesel, B100, B50, B20, and B5.

Time (hr)	Diesel	B100	B20	B50	B5
24	578.13	1073.54	1074.31	NC	780.67
48	350.38	756.68	659.02	491.11	463.30
72	133.52	555.19	541.27	348.32	234.47
96	NC	455.28	497.60	276.71	129.57

Notes: NC = not calculable.

Khan et al 2007

- In general, pure biodiesel is less toxic than petroleum diesel
- Toxicity for blend is not linear with blend percentage
- Different species have different sensitivities (different feedstocks can also change toxicity)
- Increased exposure duration resulted in increased toxicity for rainbow trout
- Lab tests with filtered water-soluble fraction biodiesel show lower toxicity likely due to removal of droplets that can smother
- Little chronic data

Toxicity Data for Neste Renewable Diesel as Listed on SDS

Organism	Acute Toxicity	Chronic Toxicity	Reference
Fish	LL_{50}, 96 hr: >1000 mg/L, WAF (OECD 203)	NA	Neste SDS
Aquatic invertebrate	EL_{50}, 48 hr: >100 mg/L, WAF (OECD 202)	NOEC, 21 days: 1 mg/L LOEC, 21 days: 3.2 mg/L, WAF (OECD 211)	Neste SDS
Aquatic plants	EL_{50}, 72 hr: >100 mg/L, Fish WAF (OECD 201)	NA	Neste SDS
Microorganisms	EC_{50}, 30-180 min: >1000 mg/L,(wastewater sludge) (OECD 209)	NA	Neste SDS
Sediment organisms	NOEC, 10 days: 373 mg/kg; LOEC, 10 days: 1165 mg/kg; LC50, 10 days 1200 mg/kg (OSPAR Protocols, Part A: Sediment Bioassay, 2005)		Neste SDS

Malk et al., 2014 reported no clear toxicity to earthworms (*E. fetida*) when exposed to renewable diesel via soil and no clear toxicity to *Daphnia magna* or bioluminescent bacteria (*V. fischeri)* when exposed to renewable diesel WAF.

Need more studies!!!!!

Toxicity continued….

- Very limited data, need more chronic data for biodiesel
- Need more study on renewable diesel
- Limited data from spills
- Consider physical impacts and DO issues, not just chemical toxicity

Thank you!

Questions?

References:

Malk, V., Tejera, E.B., Simpanen, S., Dahl, M., Makela, R., Hakkinen, J., Kiiski, A., Penttinen, O.P., 2014. NAPL migration and ecotoxicity of conventional and renewable fuels in accidental spill scenarios. Environmental Science Pollution Research 21: 9861-9876.

Nalissa Khan , Mostafa A. Warith & Grace Luk (2007) A Comparison of Acute Toxicity of Biodiesel, Biodiesel Blends, and Diesel on Aquatic Organisms, Journal of the Air & Waste Management Association, 57:3, 286-296, DOI: 10.1080/10473289.2007.10465333

Neste. 2017. Safety Data Sheet, Neste renewable diesel.