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Detection of Crude Oil Contamination in St. Lawrence Estuary Sediments Using n-Alkanes and PAHs Diagnostic and Isotopic Ratios

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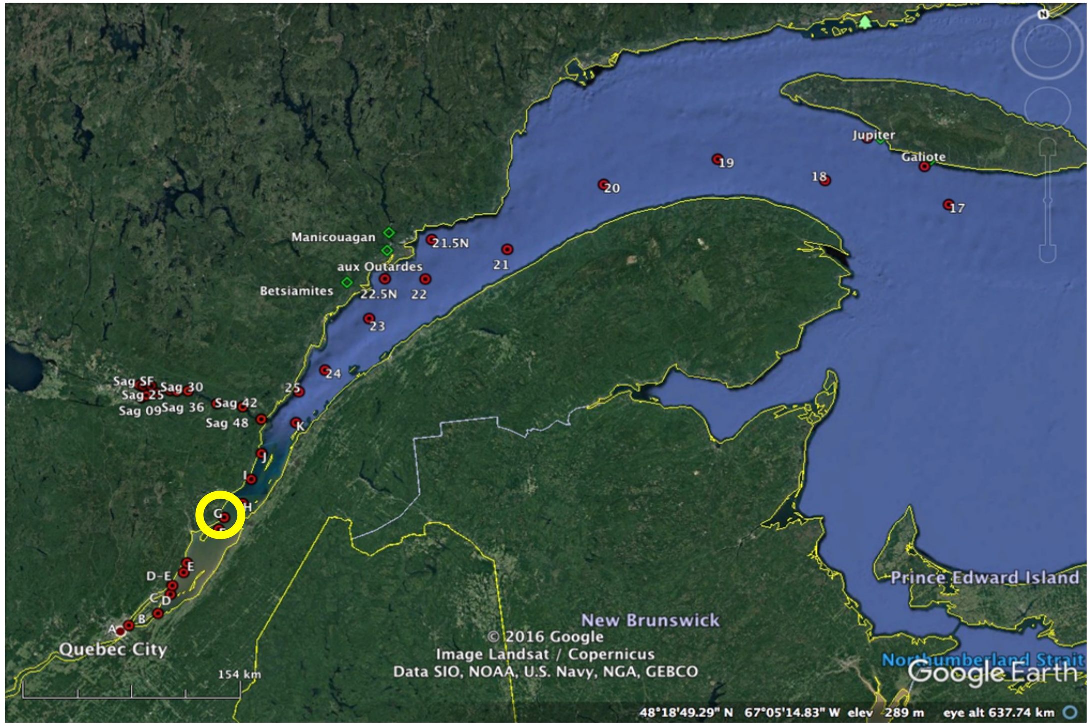
Introduction

St. Lawrence River/Estuary

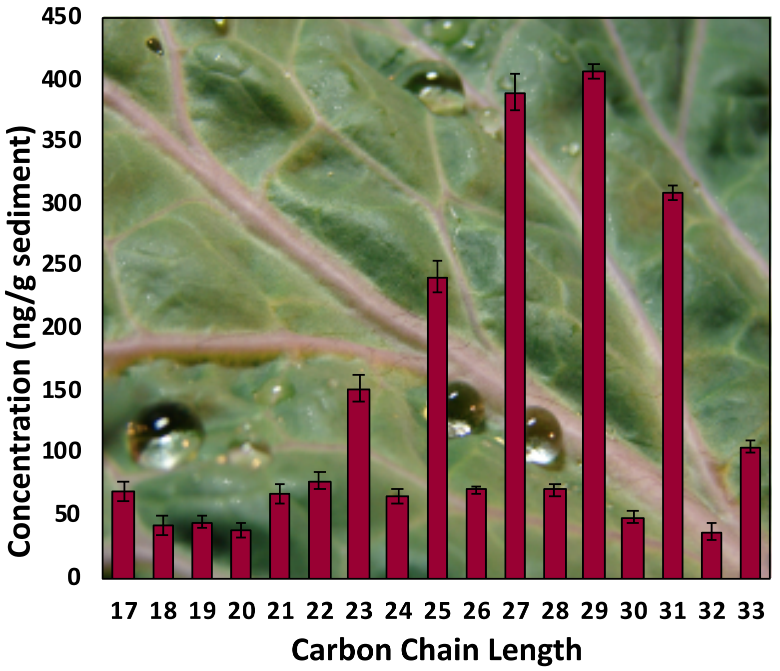
- Large quantities of petroleum hydrocarbons in the form of crude oil and dilbit are transported through the St. Lawrence River, Estuary and Gulf
- Risk of spills from tanker transport will increase in the coming years due to governments interest in transporting petroleum by ships rather than railroads
- There is an increased need for source identification for determining contamination presence and levels

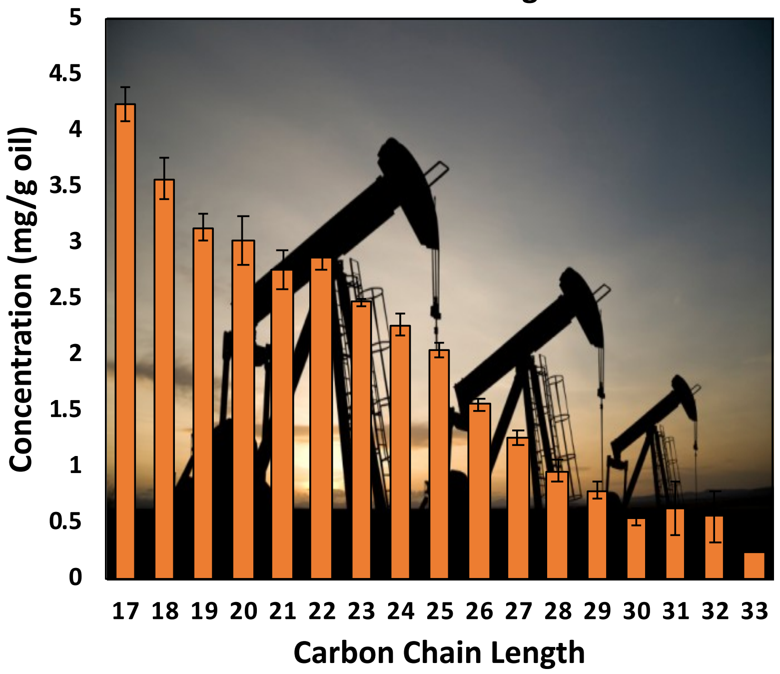


Introduction

Diagnostic Ratios

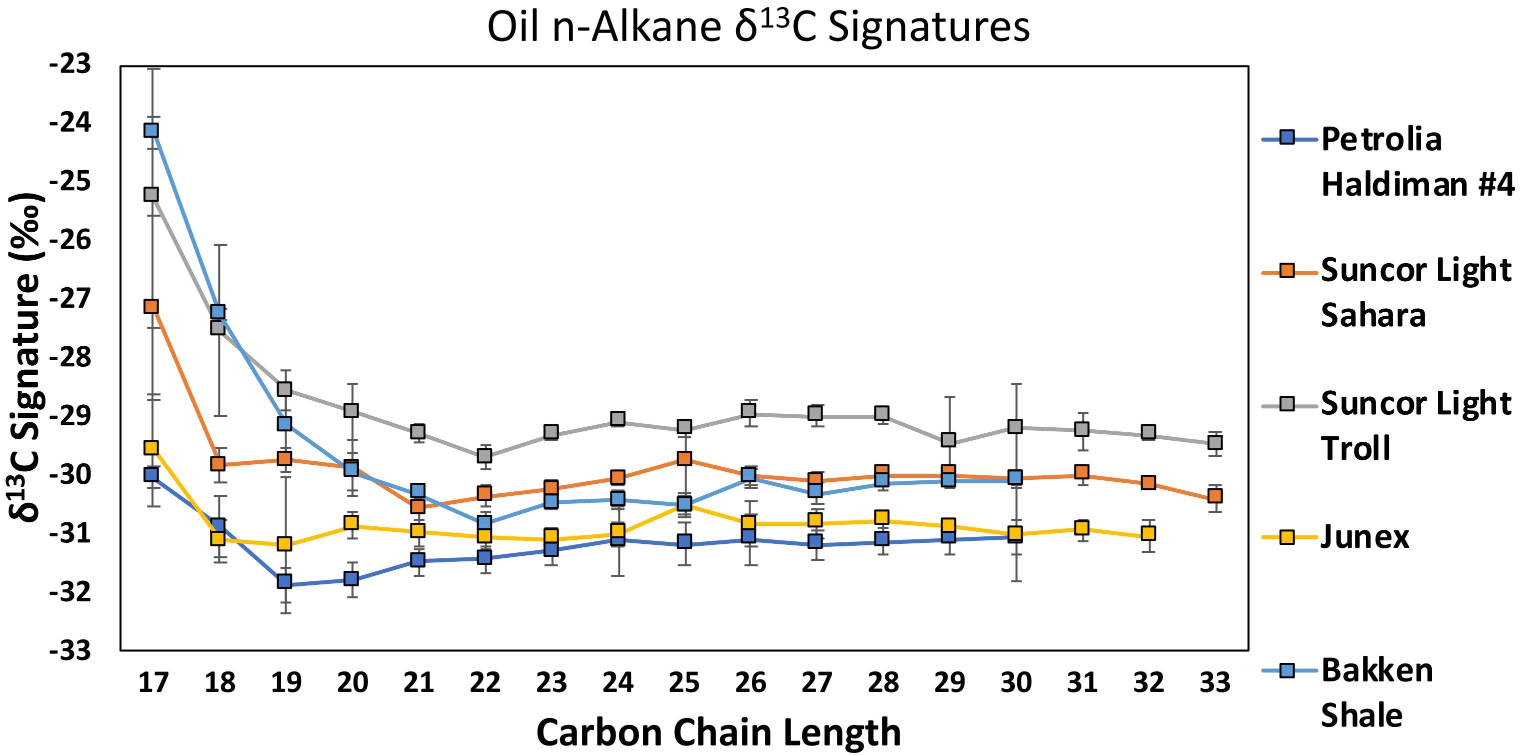
- Straight-chain n-alkanes can originate from natural or petroleum-derived sources
- Polycyclic aromatic hydrocarbons (PAHs) are common environmental pollutants, originating from natural (biomass burning, volcanism, diagenesis) and anthropogenic (fossil fuels, etc.) processes
- Diagnostic ratios have been used for hydrocarbon source identification to differentiate terrestrial from marine and biogenic from petrogenic

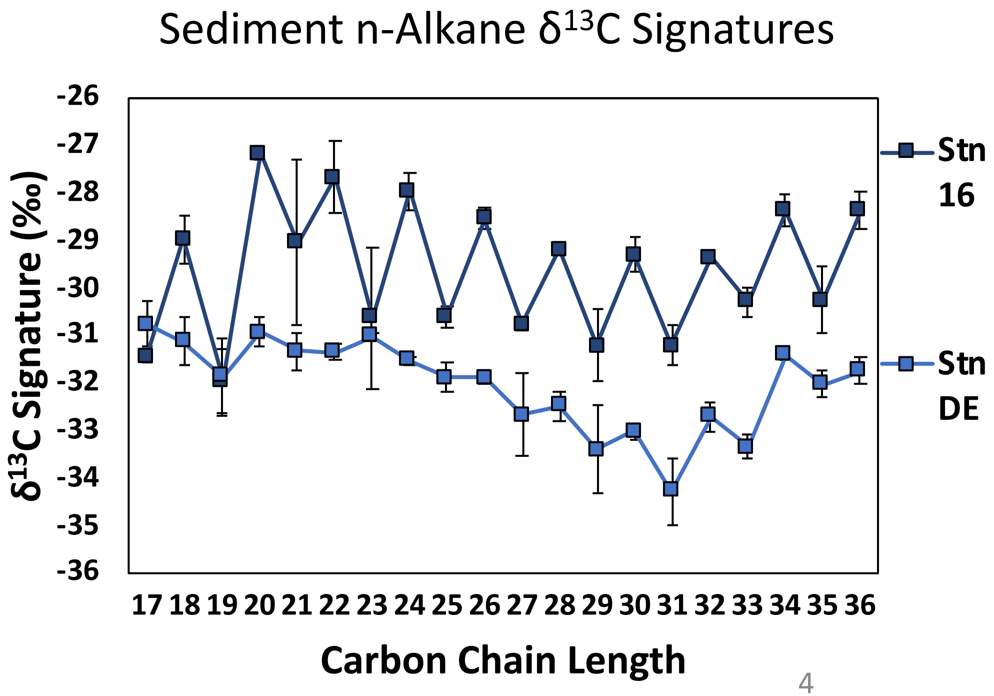




Research Goals

- Evaluate the effectiveness of n-alkane and PAH diagnostic ratios and n-alkane $\delta^{13}C$ signatures in detecting crude oil contamination
- Determine the level of contamination at which a significant difference in the diagnostic ratios and isotopic signatures is detected

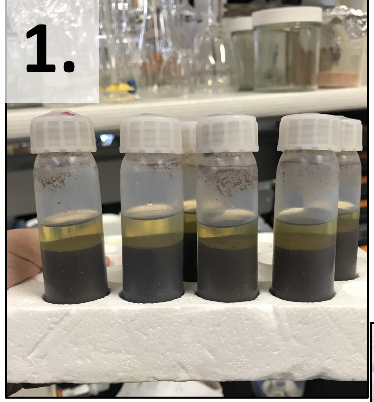


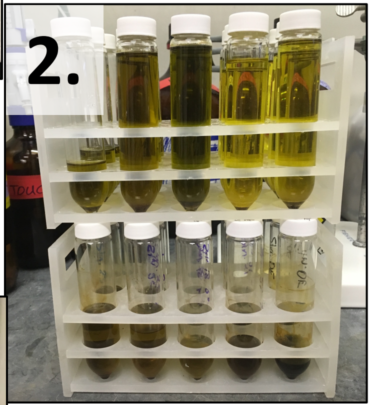


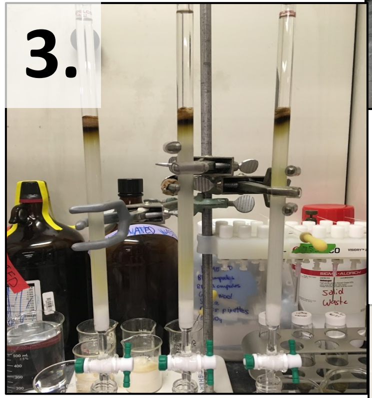
Methods

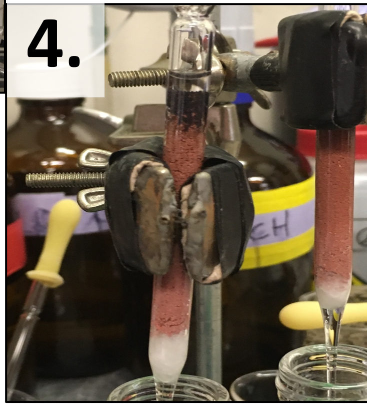
Sample Preparation

1. Extraction of sediment from the St. Lawrence River (Station G) using acetone and hexane, sonicated for 3hrs
2. Liquid-liquid extraction (x3) to separate aqueous and organic phases
3. Silica gel column chromatography of sediment organic phase and crude oil to separate the aliphatic and aromatic fractions
4. Copper column on aliphatic fractions to remove elemental sulphur
5. Quantitation of hydrocarbons in sediment and oil samples using external standards and GC-FID, equalizing of the hydrocarbon concentrations between the two sample types, and then mixed at varying levels (0-100% oil)





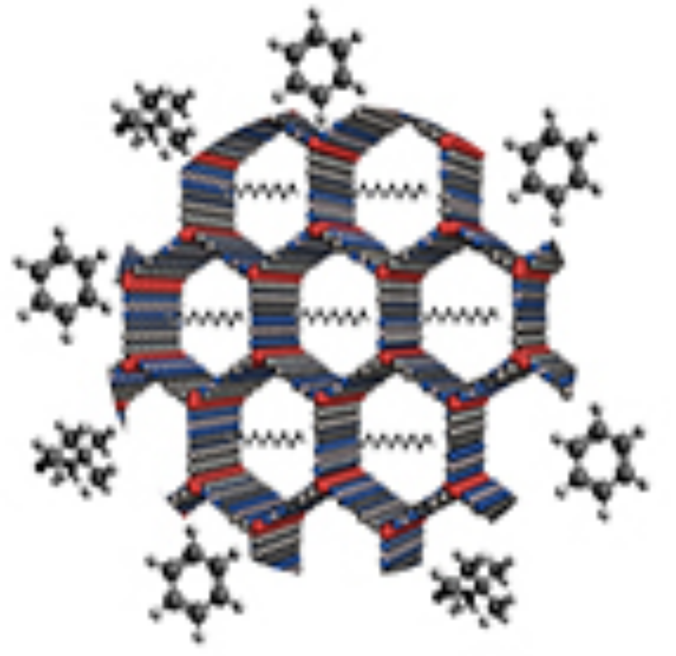


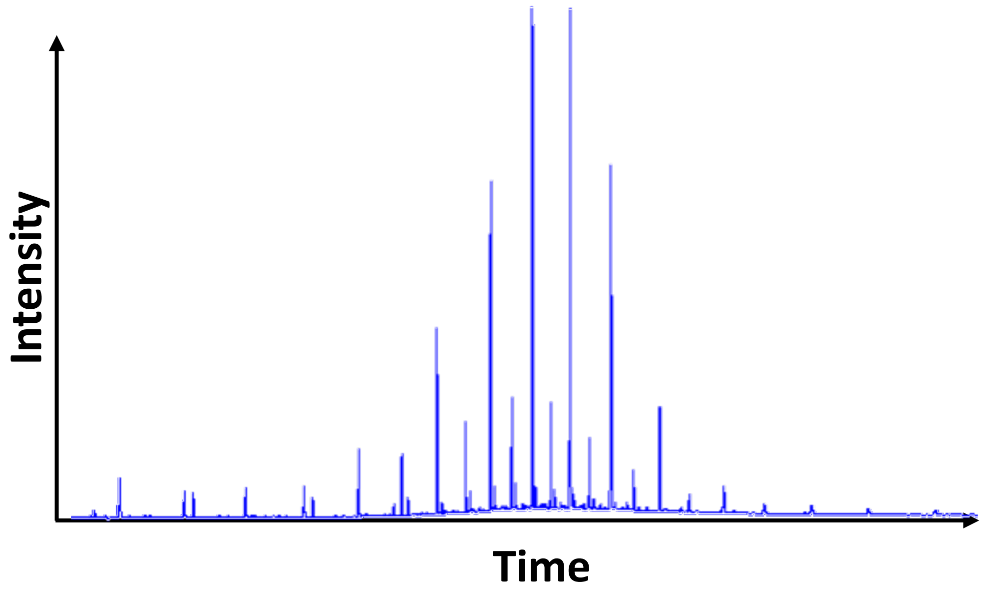


Methods

Analysis

1. Individual compounds in mixed samples were identified using GC-MS and quantified with an external standard
2. Urea adduction was performed on the aliphatic fractions to separated the straight-chained alkanes
3. $\delta^{13}C$ signatures of n-alkanes were measured using GC-IRMS and quantified with certified external standards





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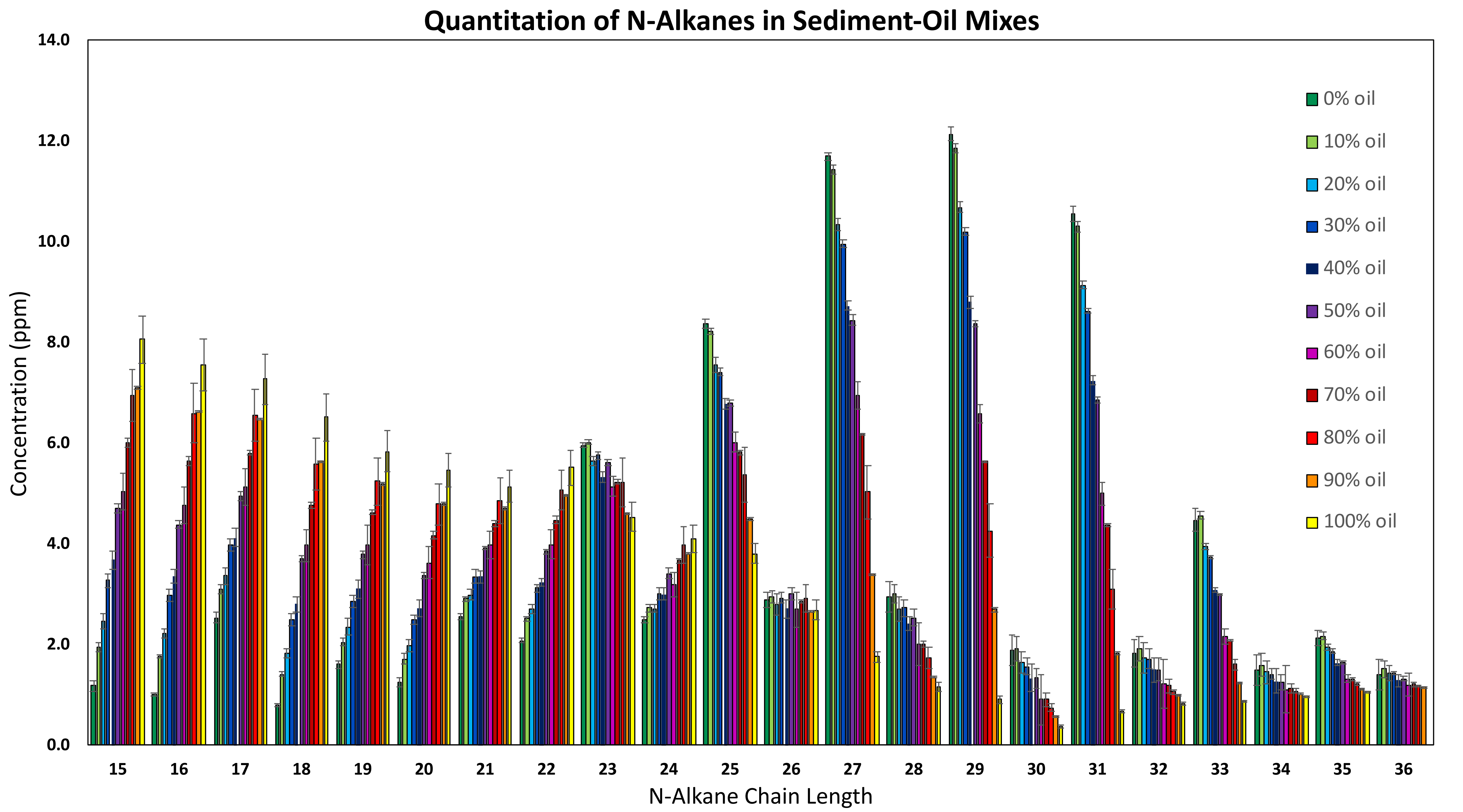
Abbreviations

PAH	Abbr.	PAH	Abbr.	Other	Abbr.
Naphthalene	NP	Benzo(a)anthracene	BaA	Carbon Preference Index	CPI
2-Methylnaphthalene	2-MNP	Chrysene	CHR	Average Chain Length	ACL
1-Methylnaphthalene	1-MNP	Benzo(b)fluoranthene	BbF	Natural n-Alkane Ratio	NAR
Fluorene	FL	Benzo(k)fluoranthene	BkF	Terrestrial Aquatic Ratio	TAR
Phenanthrene	PHE	Benzo(a)pyrene	BaP	Polycyclic Aromatic Hydrocarbons	PAHs
Fluoranthene	FLA	Perylene	PER	Low Molecular Weight	LMW
Retene	RET	Indeno(1,2,3-CD)pyrene	IcdP	Hight Molecular Weight	HMW
Pyrene	PYR	Benzo(g,h,I,)perylene	BghiP	Dilbit	Diluted bitumen



Quantitation of N-Alkanes in Sediment-Oil Mixes
Concentration (ppm)
N-Alkane Chain Length
0% oil
10% oil
20% oil
30% oil
40% oil
50% oil
60% oil
70% oil
80% oil
90% oil
100% oil

Diagnostic Ratios of n-Alkanes

N-Alkanes Ratios:

$$CPI_{23\text{-}33} = \frac{\sum(C_{23}-C_{31})_{odd} + \sum(C_{25}-C_{33})_{odd}}{2\bullet\sum(C_{24}-C_{32})_{even}}$$

$$ACL = \frac{(25\bullet C_{25})+(27\bullet C_{27})+(29\bullet C_{29})+(31\bullet C_{31})+(33\bullet C_{33})}{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}$$

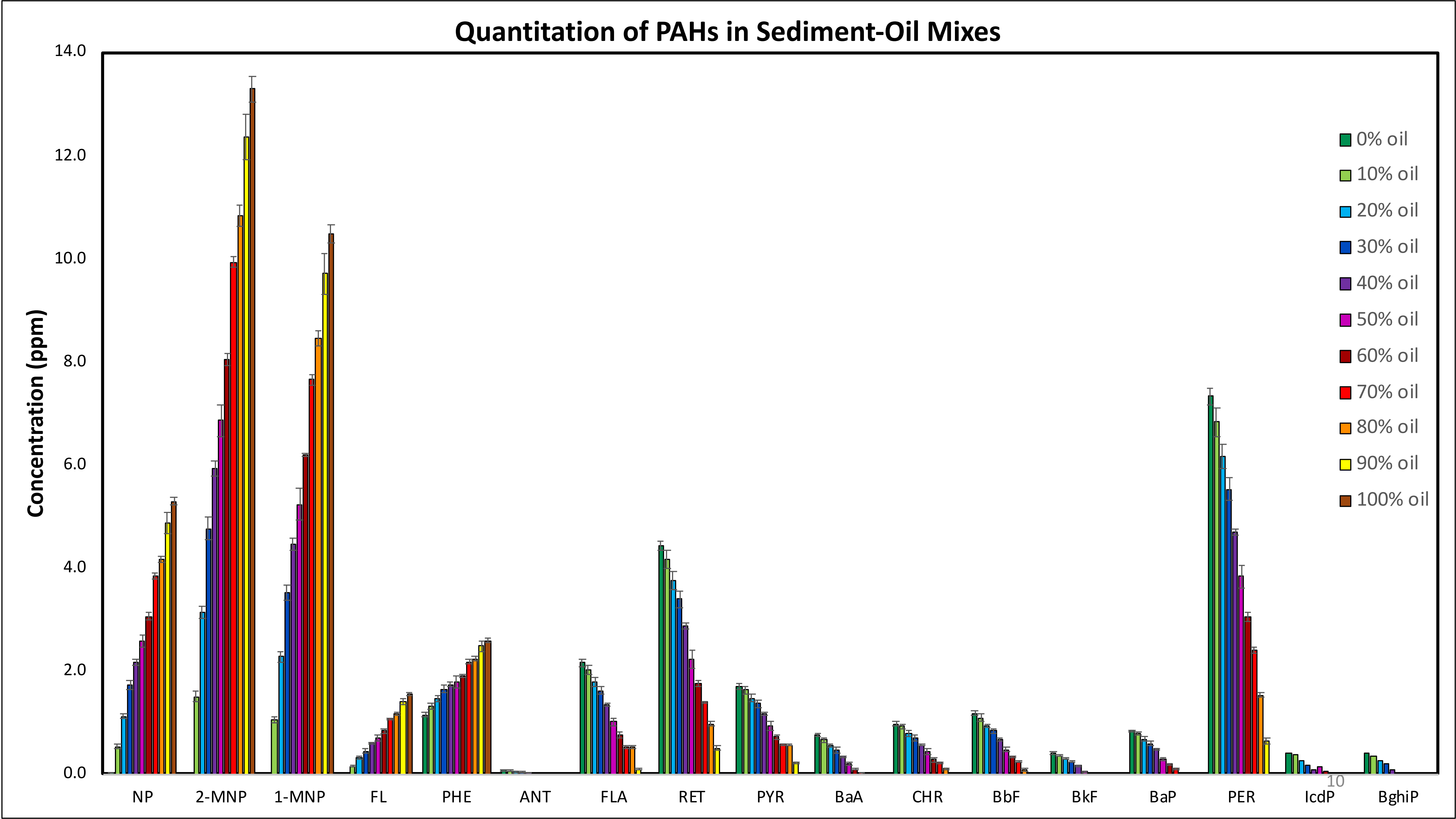
$$NAR = \frac{\sum(C_{19}-C_{32})-2\bullet\sum(C_{19}-C_{32})_{even}}{\sum(C_{19}-C_{32})}$$

$$TAR = \frac{C_{27}+C_{29}+C_{31}}{C_{15}+C_{17}+C_{19}}$$

Legend
Undefined
Marine or petrogenic
Petrogenic
Terrestrial
Aquatic

Diagnostic Ratio	%Oil	Value	Diagnostic Ratio	%Oil	Value
CPI(25-33)	0%	4.26	ACL	0%	28.62
	10%	4.08		10%	28.64
	20%	4.04		20%	28.60
	30%	3.84		30%	28.56
	40%	3.72		40%	28.49
	50%	3.41		50%	28.45
	60%	3.30		60%	28.28
	70%	2.89		70%	28.23
	80%	2.45		80%	28.03
	90%	1.93		90%	27.82
	100%	1.13		100%	27.29
NAR	0%	0.55	TAR	0%	6.46
	10%	0.52		10%	4.74
	20%	0.50		20%	3.69
	30%	0.47		30%	2.84
	40%	0.44		40%	2.27
	50%	0.39		50%	1.76
	60%	0.36		60%	1.31
	70%	0.31		70%	0.99
	80%	0.24		80%	0.66
	90%	0.17		90%	0.42
	100%	0.06		100%	0.16

El Nemr, A.; Moneer, A. A.; Ragab, S.; El Sikaily, A. *Egypt. J. Aquat. Res.* **2016**, *42* (2), 121–131.



Quantitation of PAHs in Sediment-Oil Mixes
Concentration (ppm)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
NP
2-MNP
1-MNP
FL
PHE
ANT
FLA
RET
PYR
BaA
CHR
BbF
BkF
BaP
PER
IcdP
BghiP
0% oil
10% oil
20% oil
30% oil
40% oil
50% oil
60% oil
70% oil
80% oil
90% oil
100% oil

Diagnostic Ratios of PAHs

PAH Ratios:

$$\frac{\sum \mathrm{LMW}\ (\leq 3\ \text{rings})}{\sum \mathrm{HMW}\ (\geq 4\ \text{rings})} \qquad \frac{\mathrm{FLA}}{\mathrm{FLA+PYR}}$$

$$\frac{2\mathrm{-MNP}}{\mathrm{PHE}} \qquad \frac{\mathrm{BbF}}{\mathrm{BkF}}$$

$$\frac{\mathrm{BaA}}{\mathrm{BaA+CHR}} \qquad \frac{\mathrm{RET}}{\mathrm{RET+CHR}}$$

Diagnostic Ratio	%Oil	Value	Interpretation	Diagnostic Ratio	%Oil	Value	Interpretation
lmw/hmw	0%	0.35	Pyrogenic	fla/fla+pyr	0%	0.56	Grass, wood, coal burn.
	10%	0.58			10%	0.55	
	20%	0.92			20%	0.55	
	30%	1.33	Petrogenic		30%	0.54	
	40%	1.86			40%	0.54	
	50%	2.63			50%	0.52	
	60%	4.00			60%	0.51	
	70%	6.42			70%	0.47	Fossil fuel combustion
	80%	10.00			80%	0.48	
	90%	33.42			90%	0.28	Petrogenic
	100%	N/A			100%	N/A	
2mnp/phe	0%	N/A		bbf/bkf	0%	2.87	Aluminum smelters
	10%	1.14	Undefined		10%	3.11	Undefined
	20%	2.16	Fossil fuels		20%	3.21	
	30%	2.88			30%	3.51	
	40%	3.41			40%	4.12	
	50%	3.87			50%	11.18	
	60%	4.23			60%	N/A	
	70%	4.56			70%		
	80%	4.85			80%		
	90%	4.98			90%		
	100%	5.13			100%		
baa/baa+chr	0%	0.43	Combustion/ Vehicle emisssion	ret/ret+chr	0%	0.82	Undefined
	10%	0.42			10%	0.82	
	20%	0.42			20%	0.83	
	30%	0.39			30%	0.83	
	40%	0.37			40%	0.84	
	50%	0.32	Coal combustion		50%	0.84	
	60%	0.26			60%	0.86	
	70%	0.08	Petrogenic		70%	0.87	
	80%	N/A			80%	0.91	Wood burning
	90%				90%	N/A	
	100%				100%		

Tobiszewski, M.; Namieśnik, J. *Environ. Pollut.* **2012**, *162*, 110–119.
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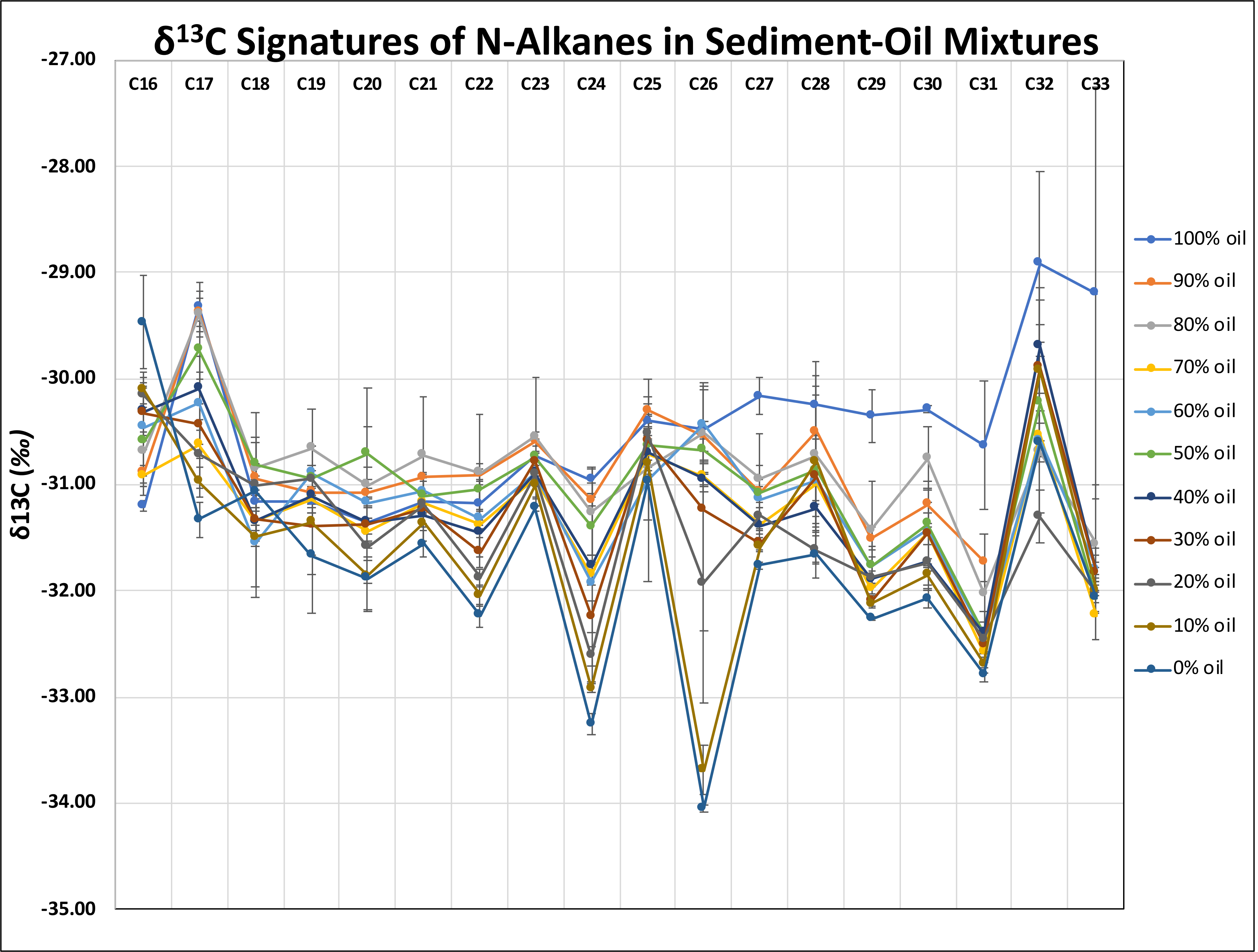
Yan, B.; Abrajano, T. A.; Bopp, R. F.; Chaky, D. A.; Benedict, L. A.; Chillrud, S. N. *Environ. Sci. Technol.* **2005**, *39* (18), 7012–7019.



- While this first run shows promise for using isotope signatures to differentiate natural and petroleum-based hydrocarbons (e.g. C22 and C24), the difference in $\delta^{13}C$ signature is not significant enough to tell, since Station G is likely somewhat contaminated, and the 100% oil replicates show a wide spread.

Conclusions and Future Work

- Diagnostic ratios detect a difference in hydrocarbon composition starting at 30% contamination, demonstrating that they are not discerning enough to determine the extent of crude oil contamination in sediments
- The isotope portion of this experiment needs to be rerun with a more marine, less contaminated sediment (e.g. Station 16)
- The molecular and isotopic fingerprints, as well as temporal variations of sedimentary hydrocarbons along the St. Lawrence River, Estuary and Gulf can be mapped to track future changes due to contamination

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