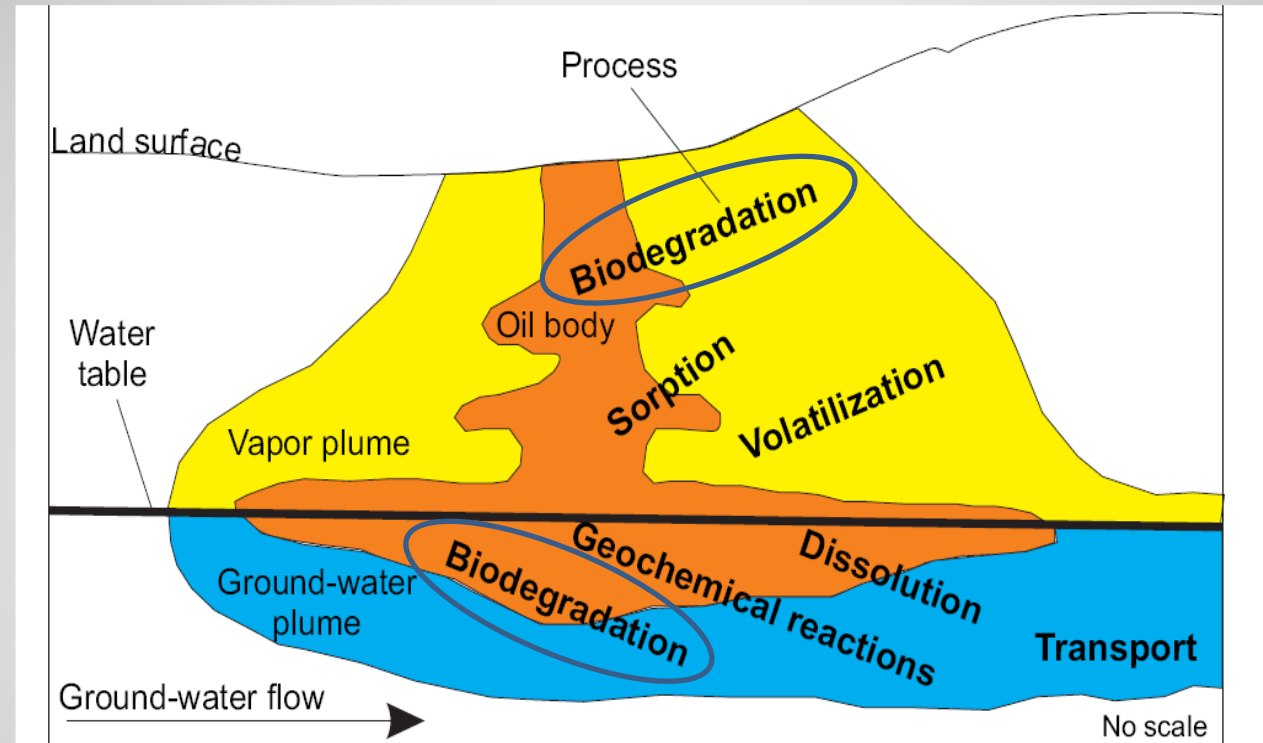


# FATE AND BIOEFFECTS OF OXYHYDROCARBONS AT A CRUDE OIL SPILL SITE



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# Methods Issues: Total Petroleum Hydrocarbons in the diesel range (TPHd) is required at oil spill sites

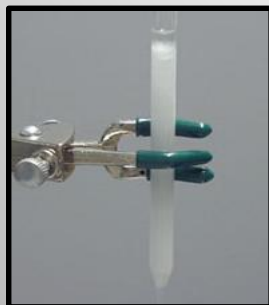
## Silica Gel clean-up has been proposed

### TPHd Method

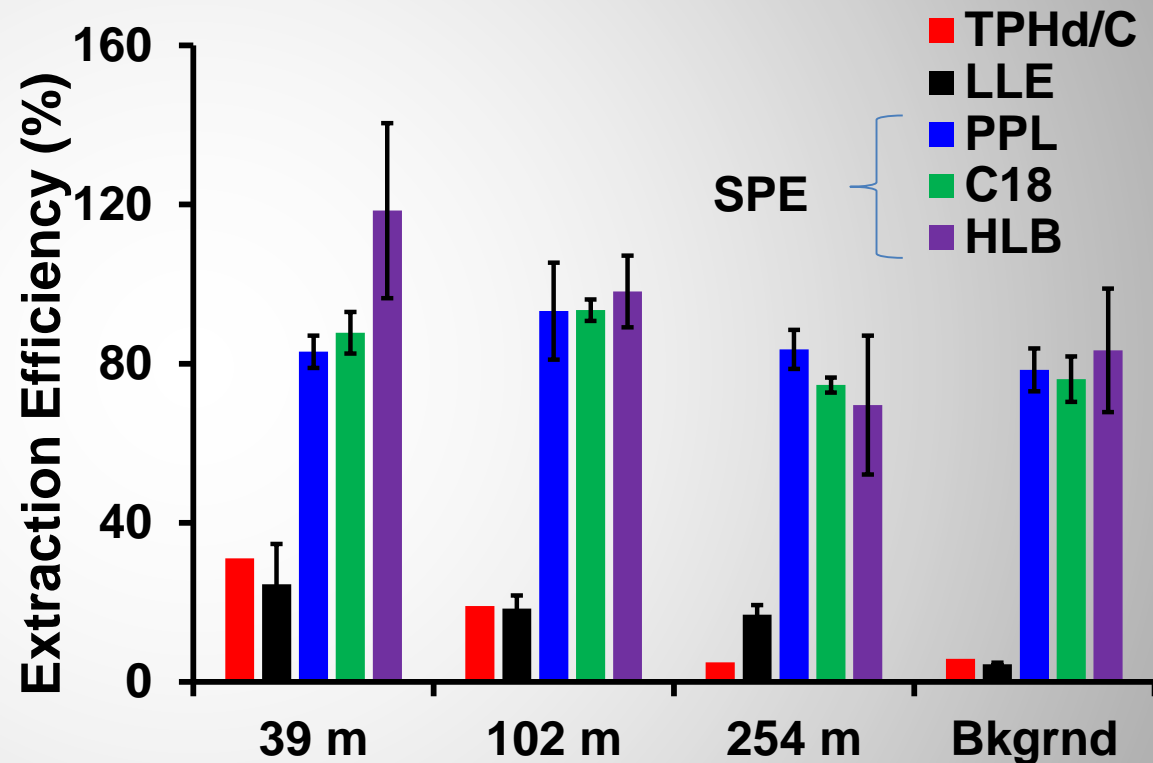
- Liquid-liquid extraction (LLE) with methylene chloride or hexane
- GC-FID chromatographic response between  $n\text{-C}_{10}$  and  $n\text{-C}_{28}$

### Silica Gel Clean-up

- Removes the polar transformation products
- Leaving the true hydrocarbons

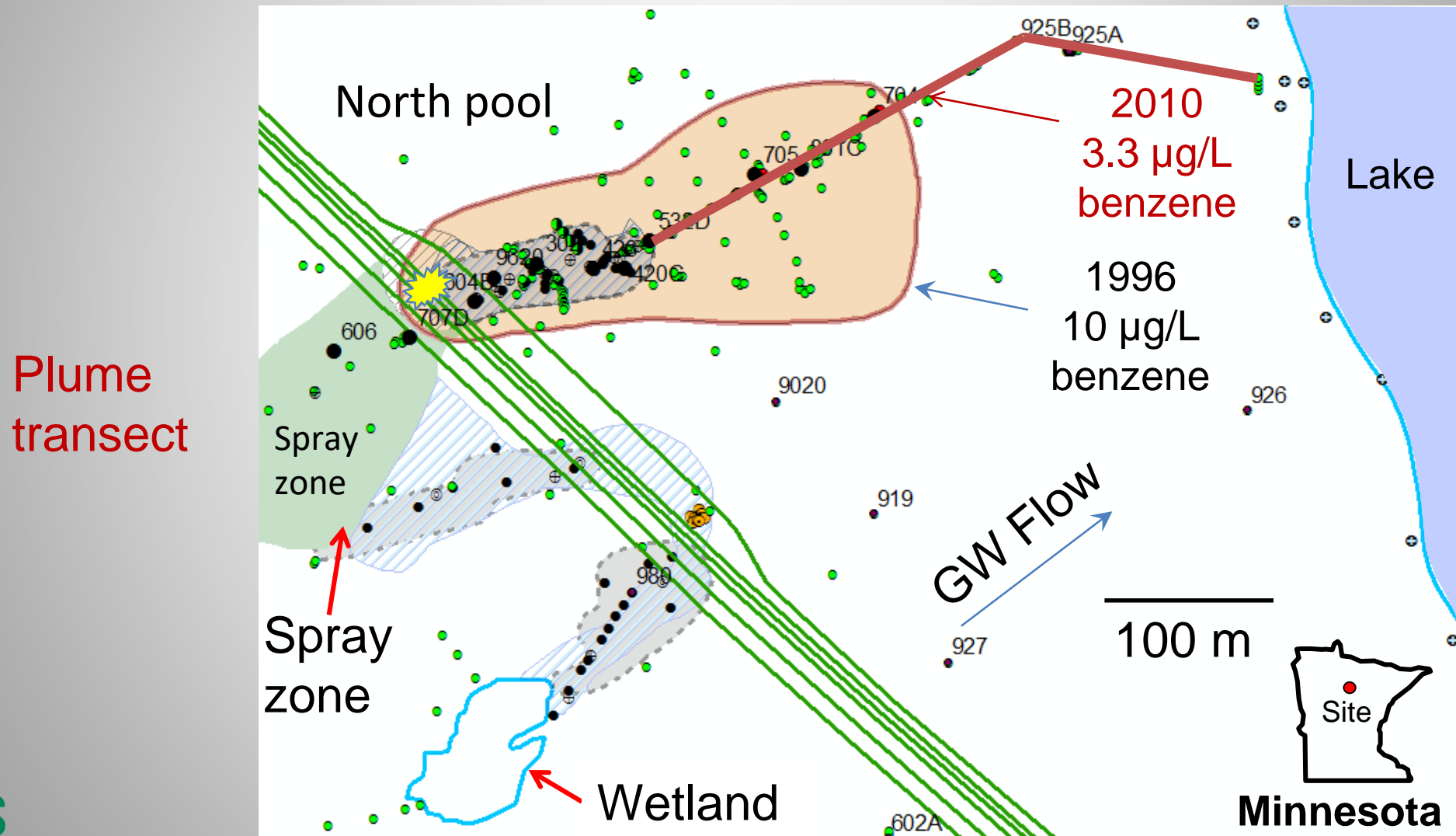


Silica gel column



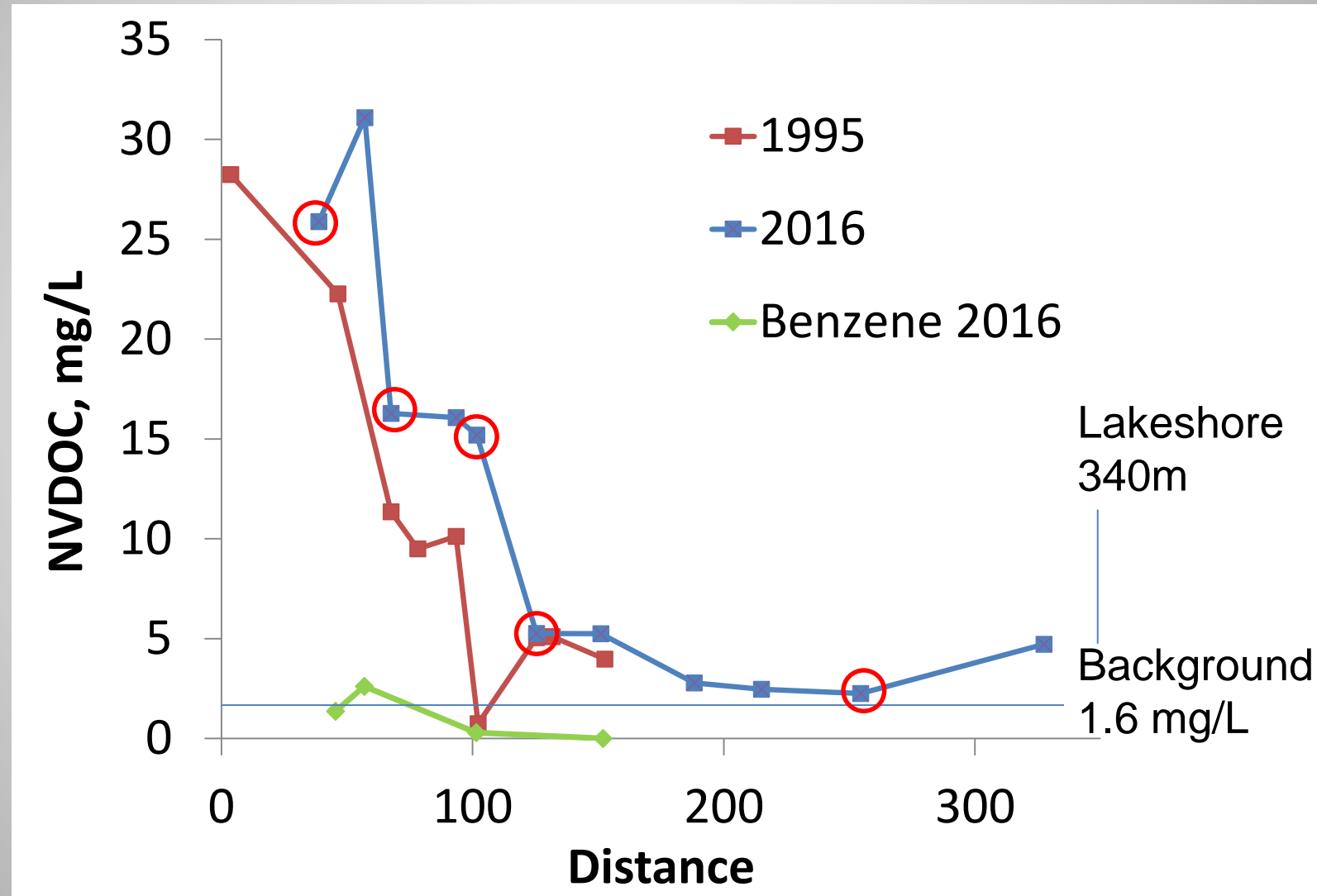
Zito et al., 2019

1979 pipeline rupture spilled 10,500 barrels light crude onto an unconfined sand and gravel aquifer



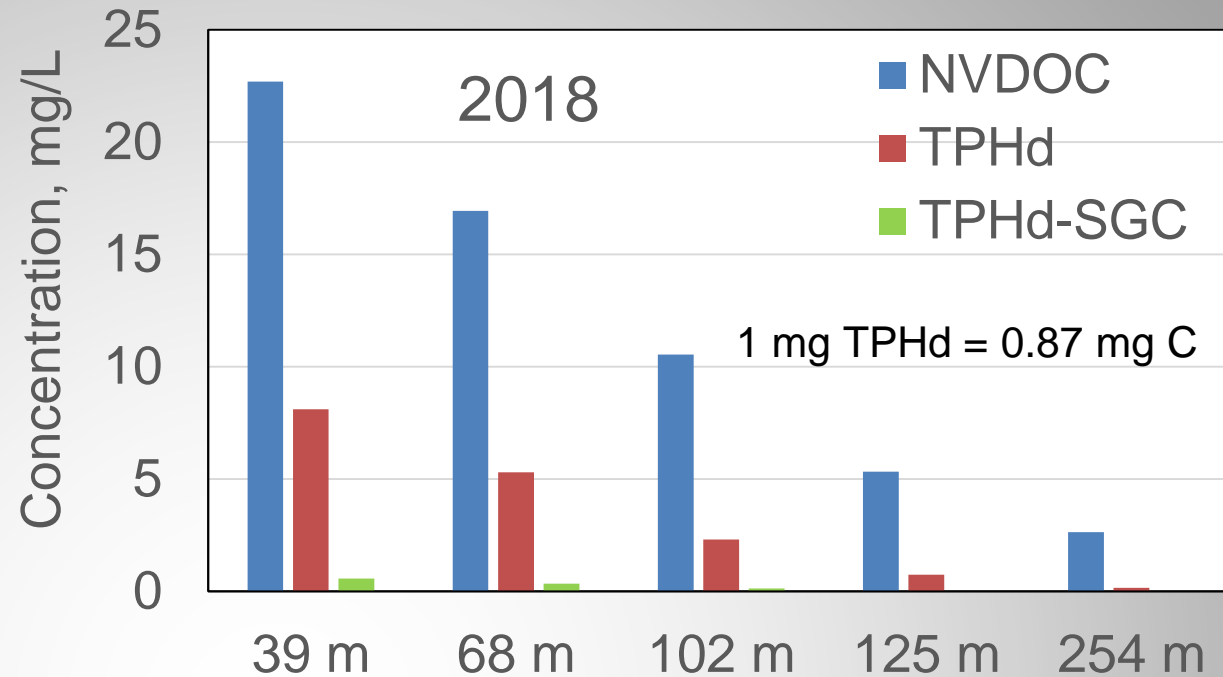
# Nonvolatile dissolved organic carbon (NVDOC) dominates the plume

The front advanced ~1 m/year in 1995-2016 with ~3 mg/L residual

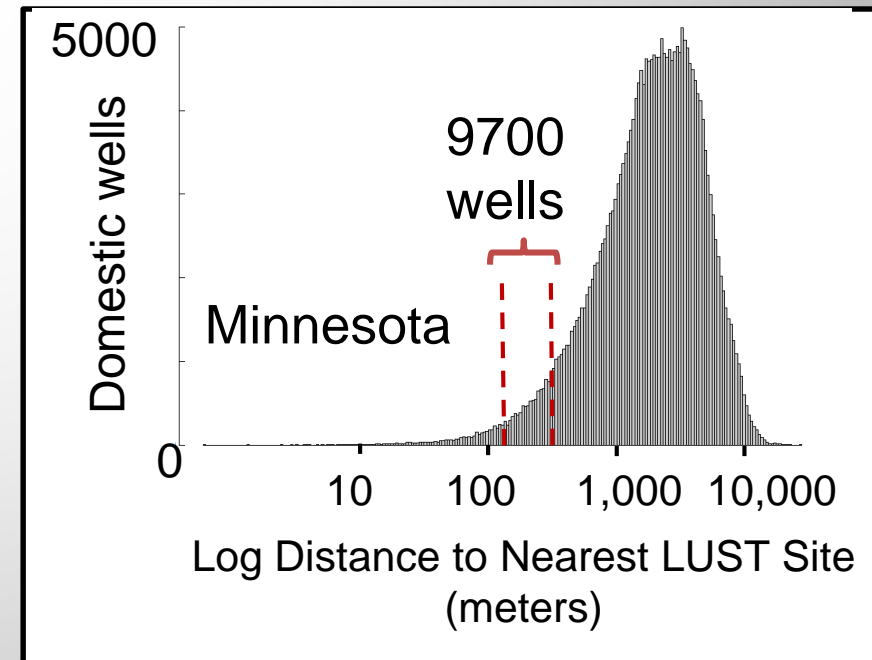


# Implications for regulatory method

- NVDOC is always much higher than TPHd.
- Hydrocarbons isolated with Silica Gel Cleanup (SGC) are a tiny fraction

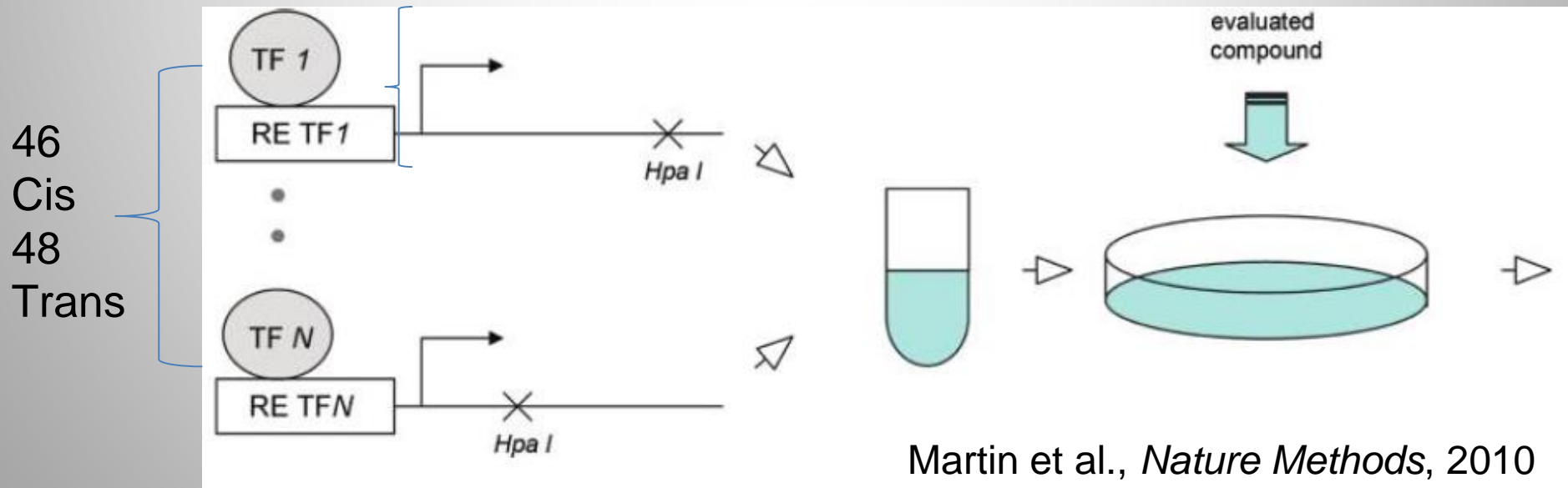


150 – 340 m,  
metabolites  
detected, but  
no TPHd or  
BTEX



# Bioeffects screening

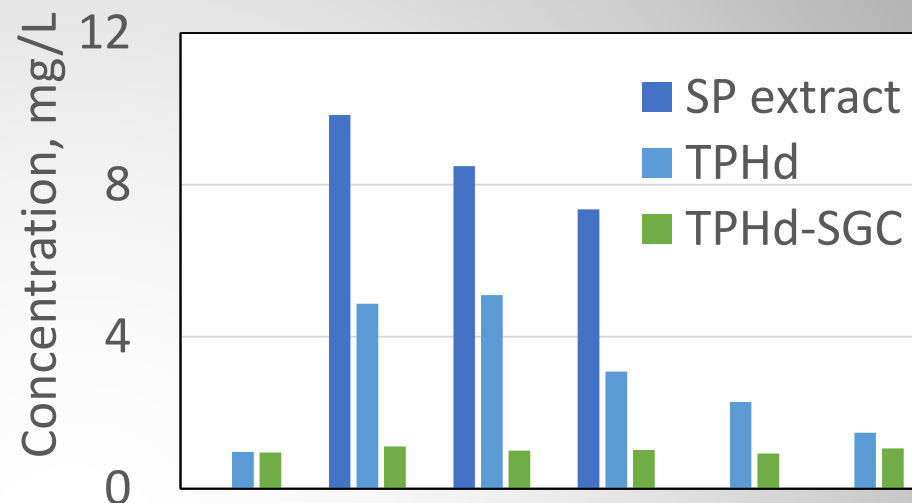
- Human liver cells are used as a model of liver metabolism
- The method detects activities of 94 proteins that regulate genes (transcription factors)
- Activities are reported as the ratio of induction values to unexposed cells.



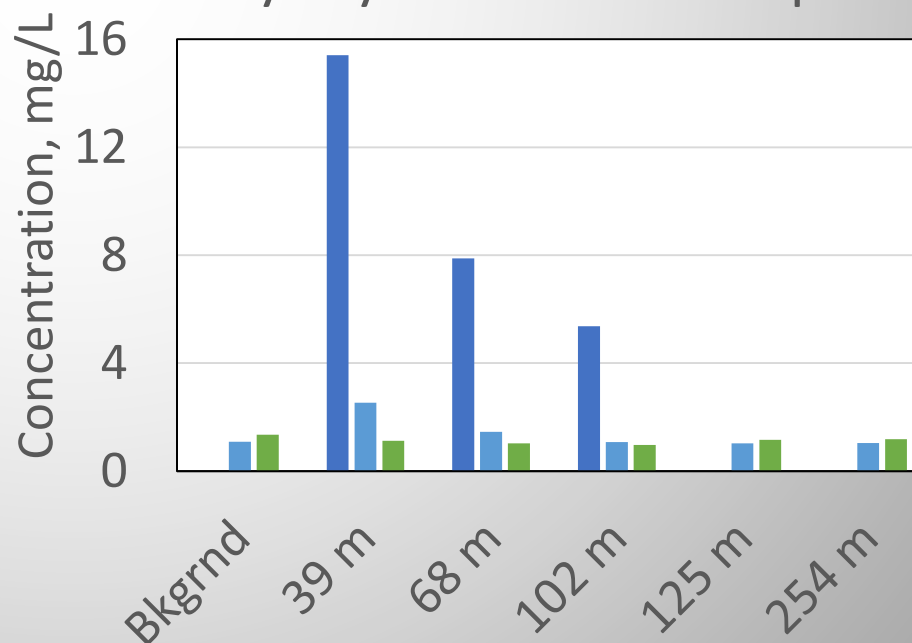
# Bioeffects screening results

- Non polar fraction from SGC is like background
- In both cases much of the response is in the fraction extracted with HLB

Pregnane xenobiotic receptor



Aryl Hydrocarbon Receptor





# What we knew about the NVDOC in 2016

- Most of the DOC mass consists of nonvolatile organic acids (NVOA's) formed as partial oxidation products of the crude oil constituents.
- The NVOA's downgradient from the oil body differ from the naturally occurring DOC.
- >14,000 compounds in plume, >12,000 in background

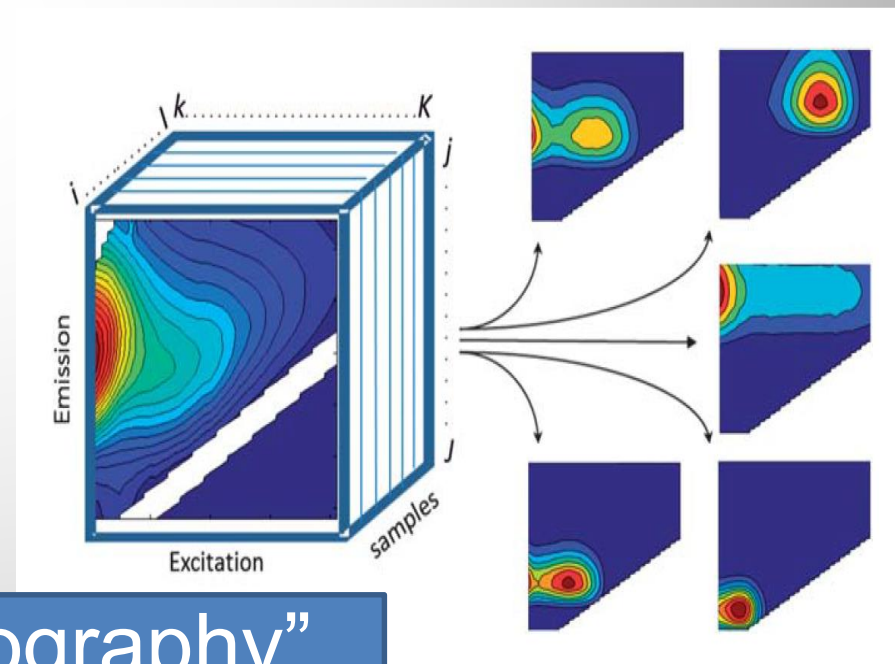
Bond types of  
most polar  
fraction from  
 $^{13}\text{C}$  NMR

<i>ketone, quinone</i>	7%
<i>ester, amide carboxyl</i>	16%
<i>alcohol, ether, carbohydrate</i>	17%
<i>aliphatic</i>	36%
<i>aromatic,olefinic</i>	16%



# Approach 1: Excitation Emission Matrix (EEM) Spectra and Parallel Factor (PARAFAC) Analysis

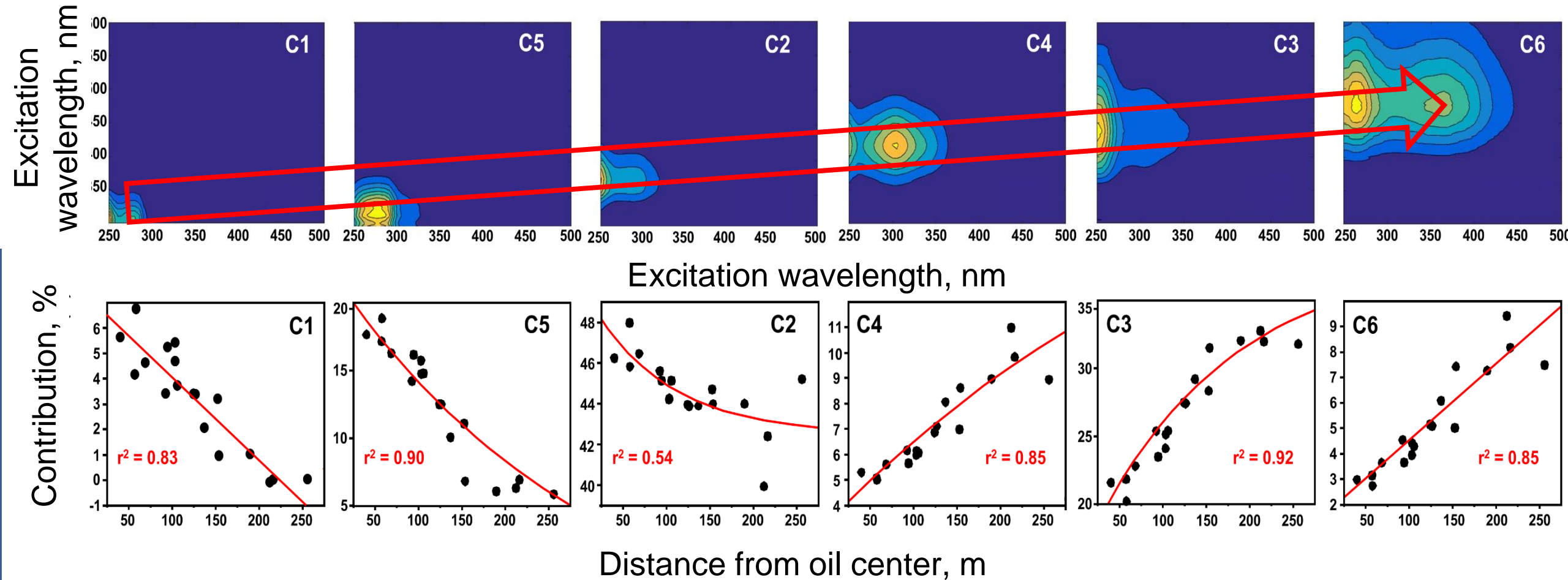
- EEMs – Measures properties of chromophoric dissolved organic matter via optical responses of absorbance and fluorescence.
- PARAFAC - Decomposes EEMs into underlying chemical components.



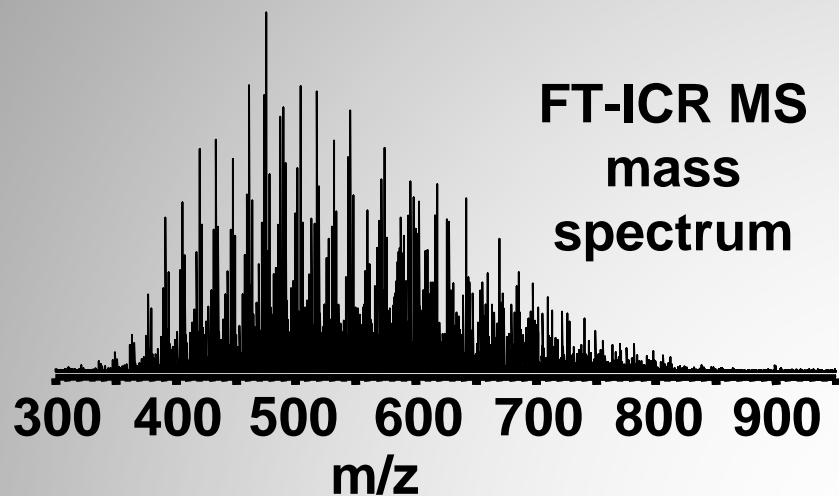
“Mathematical Chromatography”

Stedmon and Wünsch <urbw@aqua.dtu.dk>

# The contribution of each factor changes continuously with distance from the source



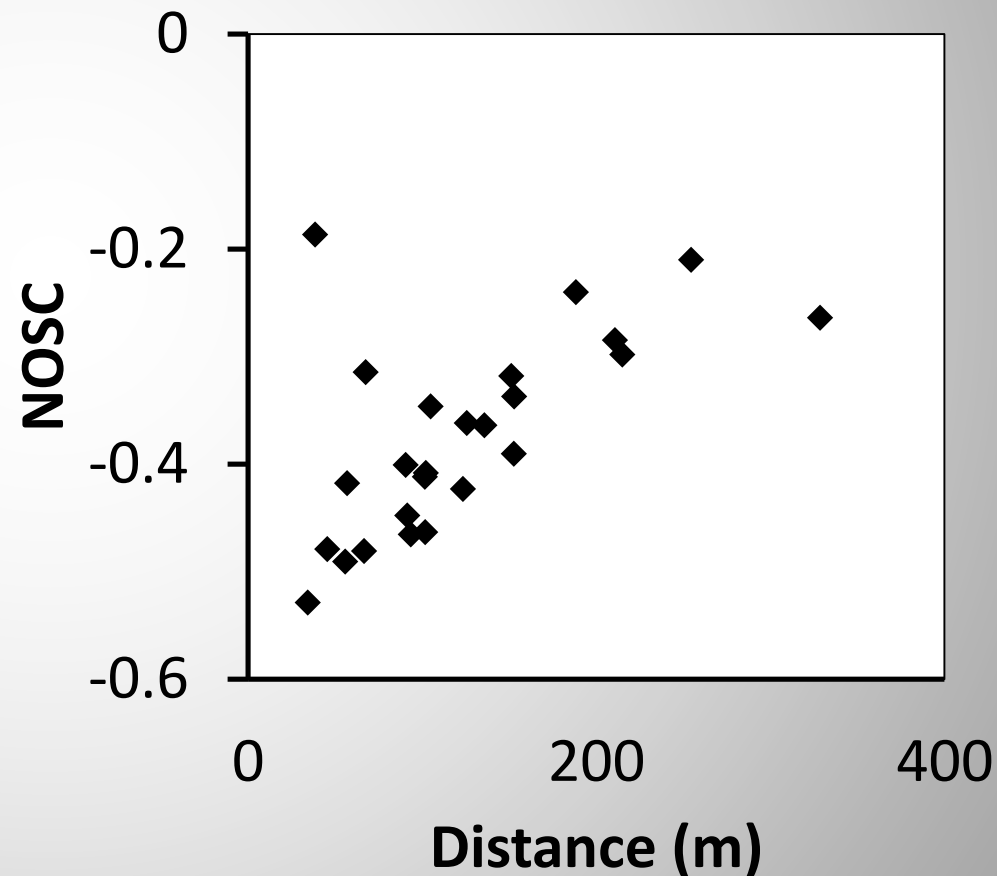
# Approach 2: Ultrahigh Resolution MS



↓

m/z	Formula
475.45202	C <sub>32</sub> H <sub>59</sub> O <sub>2</sub>
475.41553	C <sub>31</sub> H <sub>55</sub> O <sub>3</sub>
475.39455	C <sub>34</sub> H <sub>51</sub> O <sub>1</sub>
475.36155	C <sub>30</sub> H <sub>51</sub> S <sub>1</sub> O <sub>2</sub>
475.30406	C <sub>32</sub> H <sub>43</sub> S <sub>1</sub> O <sub>3</sub>

NOSC (Nominal oxidation state carbon)  
=  $4 - [(4c + h - 3n - 2o - 2s)/c]$  where:  
h=H(+1), c=C(+4), s=S(-2),  
o=O(-2), n=N(-3)



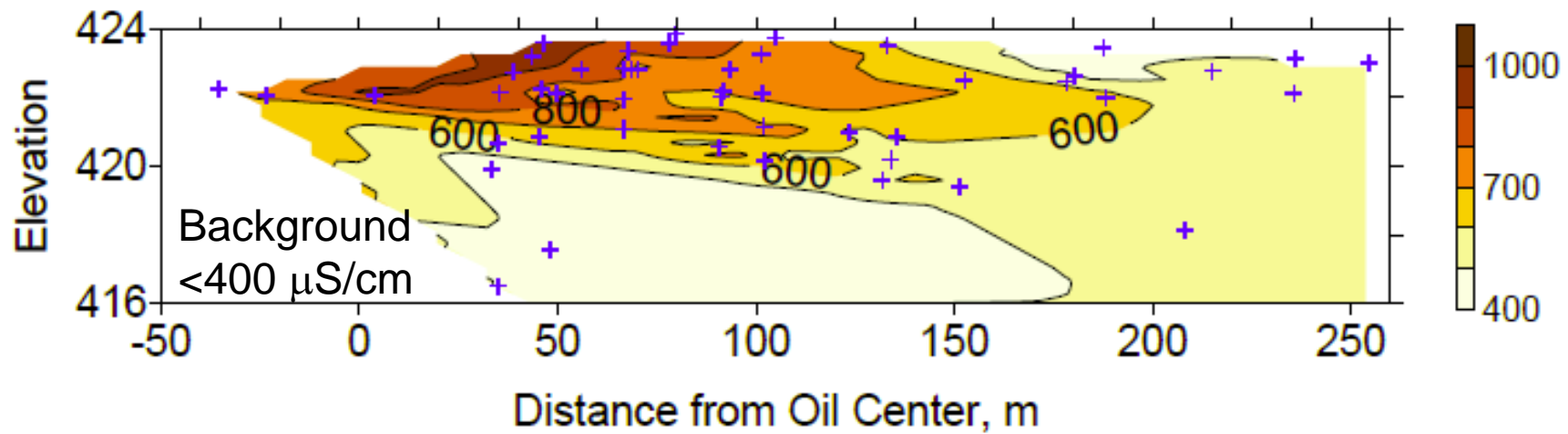
## Approach 4: Geophysical Survey of Lake

- Electromagnetic induction (EMI) to detect variations in SpC
- Ground penetrating radar (GPR)
- conducted from kayaks paddled in several loops around the lake, producing several linear km of data
- Vertical profiles of SpC measured with a YSI Proplusconductivity/temperature sensor driven through the organic sediments at 0.5 m depth increments

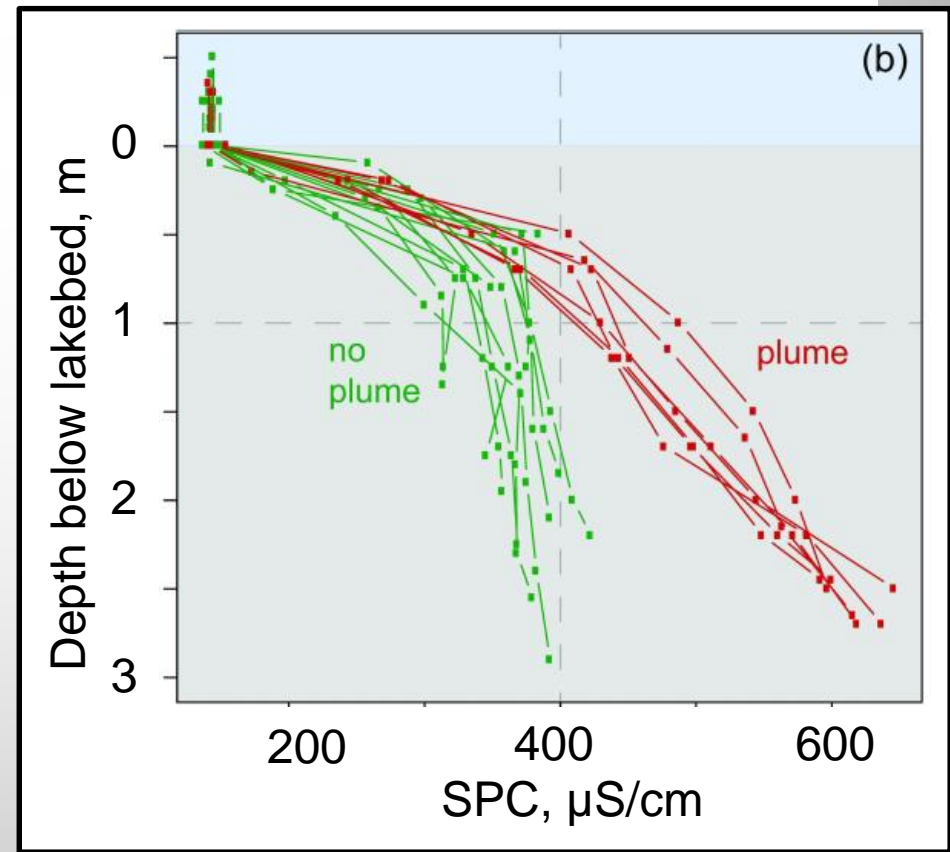


Terry et al., Geophysics, 2019



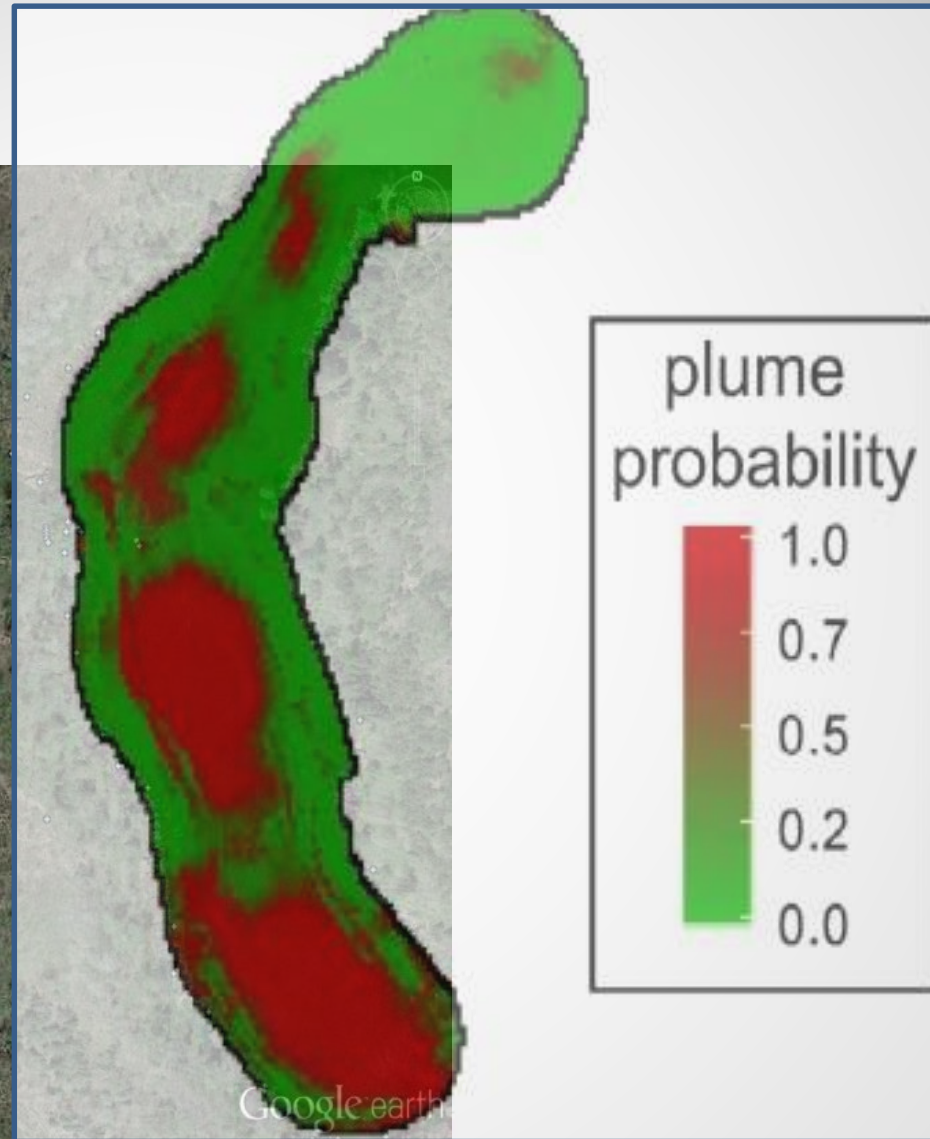
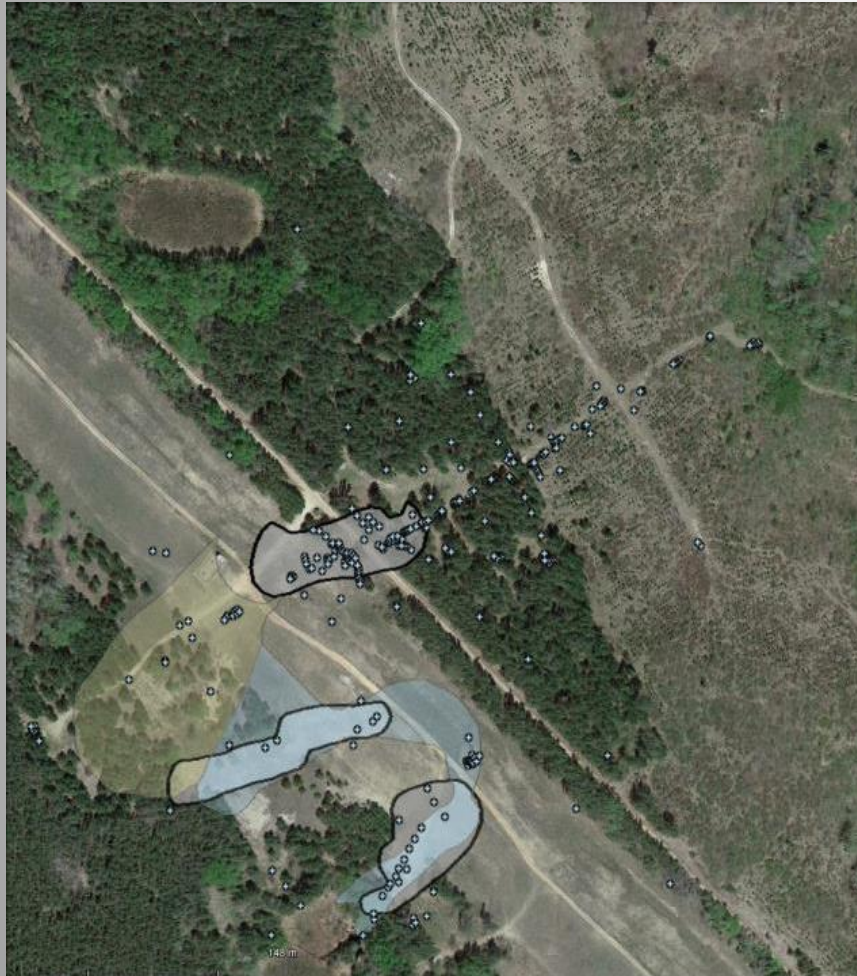


Specific  
conductance is high  
in the plume  
making it a cheap  
natural tracer



Interpreted  
conductance data  
suggest 3 plumes

June, 2018



# Conclusions

- Required analyses at hydrocarbon sites underestimate polar transformation products
- A crude oil research site has an expanding plume of transformation products discharging to a lake 340 m downgradient
- Optical and high resolution mass spectrometry show progressive oxidation with selective preservation of a refractory component.
- Cell assays show that the transformation products should be assessed for toxicity.



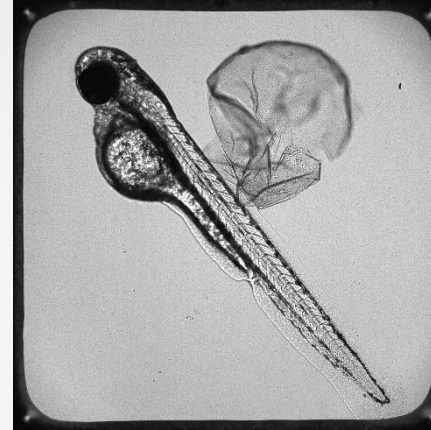
# Work in Progress

- Bioscreening:  
Developmental stage *in vivo* assays

- Chemistry:  
Solid phase NMR and black carbon analyses

- Implications:  
Refined fuel sites  
Minnesota

Funding:  
American Petroleum Institute  
USGS Toxics Substances  
Hydrology Program



Questions?