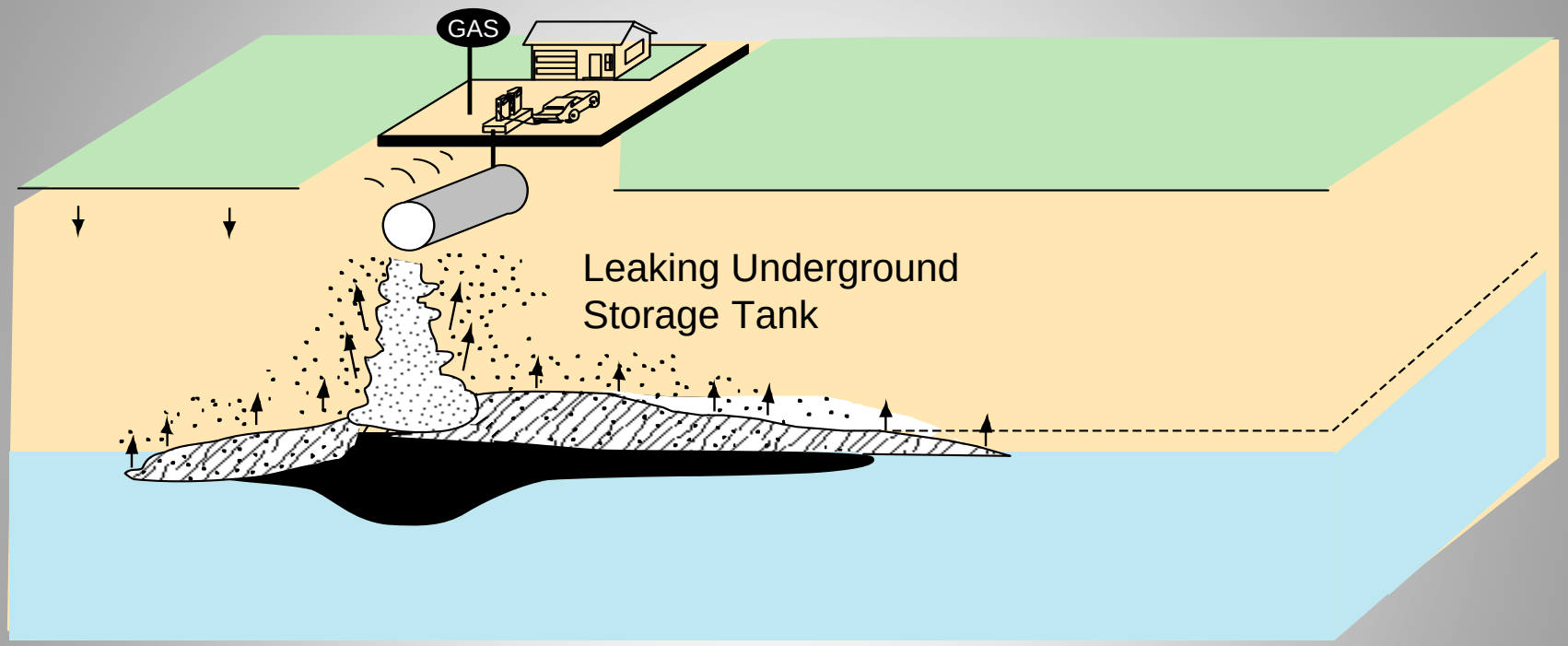
The Legacy of Spilled Oil and Fuel in Groundwater: Source Zone Persistence and Plume Growth



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Outline of Talk

- How many legacy sites are there?
- Potential issues from crude oil study
  - –Source zone longevity
  - –Groundwater plume growth
- Ongoing studies
  - –Plume fate
  - –Oil degradation rate (poster)
  - –Plume toxicity (poster)

Leaking Underground Storage Tank

http://www.epa.gov/reg5rcra/wptdiv/r5lust/index.htm

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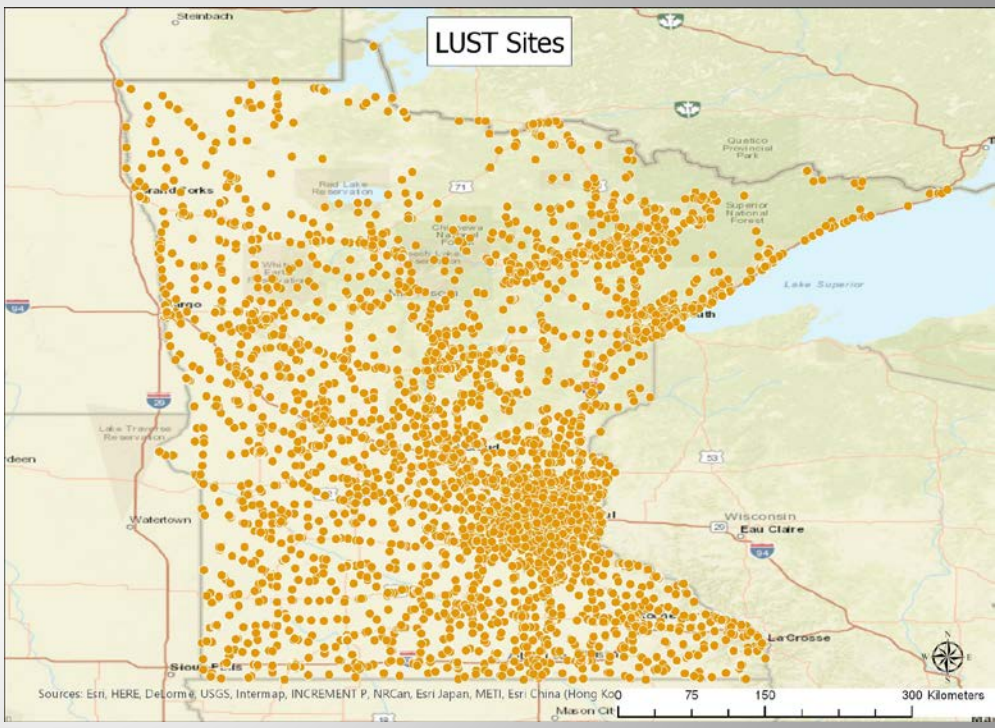
LUST = Leaking Underground Storage Tanks

- 535,320 releases nationwide
- Risk-Based Corrective Action for cleanup
- MN 19,044 LUST Sites, including open and closed
- MN 8,360 (~44%) sites (both open and closed) are marked as having contaminant remaining*



*based on the best readily available information, may represent a minimum.

MN Source: Remediation sites, including leak sites, https://www.pca.state.mn.us/waste/petroleum-tanks-and-leaks-site-search

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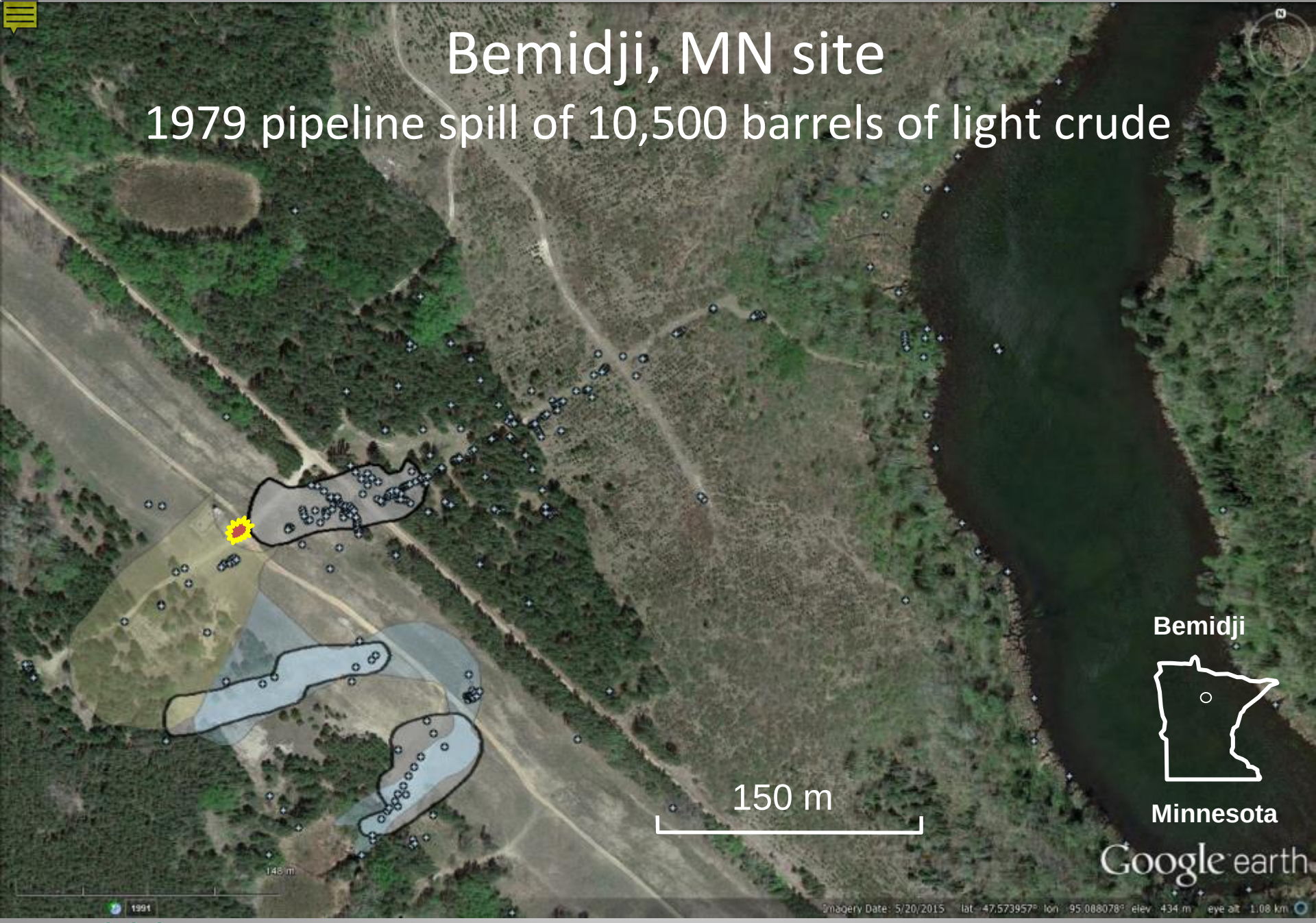
Bemidji, MN site

1979 pipeline spill of 10,500 barrels of light crude



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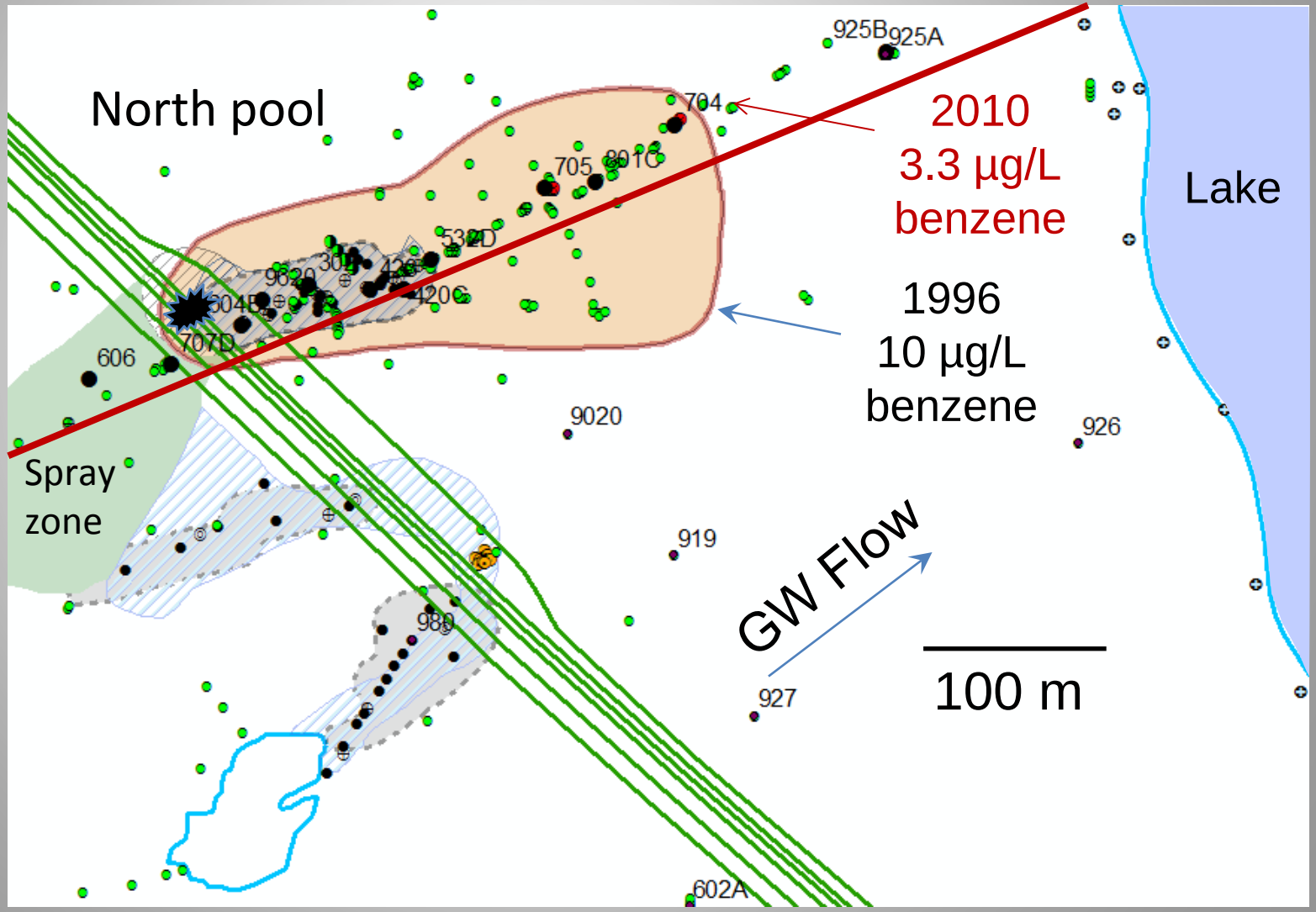
Most research is on the North oil pool and plume

Cross section line



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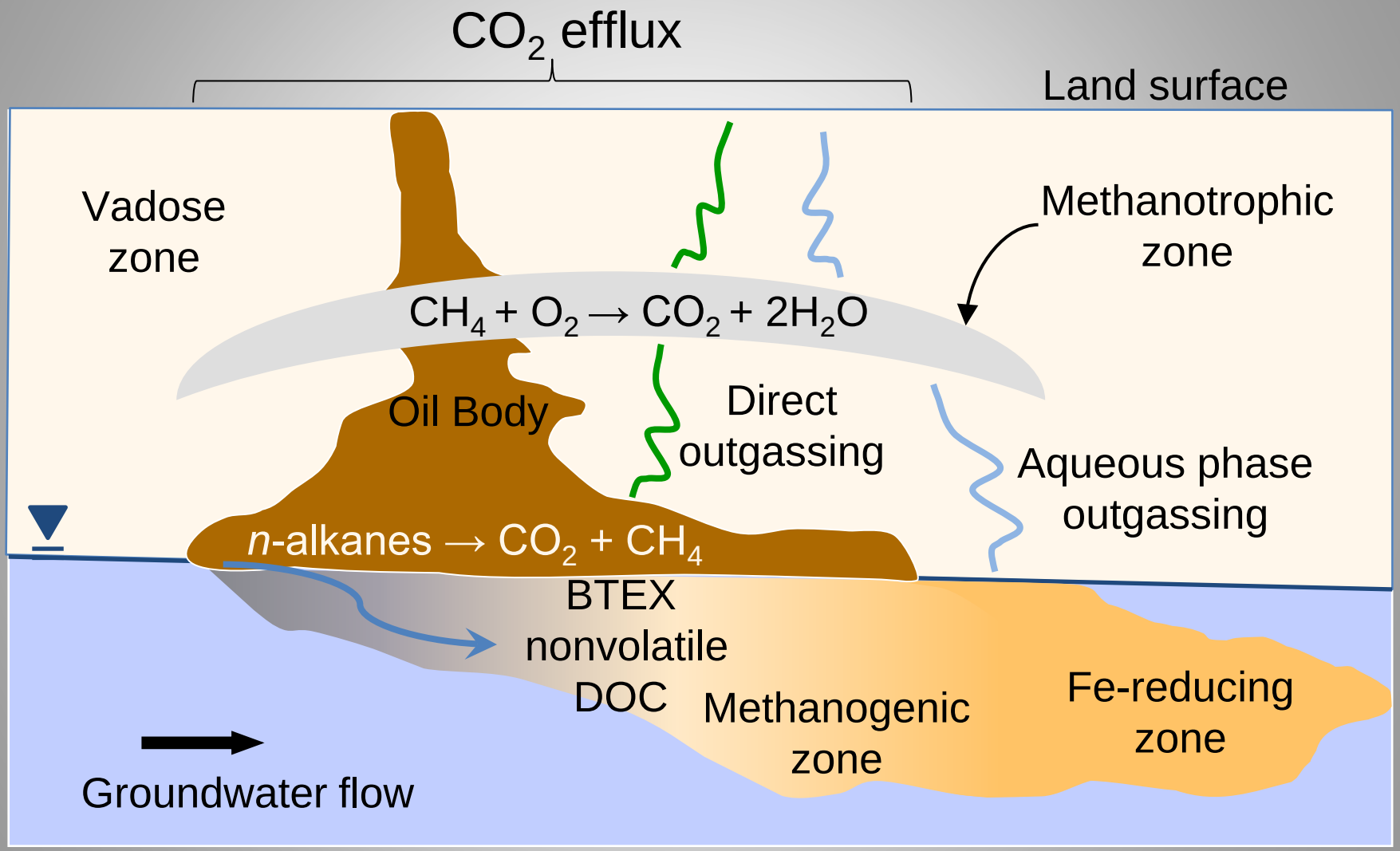
Conceptual model of site processes



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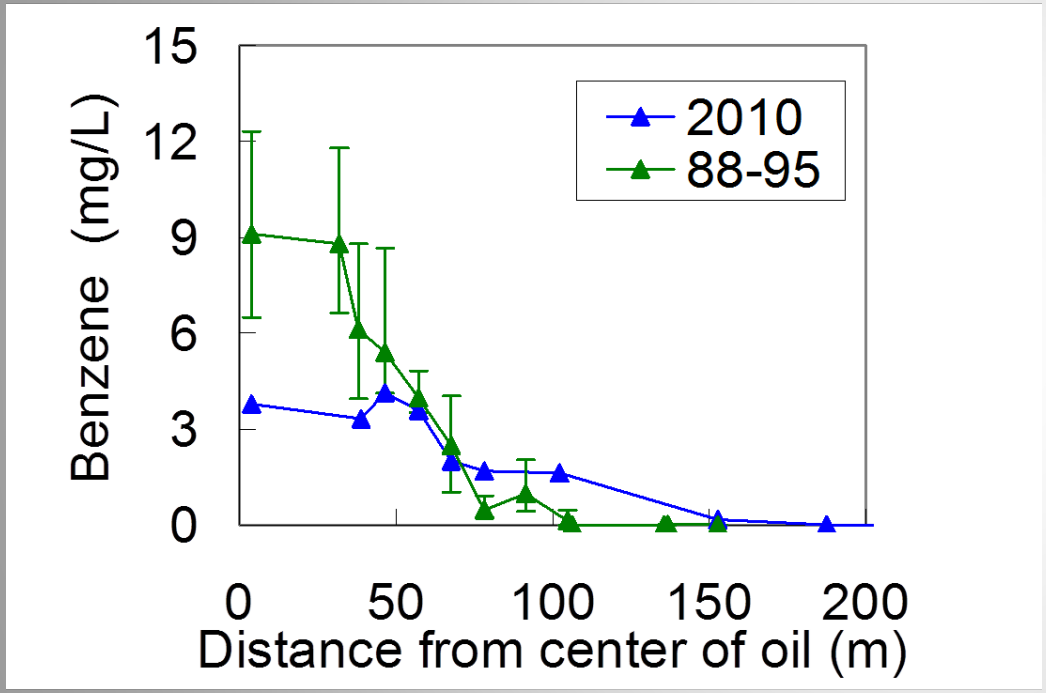
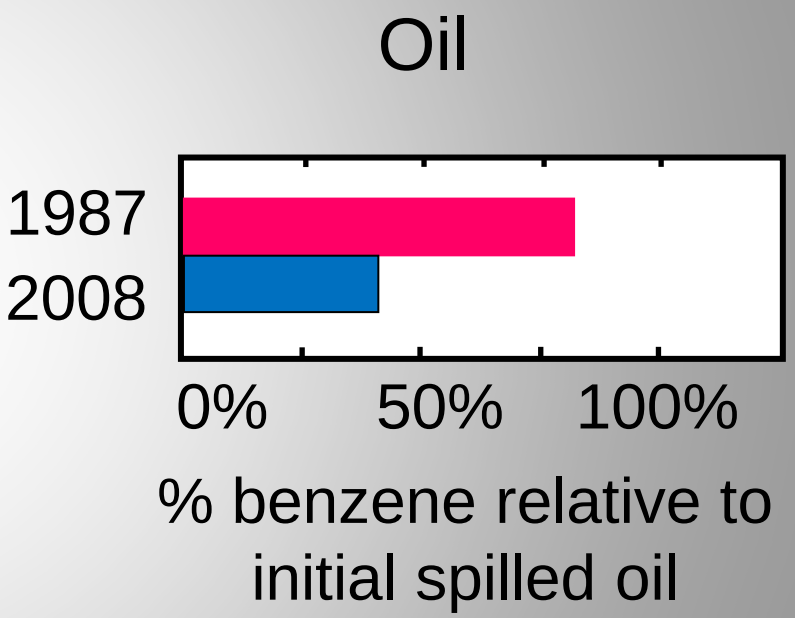
Ng et al., 2015, DOI: 10.1002/2015WR016964

The benzene plume has expanded slightly but concentrations near the oil are dropping





Baedecker et al., 2011
Bekins et al., 2011

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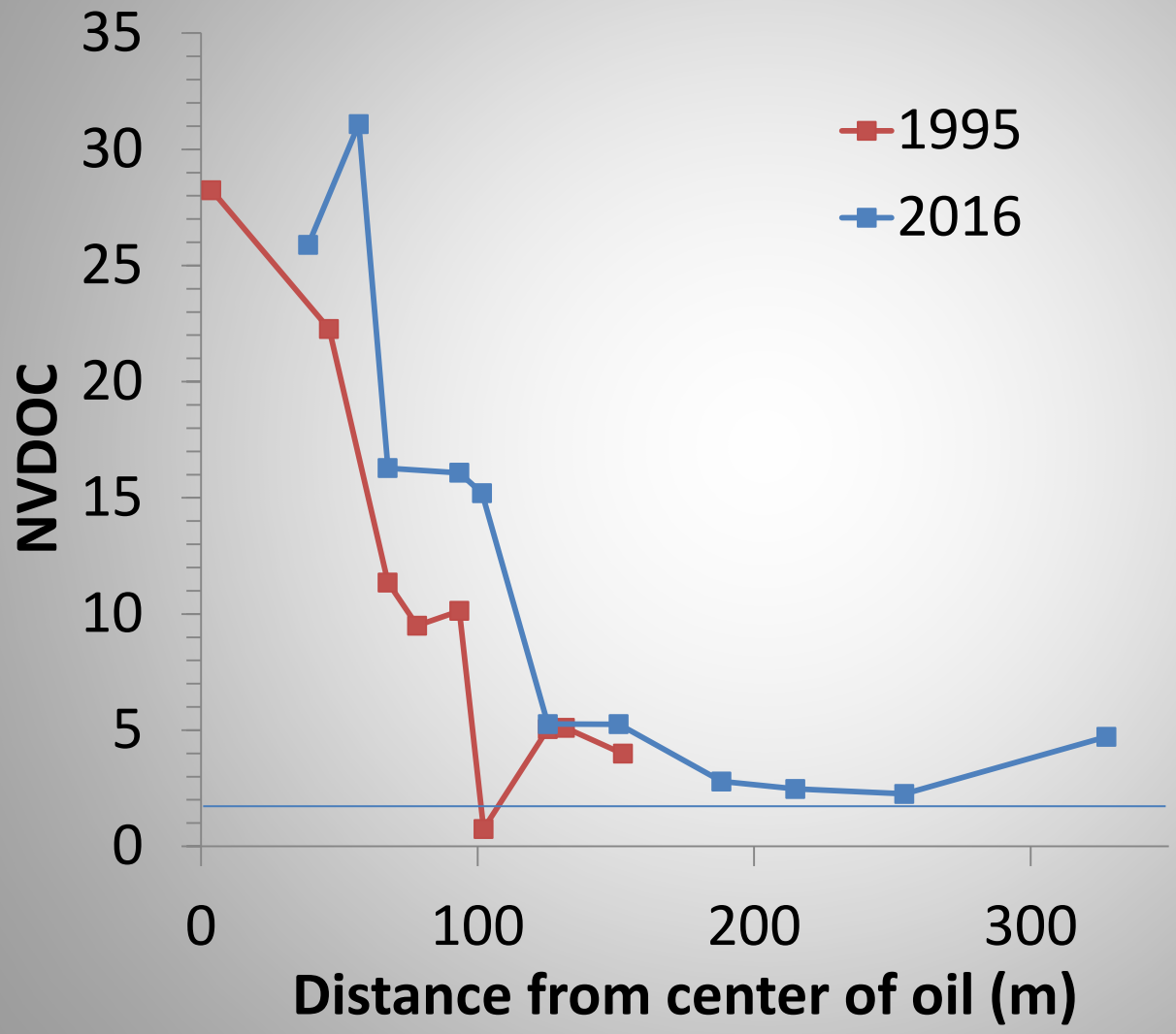
A nonvolatile organic carbon (NVDOC) plume grew by about 1m/year and has a refractory component



Background = 1.6 mg/L

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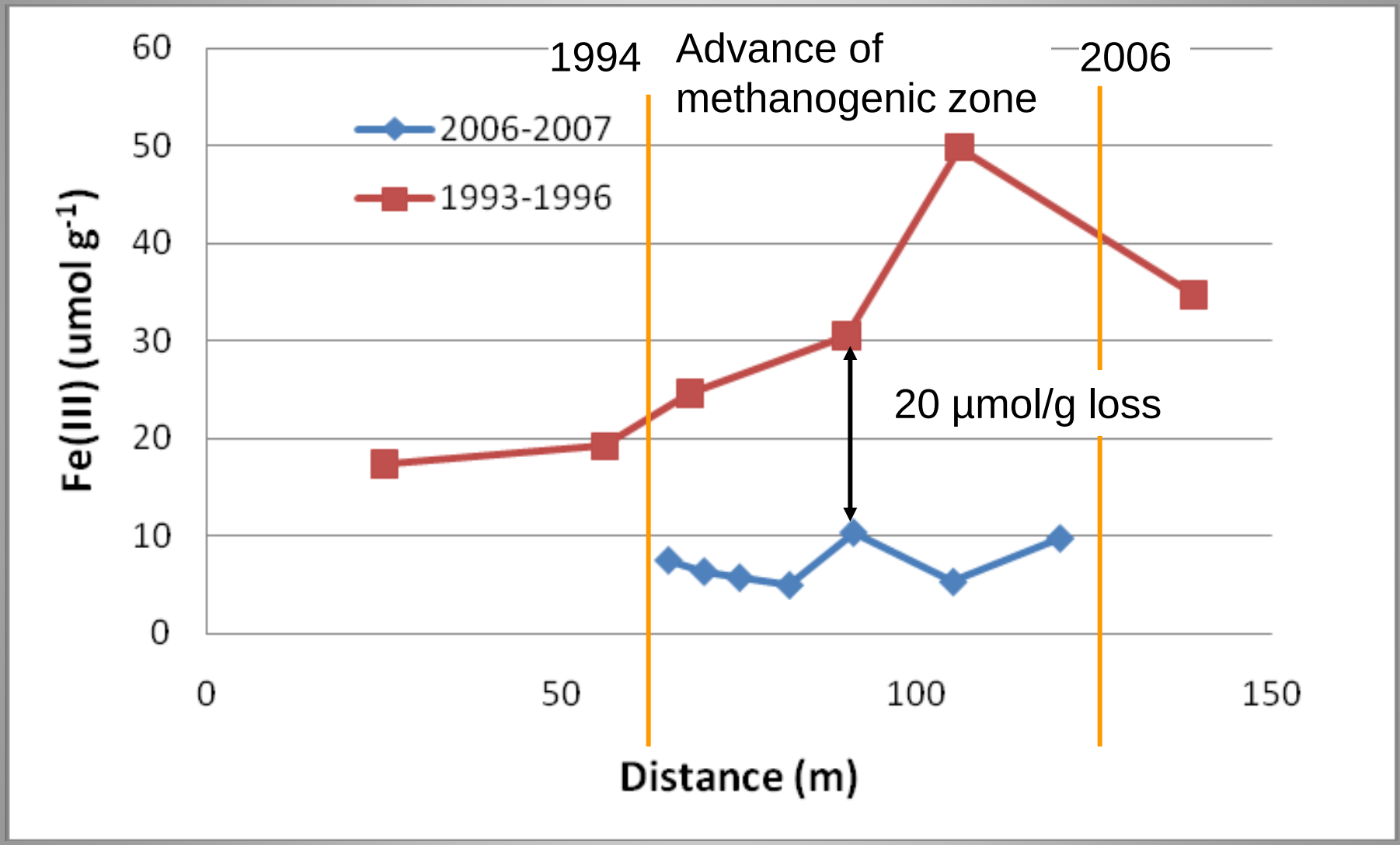
Fe oxy-hydroxide is the main electron acceptor
In 12 years 20 umol/g sediment was consumed



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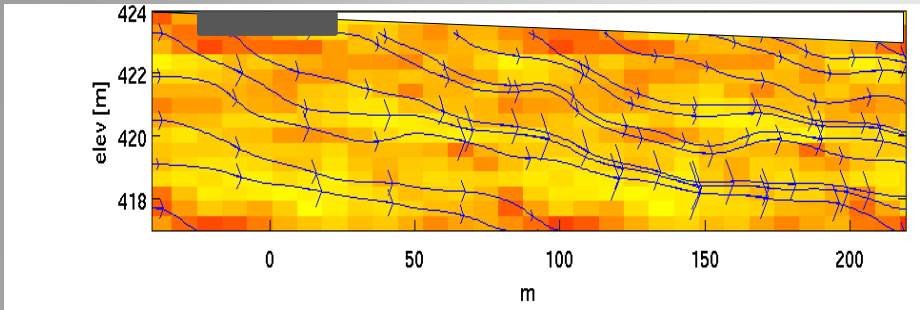
Bemidji Reactive Transport Model

Flow:



Data

Dissolved BTEX
NVDOC
CO_2 surface efflux
Oil composition
Sediment Fe
Major ions, pH, alkalinity

Geochemistry:

- Kinetic oxidation of OC (BTEX, NVOC, n-Alkanes)
- Out-gassing of CH_4 and CO_2
- Mineral dissolution of electron acceptors (Mn, Fe)
- Mineral precipitation of reduced species
- Sorption of reduced species via cation exchange
- Plume also controlled by carbonate chemistry and reoxidation

PHT3D Model

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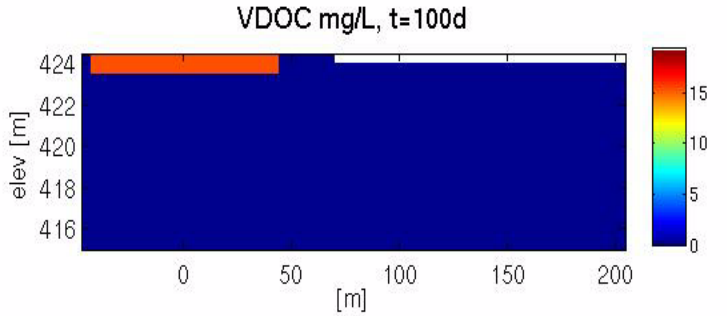
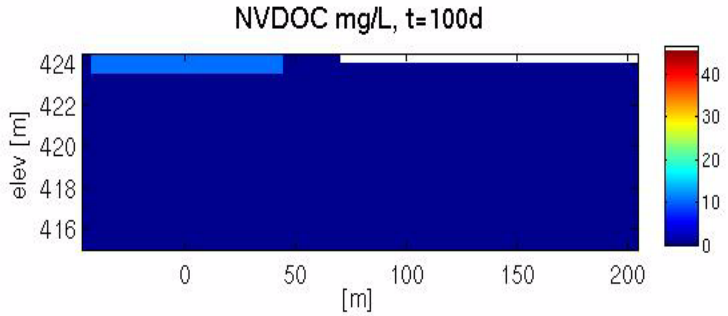
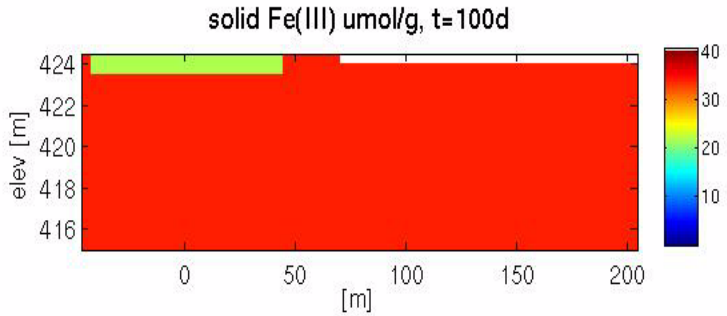
Ng et al. (2015)

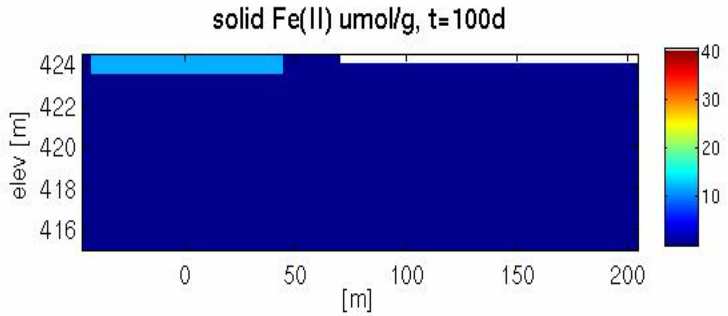
Model results

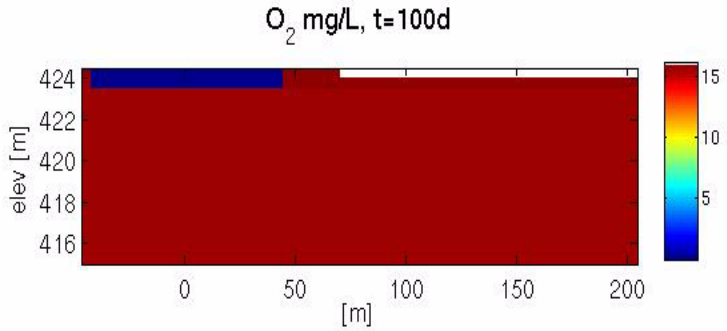
NVDOC degradation rate =0.13%/day

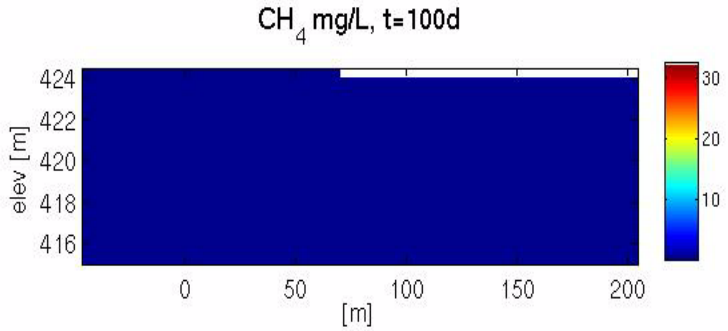






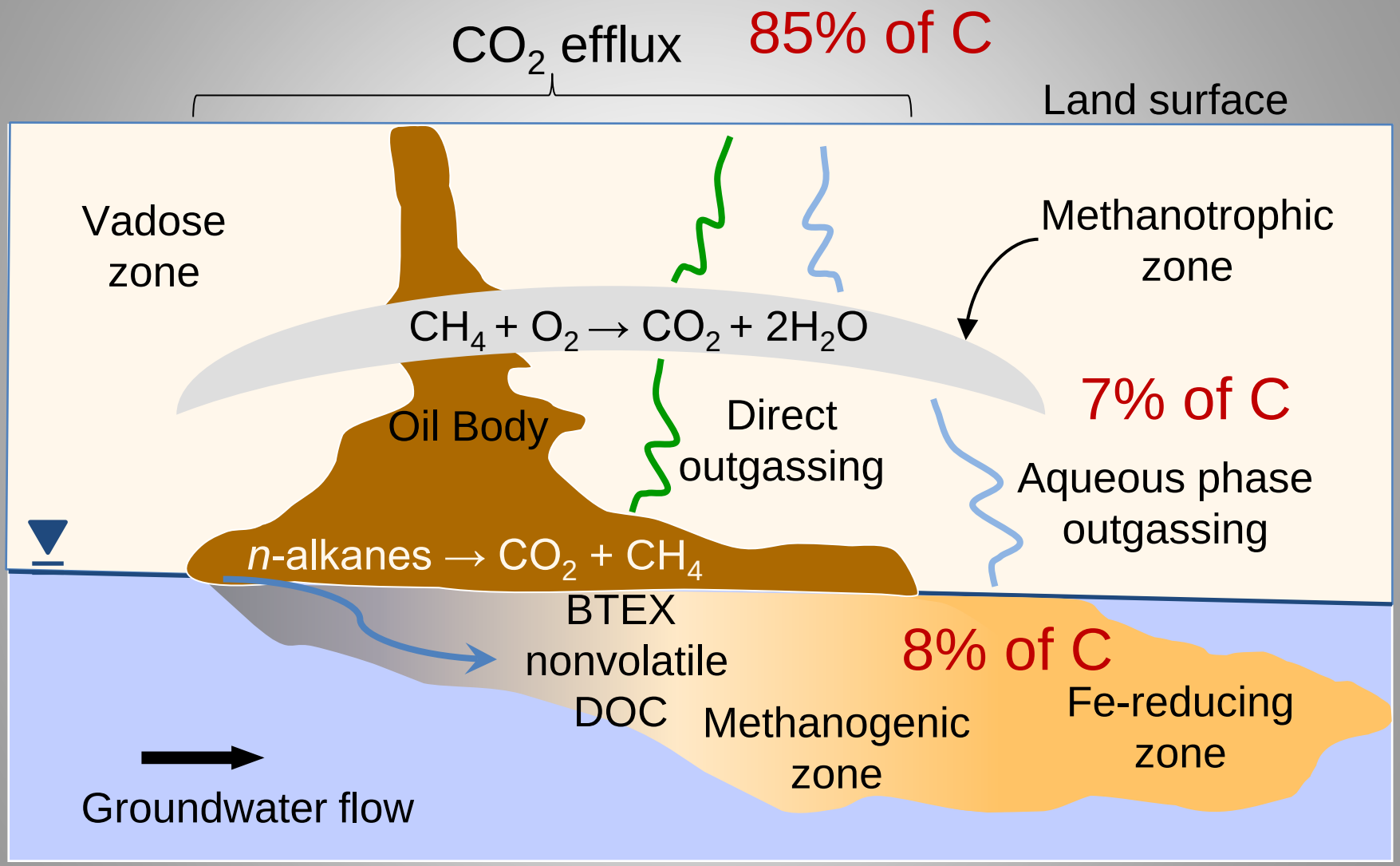






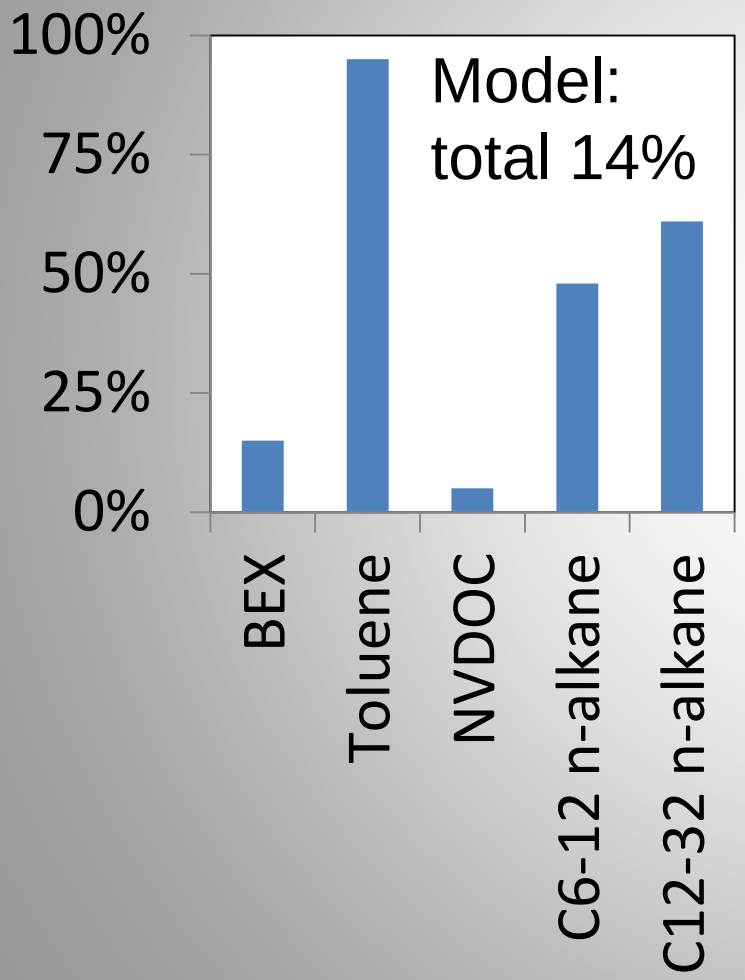
Ng et al., WRR, 2015

Model results: Carbon fate



Ng et al., 2015, DOI: 10.1002/2015WR016964

Model results: Percent lost from oil by 2010



Ng et al., 2010, *WRR*

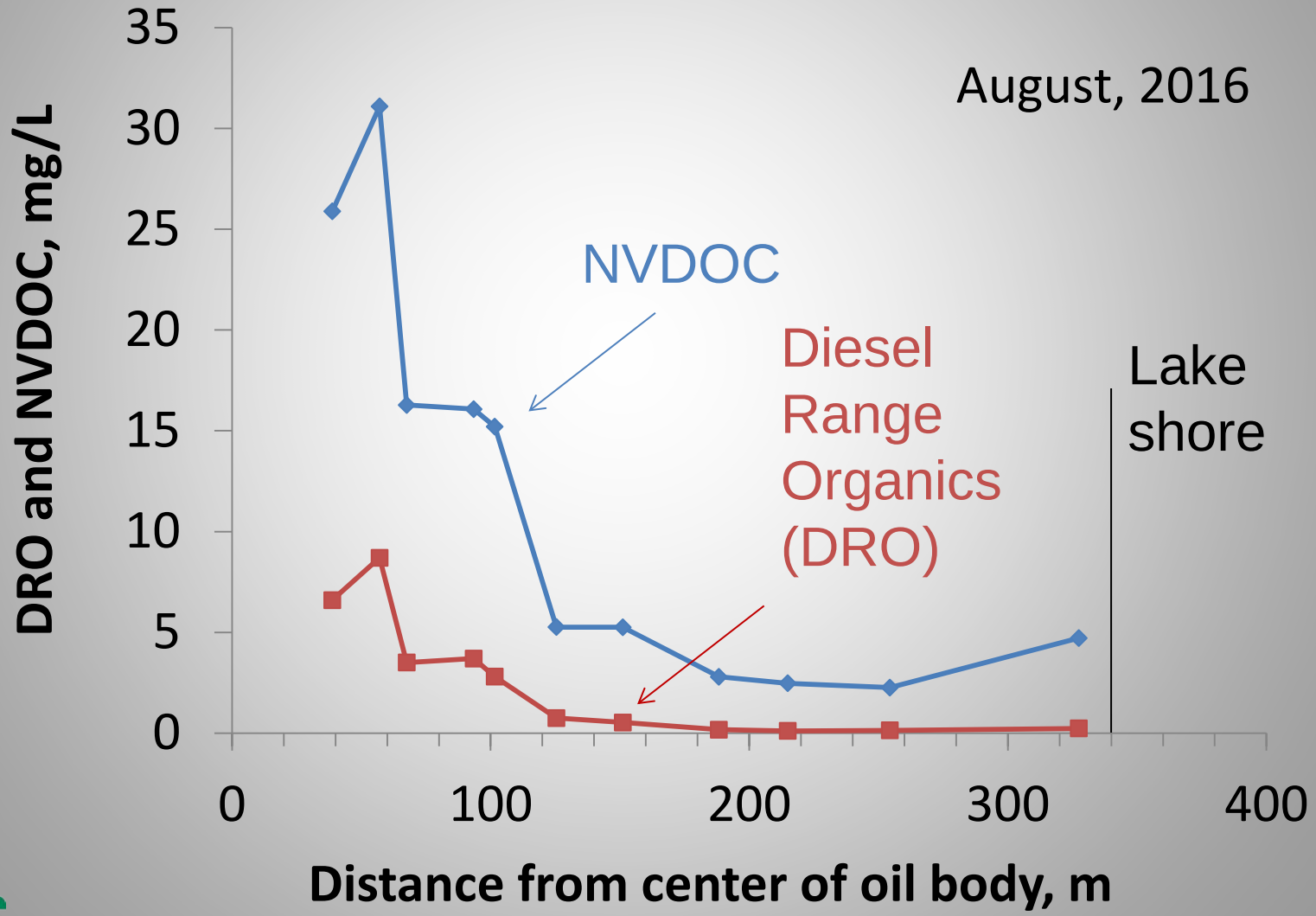
Oil data

- Normalized to 1-methyl-napthalene,
- 19-46% at 13 sites
- Saturation-weighted average 32%

Baedecker et al., in final review *Groundwater*

Motivation for ongoing work on NVDOC:

The MN required analysis method (DRO) reflects only 1/3 the nonvolatile DOC in the plume



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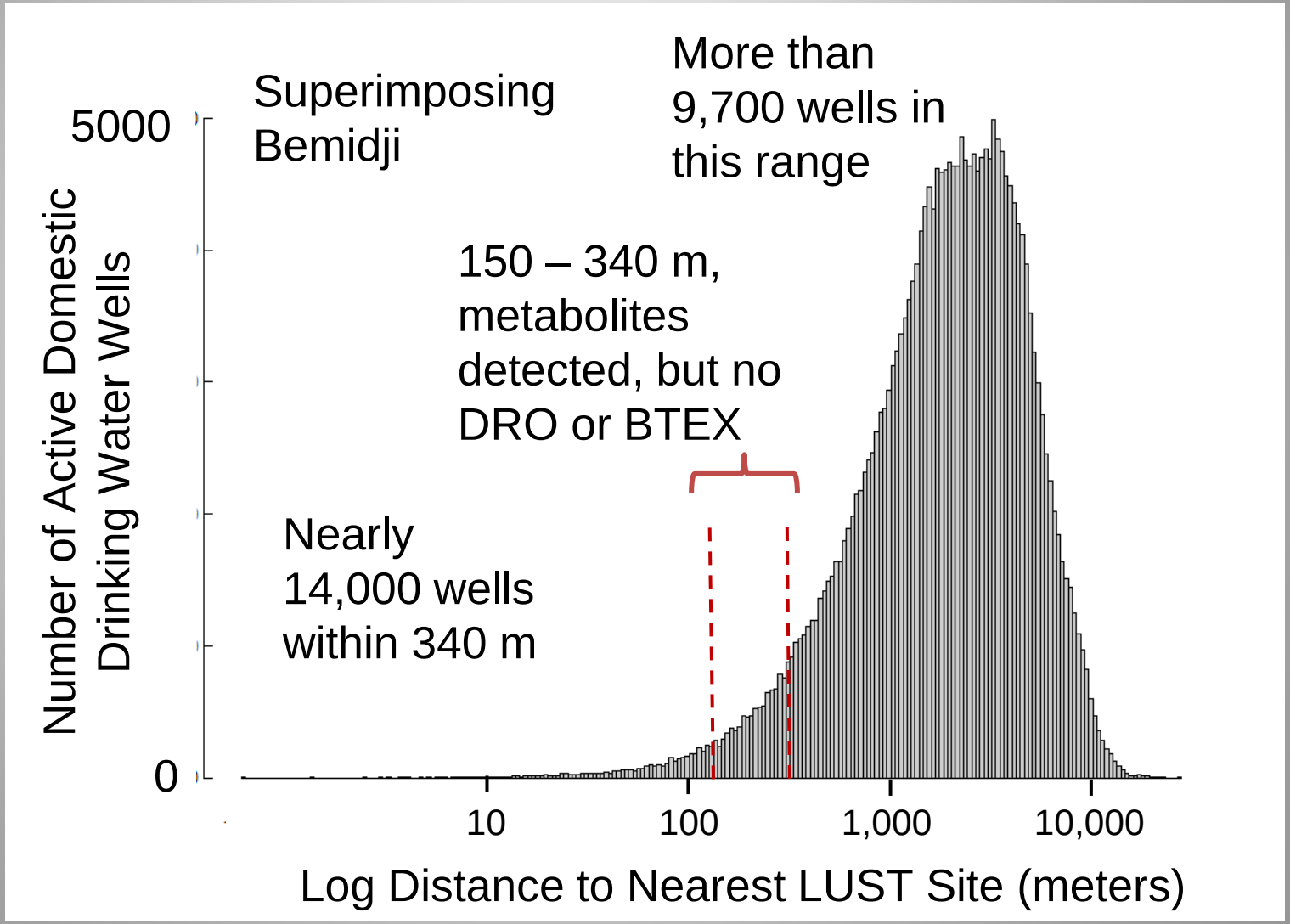
Distance to Nearest LUST Site From Domestic Drinking Water Wells in MN



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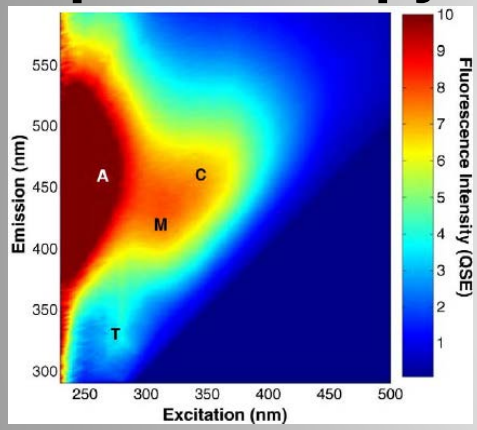
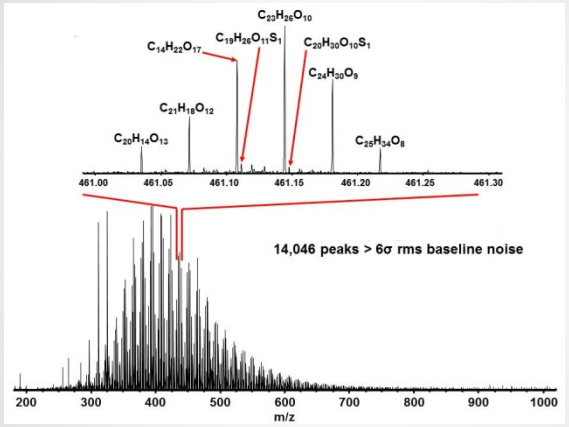
Ongoing work: Degradation pathways
Using several advanced analytical approaches

Optical Spectroscopy



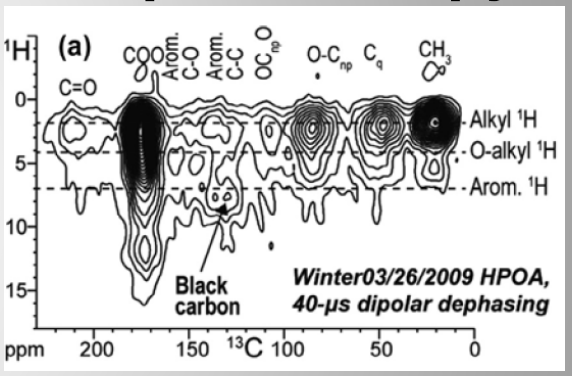
Shank, G.C., et al. 2010

Ultrahigh Resolution Mass Spectroscopy



Over 14,000 individual peaks

Nuclear Magnetic Resonance Spectroscopy



Cao, et al. 2016

David Podgorski
Phoebe Zito
University of New Orleans

Xiaoyan Cao
Klaus Schmidt-Rohr
Brandeis University

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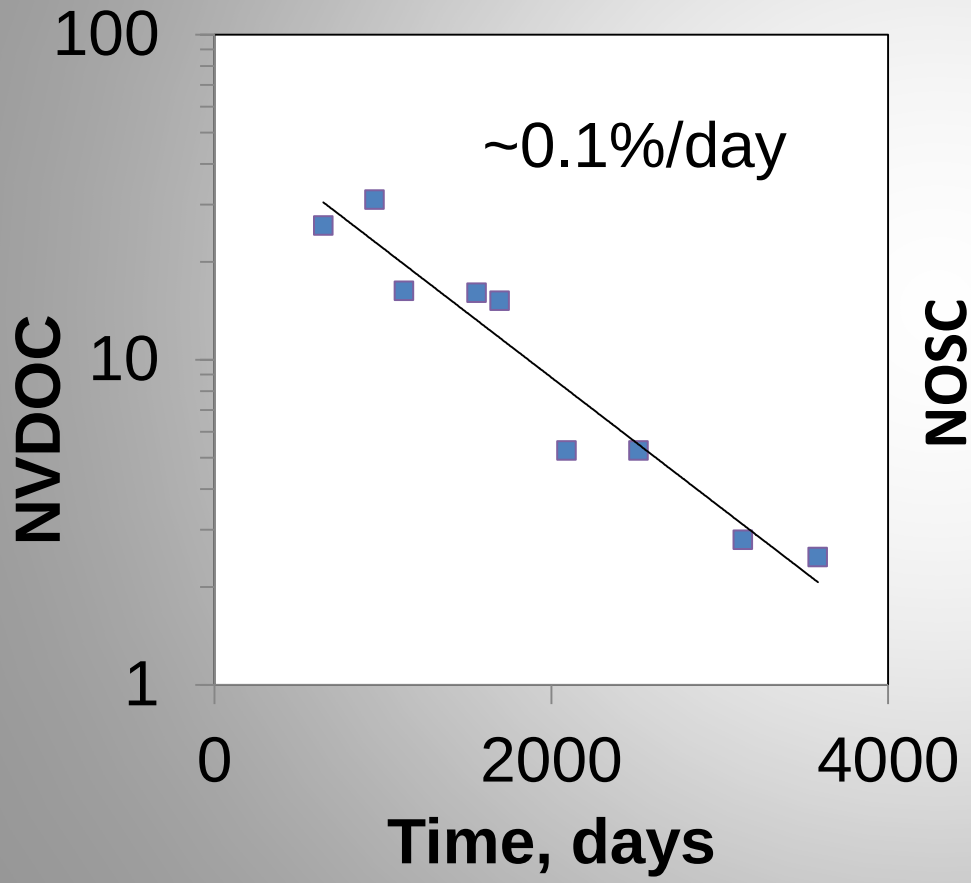
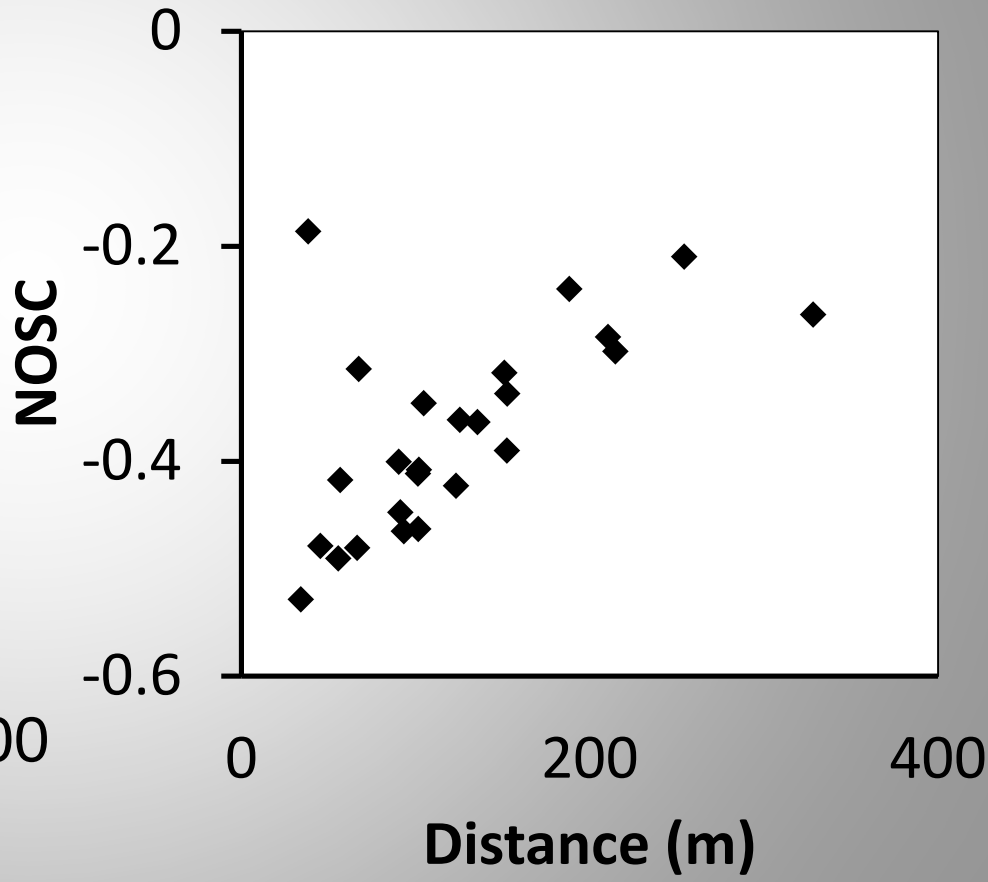
Ongoing work: Degradation processes

NOSC (Nominal oxidation state carbon)= $4-[(4c+h-3n-2o-2s)/c]$

Number of H(+1)=h, C(+4)=c, S(-2)=s, O(-2)=o, N(-3)=n





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Ongoing work: Lake sampling

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Conclusions

- Many spill sites have residual hydrocarbon
- A long term crude oil study shows
  - After almost 40 years the residual oil continues to be a source of groundwater contaminants
  - The organic carbon plume is expanding as iron oxy-hydroxides are depleted
- Required analyses do not adequately measure the degree of contamination at these sites
- The plume of NVDOC at the Bemidji Site is discharging to a lake.

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