Learning about Secondary Water Quality Impacts from the Bemidji Oil Spill

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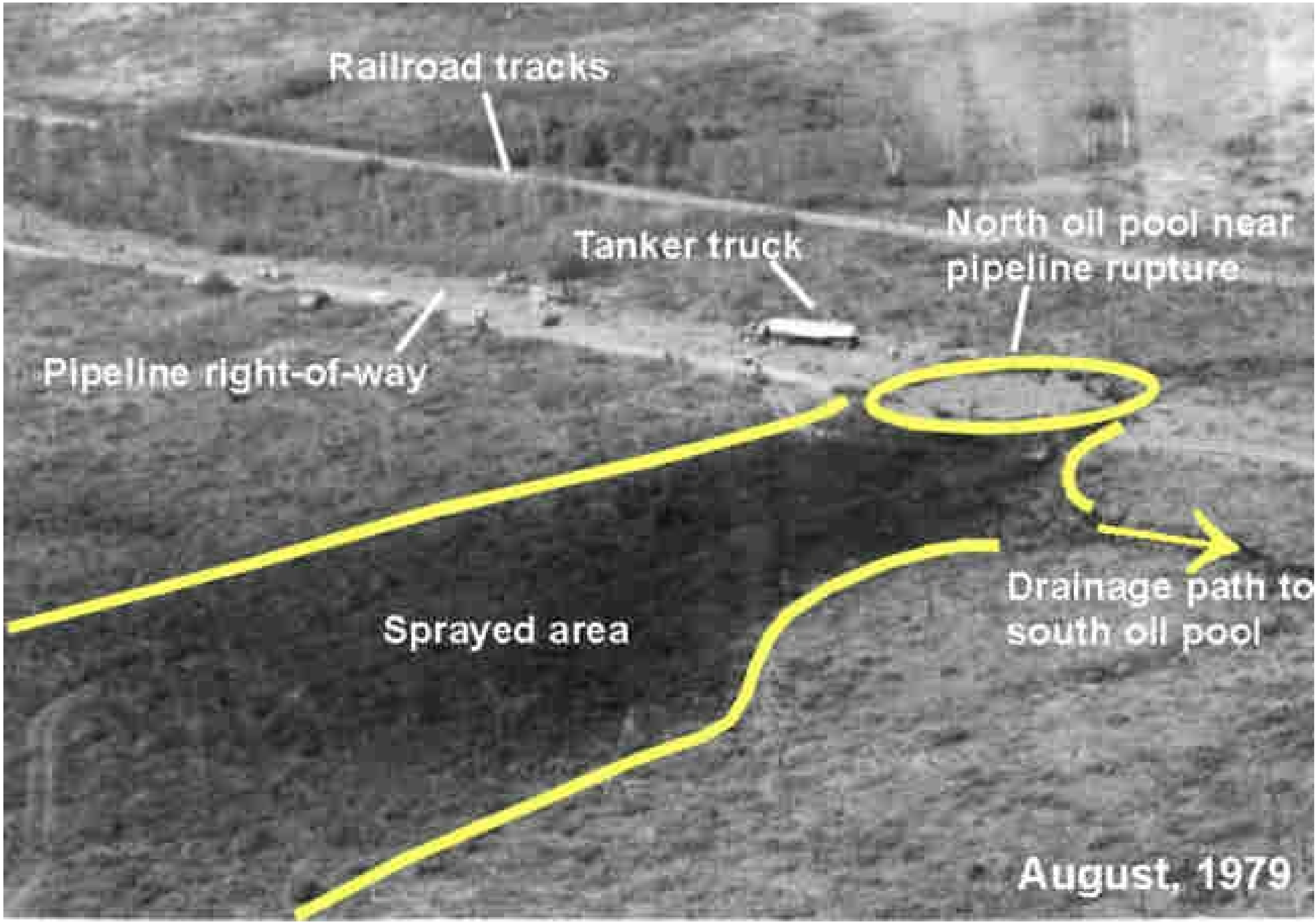
Crude-oil pipeline broke in August, 1979

- Spilled 1.7 million L (441,000 gallons) light crude oil onto glacial outwash deposits
- After cleanup efforts in 1980, 400,000 L remain
- North and South oil pools along water table

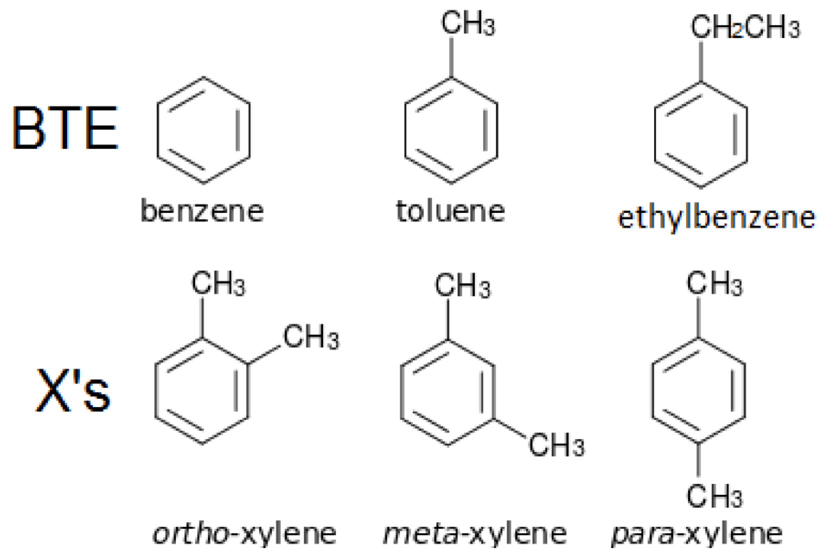


http://mn.water.usgs.gov/projects/bemidji/PhotoGallery/1990.html

Learning about BTEX from the Bemidji Oil Spill

BTEX = Benzene, Toluene, Ethylbenzene, and Xylene

- Volatile organic carbons found in petroleum products
- Adverse health effects: sensory irritant and carcinogen (benzene)
- Highest solubility, easily spread through groundwater (benzene)

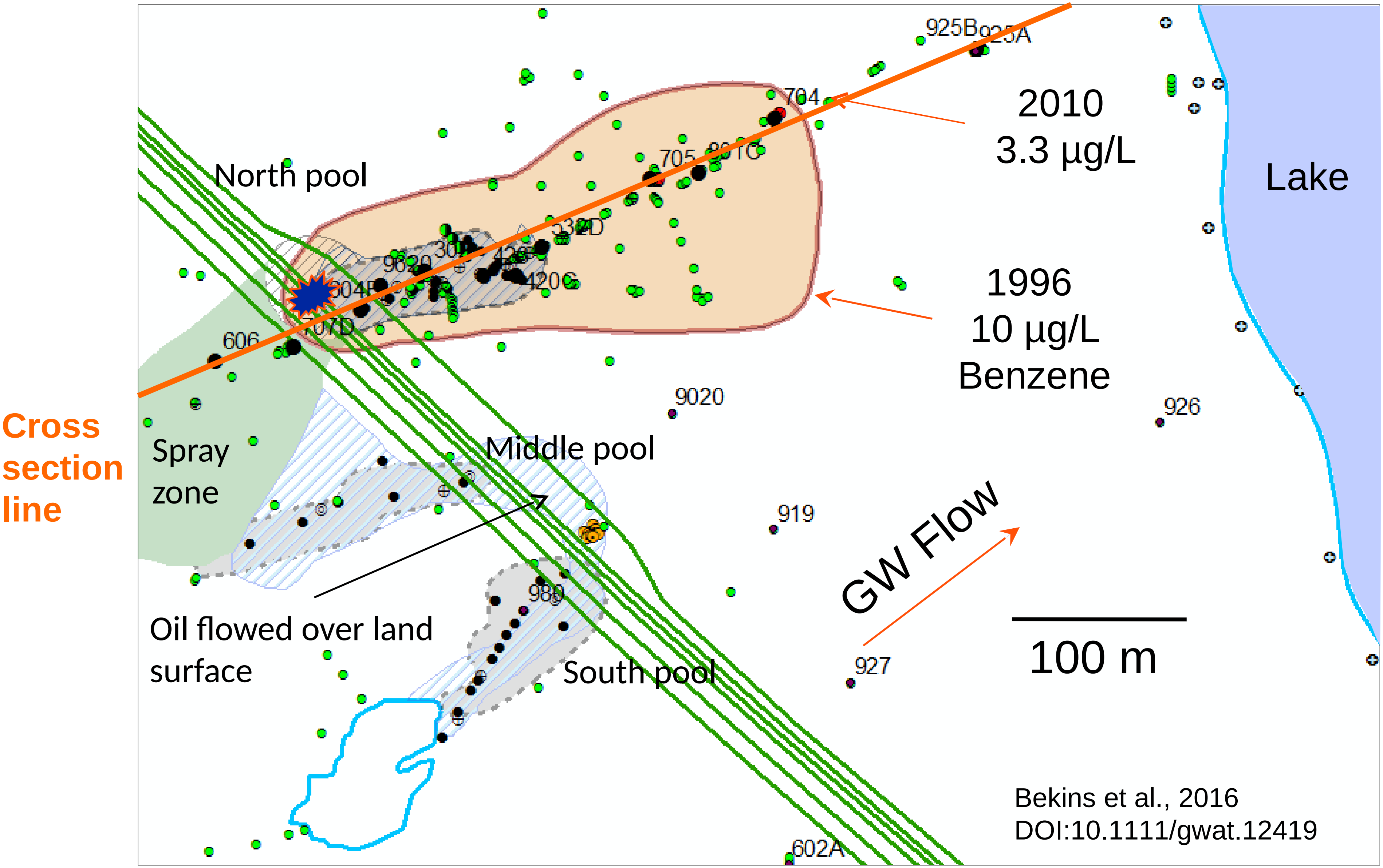


http://www.gcesystems.com/wp-content/uploads/2016/08/BTEX.png

Misconceptions about BTEX plumes at the time of the Bemidji Oil Spill

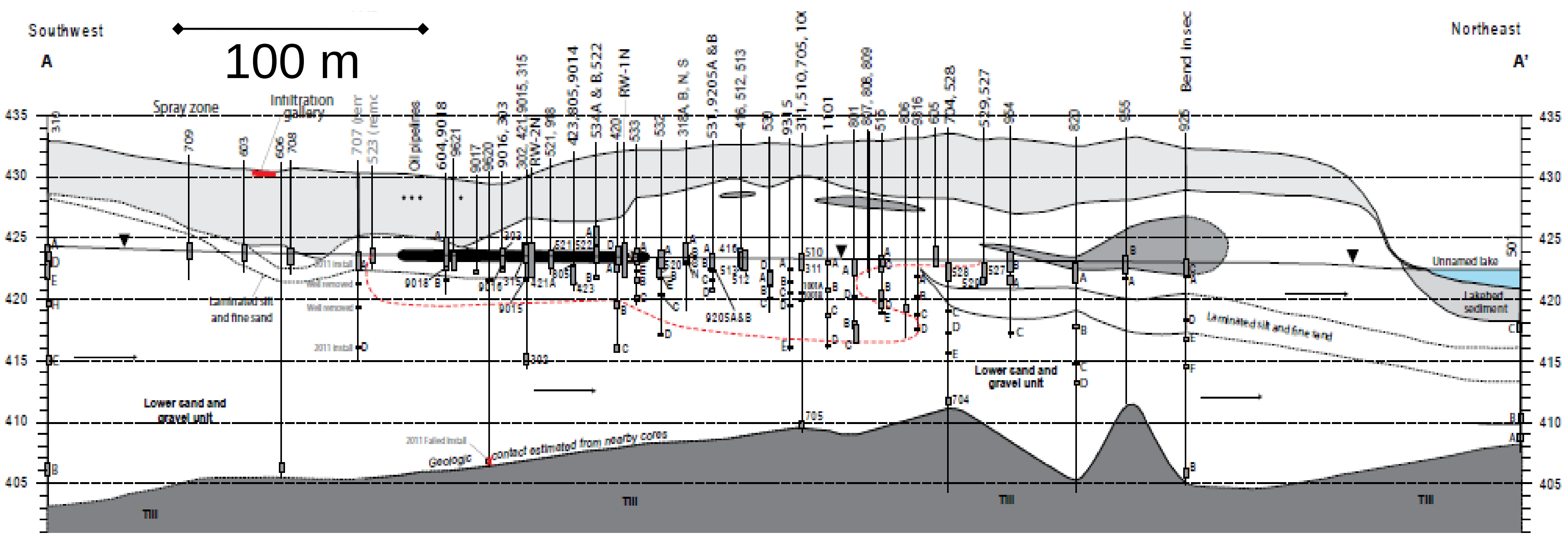
- BTEX biodegradation requires **oxygen**
- **Oxygen** is plentiful in shallow aquifers
- Plumes mix readily with **oxygen** in background water

Research at the Bemidji Oil Spill Site: Focus on the North Oil Pool and Plume



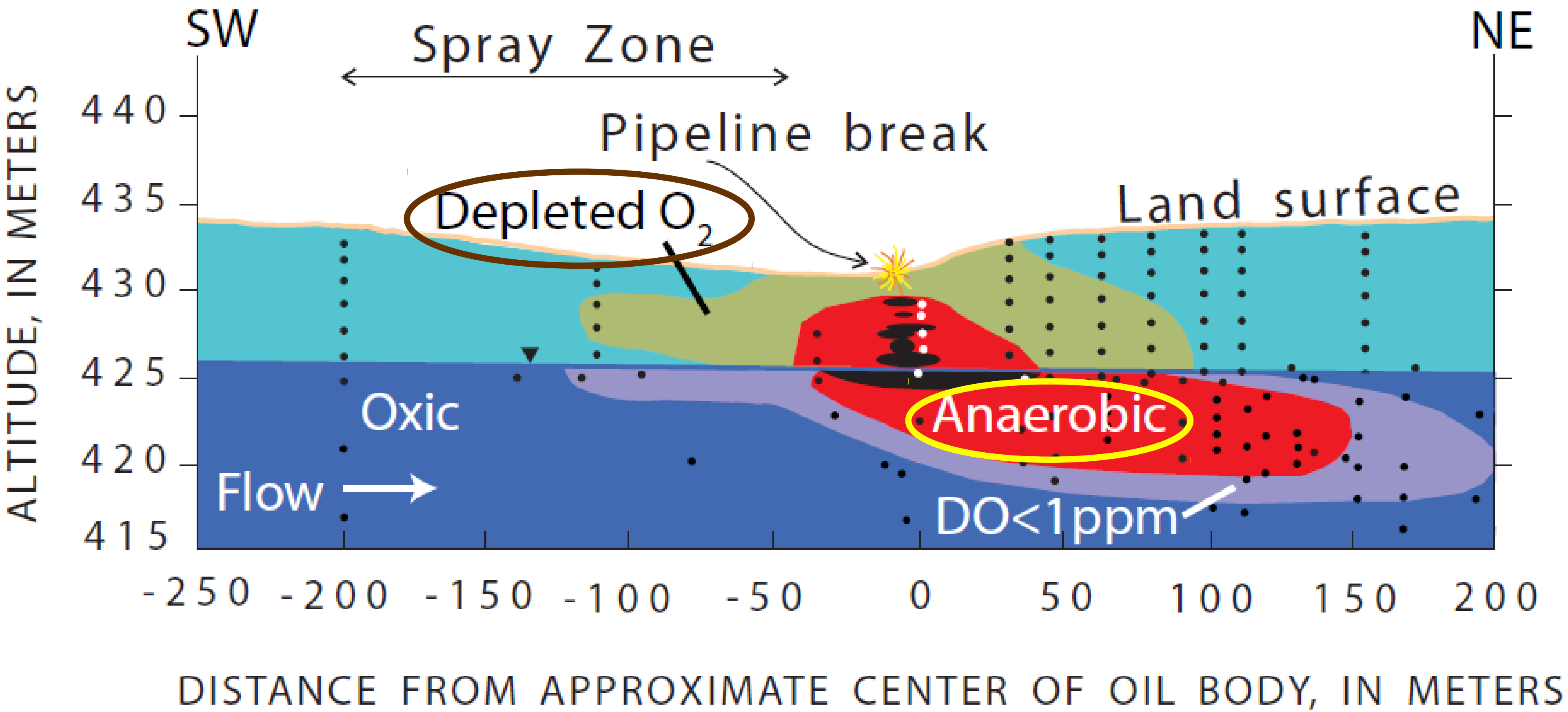
Bekins et al., 2016
DOI:10.1111/gwat.12419

Bemidji North Pool Well Transect



http://mn.water.usgs.gov/projects/bemidji/spatial/Current/xsection.pdf

Anaerobic conditions

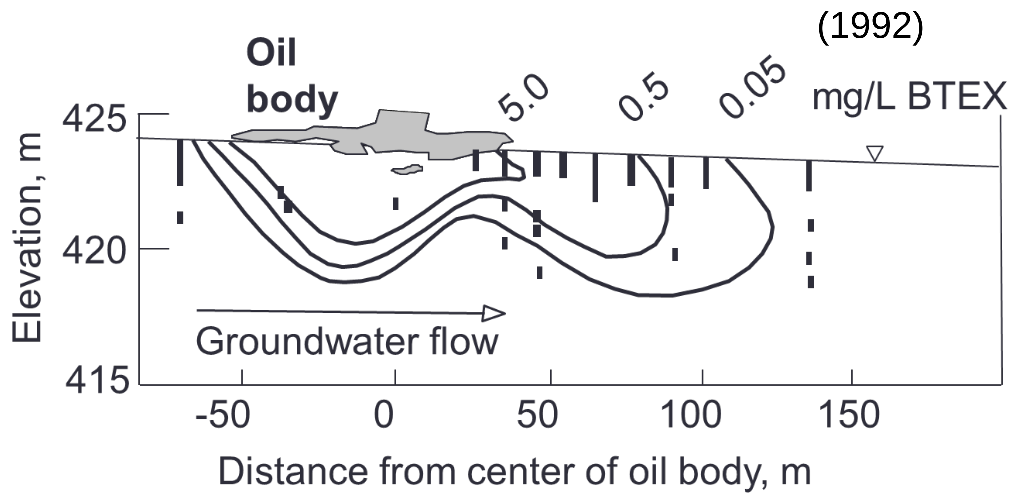


Groundwater from: Cozzarelli et al., 2015, Arsenic Cycling in Hydrocarbon Plumes: Secondary Effects of Natural Attenuation, Groundwater, doi: 10.1111/gwat.12316

Lessons Learned About BTEX Degradation from Bemidji

Naturally: BTEX degrades <u>anaerobically</u>

- 1993: Eganhouse et al., Bennett et al., Baedecker et al.
- <u>First</u> demonstration of BTEX degradation coupled to iron reduction [Lovely et al. Nature 1989]
- Anaerobic metabolites (non-volatile DOC) present in plume [Cozzarelli et al. 1994]
- CH_4 in plume indicates (anaerobic) methanogenesis [Amos et al. 2005]
- Models indicate 60% of degradation is anaerobic [Essaid et al, 1995]

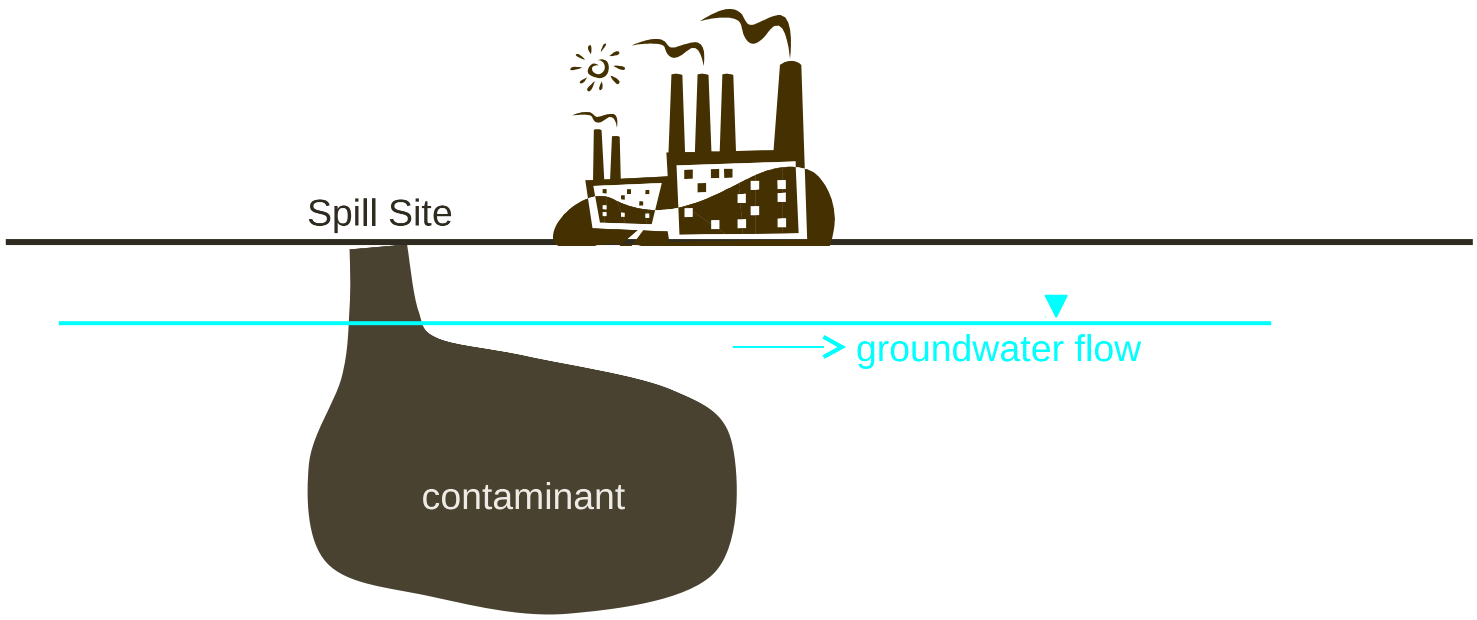


➢ **Natural attenuation established as an effective BTEX remediation strategy**
[National Research Council, 2000]

What can we learn about BEYOND BTEX degradation from the Bemidji Oil Spill Site?

Emerging Concern:

Secondary Water Quality Impacts (SWQI's) of Anaerobic Bioremediation?



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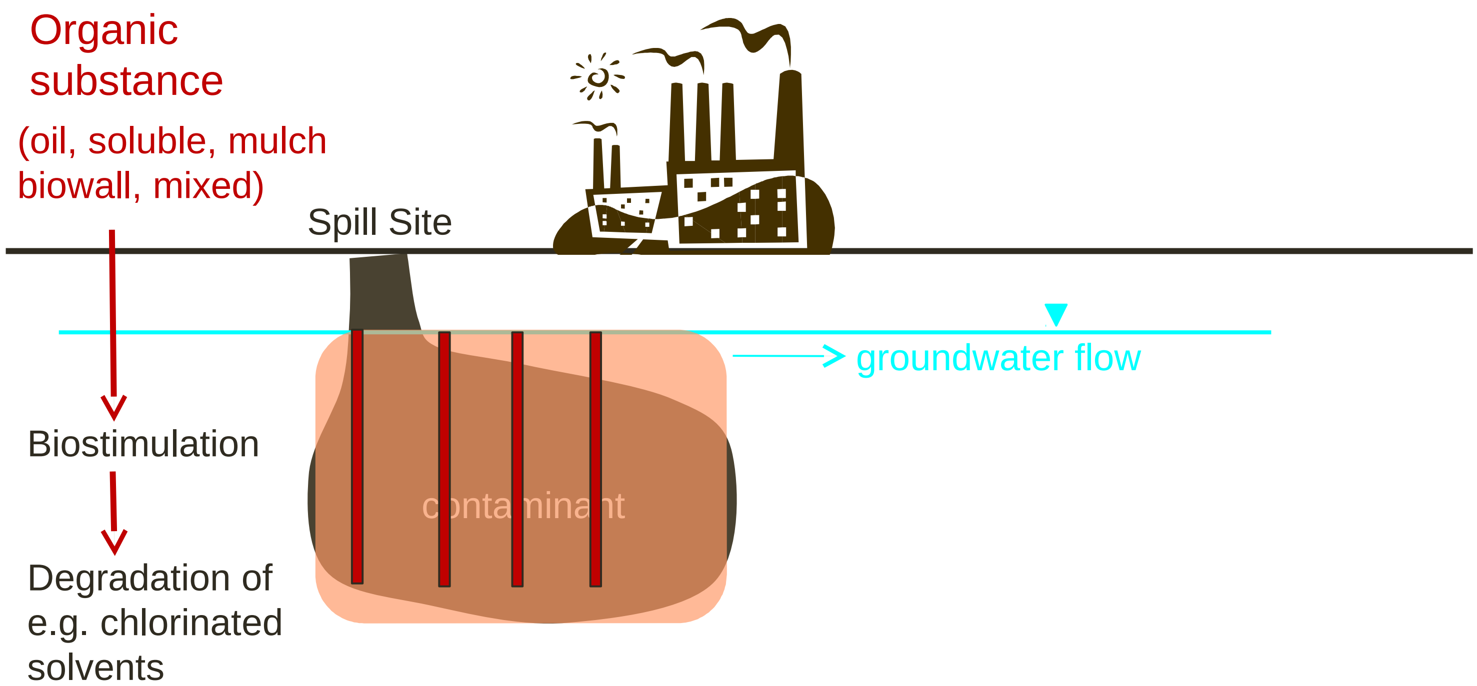

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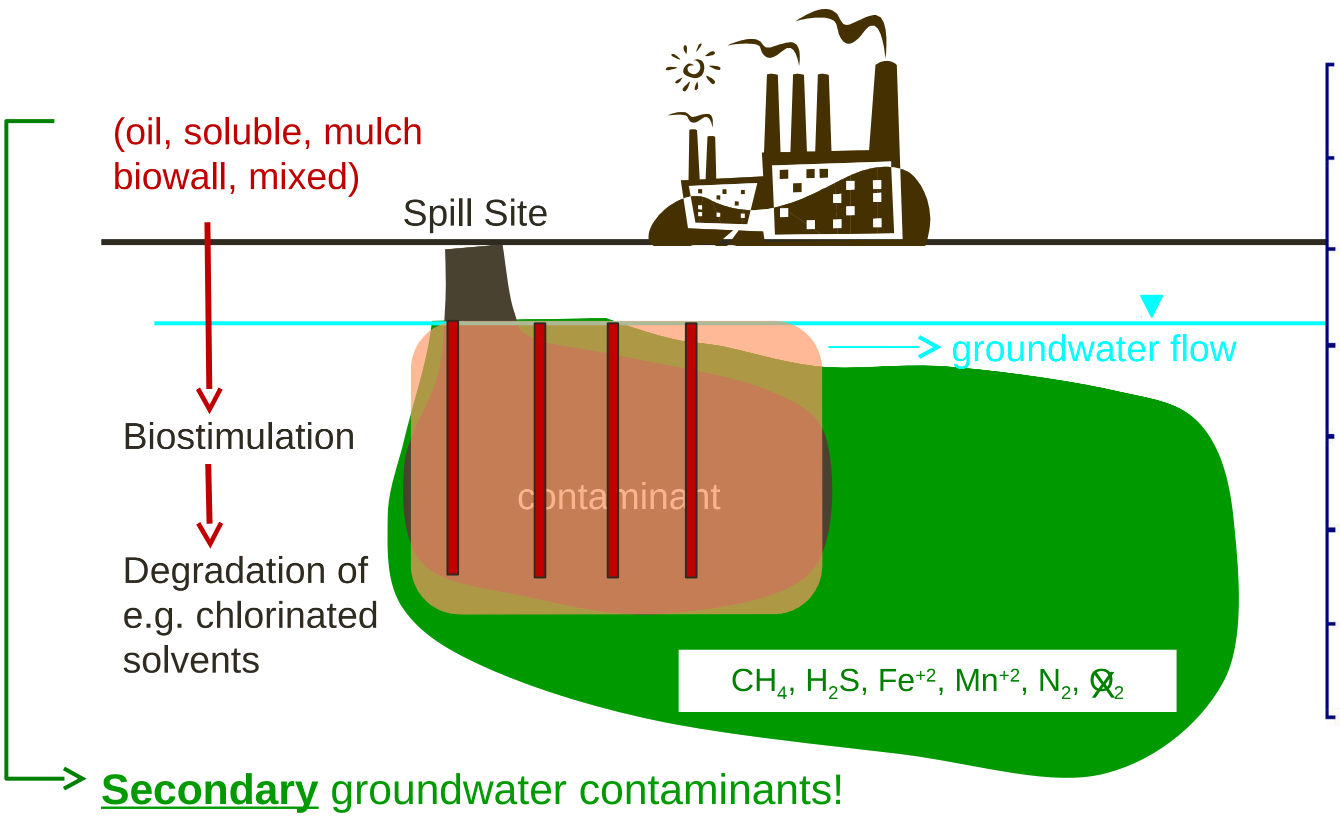

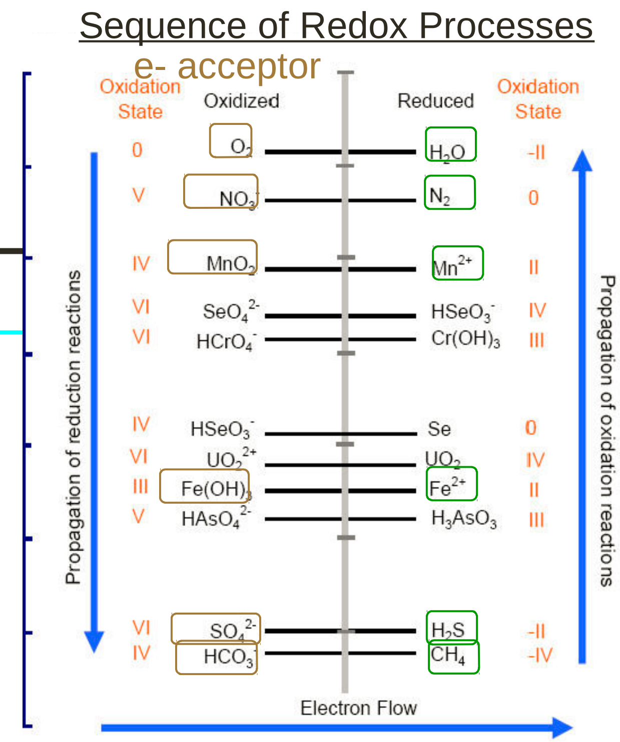

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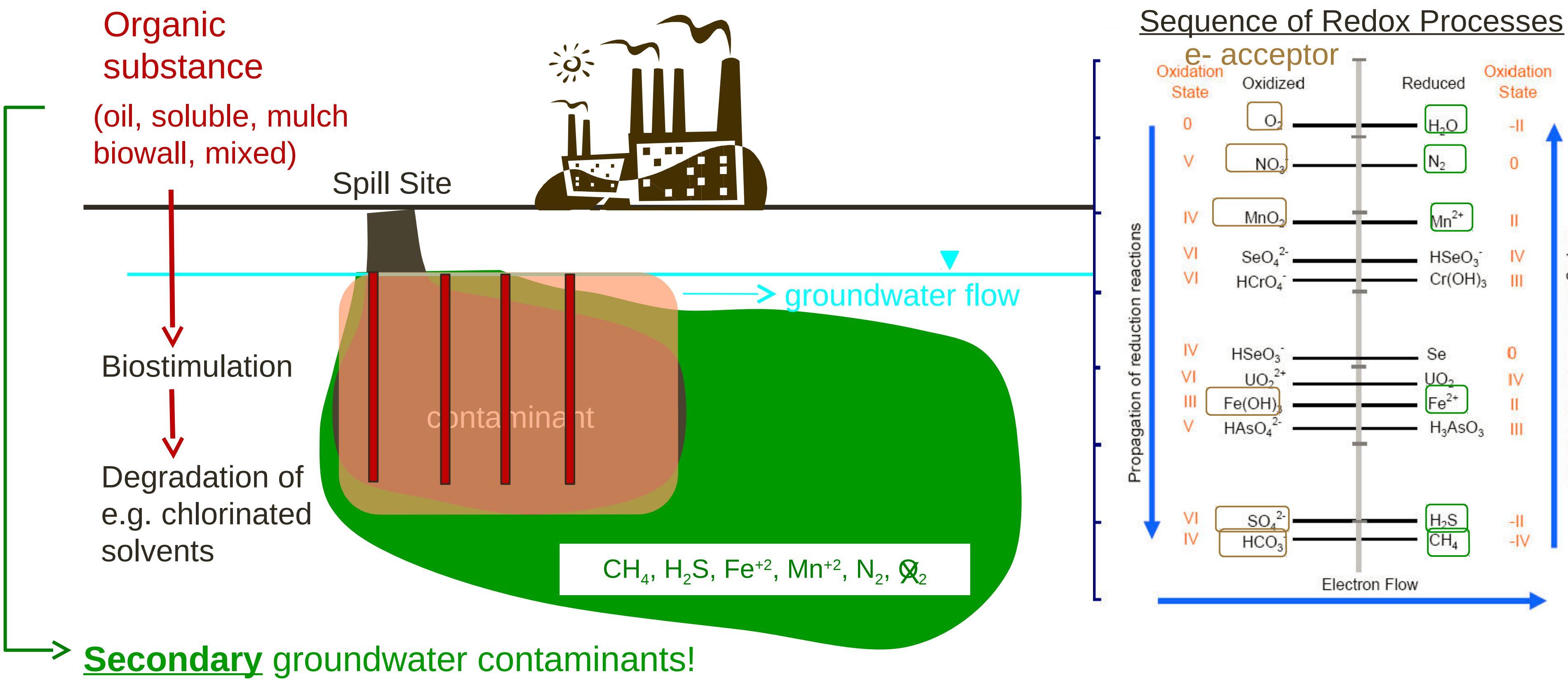
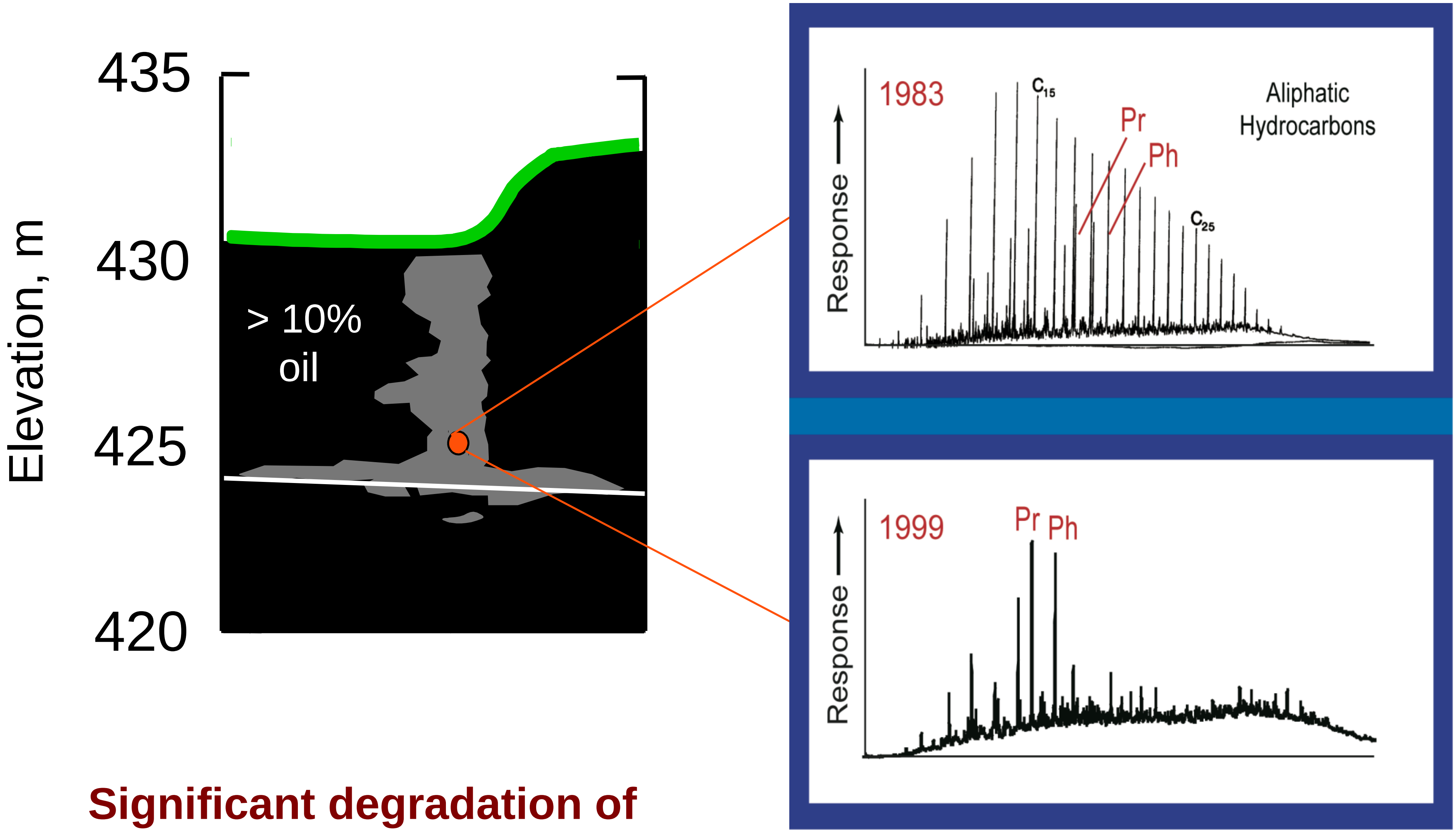


- ☐ Bioremediation site monitoring: some (limited) data

- ➢ **Intensively monitored analogue: Bemidji oil spill**
- ➢ **Long-term secondary water quality impacts of Bemidji oil spill?**

Observations beyond BTEX at Bemidji: Composition of Degrading Oil

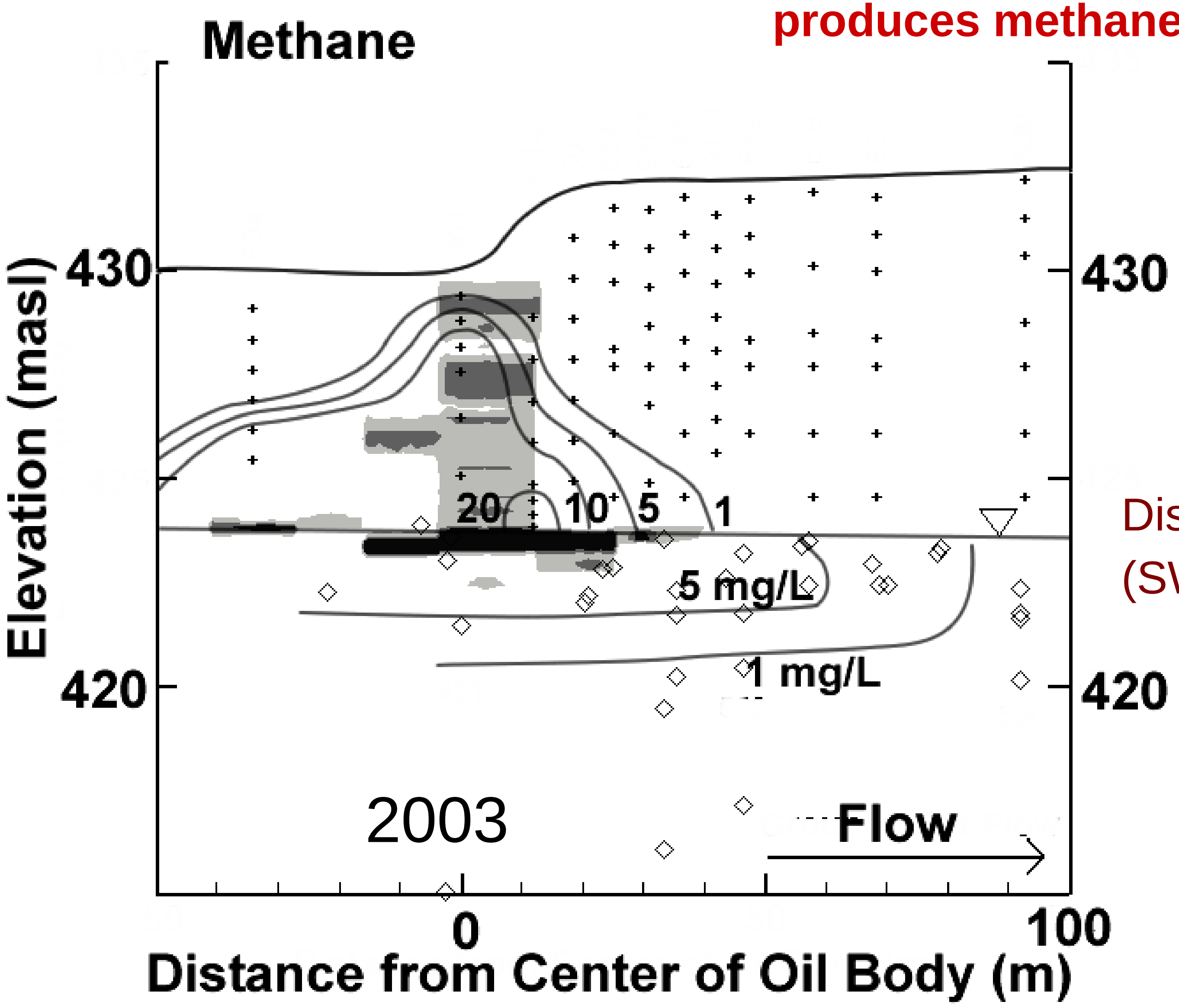


Significant degradation of *n*-alkanes 1983-1999

Hostettler et al, 2008,
DOI:10.1080/15275920802115738

Observations beyond BTEX at Bemidji: Methane

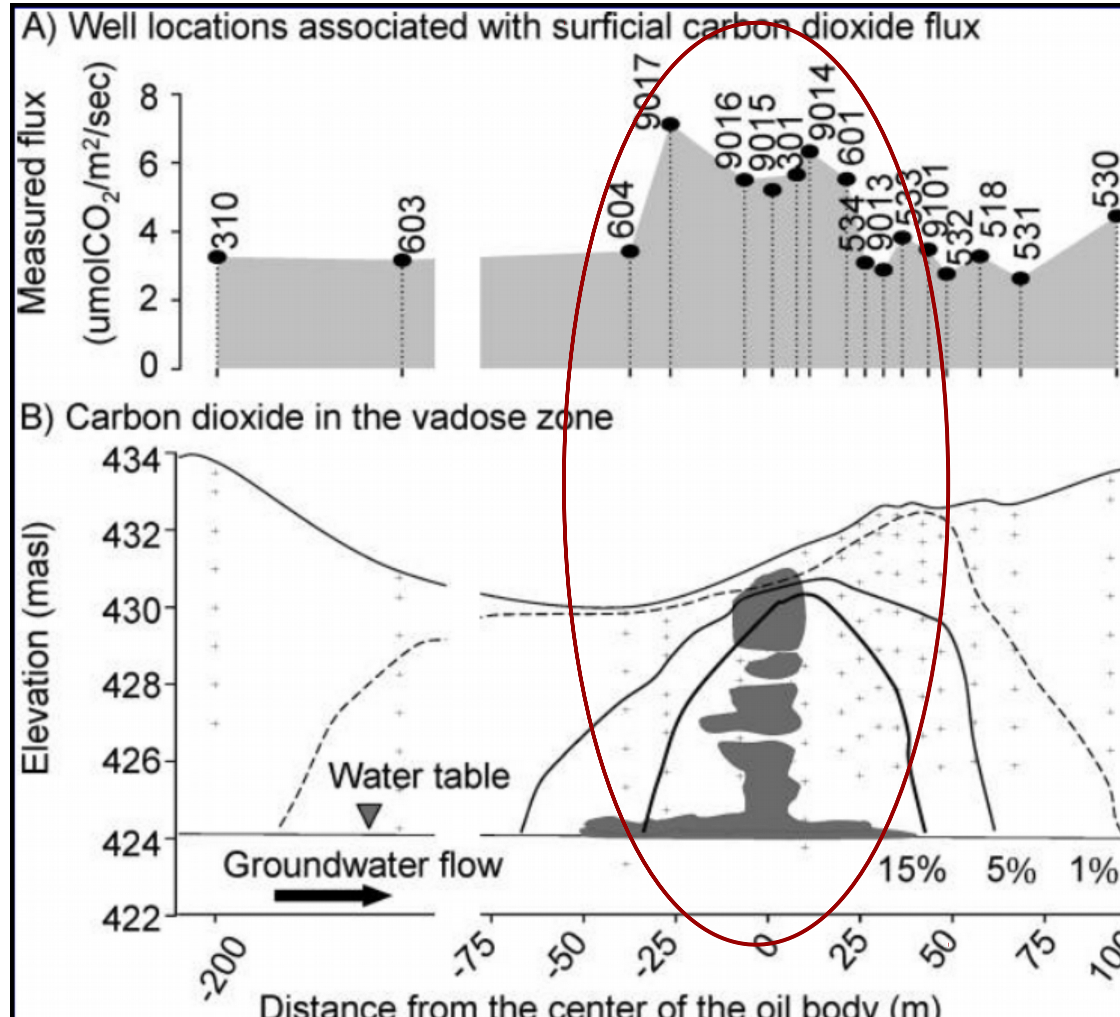
Oil degradation produces methane



Dissolved CH_4 (SWQI)

Amos et al, 2005, DOI:10.1029/2004WR003433

Observations beyond BTEX at Bemidji: Surface CO_2 gas efflux



Elevated surface efflux of CO_2 measured above oil body

[Sihota et al. 2011]

Dissolved and Sediment Fe

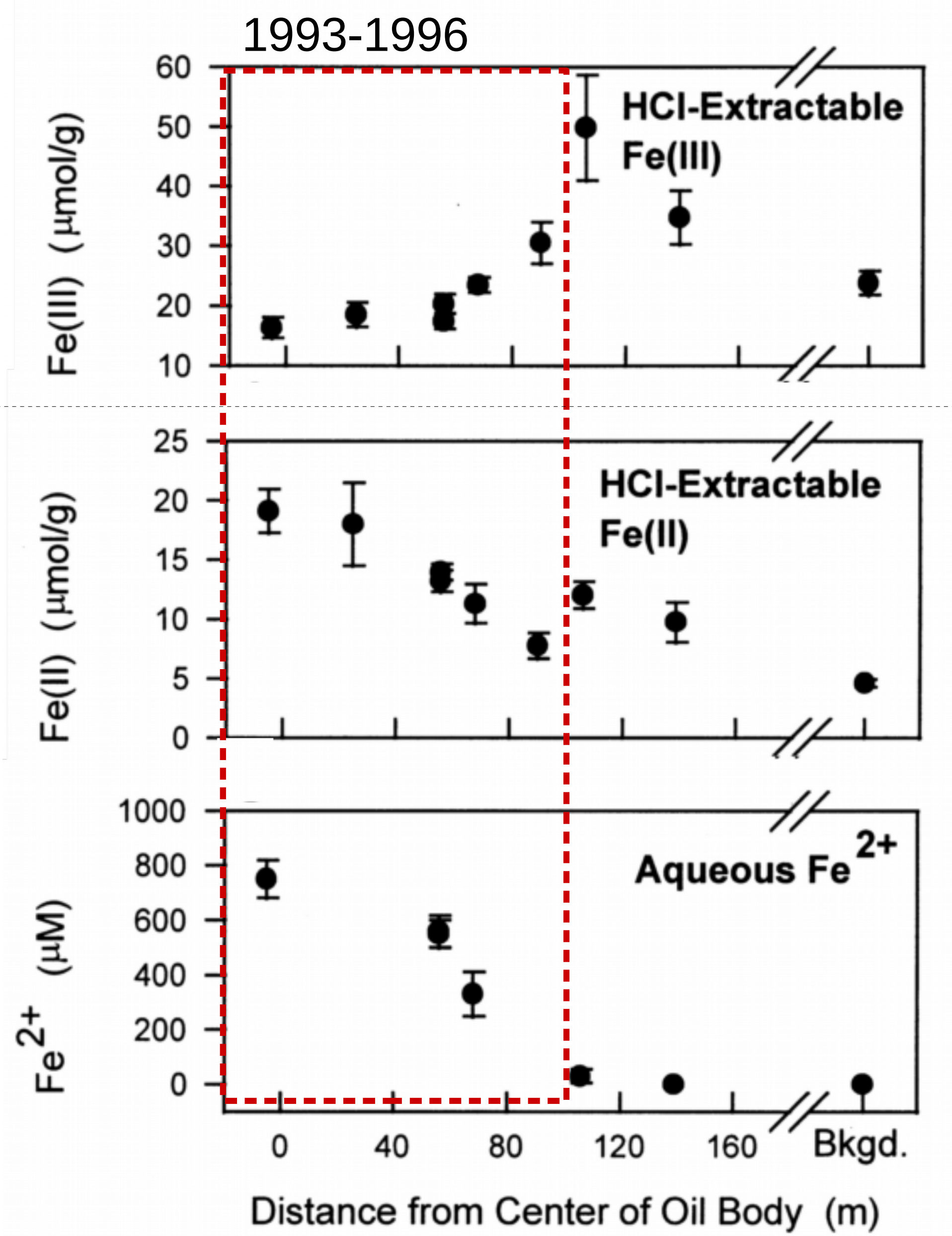
Coupled to anaerobic oil degradation:

Fe(III) reduction

Sediment-bound Fe(II)

+

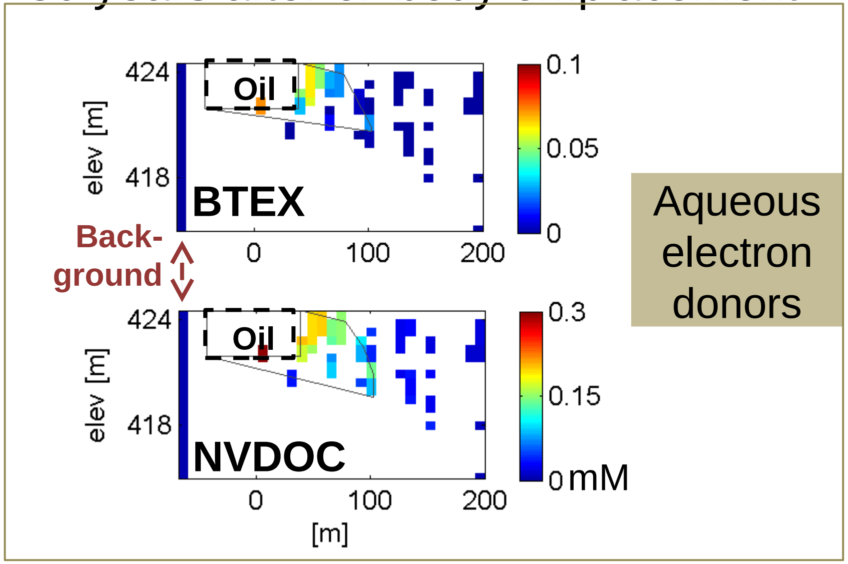
Dissolved Fe(II) (SWQI)



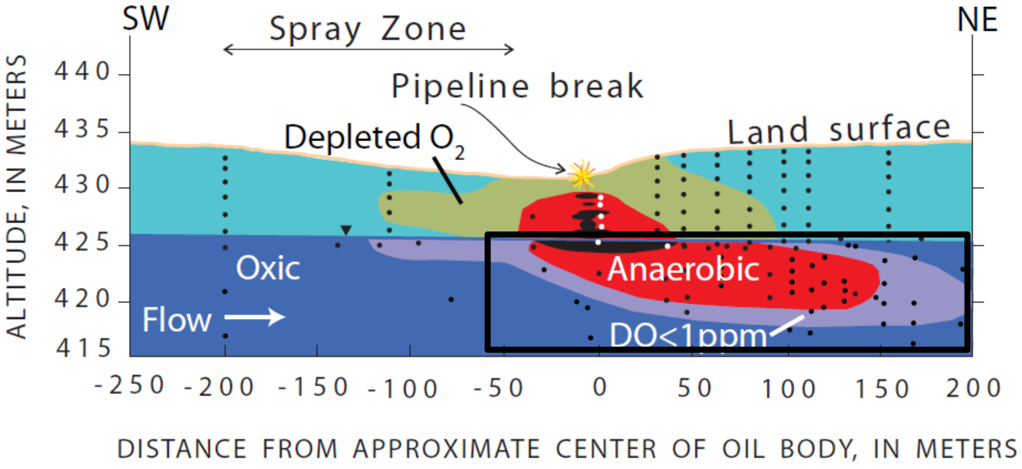
Tuccillo et al. 1999

Observed Long-Term SWQIs at Bemidji

30 years after oil body emplacement



Cozzarelli et al., 2015



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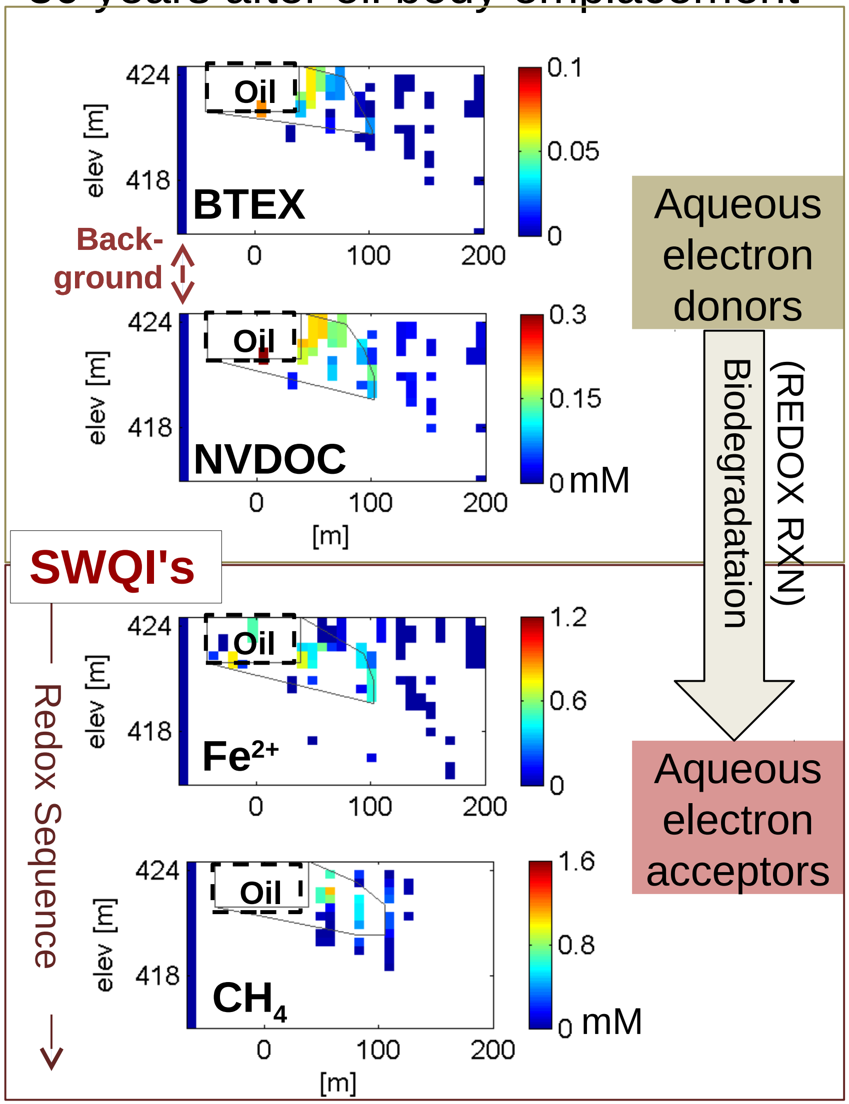
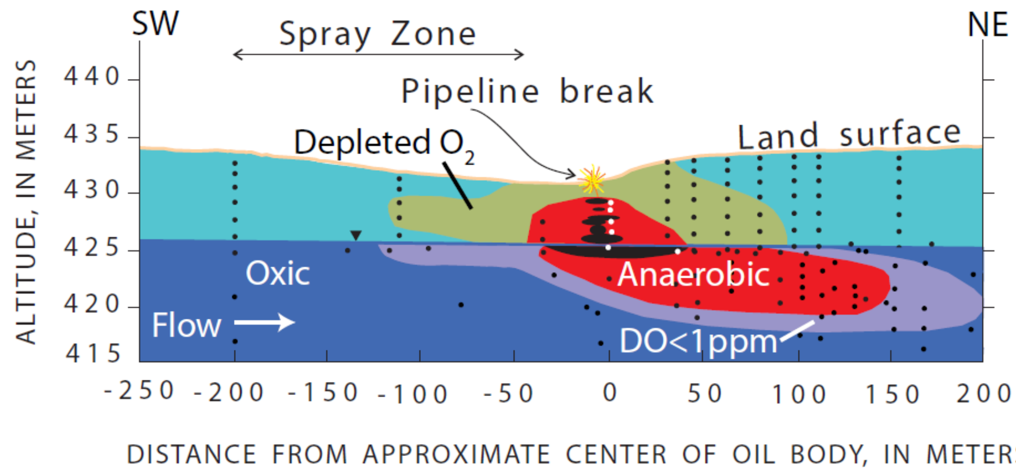


Cozzarelli et al., 2015



What controls production and limit of secondary plumes (Fe^{2+}, CH_4)?

Data Compiled to Constrain SWQI Processes

Sources

- **Oil components and saturation**
  - Initial oil[a,b,c], 2008[d,e,f]
- **BTEX**
  - 1987[a,g], 1993[h], 2008[c]
- **Nonvolatile organic carbon**
  - 1987[a,g], 1993[h], 2008[i]

SWQI processes

Sinks

- **Inorganic and CH_4 aqueous chemistry**
  - Initial[c], 1987[g,j], 1993[c,h], 2008[c,k]
- **Sediment Fe**
  - Initial[l], 1993[l], 2008[c,i]
- **CO_2 surface efflux**
  - 2008[m,n]

[a]Eganhouse et al. [1993]
[b]Essaid et al. [2003]
[c]Ng et al. [2014]
[d]Baedecker et al. [2011]
[e]Thorn and Aiken [1998]
[f]Bekins et al. [2005]
[g]Baedecker et al. [1993]
[h]Cozzarelli et al. [2001]
[i]Amos et al. [2012]
[j]Bennett et al. [1993]
[k]Amos et al. [2011]
[l]Tuccillo et al. [1999]
[m]Sihota et al. [2011]
[n]Sihota et al. [2014]

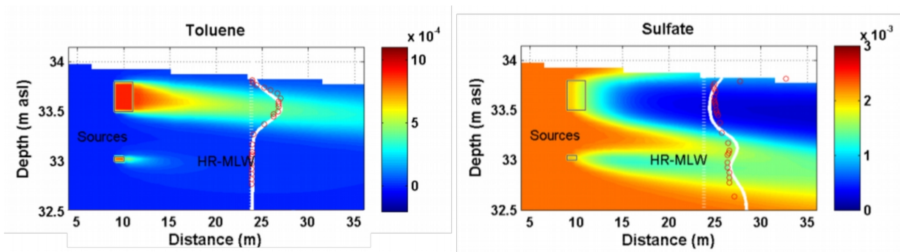
Requires extensive and complete data on plume sources and sinks

Ng et al. 2014 (JCH)

Synthesize Extensive Data: Geochemical Mass Balance and Reactive Transport Modeling

PHT3D: 3D Reactive Multicomponent Transport Model

[Prommer and Post 2010]



- Suitable for complex hydrologic, geochemical apps
- Incorporates well-established models

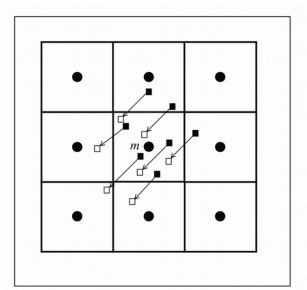
Coupling

Flow / Transport

Geochemical Reactions

MODFLOW/ MT3DMS v5.3
[Zheng and Wang, 1999]

- Groundwater flow (MODFLOW)
- Advective-dispersive transport

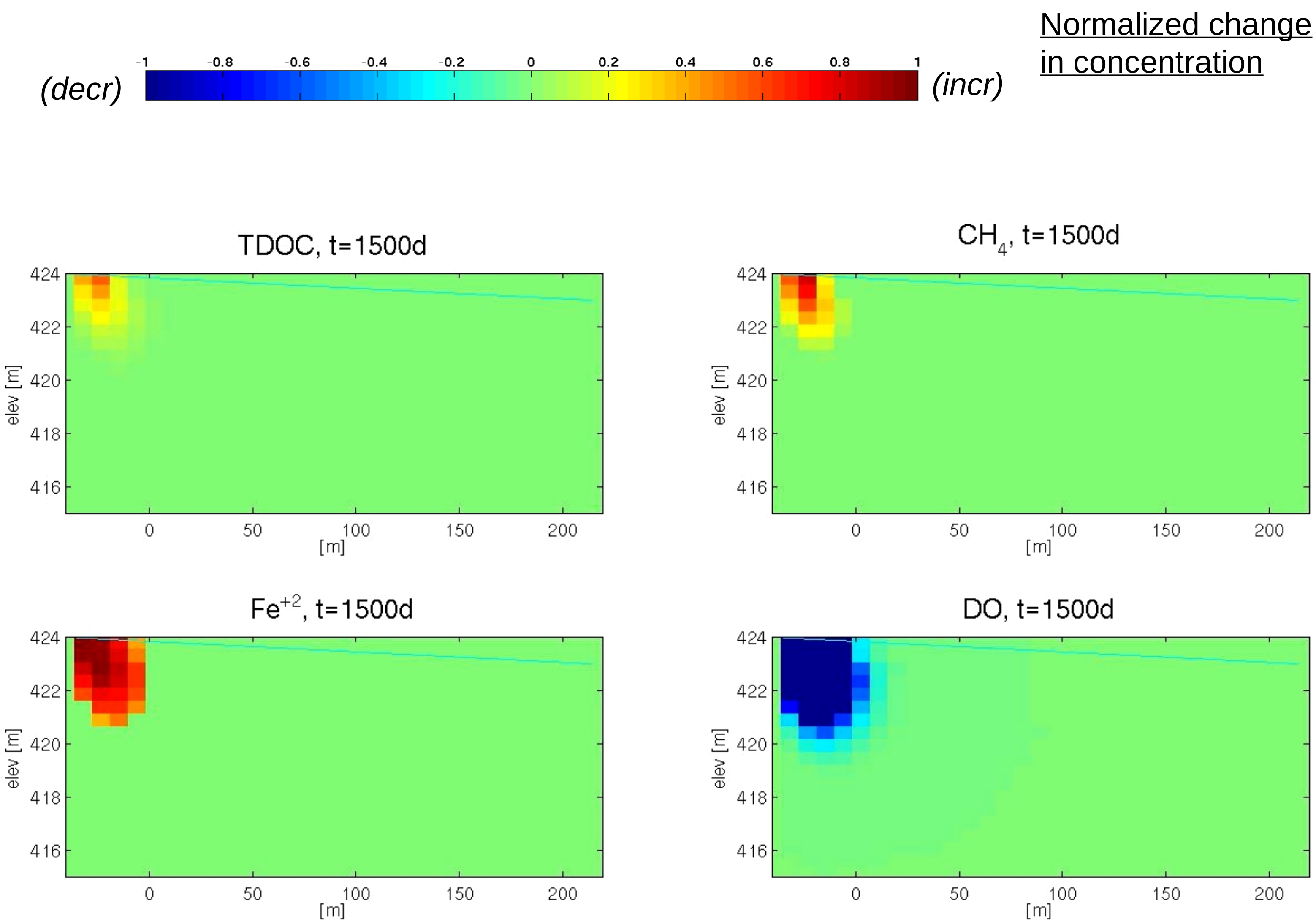


PHREEQC-2 [Parkhurst and Appelo, 1999]

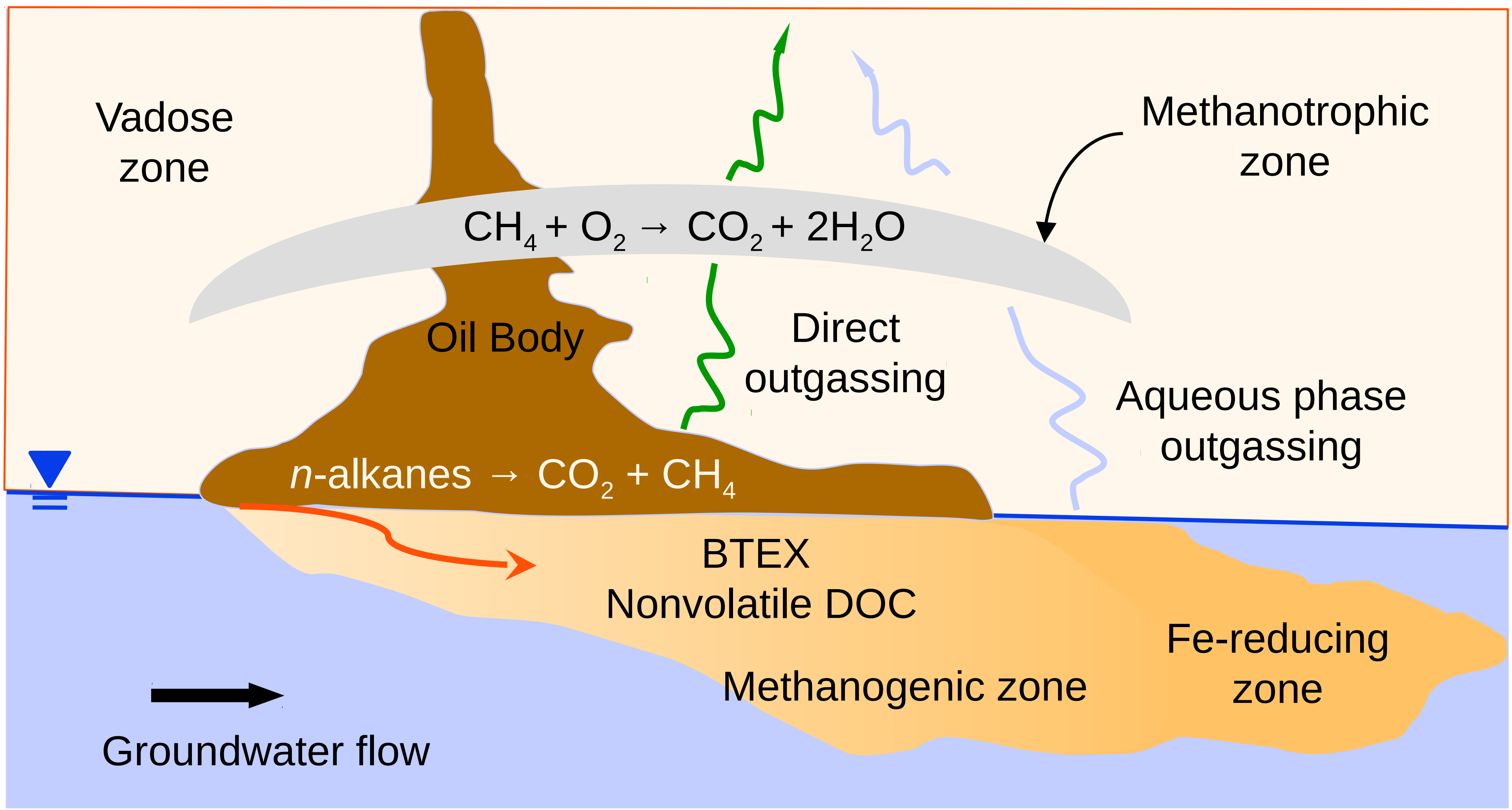
- Geochemical processes (equilibrium, kinetic)

Element or element valence state	PHREEQC notation	Formula used for default gram formula weight
Alkalinity	Alkalinity	$Ca_{0.5}(CO_3)_{0.5}$
Aluminum	Al	Al
Barium	Ba	Ba
Boron	B	B
Bromide	Br	Br
Cadmium	Cd	Cd
Calcium	Ca	Ca
Carbon	C	HCO_3
Carbon(IV)	C(4)	HCO_3
Carbon(-IV), methane	C(-4)	CH_4
Chloride	Cl	Cl

Example Plume Simulation

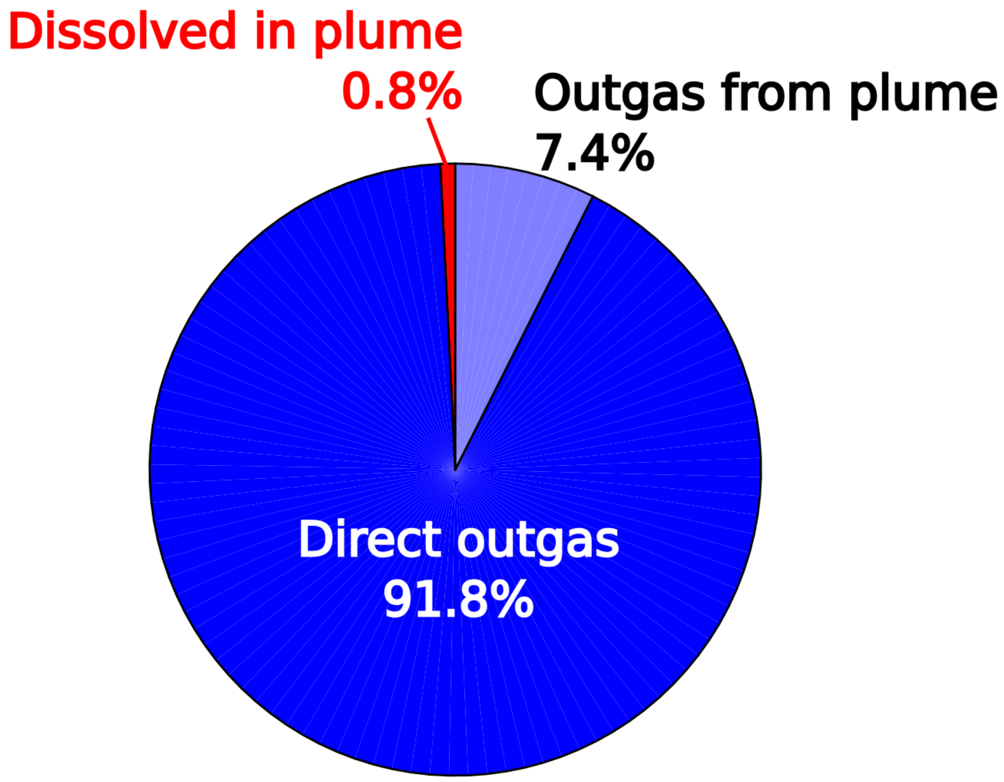


Overview of Site Processes



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

CH_4 Plume Production and Fate



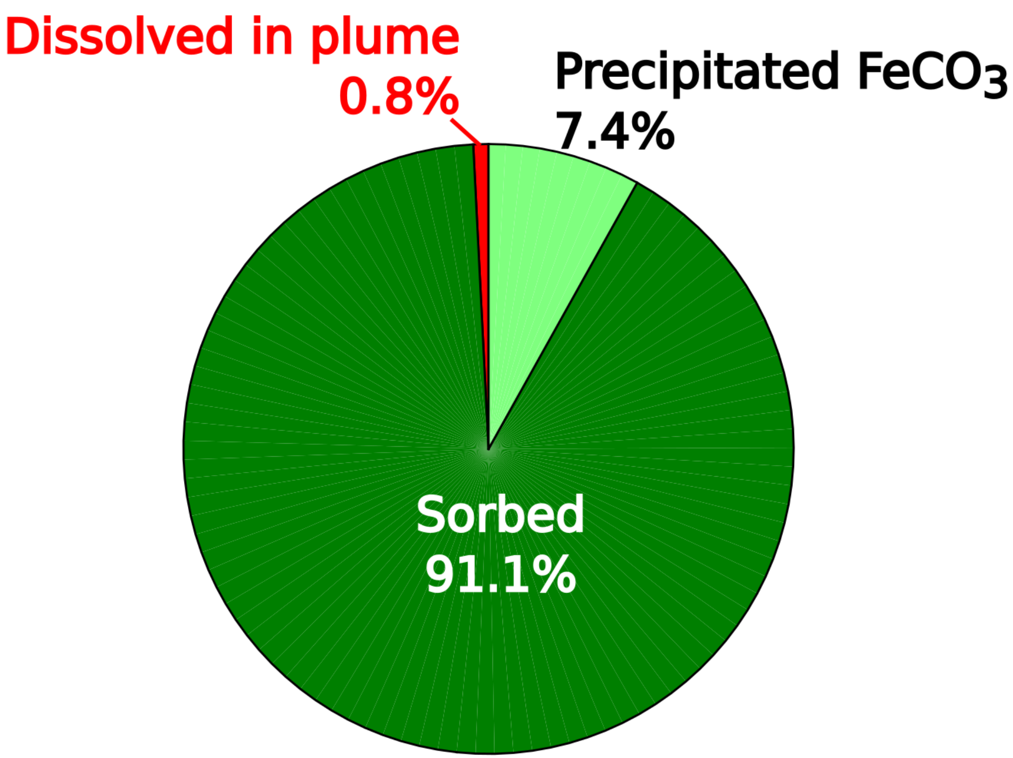
Compare: Diluent spill in Guadalupe Oil Field (CA)

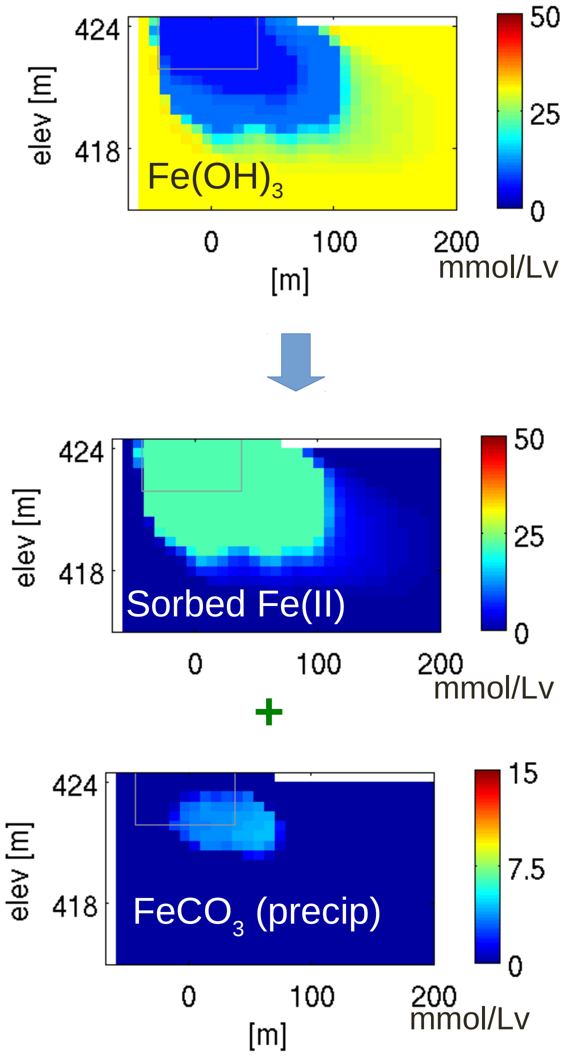
C Mass flux in

- Groundwater: 1-10%
- Vapor: 90-99%

[Lundegard and Johnson, 2006]

Fe(II) Plume Production and Fate





Ng et al. 2014 (JCH); Ng et al. 2015 (WRR)

Learning about Secondary Water Quality Impacts from modeling the Bemidji Oil Spill

- Secondary Water Quality **Impacts**:
  - **30+ yrs Fe^{2+}, (early!) CH_4**

- Secondary Water Quality **Controls**:

CH_4 Plume -

- Driven by diverse degrading oil components
- Attenuated by out-gassing
  (>99% of CH_4 exits as surface CO2 efflux)

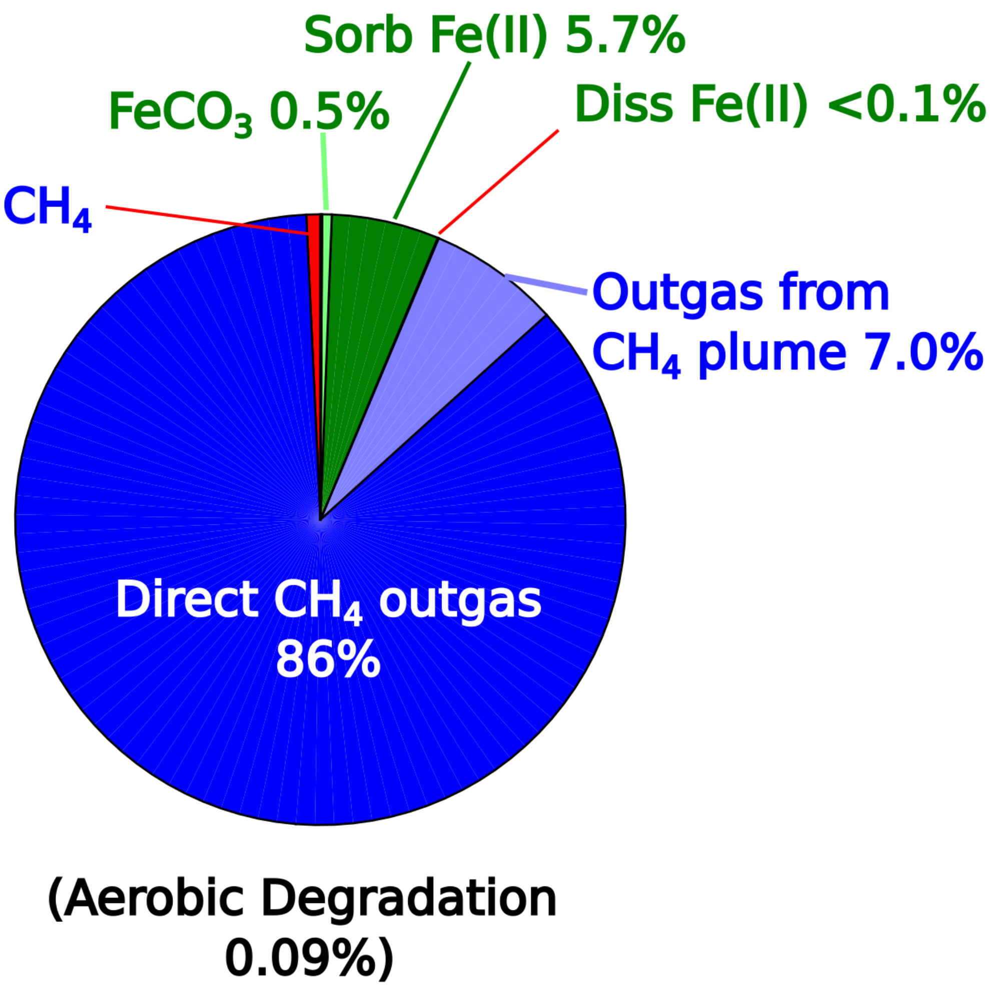
Fe plume -

- Driven by reduction of (depleting) Fe(III) oxide minerals
- Attenuated by immobilization on sediments
  (>99% of reduced Fe is attenuated on sediments)

Ng et al. 2014 (JCH); Ng et al. 2015 (WRR)

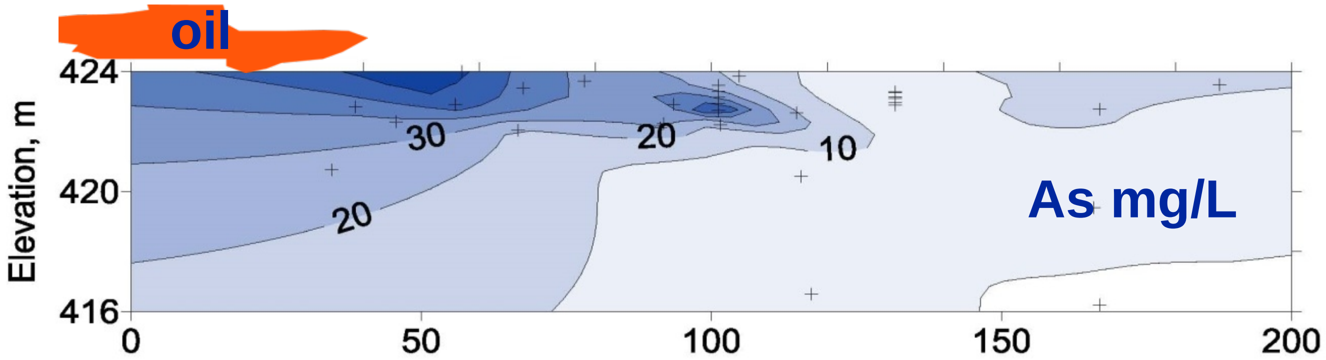
Learning about oil degradation from the SWQI model

Fate of oil lost from pool (e^- balance):



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

Ongoing Lessons: Groundwater Plume



- Arsenic immobilization*
- Heat generated from biodegradation
- Fate of oil metabolites**
- Mixed BTEX ethanol plume experiments

*Cozzarelli et al., 2015, Arsenic Cycling in Hydrocarbon Plumes: Secondary Effects of Natural Attenuation, Groundwater, doi: 10.1111/gwat.12316

**Bekins et al., 2016, Crude Oil Metabolites in Groundwater at Two Spill Sites, Groundwater, doi: 10.1111/gwat.12419

Ongoing Lessons: Oil

Hydrophobic soils:

- Mapped areas of hydrophobic soils*
- Pilot remediation plots

Water ponded on hydrophobic soil

Source Zone

- Seasonal gas efflux cause
- Oil composition changes

Hydrophobicity inhibits plant growth

*Adams et al., 2016, International Journal of Environmental Science and Technology.

Ongoing Lessons: Methods Development

- Biogeophysics
- Freezing drive shoe
- Colloidal boroscope flowmeter
- Optical fluoresence probe
- Hydraulic conductivity profiling
- Low cost ^{14}C analysis

Collaborative Agreement

- Maintain the research site
- Promote/advance science, research, education related to the fate, transport, and natural attenuation of crude oil contamination in the subsurface
- Make results widely available to researchers, industry, consultants, regulators, teachers, and students

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http://mn.water.usgs.gov/projects/bemidji/policy.html

Continuing to learn from Bemidji oil spill

Use the site's capabilities to develop new methods and understanding about oil degradation and beyond

Groundwater
- 255 Monitoring wells

Oil
- 35 Oil monitoring wells

Gases
- 22 Vapor wells
- Surface CO_2 efflux
- 14 continuous CO_2 and O_2

Recharge
- 4 Moisture probe arrays
- 4 Suction lysimeter arrays
- 6 Temperature profile arrays

Geophysics
- Self potential
- Magnetic susceptibility
- Electrical resistivity

Spatially referenced database
- DO, pH, SpCond
- Water levels
- Oil thicknesses

http://mn.water.usgs.gov/projects/bemidji/