Integrated Investigation of Natural Attenuation Processes at the Bemidji Crude Oil Spill Site:

Closing Gaps in Conceptual Models and Quantification of Degradation Rates

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Contributors

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- Barbara Bekins, Geoff Delin (USGS)

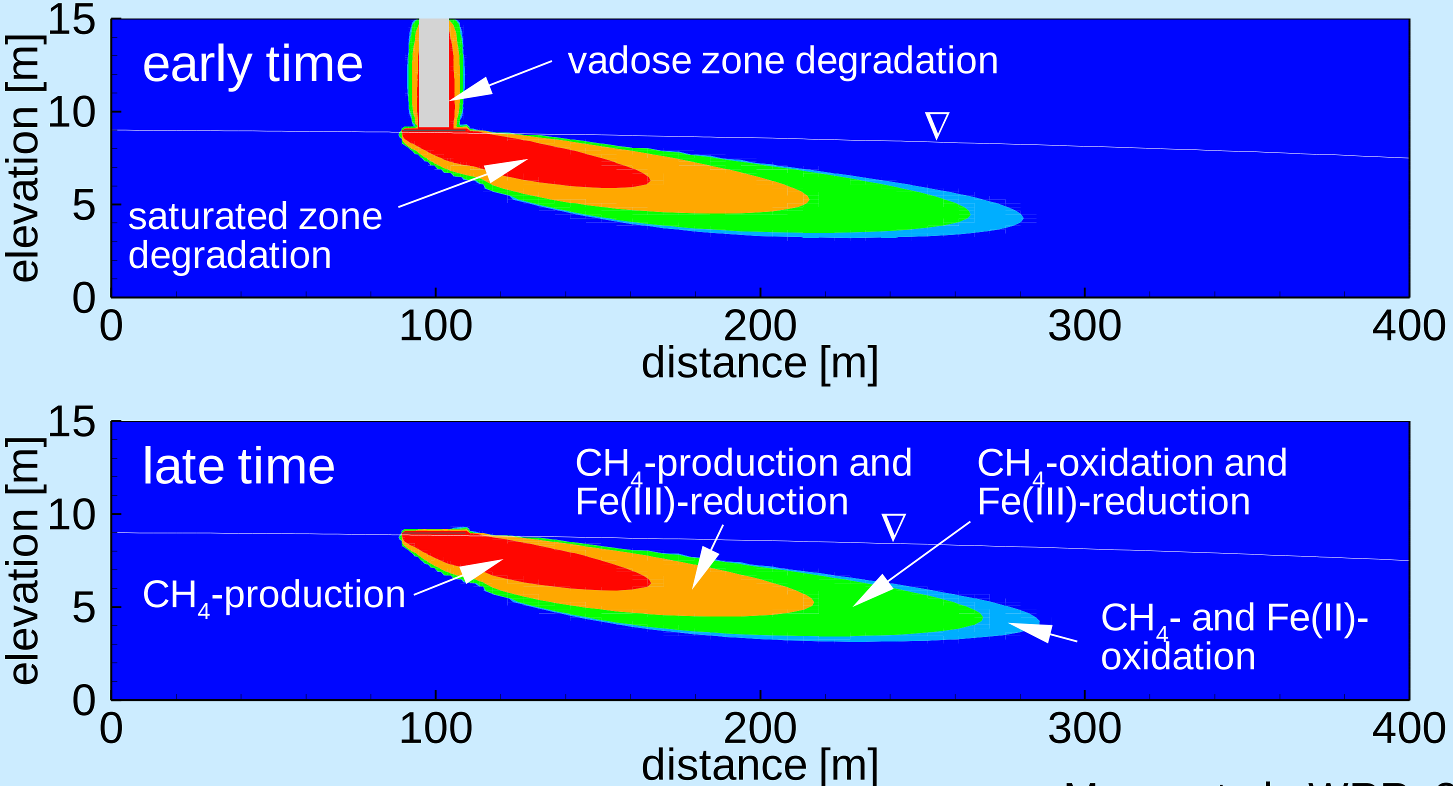
Bemidji Crude Oil Spill

- One of the key goals: Degradation rates and source zone longevity

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

Original Research Idea

- Integrated investigation of natural attenuation in shallow unconfined aquifers
- Reactive transport modeling in variably saturated media constrained by field data

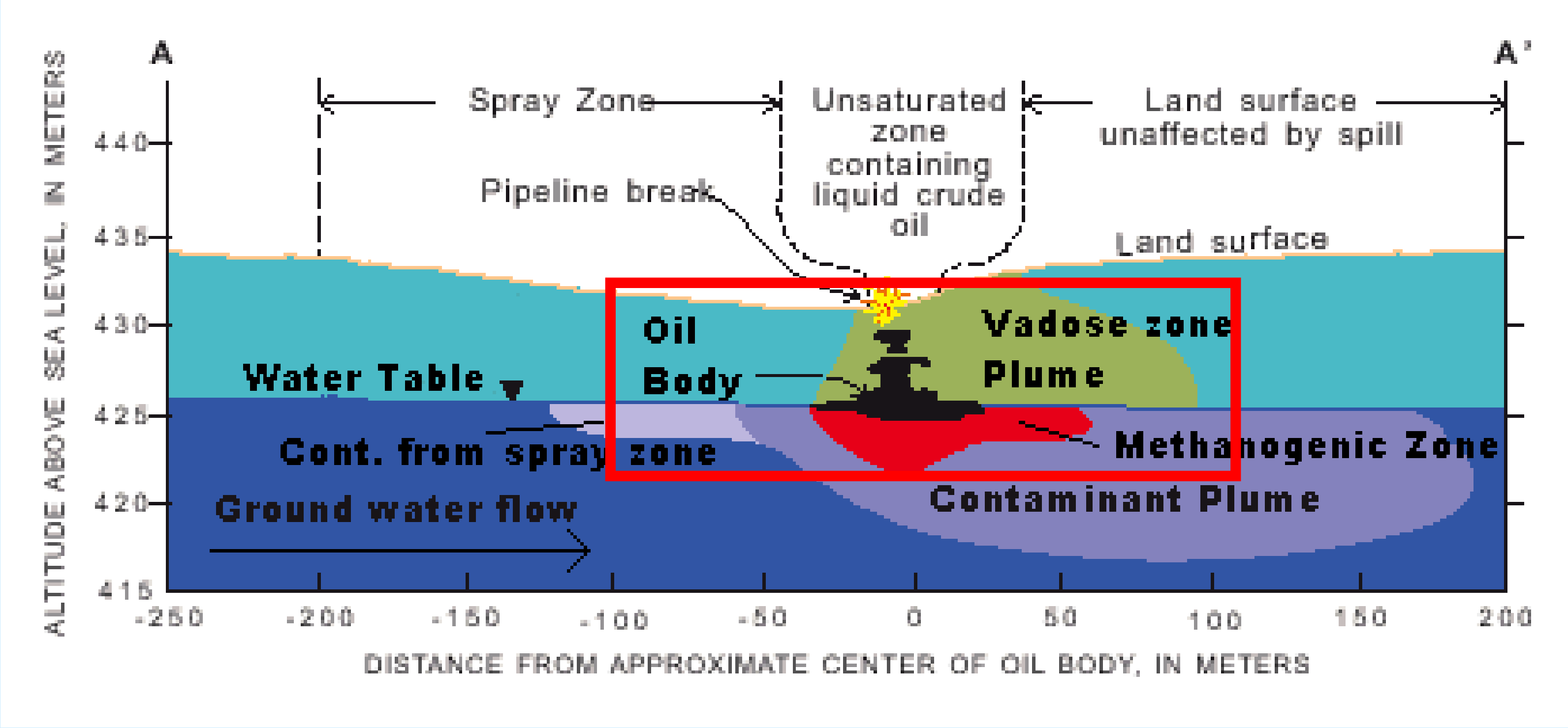


Mayer et al., WRR, 2002

Knowledge Gaps: Methanogenesis and mass transfer across capillary fringe

- Saturated zone: a general assumption is that no gas phase is present
- Mass transfer across capillary fringe: a top-down process?
- Blicher-Mathiesen et al., 1998, J. Hydrol, observed depletion of argon in zone of denitrification – attributed to gas exsolution
- Does this process occur at the Bemidji site in the region of active methanogenesis?

Groundwater and Vadose Zone Contamination at the Bemidji Site



Modified from USGS Fact Sheet 084-98

Research Questions

- What is the contribution of methanogenesis to contaminant degradation in saturated zone?
- Is gas transfer to the vadose zone ocurring?
- What is the overall rate of vadose zone contaminant degradation?
- What is the fate of methane in the vadose zone?

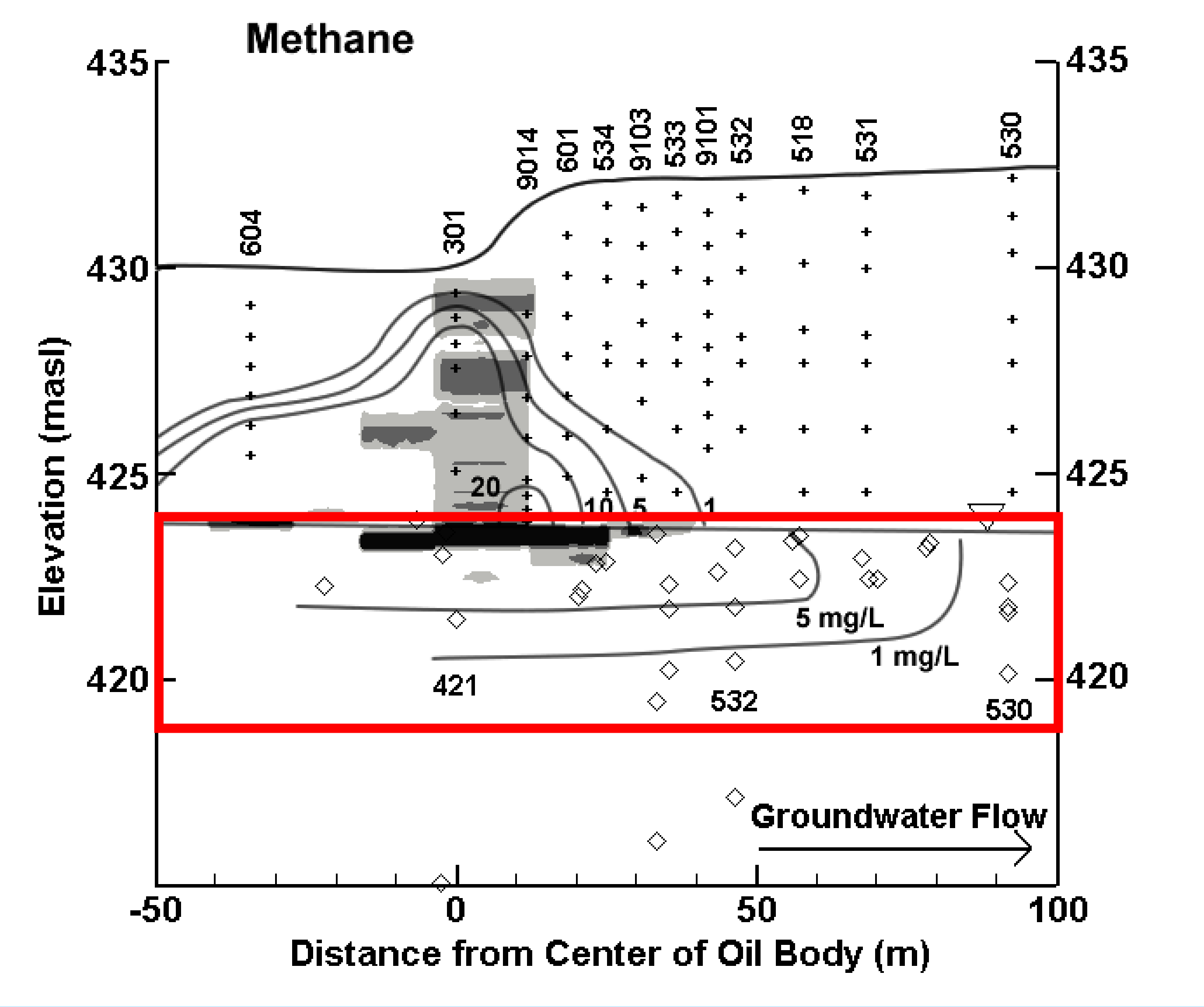
- See also poster # 34 by Amos et al.

Bemidji Field Work - Overview

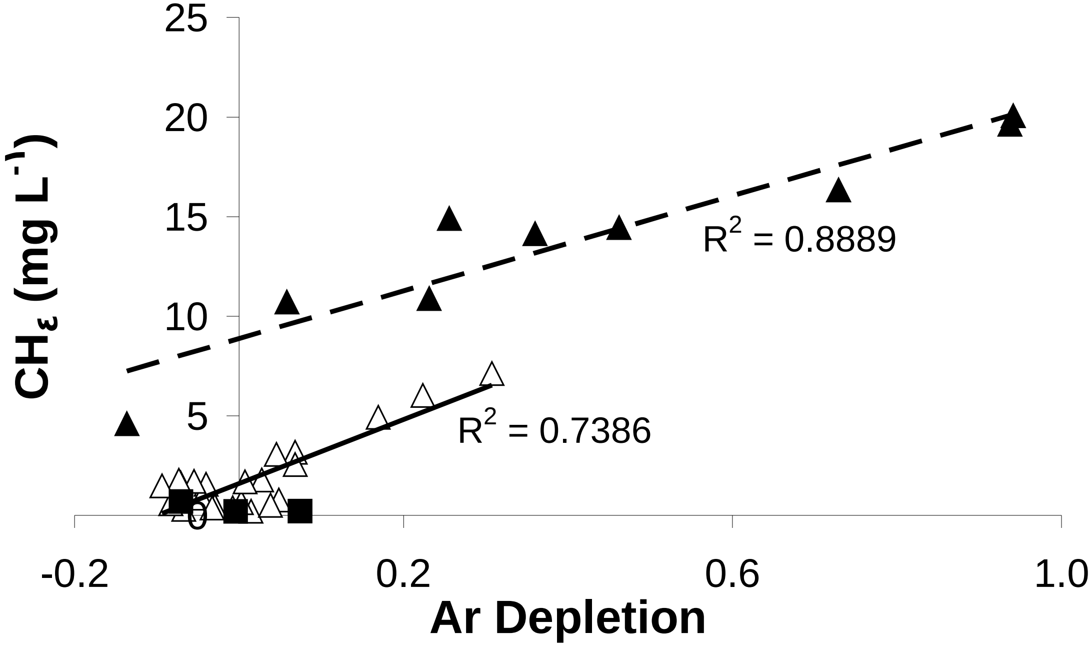
- 2002, 2003, 2004, 2007, 2008
- Dissolved Gas Data
- Vadose Zone Gas Data
- MicroGC – in field analysis
- Reactive Gases
  - CH_4, O_2, CO_2
- Inert Gases
  - Ar, N_2

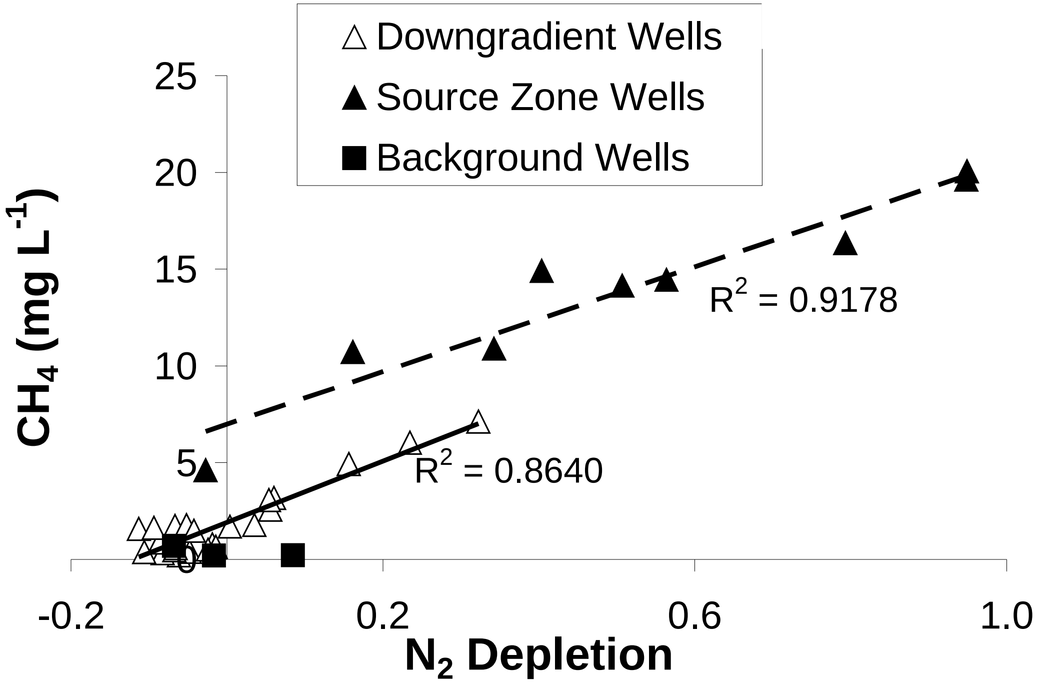
Amos et al., 2005, *Water Resour. Res.*

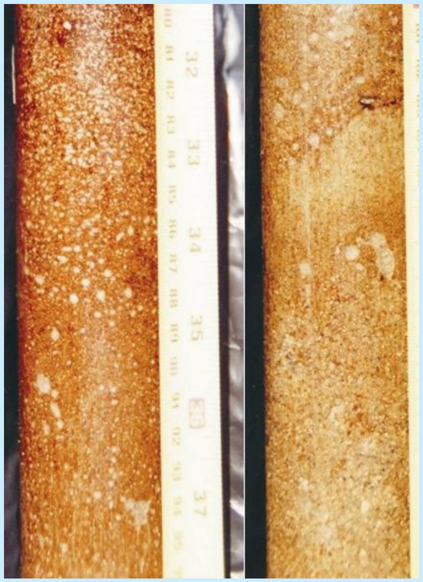
CH_4- Concentrations (2003)



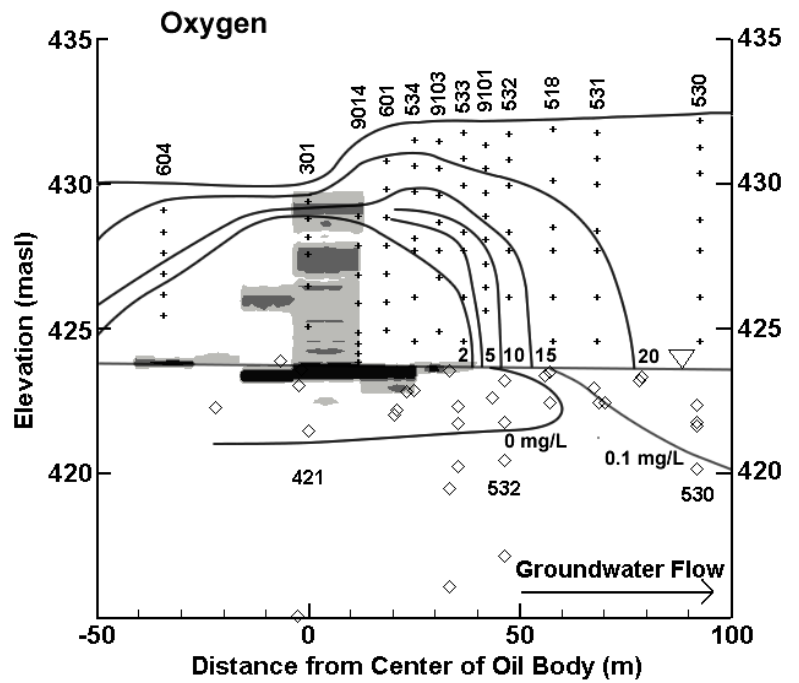
Saturated Zone: Evidence for Gas Exsolution

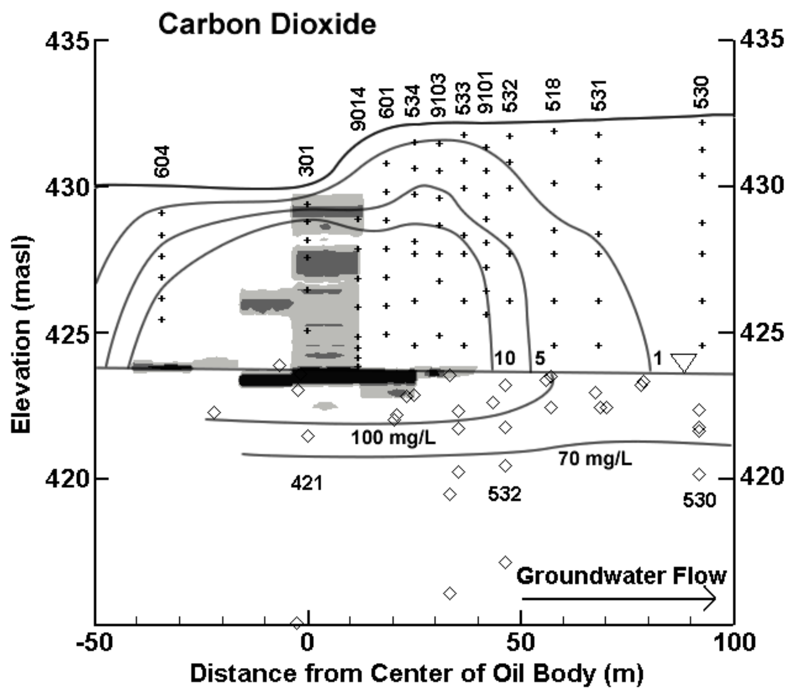


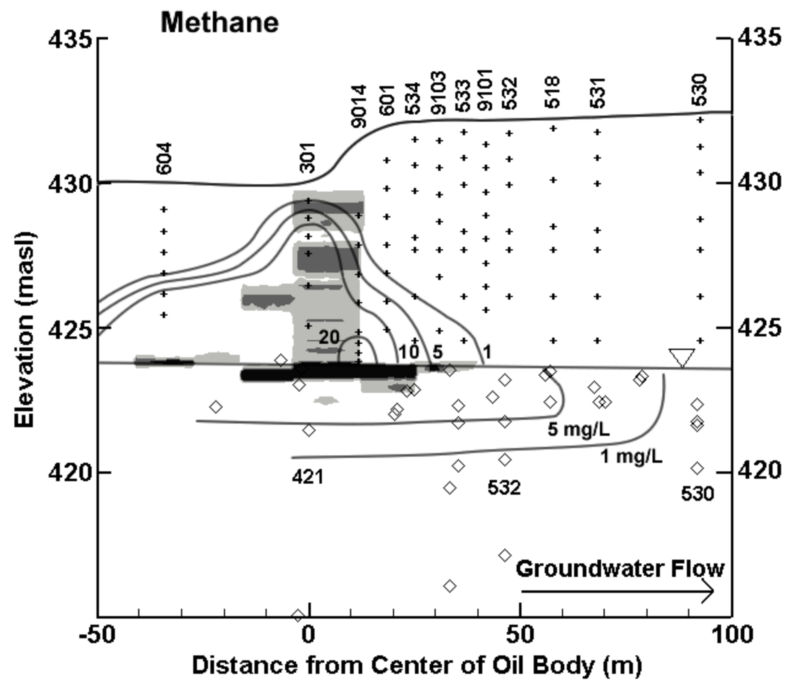




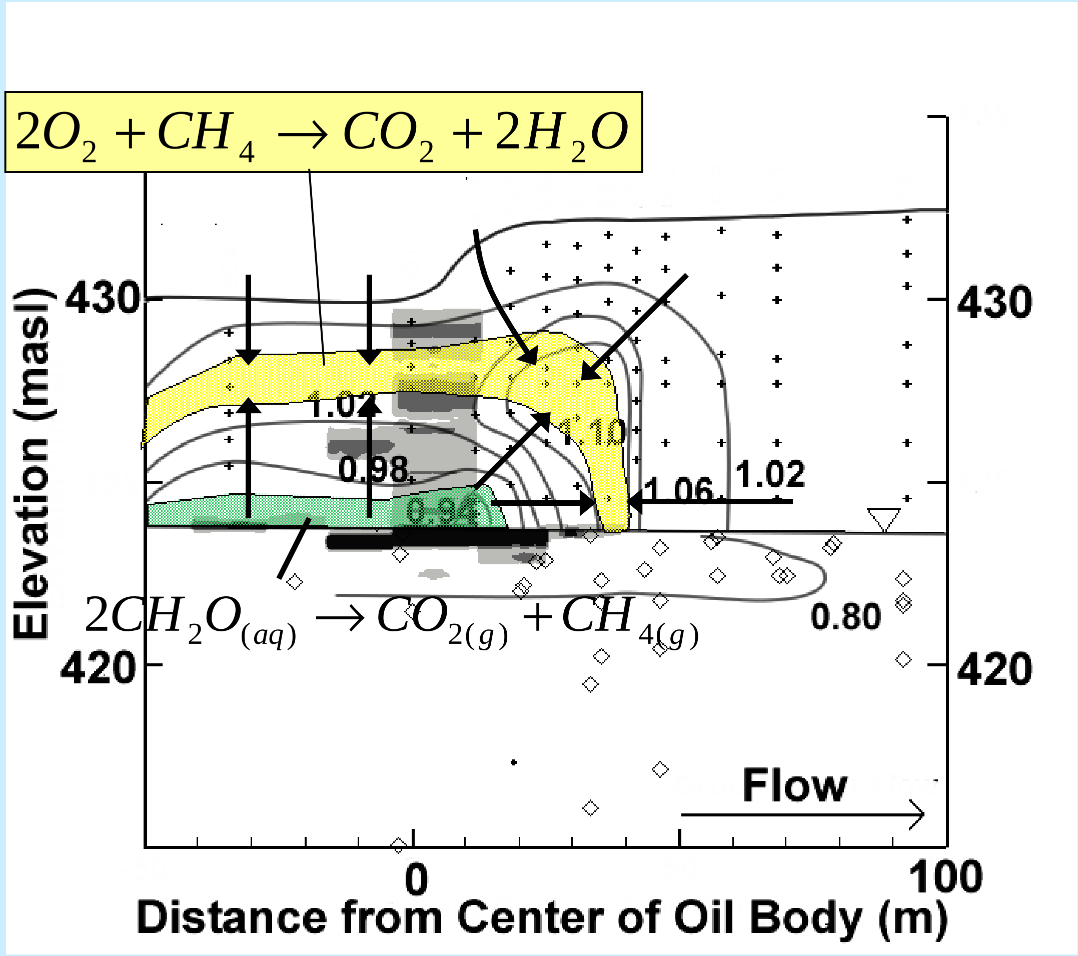
Vadose Zone
O_2, CH_4, and CO_2







Vadose Zone – Interpretation



- Methanogenic Zone
  - Increases gas pressure
  - Induces an upward advective gas flow
  - Deplete non-reactive gases
- Methanotrophic Zone
  - Decrease in gas pressure
  - Induces an inward advective gas flow
  - Enrichment non-reactive gases

Can we use depletion and enrichment of nonreactive gases to constrain the dynamics between reactions and fluxes?

Reactive Transport Modeling of Vadose Zone Processes

Mass Balance Equation

$$\frac{\partial}{\partial t}\left[S_a \; T_a^k\right] + \frac{\partial}{\partial t}\left[S_g \; T_g^k\right] + \nabla \cdot \left[\mathbf{q}_a T_a^k\right] + \nabla \cdot \left[\mathbf{q}_g T_g^k\right]$$

$$- \nabla \cdot \left[S_a \mathbf{D}_a \nabla T_a^k\right] - \nabla \cdot \left[S_g \phi \mathbf{D}_g^k \nabla T_g^k\right] - Q_{a,a}^k - Q_{a,s}^k - Q_{a,ext}^k - Q_{g,ext}^k = 0$$

$$k = 1, N_c$$

$$T_g^k$$

Momentum Balance Equation

$$\mathbf{q}_g = -\frac{k_{rg}\mathbf{k}}{\mu_g}\left(\nabla p_g + \rho_g g \nabla z\right)$$

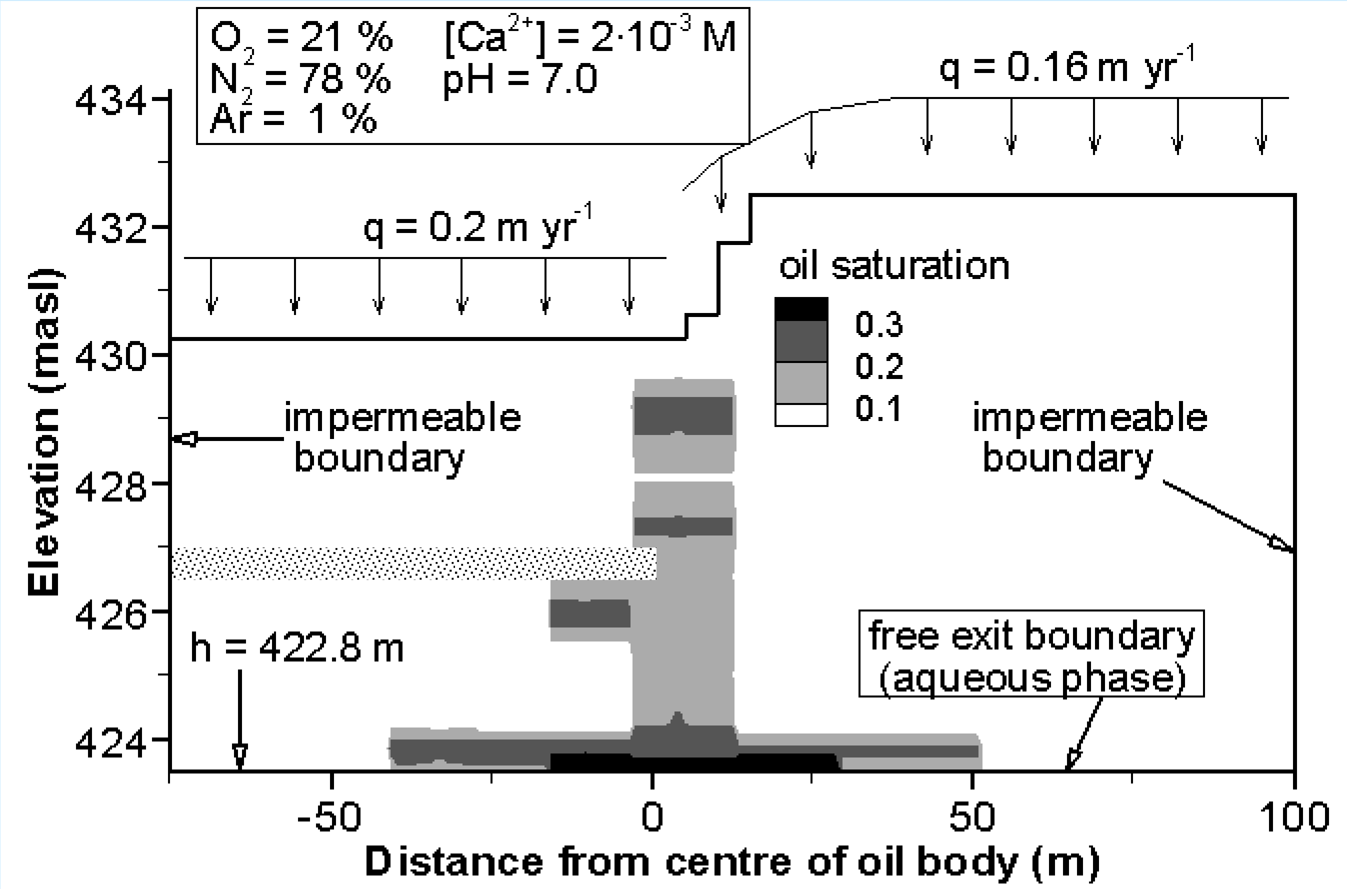
$$p_g = \sum_{i=1}^{N_g} p_g^i \qquad p_g^i = RTc_g^i$$

See also poster # 35 by Molins and Mayer

Molins and Mayer, *Water Resour. Res., 2007*

Molins et al., 2009, in preparation

Bemidji Vadose Zone Simulation



$\phi = 0.38$

$K_h = 10^{-11}\ m^2$

$K_v = 3 \cdot 10^{-12}\ m^2$

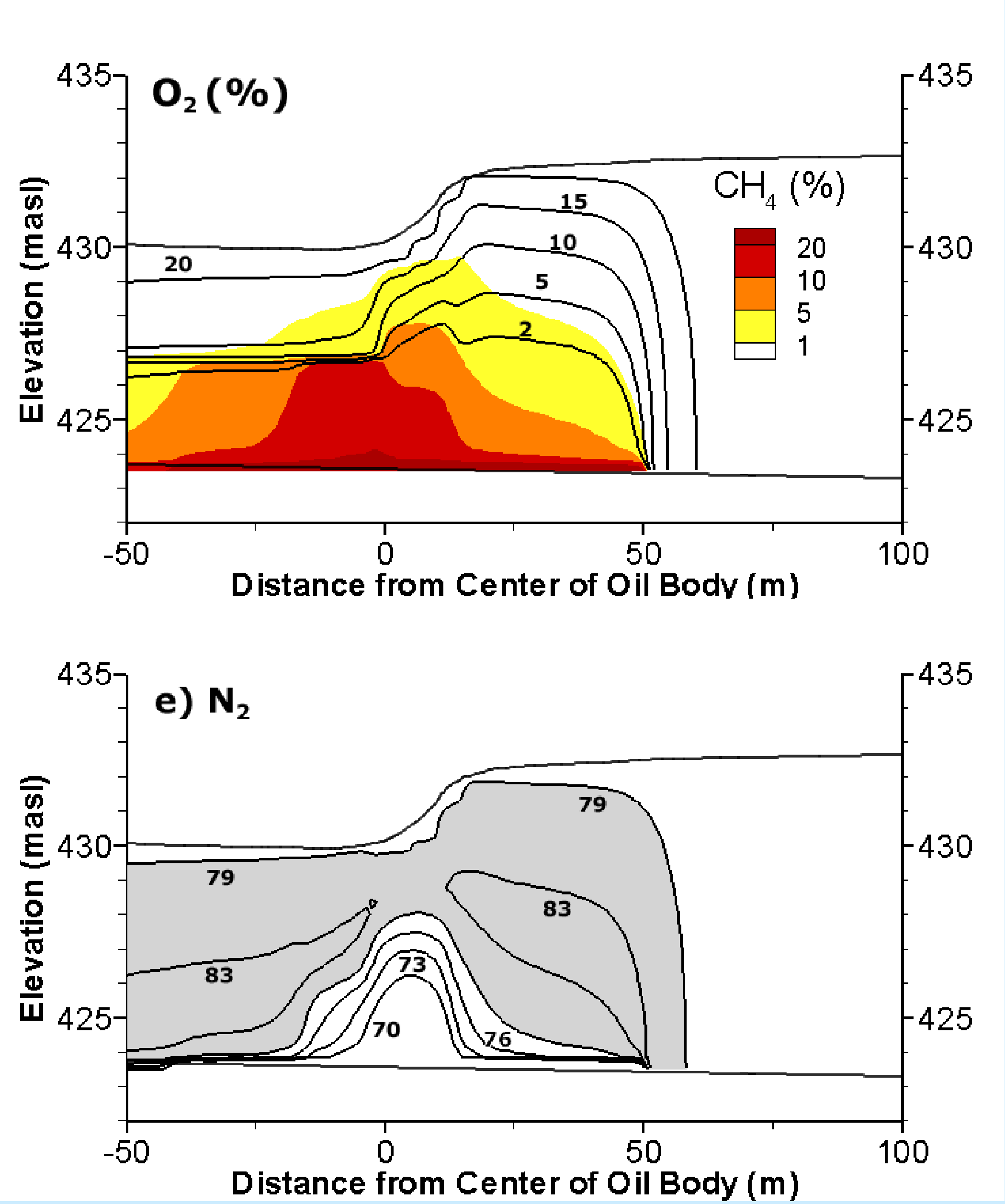
lens:

$\phi = 0.30$

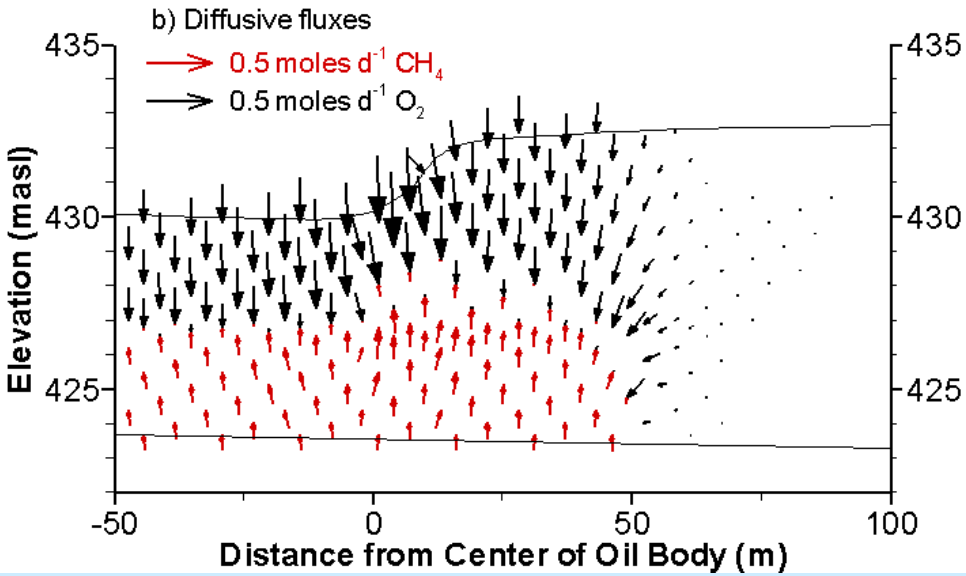
$K_h = 10^{-13}\ m^2$

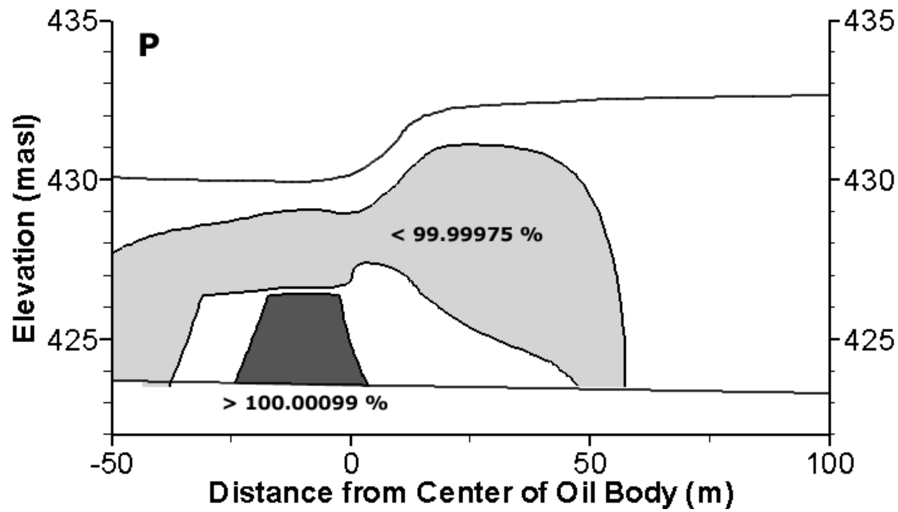
$K_v = 3 \cdot 10^{-14}\ m^2$

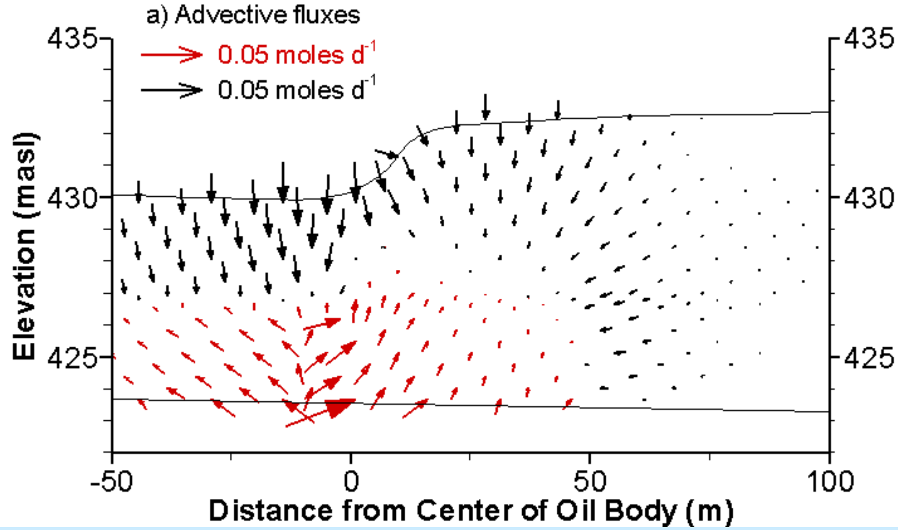
Simulated O_2, CH_4, and N_2 Concentrations in 2007



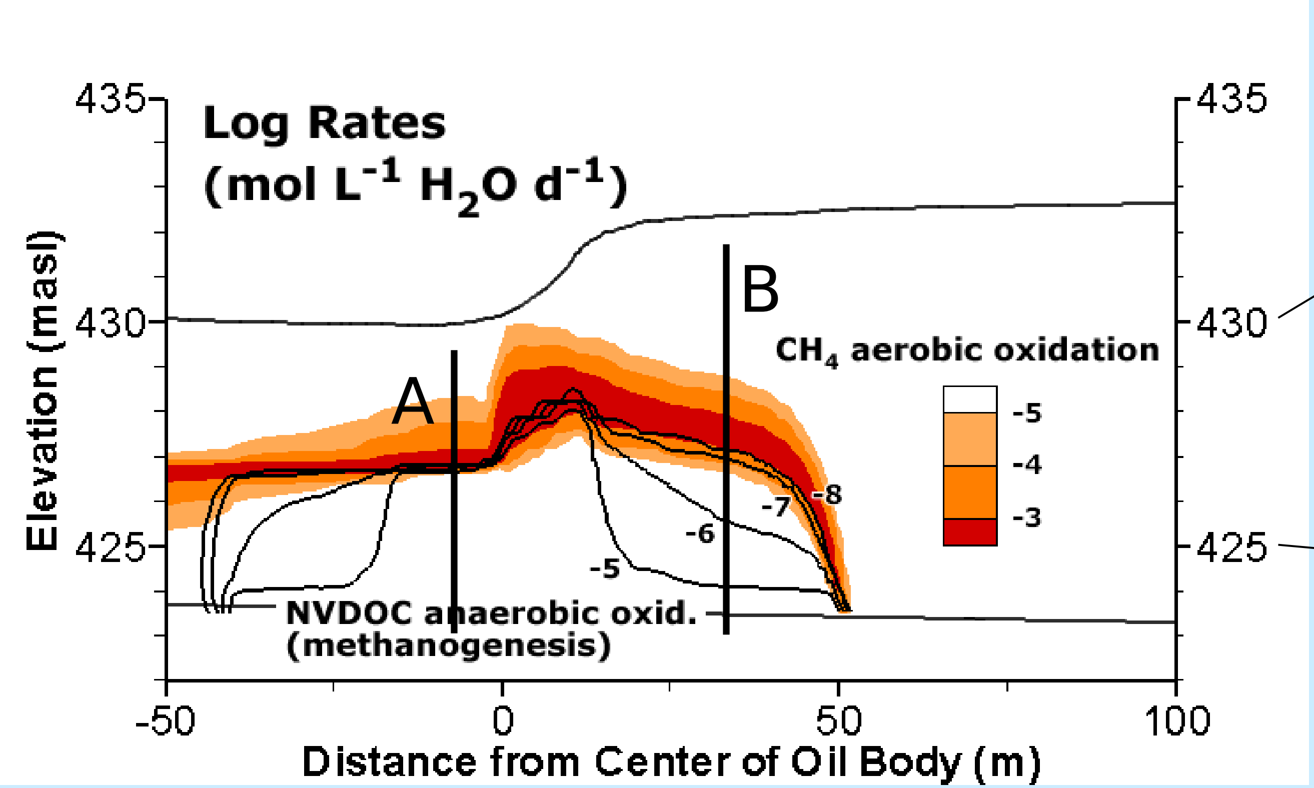
Simulated Gas Pressures and Fluxes

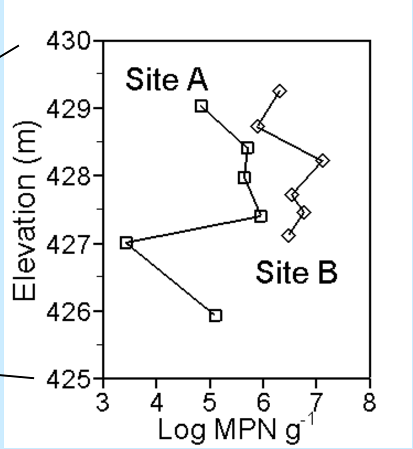






Simulated Reactions Rates (2007)

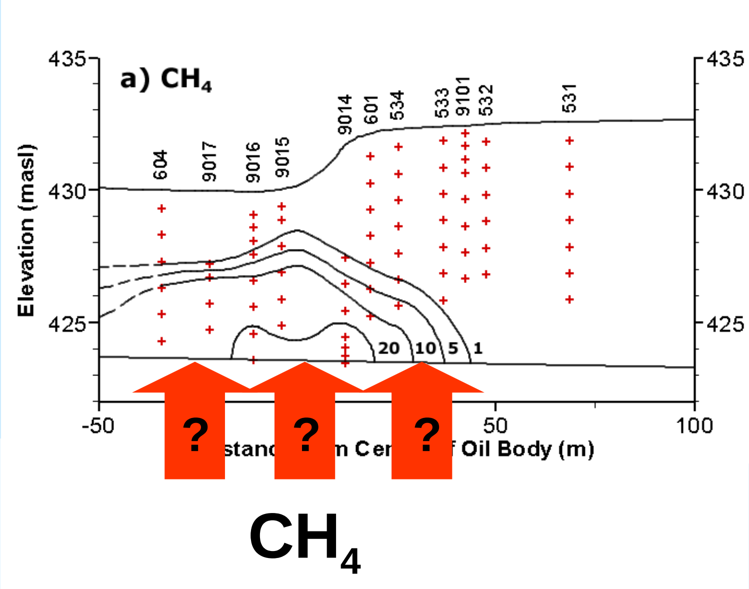


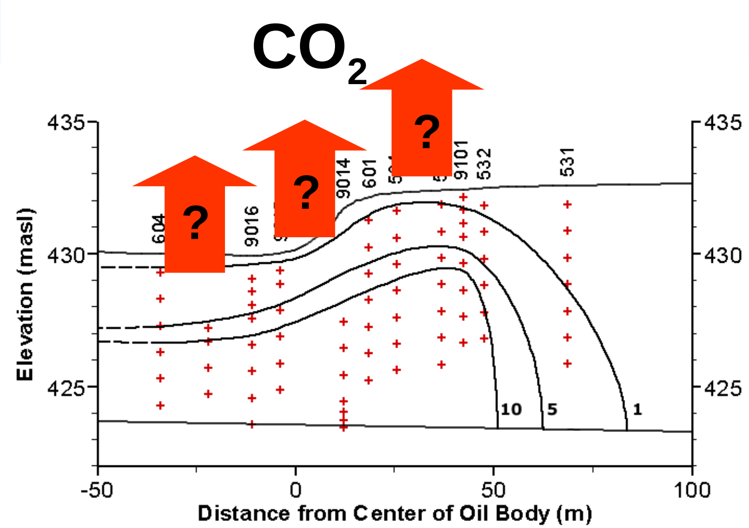


Data from Bekins, 2005

Implications for Natural Attenuation Research

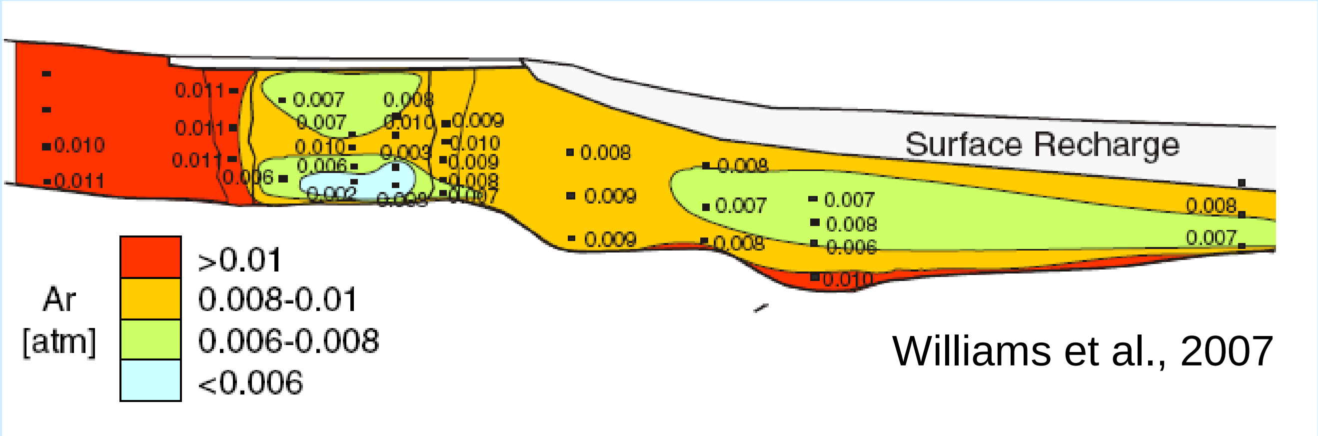
- Gas generation in saturated zone is occurring
- Simulations suggest that CH_4 generation is focused on smear zone
- Uncertainties for C-balance and fluxes, therefore also rates
- Additional field work planned for 2009: IRGA CO_2 flux chambers to provide further model constraint





Implications for GW Contamination and Remediation Research

- Use of inert gases as transport and reaction tracers in contamination and remediation studies



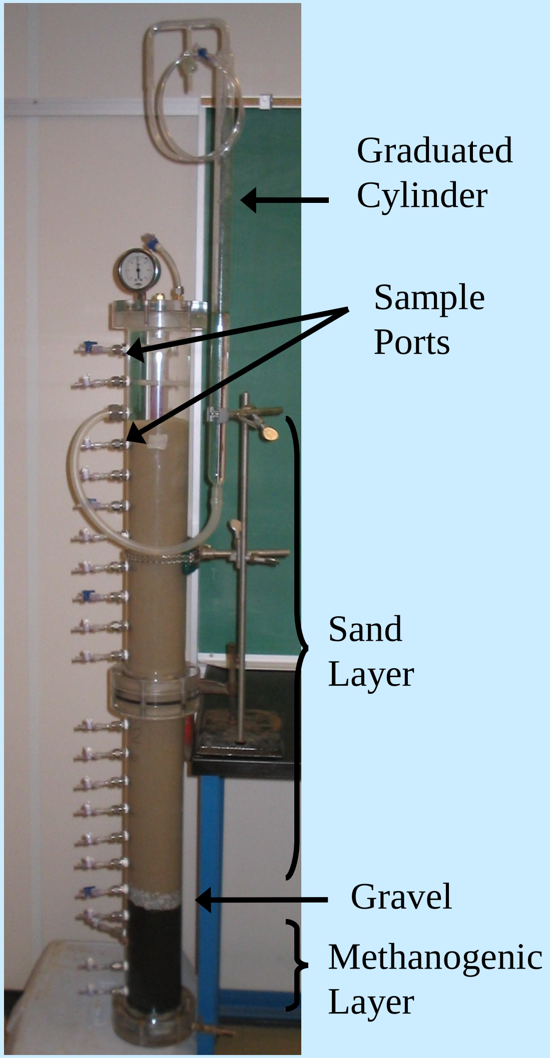
- Current research initiative: Role of gas generation and gas transfer processes in groundwater remediation and for highly degradable contaminants

Implications for Reactive Transport Modeling

- Implementation of new processes in the MIN3P reactive transport model
  - Gas exsolution, Gas entrapment and release (Amos and Mayer, JCH, 2006)
  - Gas ebullition (Amos and Mayer, ES&T, 2006)
  - Gas advection (Molins and Mayer, WRR, 2007)
- Comprehensive and long term data set provides ideal platform for model validation and quantitative assessment of natural attenuation using mechanistic reactive transport models

Thank You! Questions?

Column Experiments



- Ebullition: movement of discontinuous gas phase driven by buoyancy forces
- Objective:
  - Investigate ebullition by monitoring dissolved gases
- Column:
  - 1.2 m long
  - Methanogenic material in bottom 24 cm

Amos et al., *ES&T, 2006*

Results from Column Experiments

CO_2 CO_2 N_2
CH_4 CH_4