REACTIVE AND INERT GASES IN GROUNDWATER CONTAMINATION AND REMEDIATION STUDIES

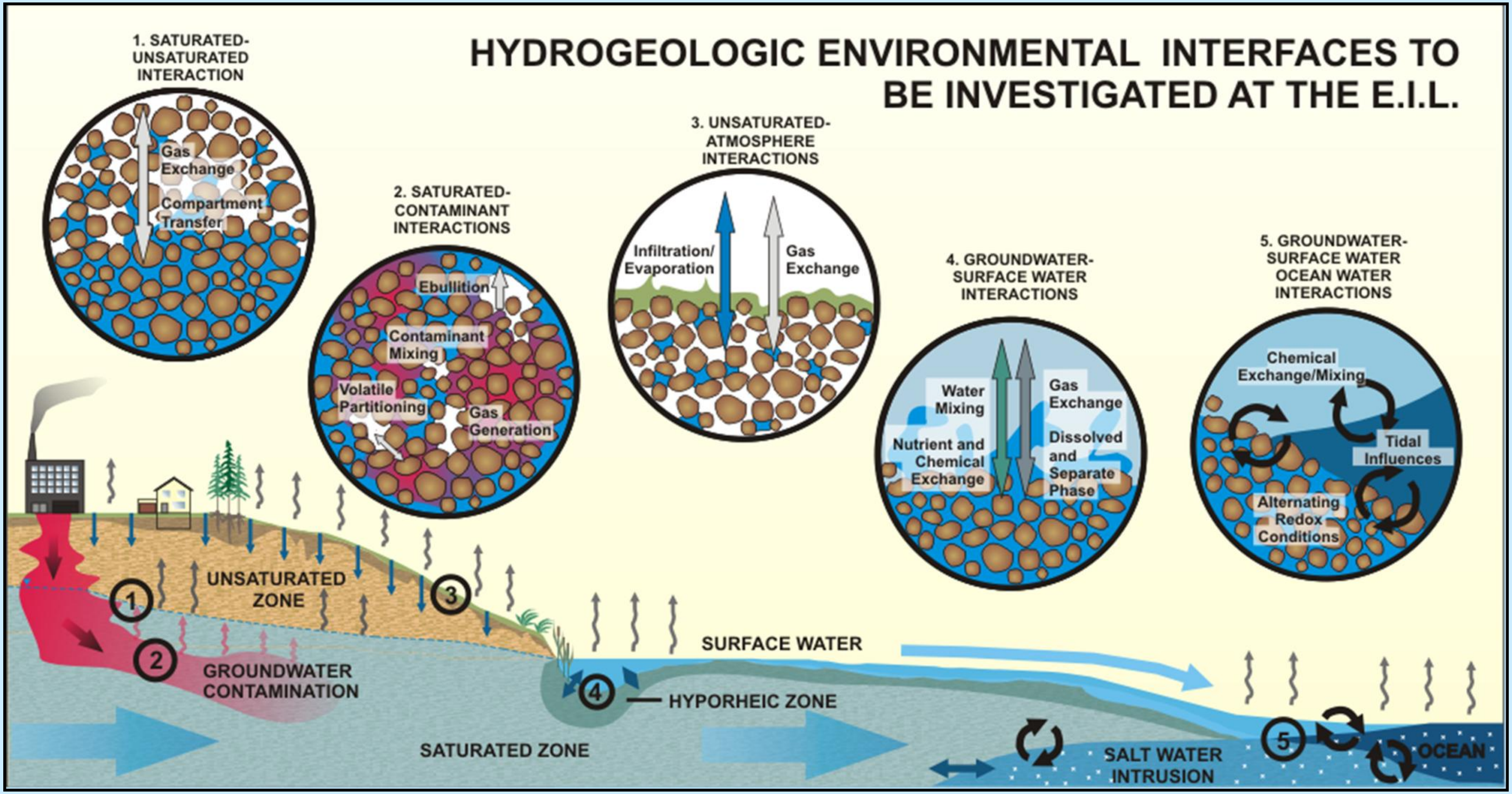
K. Ulrich Mayer

Dept. Earth, Ocean and Atmospheric Sciences
University of British Columbia

Acknowledgements

- Randi Williams, M.A.Sc., UBC, 2005, now at BGC Engineering Ltd.)
- Richard Amos (Ph.D, UBC, 2006, now at Carleton Univ)
- Sergi Molins (Ph.D., UBC, 2007, now at LBNL)
- Katie Jones (M.Sc., UBC, 2009, now at BGC Engineering Ltd.)
- Natasha Sihota (Ph.D. UBC, 2014, now at Chevron Energy Technology Company)
- Andrea Chong (M.Sc., UBC, in progress)
- Barbara Bekins, USGS, Menlo Park, CA
- Jared Trost, USGS, Minneapolis, MN

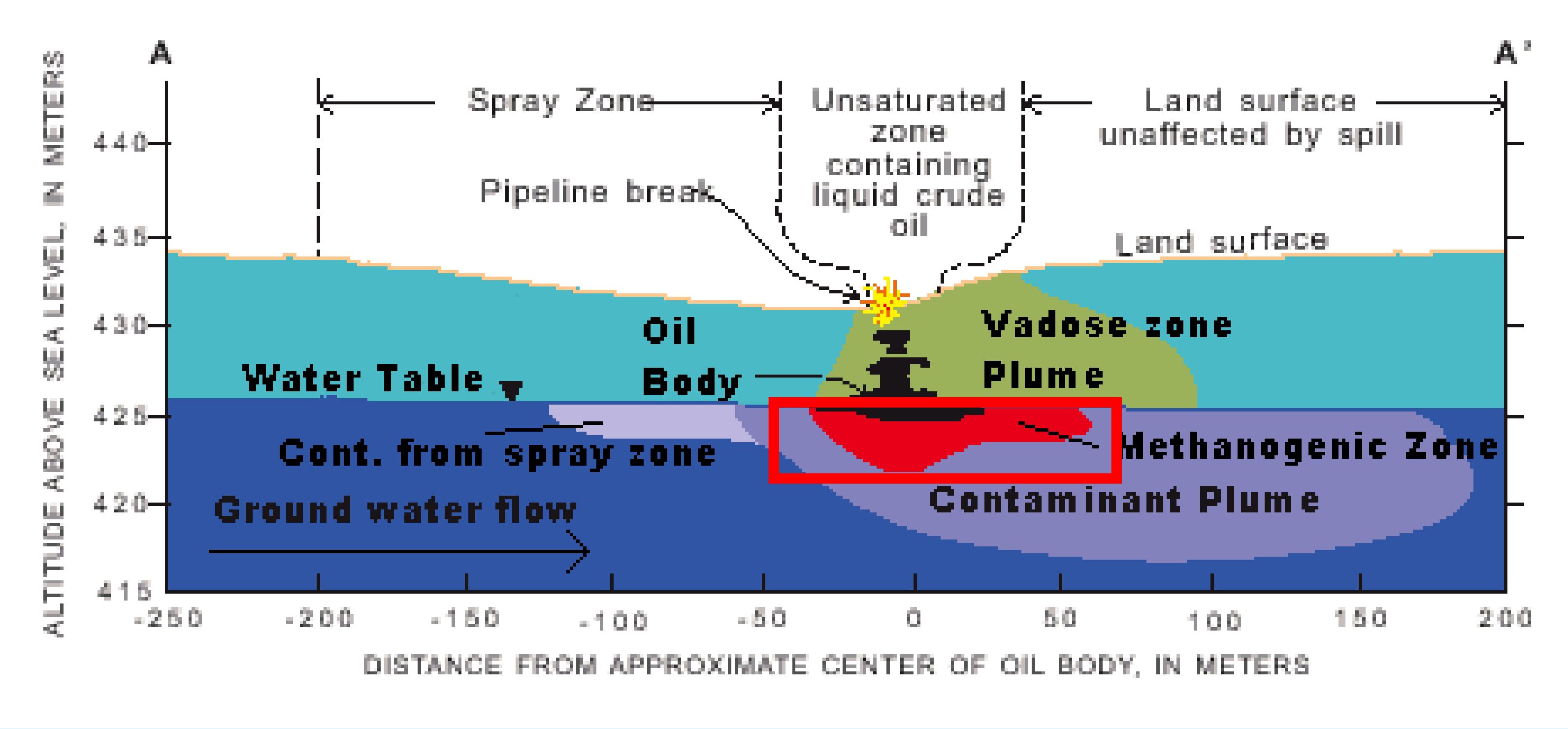
Dissolved gases and soil gas and the field of contaminant hydrogeology



Components of talk

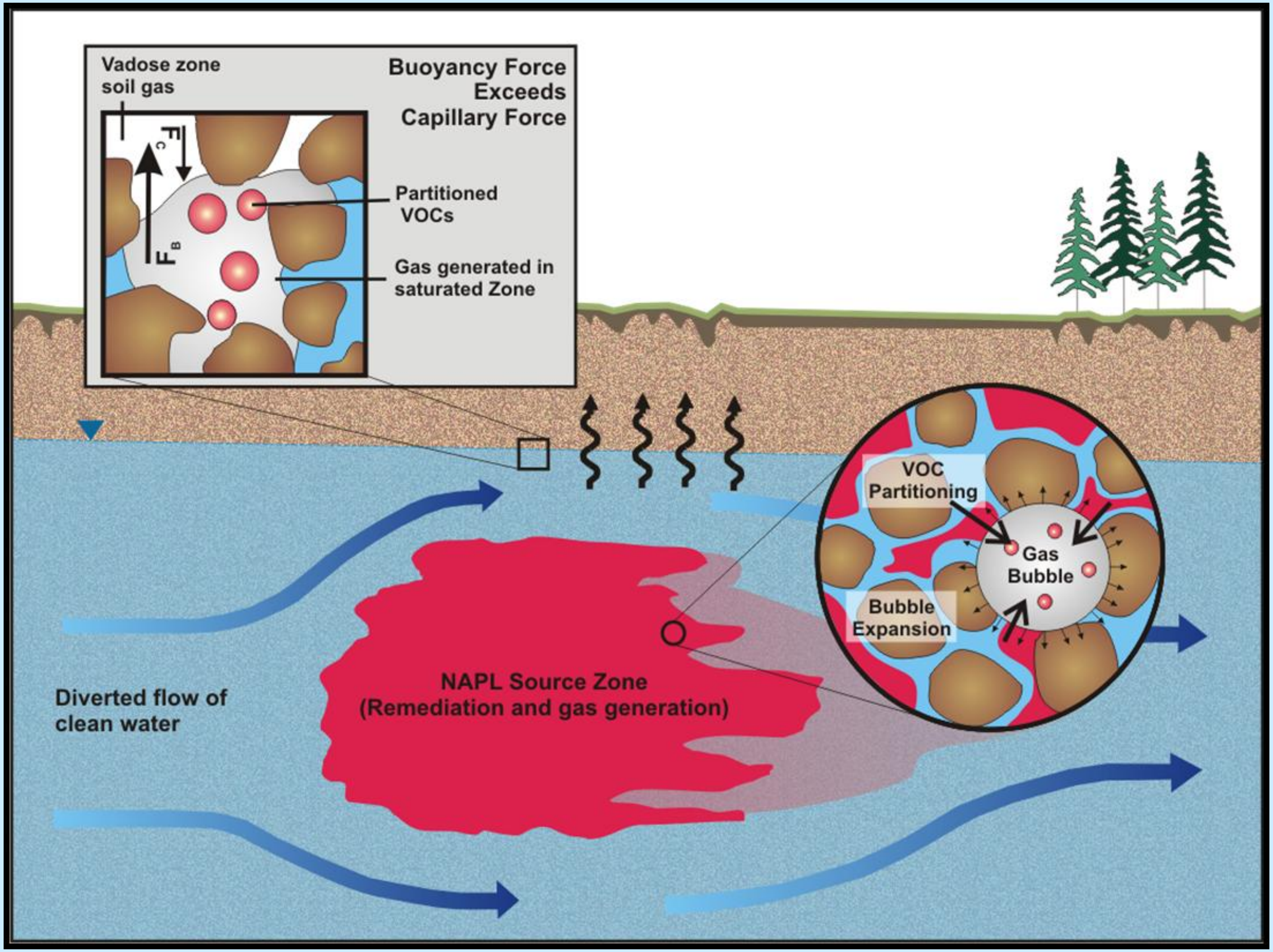
- Gas exsolution and ebullition in the saturated zone
  - Monitored natural attenuation of hydrocarbons
  - GW remediation with permeable reactive barriers
  - Gas transfer during GW remediation
- Reactive and non-reactive gases as tracers in the vadose zone
  - Monitored natural attenuation of hydrocarbons
- Surficial gas efflux measurements for source zone delineation and quantification of contaminant degradation rates

Reactive and non-reactive gases
Saturated zone processes

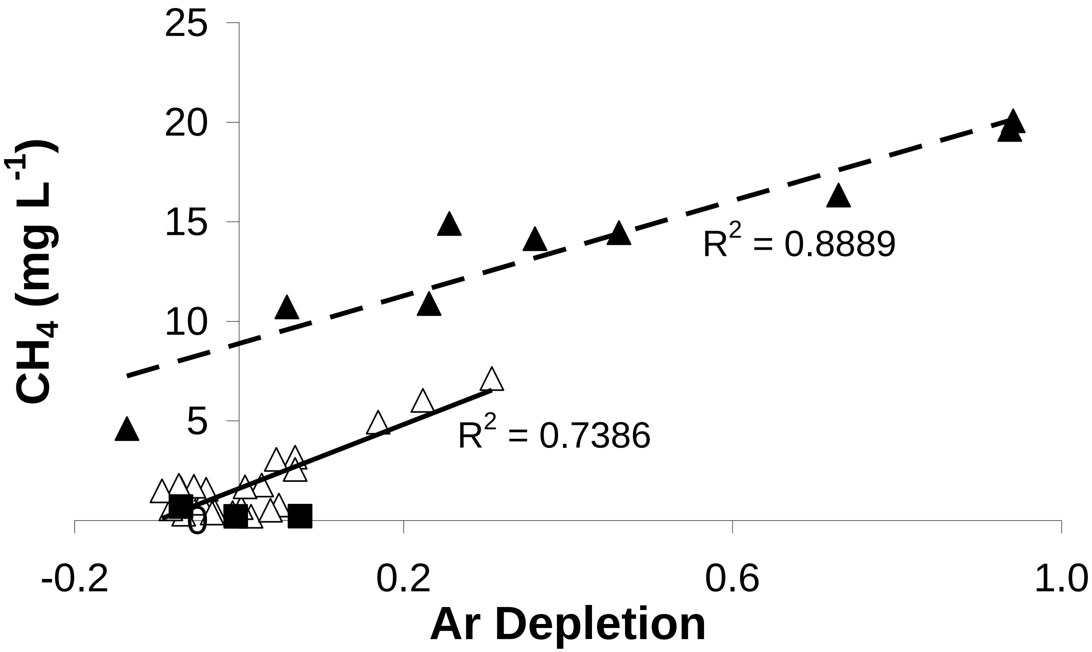


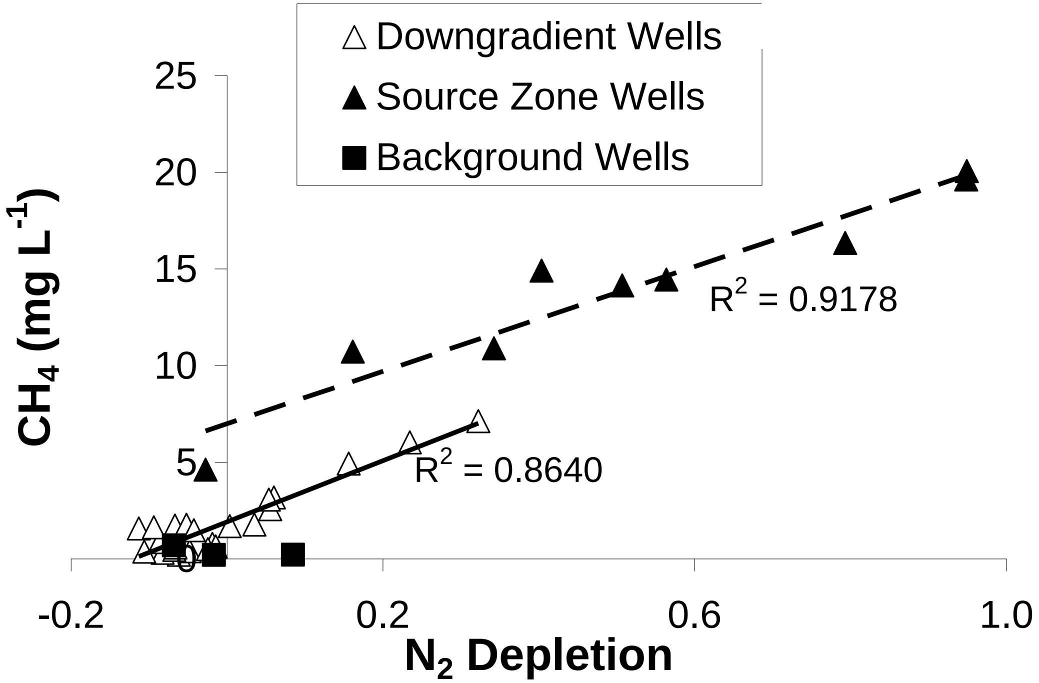
Modified from USGS Fact Sheet 084-98

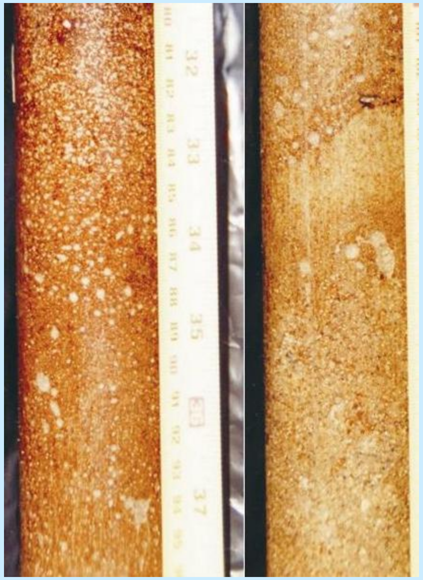
Microbially mediated gas generation
Gas exsolution and ebullition



Saturated Zone: Evidence for Gas Exsolution





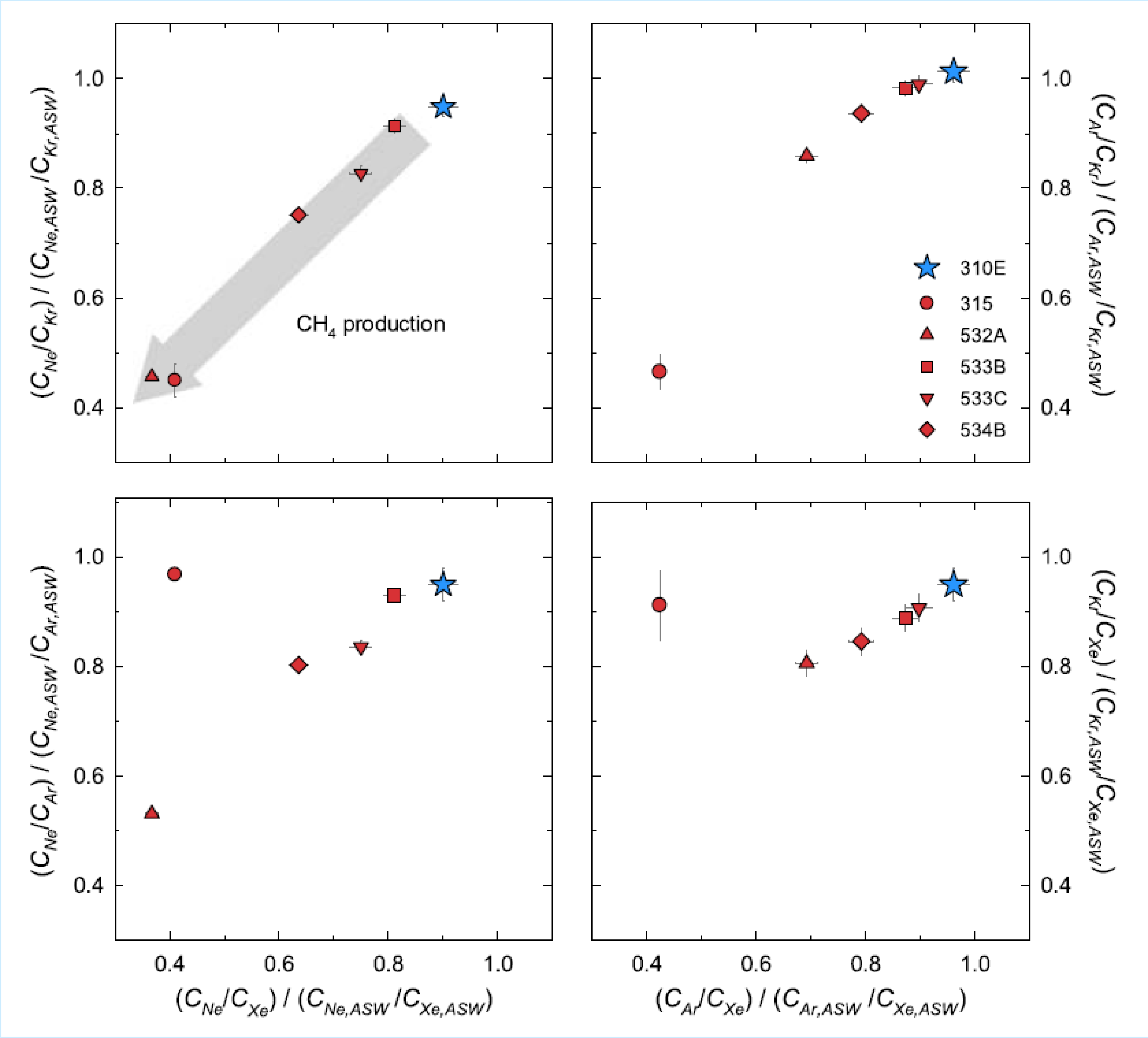


From Amos et al, *WRR*, 2005

Henry's Law constants and gas exsolution

Gas	Henry's law constant [mol L^{-1} atm^{-1}] reported as log $K_{H,cp}$
O_2	-2.77
CH_4	-2.86
CO_2	-1.47
N_2	-3.19
He	-3.40
Ne	-3.30
Ar	-2.72
Kr	-2.44
Xe	-2.17

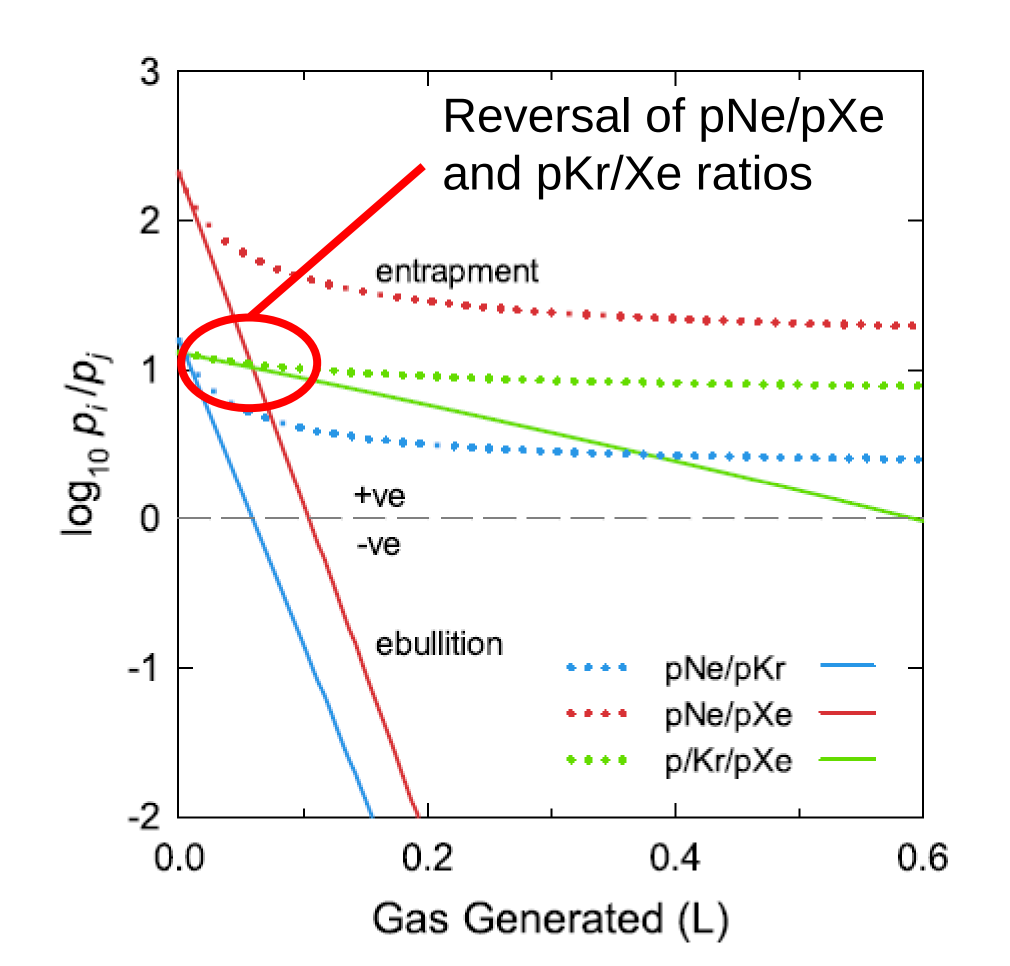
Noble gases as gas exsolution tracers



- Noble gas ratios and concentra-tions can be related to gas generation (reaction progress)
- <u>Strongest response for Ne/Kr ratio</u>

From Jones et al, GCA, 2014

Noble gas signature for ebullition

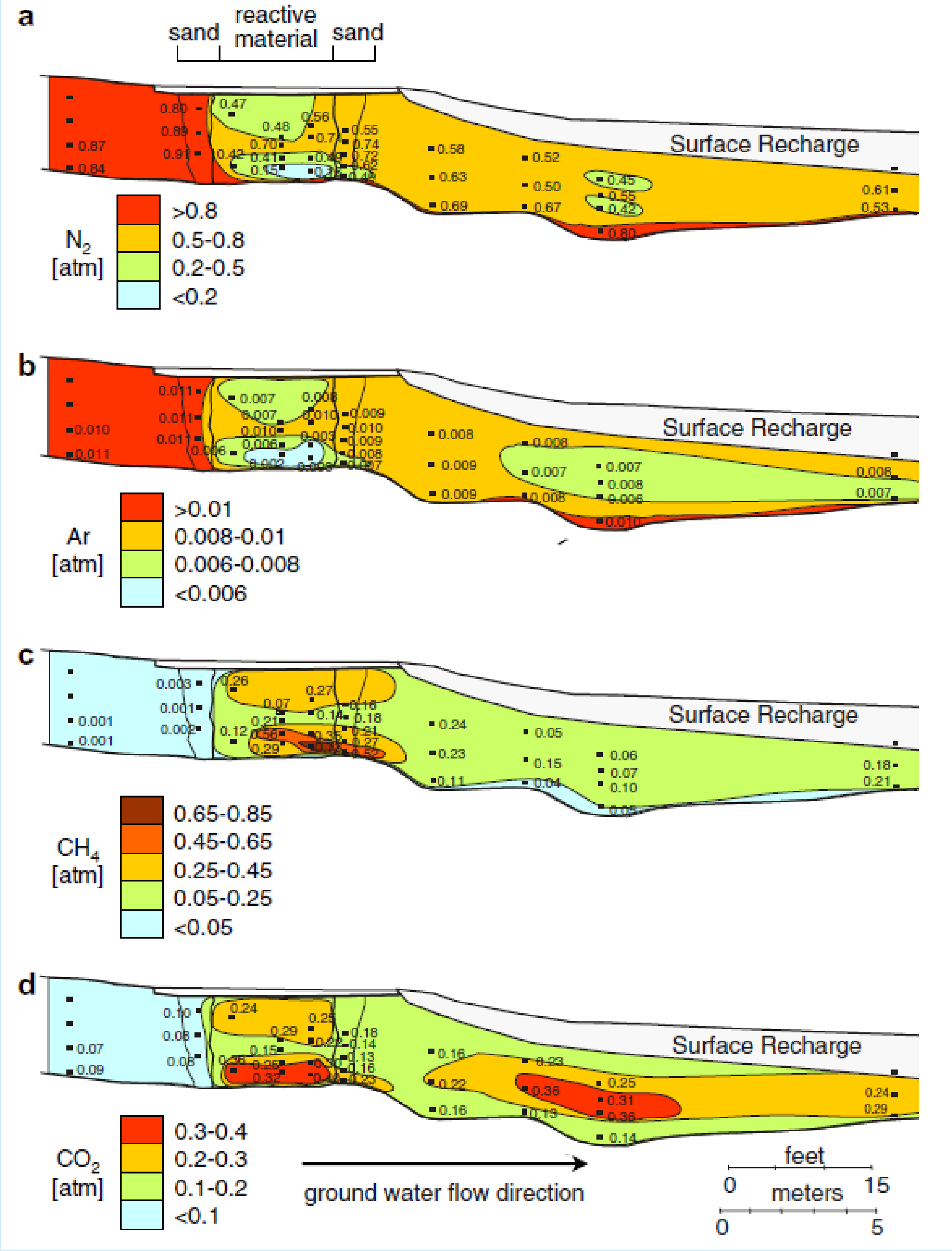


From Jones et al, GCA, 2014

- PHREEQC modeling of gas exsolution due to CH_4 and CO_2 generation by methanogenesis
- For high gas production volumes <u>noble gas ratios may be useful to prove ebullition in the field</u>

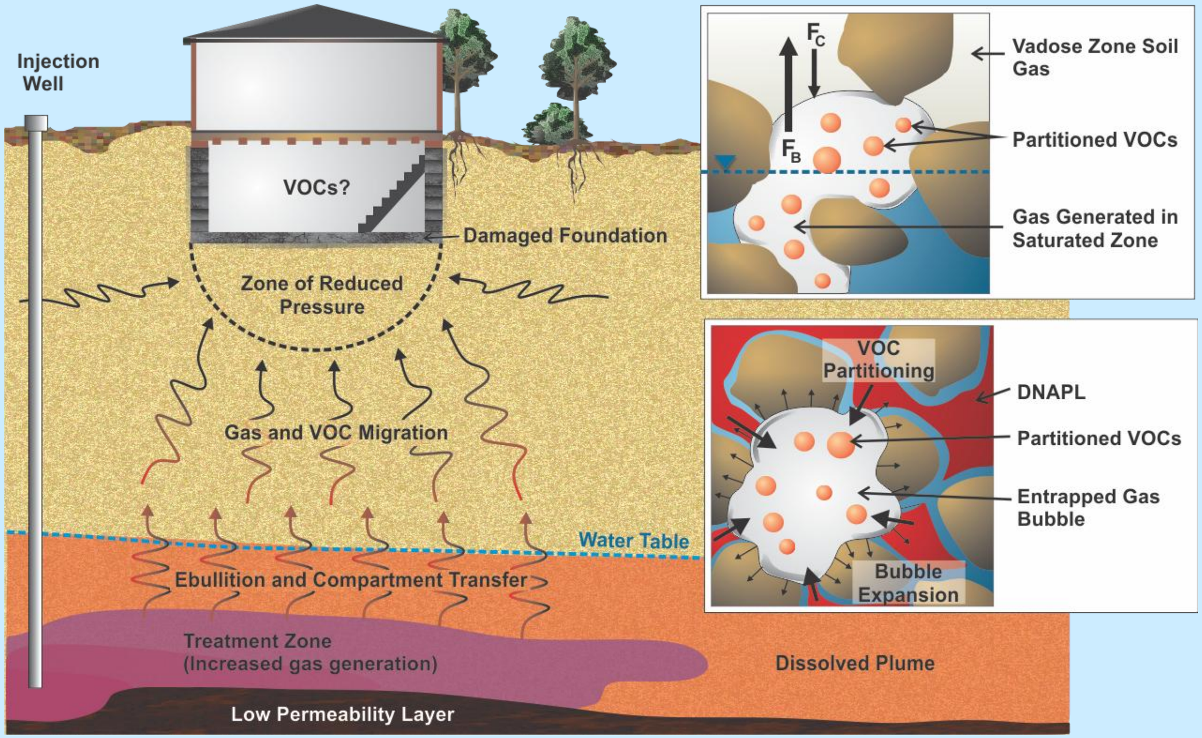
Gas exsolution in permeable reactive barriers

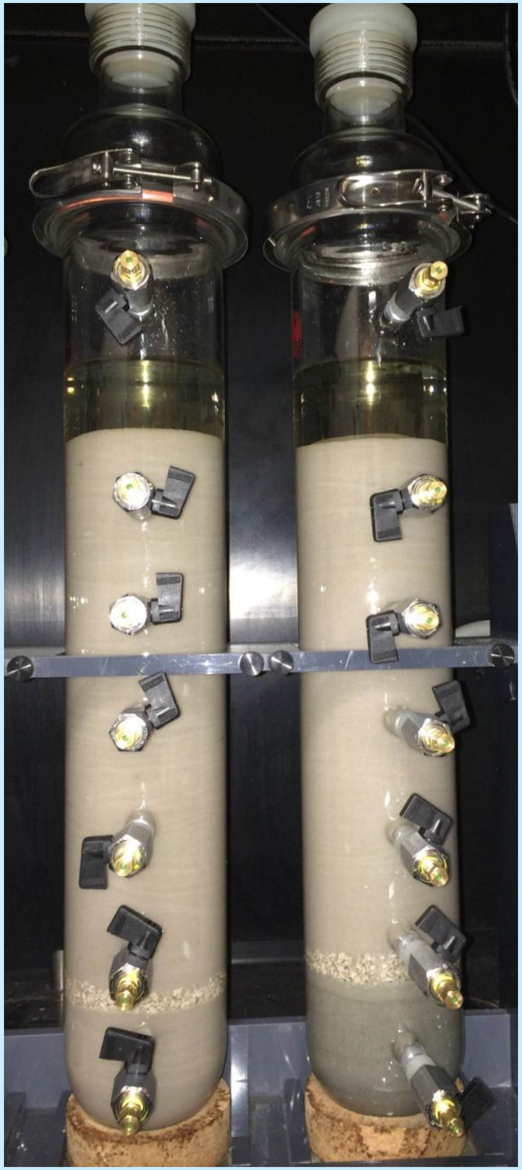
- Treatment of Fe and SO4 in mine drainage by organic carbon mixture
- Generation of CO_2 and CH_4
- N_2 and Ar indicate occurrence of gas exsolution



From Williams et al, Appl. Geochem., 2007

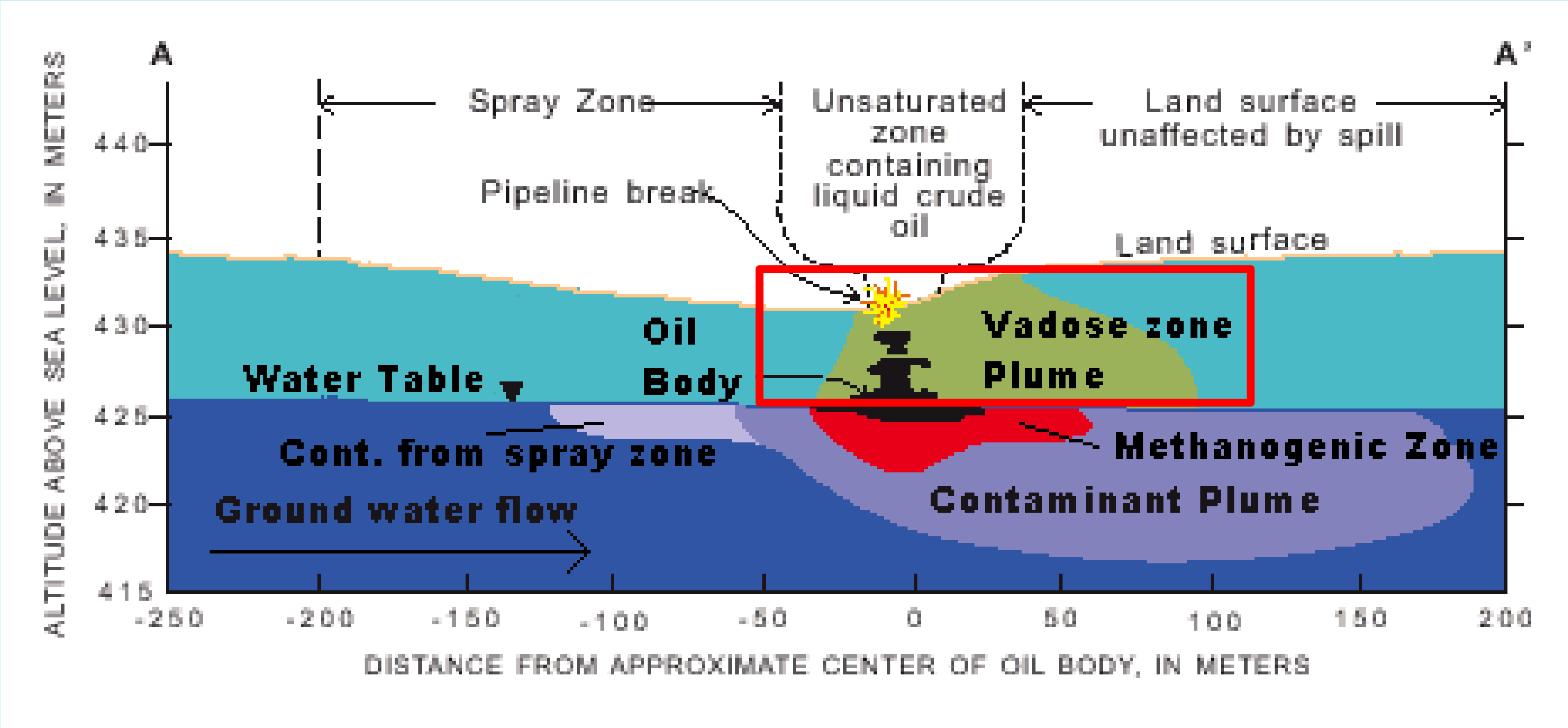
Current project: Enhanced ebullition due to groundwater remediation?





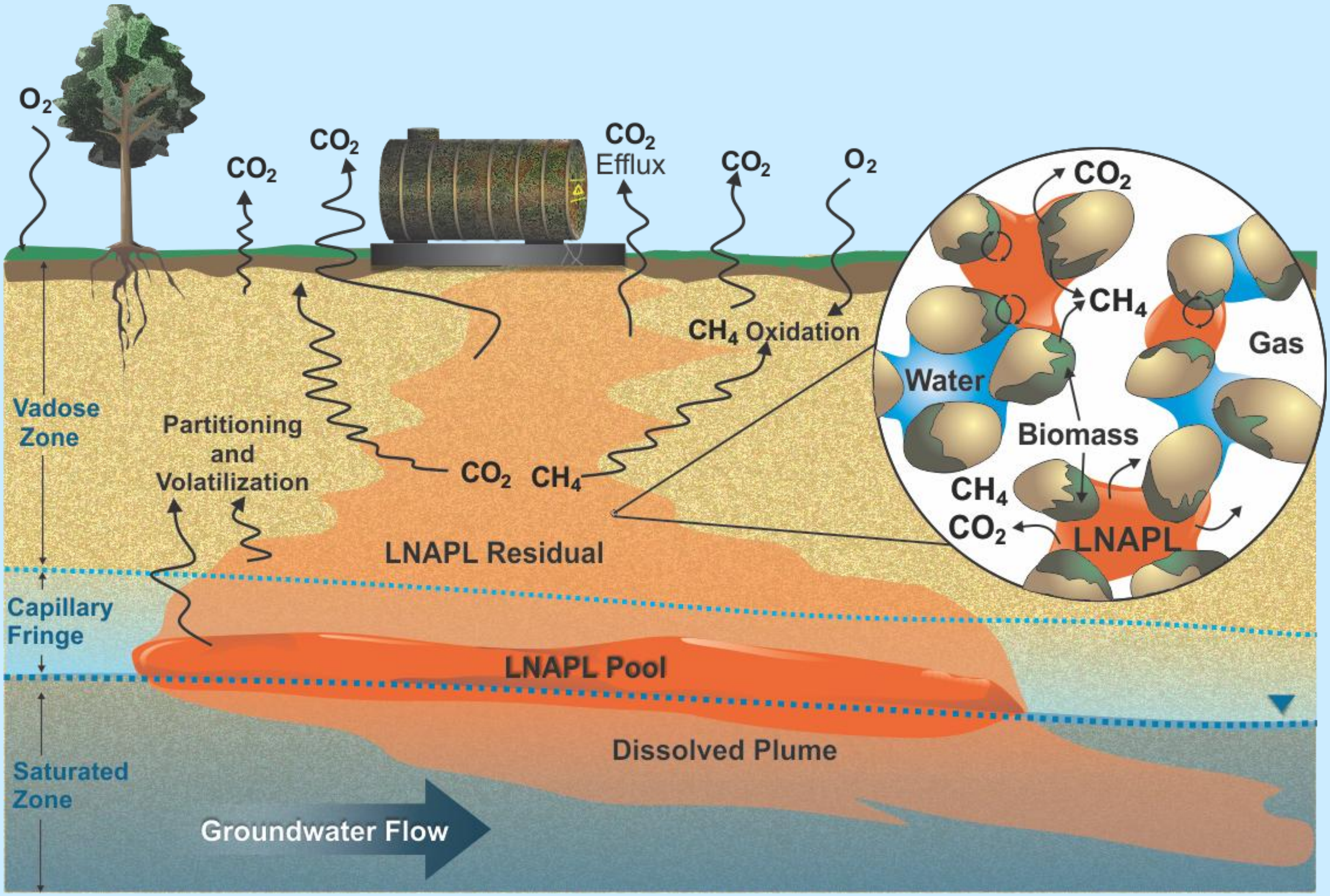
- Focus on chlorinated solvents
- Consider various treatments including permanganate and enhanced bioremediation

Reactive and non-reactive gases
Vadose zone processes

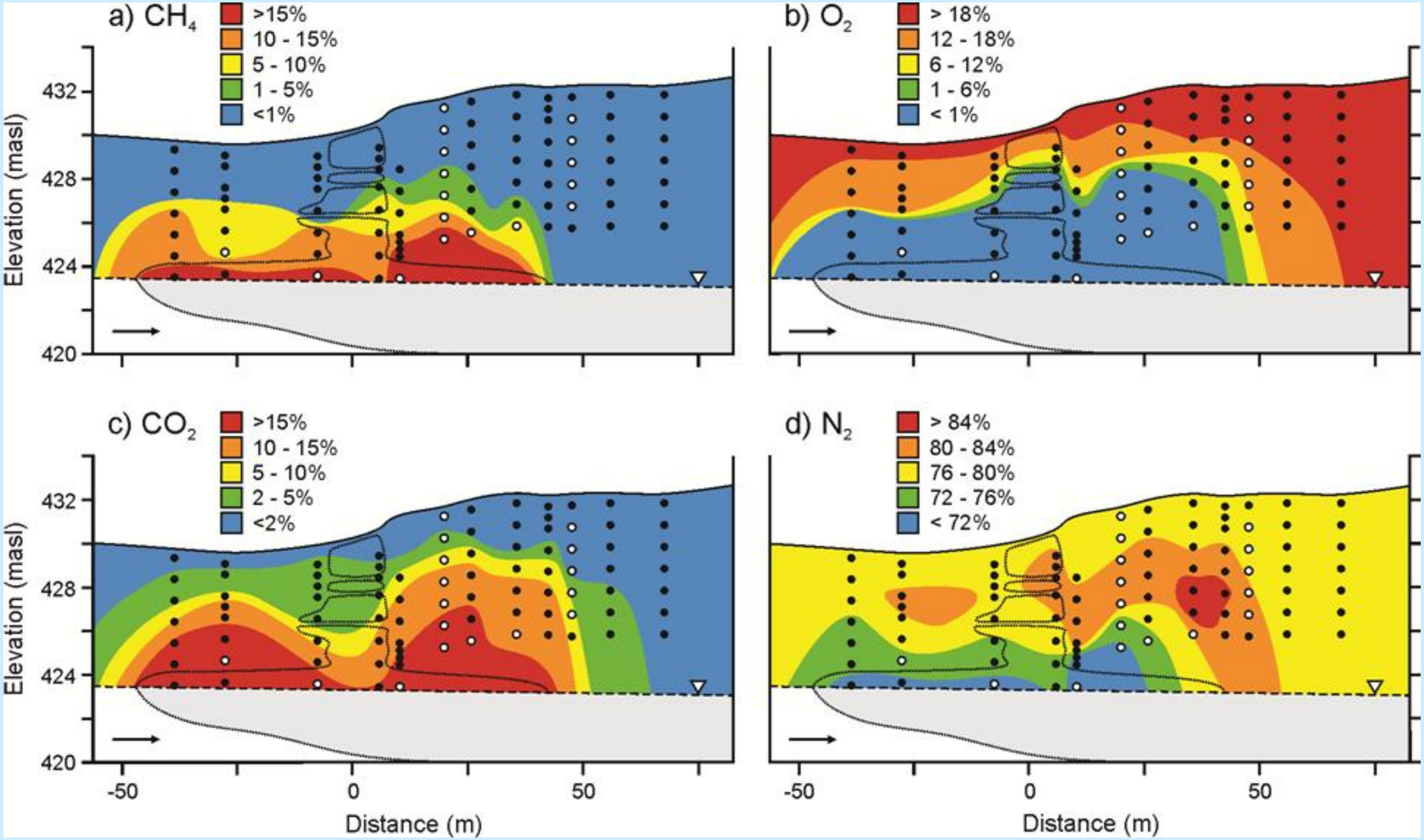


Modified from USGS Fact Sheet 084-98

Contaminant degradation in the vadose zone

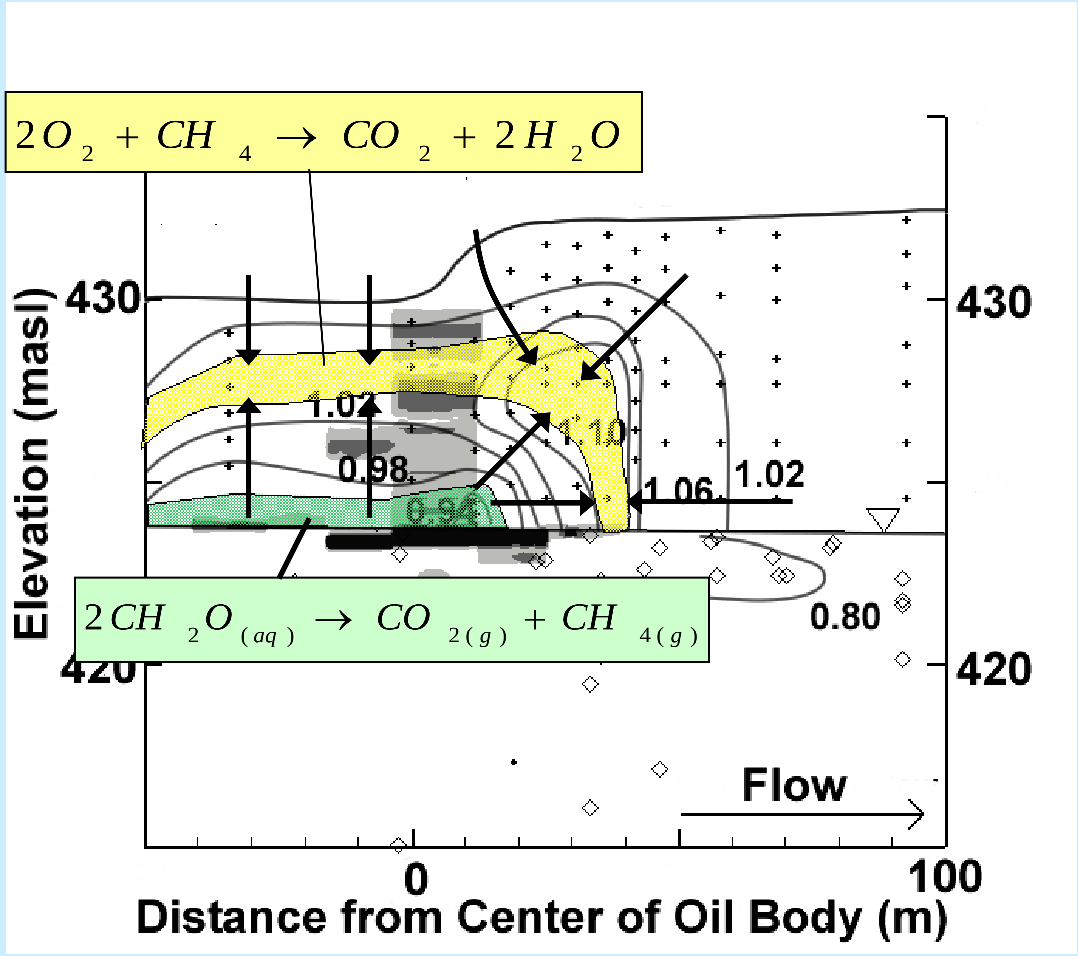


Vadose Zone
O_2, CH_4, CO_2, and N_2



From Jones et al, *GCA*, 2014

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

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

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

$$k = 1, N_c$$

T_g^k

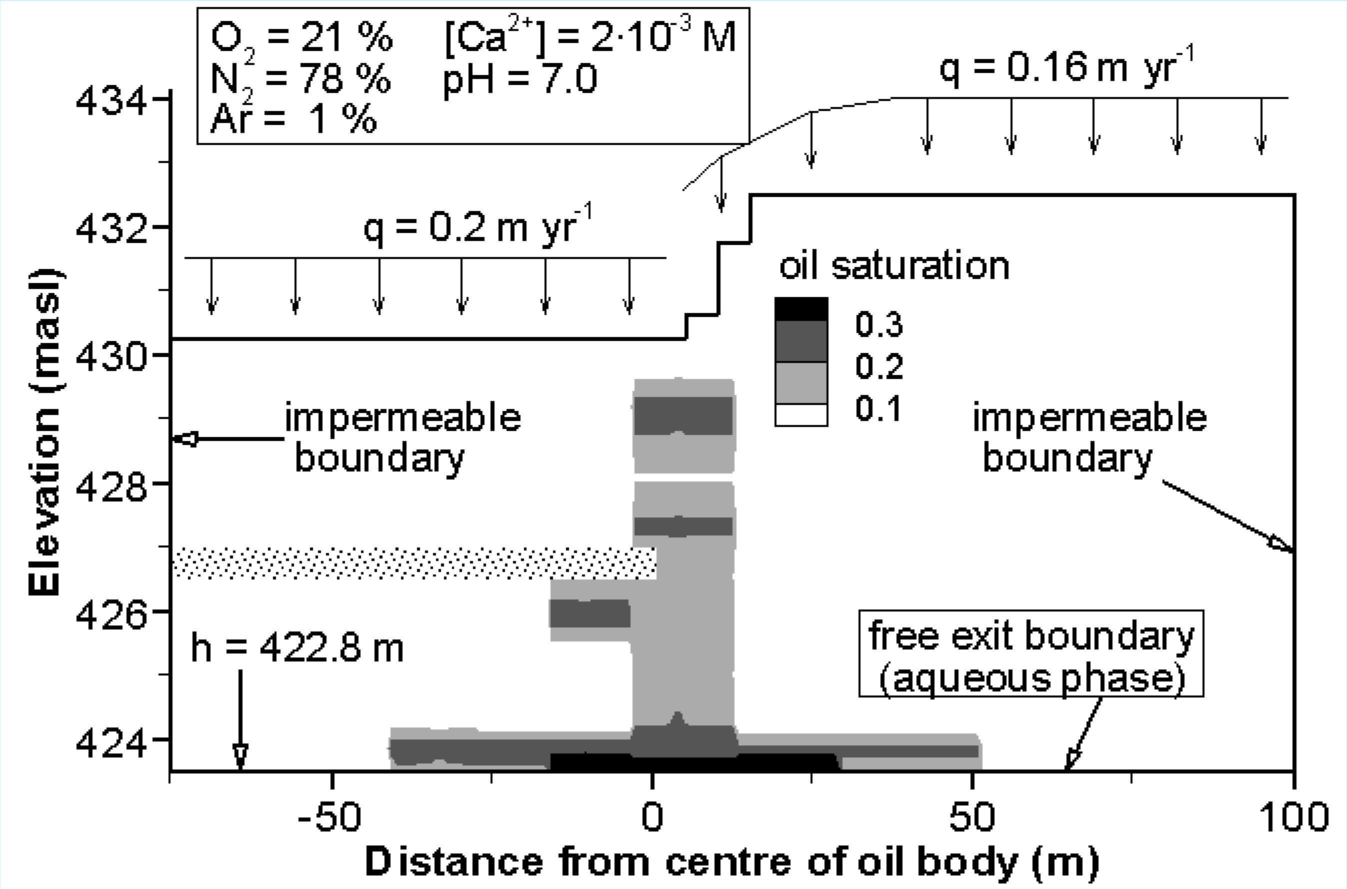
Momentum Balance Equation

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

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

Molins and Mayer, *Water Resour. Res., 2007*
Molins et al., *JCH*, 2010

Bemidji Vadose Zone Simulation



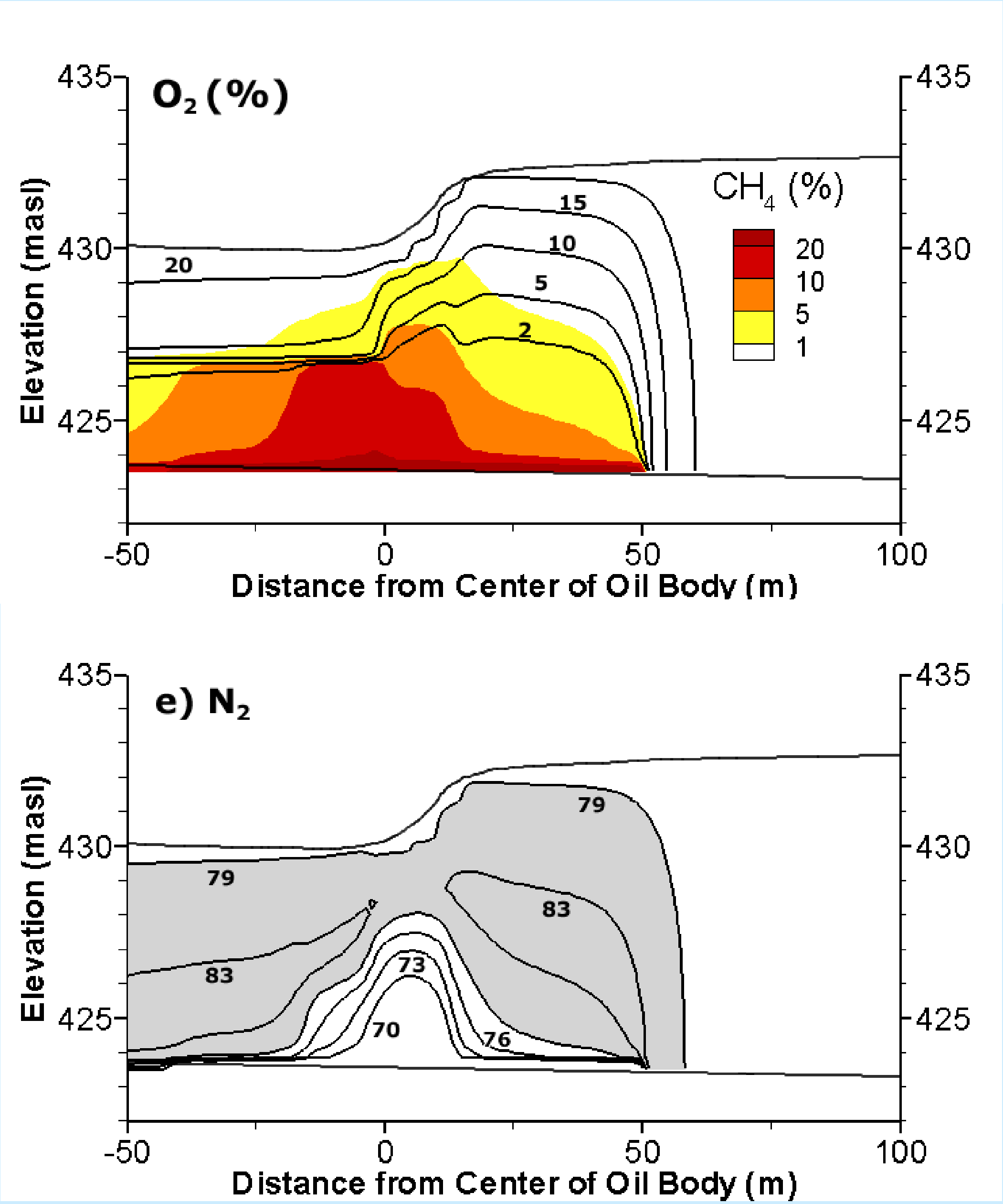
$\phi = 0.38$
$K_h = 10^{-11}$ m^2
$K_v = 3 \cdot 10^{-12}$ m^2

lens:
$\phi = 0.30$
$K_h = 10^{-13}$ m^2
$K_v = 3 \cdot 10^{-14}$ m^2

Molins et al., *JCH*, 2010

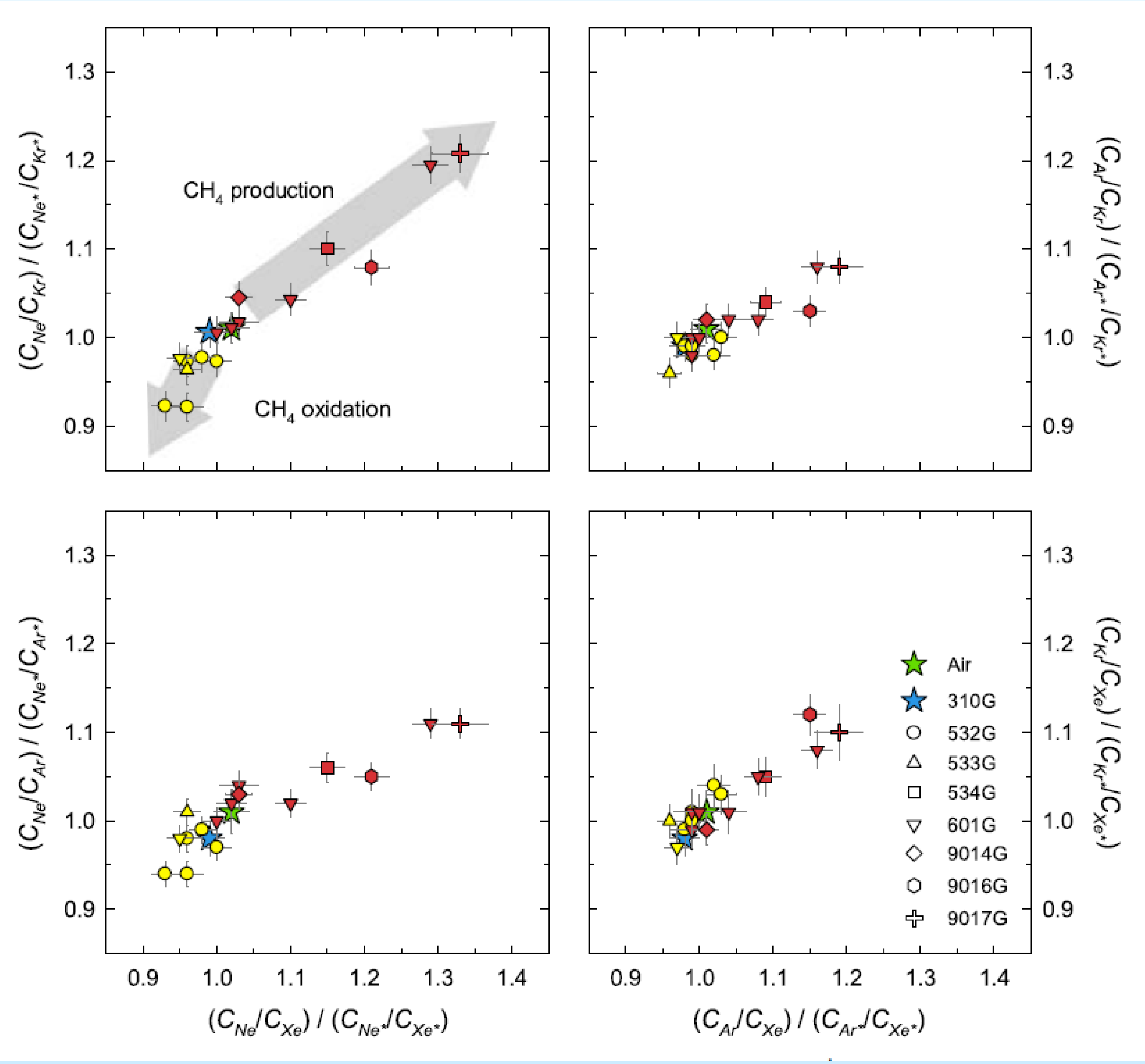
Simulated O_2, CH_4, and N_2 Concentrations

- Good qualitative agreement was obtained with the field observations
- … Model also allows to visualize fluxes and rates



Molins et al., *JCH*, 2010

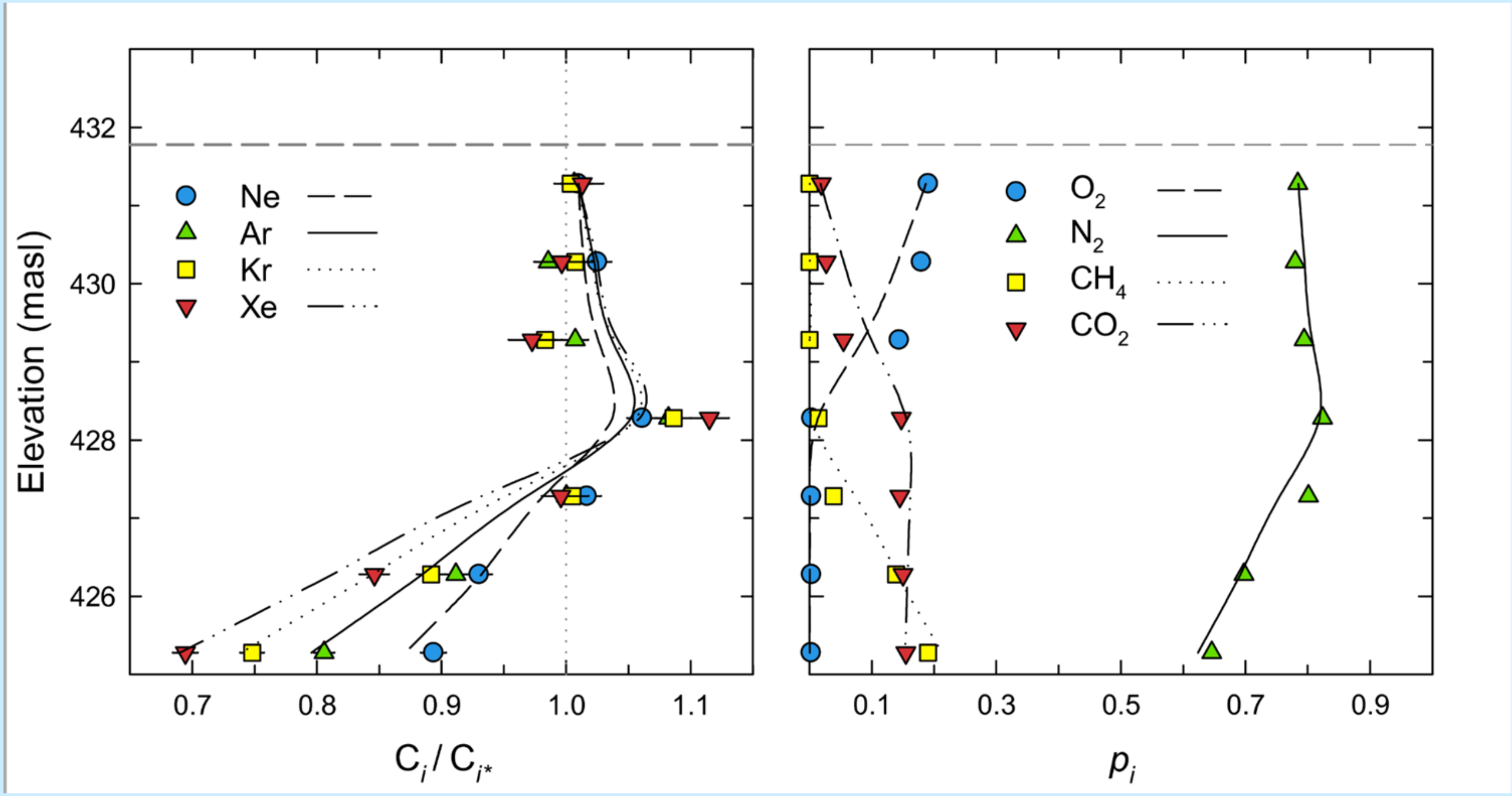
Noble gases in the vadose zone at the Bemidji site



Jones et al., GCA, 2014

- CH_4 production: preferential depletion of heavy noble gases
- CH_4 oxidation: preferential enrichment of heavy noble gases

MIN3P-Dusty simulation of gas generation and fate

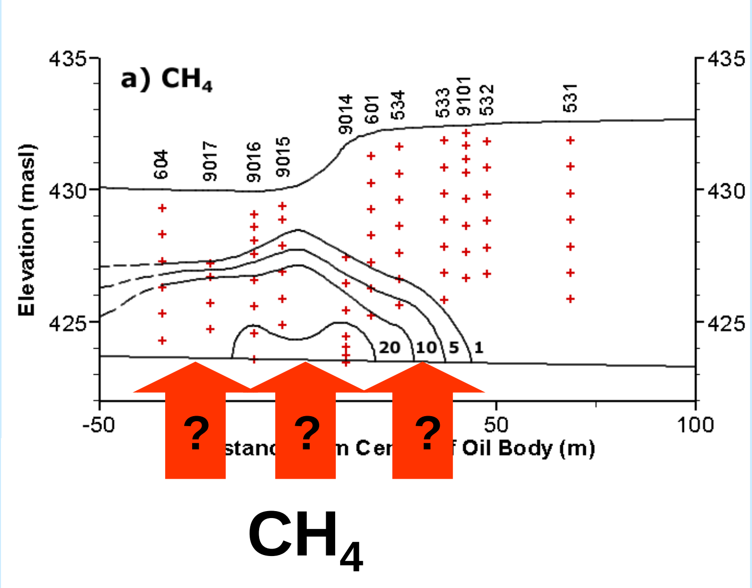


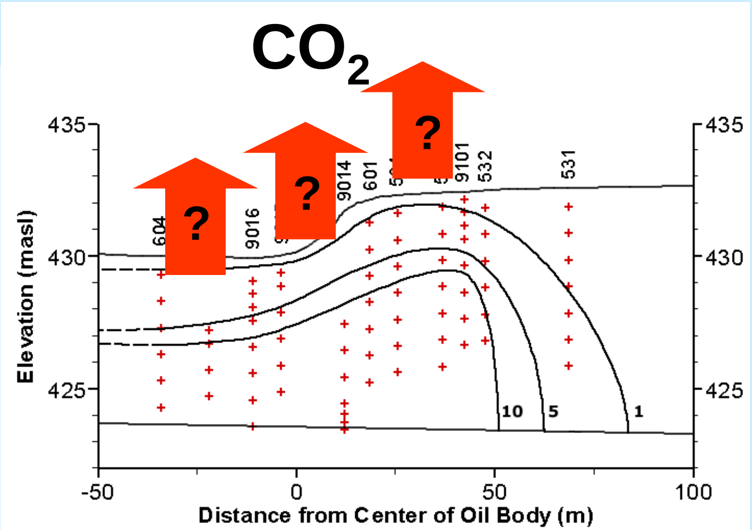
- Use of noble gases as tracers for advection/pressure gradients
- <u>Heavy noble gases are the most sensitive tracers in the vadose zone</u>

Jones et al., GCA, 2014

Implications for Natural Attenuation Research

- Simulations and field observations suggest that
  - CH_4 generation is focused on smear zone
  - More than 95% of carbon will leave via CO_2 gas efflux
- Gas migration in soil is very sensitive to soil moisture and soil structure
- Uncertainties for C-balance remain
- Need to measure rates (or fluxes)





Model results indicate that most CO_2 reports to the ground surface

	C flux/rate [moles d^{-1} m^{-1}]	C flux/rate (%)
Biodegradation	22.3	99.8
Calcite dissolution	0.033	0.2
Total source	**22.33**	
Recharge to saturated zone	0.25	1.1
Change in storage	0.13	0.6
Gas efflux to atmosphere	21.96	98.3
Total sink	**22.33**	

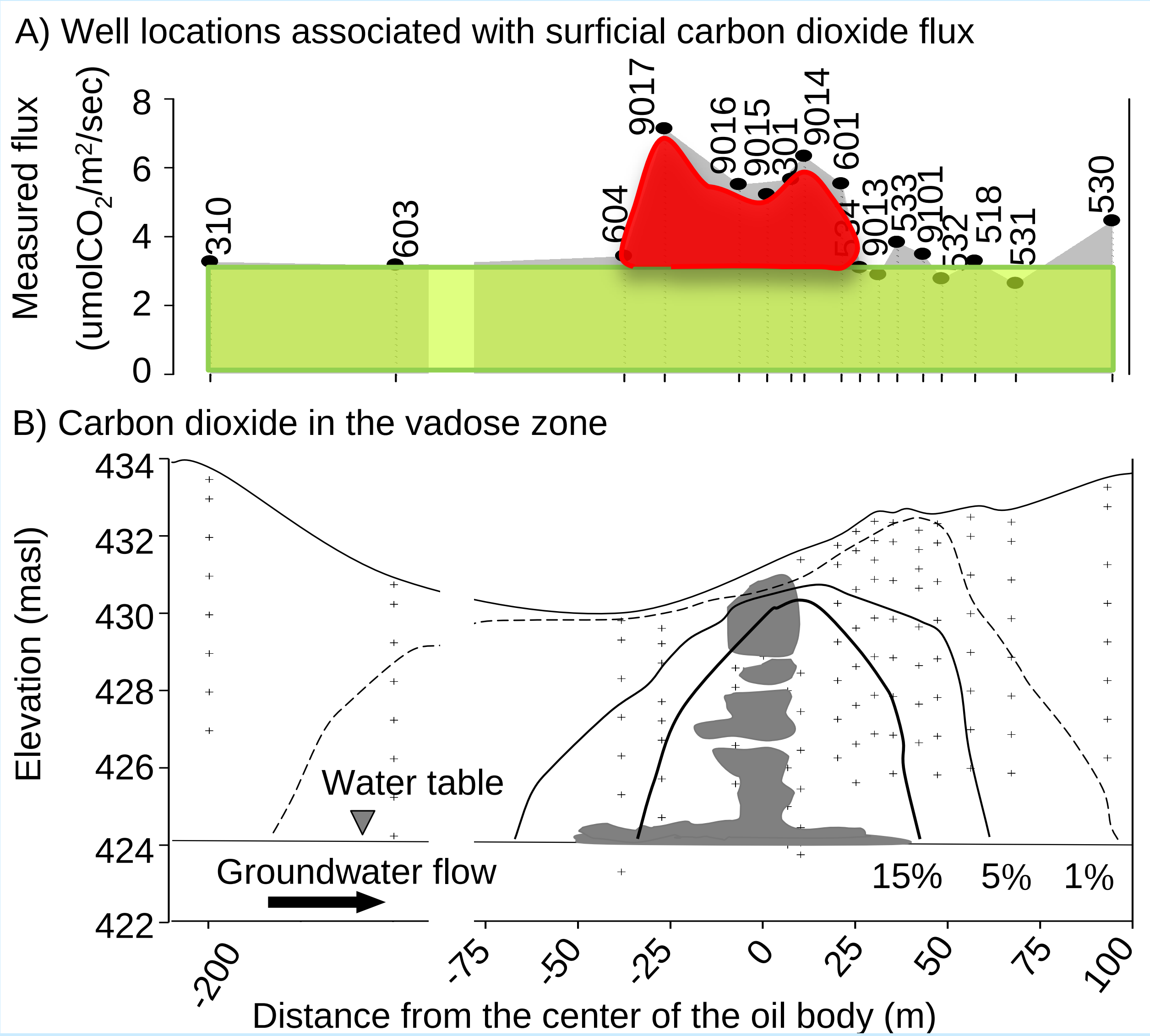
From Molins et al., 2010 and Sihota et al., 2011

How can we measure contaminant degradation rates?

- Measure CO_2 efflux above, upgradient, and downgradient of source zone

- Real-time infrared gas analysis
- Need to distinguish between background soil respiration and contaminant degradation

CO_2 Efflux Measurements
Contaminant respiration and soil respiration



- Use background correction
- Flux attributable to SZNA is 2.6 μmol m^{-2} s^{-1}
- Corresponds to depth-integrated rate of biodegradation
- Method effective for source zone and rate delineation and

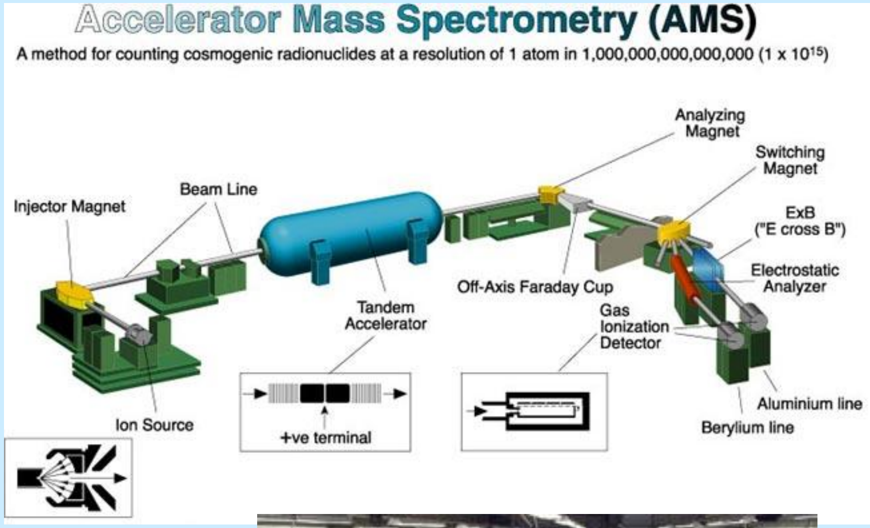
Sihota et al., ES&T, 2011

How do we know that enhanced CO_2 efflux is due to contaminant degradation?

- ^{14}C in CO_2 provides direct measurement of TPH-derived CO_2

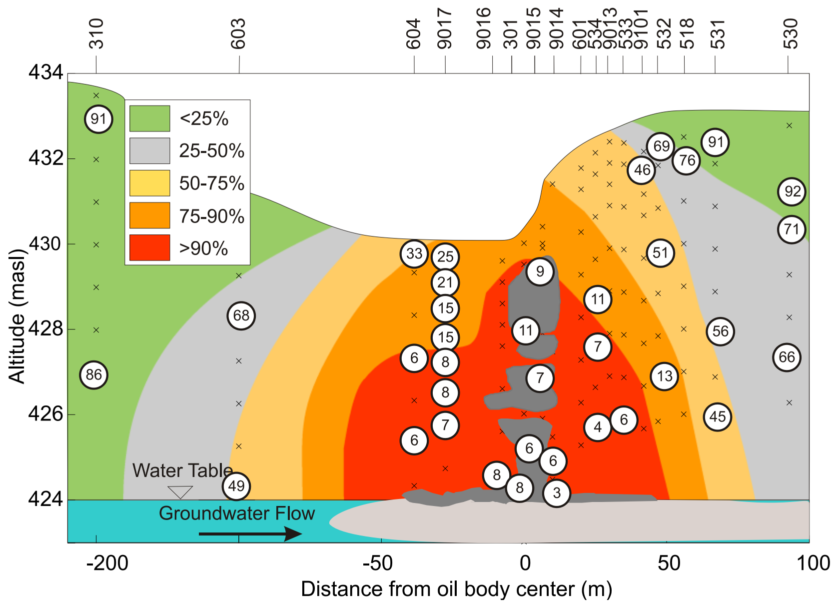
- Half-life of ^{14}C is 5,730 years

- TPH will have ^{14}C signature of 0 percent modern carbon (pmc)
    - Analyze ^{14}C contents of CO_2 in soil gas
    - Calculate rates based on ^{14}C contents
    - Compare results to rate measured using CO_2 efflux method

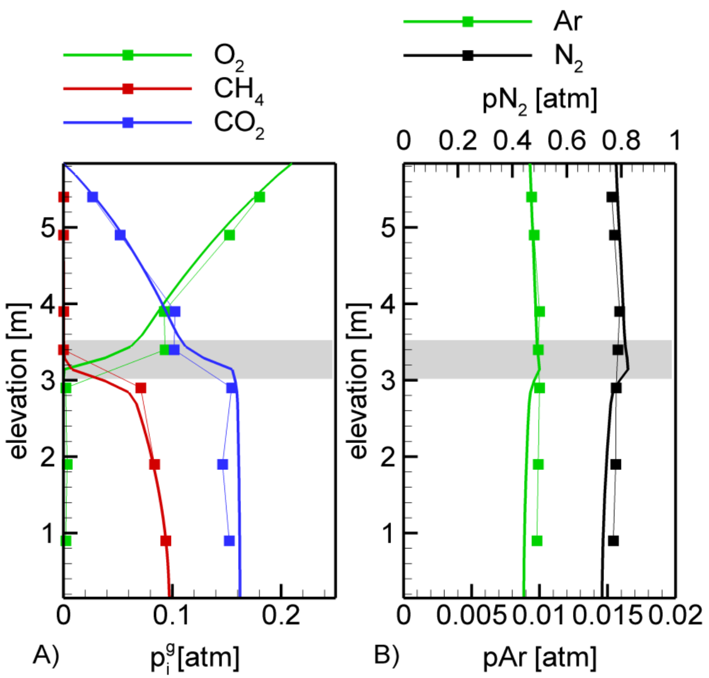


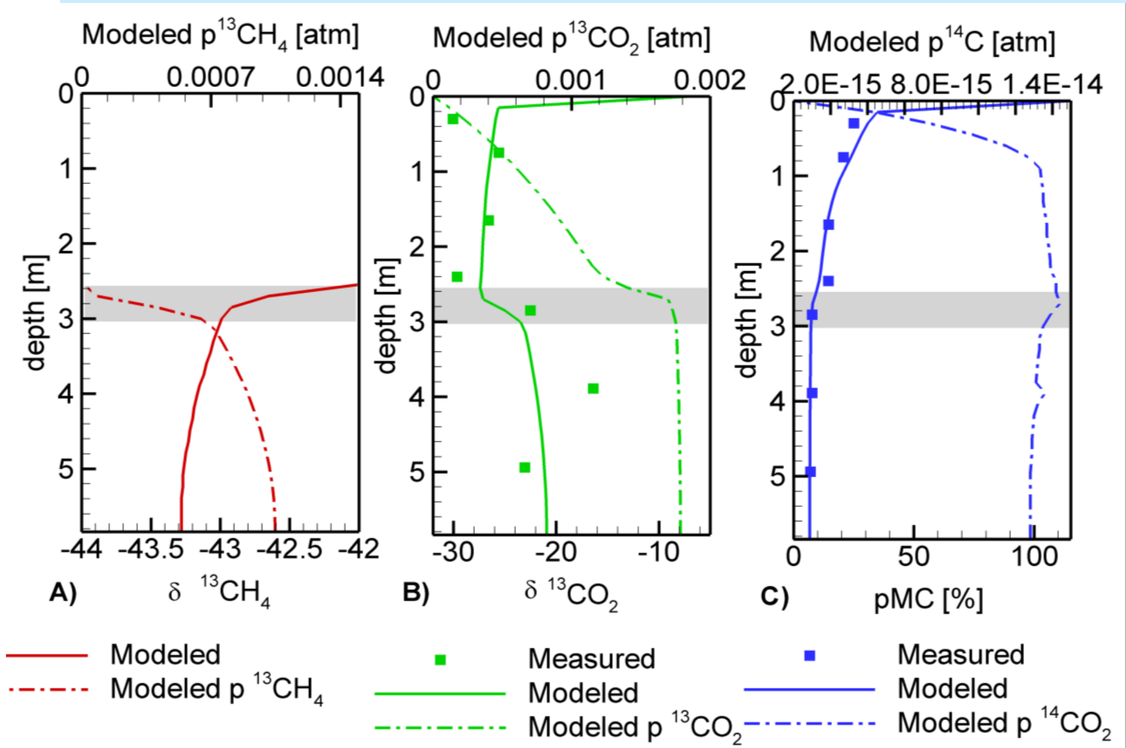
https://seaborg.llnl.gov/facilities.php

Radiocarbon and stable carbon isotopes



- Radiocarbon allows to distinguish between soil respiration and contaminant degradation
- Model highly constrained





Sihota and Mayer, VZJ, 2012

Conclusions and Outlook

- Reactive gases provide important information on contaminant fate in the vadose and GW zones
- Inert gases can serve as powerful indicators for transport and reaction processes, but are often underutilized in GW contamination studies
- Gas efflux measurements show promise for delineating contaminant degradation rates

Thank You – Questions?

- Amos, R. T., K. U. Mayer, B. A. Bekins, G. N. Delin, and R. L. Williams. 2005. Use of dissolved and vapor phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface, Water Resour. Res., 41, W02001, doi:10.1029/2004WR003433
- Williams, R. L., K. U. Mayer, R. T. Amos, D.W. Blowes, C. J. Ptacek, and J. Bain, 2007. Using dissolved gas analysis to investigate the performance of an organic carbon permeable reactive barrier for the treatment of mine drainage, Appl. Geochem., 22:90-108
- Amos, R. T., and K. U. Mayer, 2006. Investigating the role of gas bubble formation and entrapment in contaminated aquifers: Reactive transport modeling, *J. Contam. Hydrol.,* 87:123-154
- Molins, S., K. U. Mayer, R. T. Amos, and B. A. Bekins, 2010. Vadose zone attenuation of organic compounds at a crude oil spill site - Interactions between biogeochemical reactions and multicomponent gas transport, *J. Contam. Hydrol,* 112:15-29
- Sihota, N.J., O. Singurindy, and K. U. Mayer, 2011. CO_2 efflux measurements for evaluating source zone natural attenuation rates in a petroleum hydrocarbon contaminated aquifer, *Environ. Sci. Technol.*, 45:482-488
- Sihota, N.J., and K.U. Mayer, 2012. Characterizing vadose zone hydrocarbon biodegradation using CO_2-effluxes, isotopes, and reactive transport modeling, *Vadose Zone J.*, 11, doi:10.2136/vzj2011.0204.
- Jones, K.L., M.B.J. Lindsay, R. Kipfer, and K.U. Mayer, 2014. Atmospheric noble gases as tracers of biogenic gas dynamics in a shallow unconfined aquifer, Geochimica Cosmochimica Acta, 128:144-157