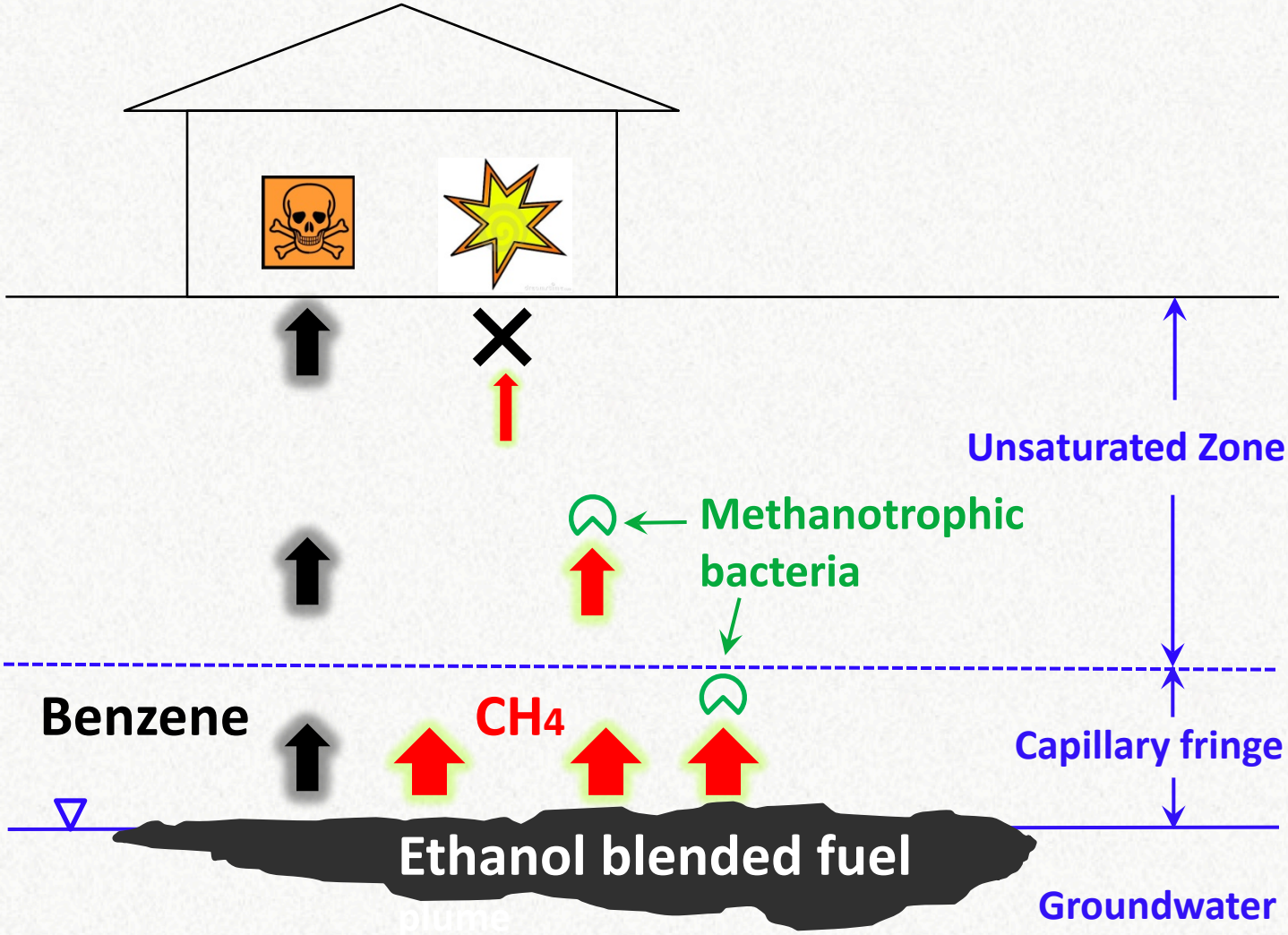
Ethanol Blended Fuel Spills and Potential for Methane Generation and Transport

Bill Rixey
Dept. Civil & Environmental Engineering
Univ. of Houston

Methane From Biofuels Webinar
October 8, 2014

Ethanol fuel releases & methane



Ma, J., et al. *Environmental Science & Technology* (2012); & (2014)

Outline

- **Pilot-scale Aquifer continuous EtOH release studies**
  - **Groundwater impacts**
  - **Flux measurements & modeling**
  - **Response to source removal**

Continuous Release:

The Pilot-Scale Aquifer

Channel 1:

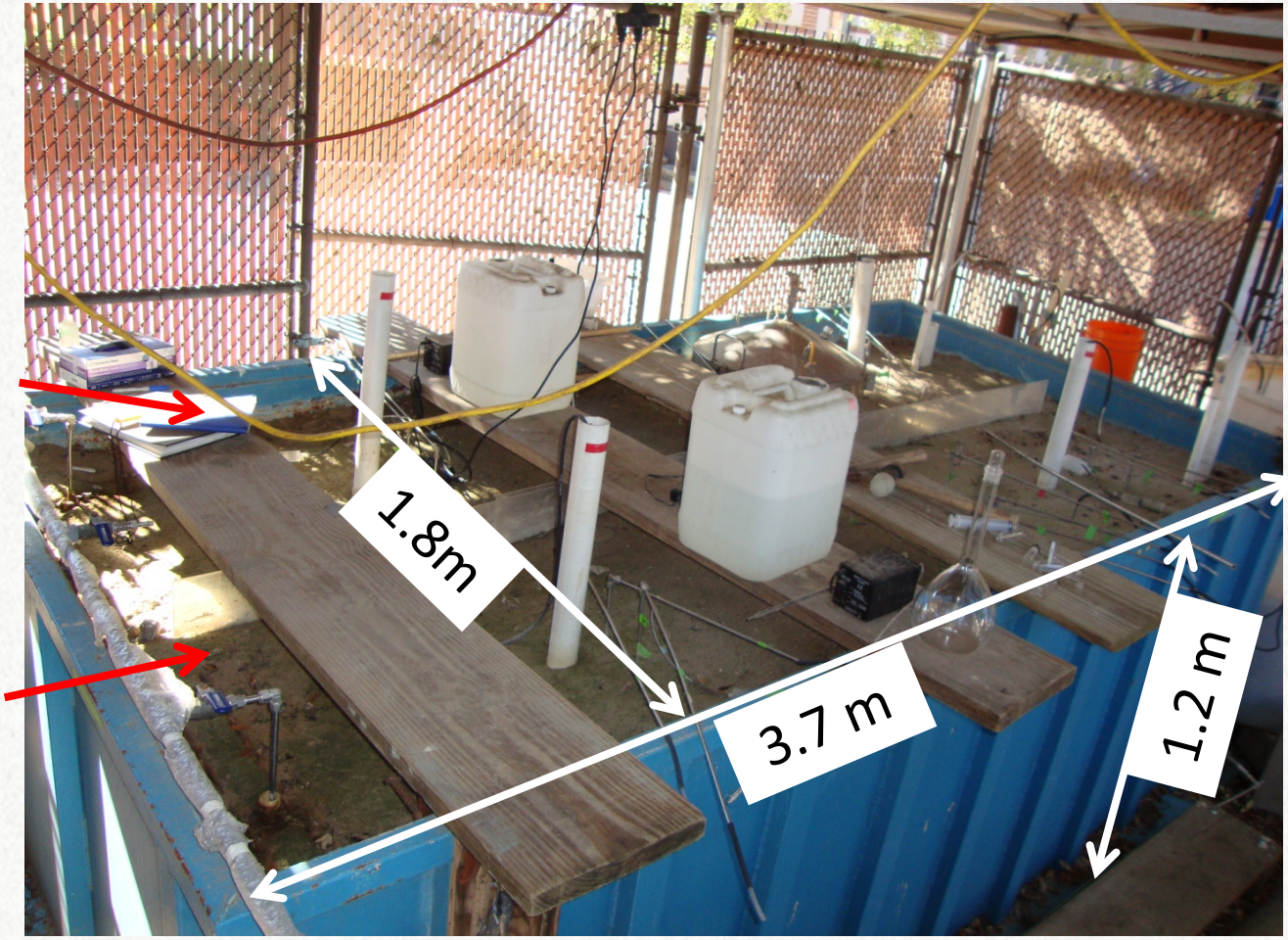
Rate = 0.1 L/day

10% (V:V)ethanol

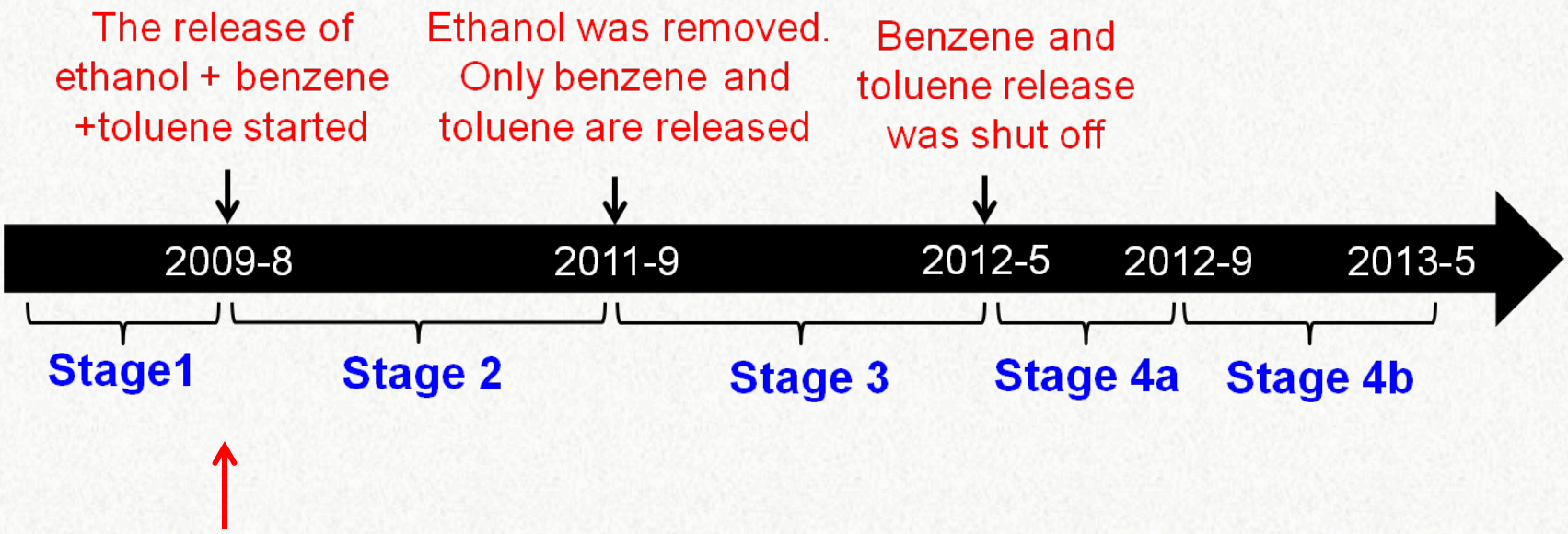
50 ppm benzene
50 ppm toluene

Channel 2:

50 ppm benzene
50 ppm toluene

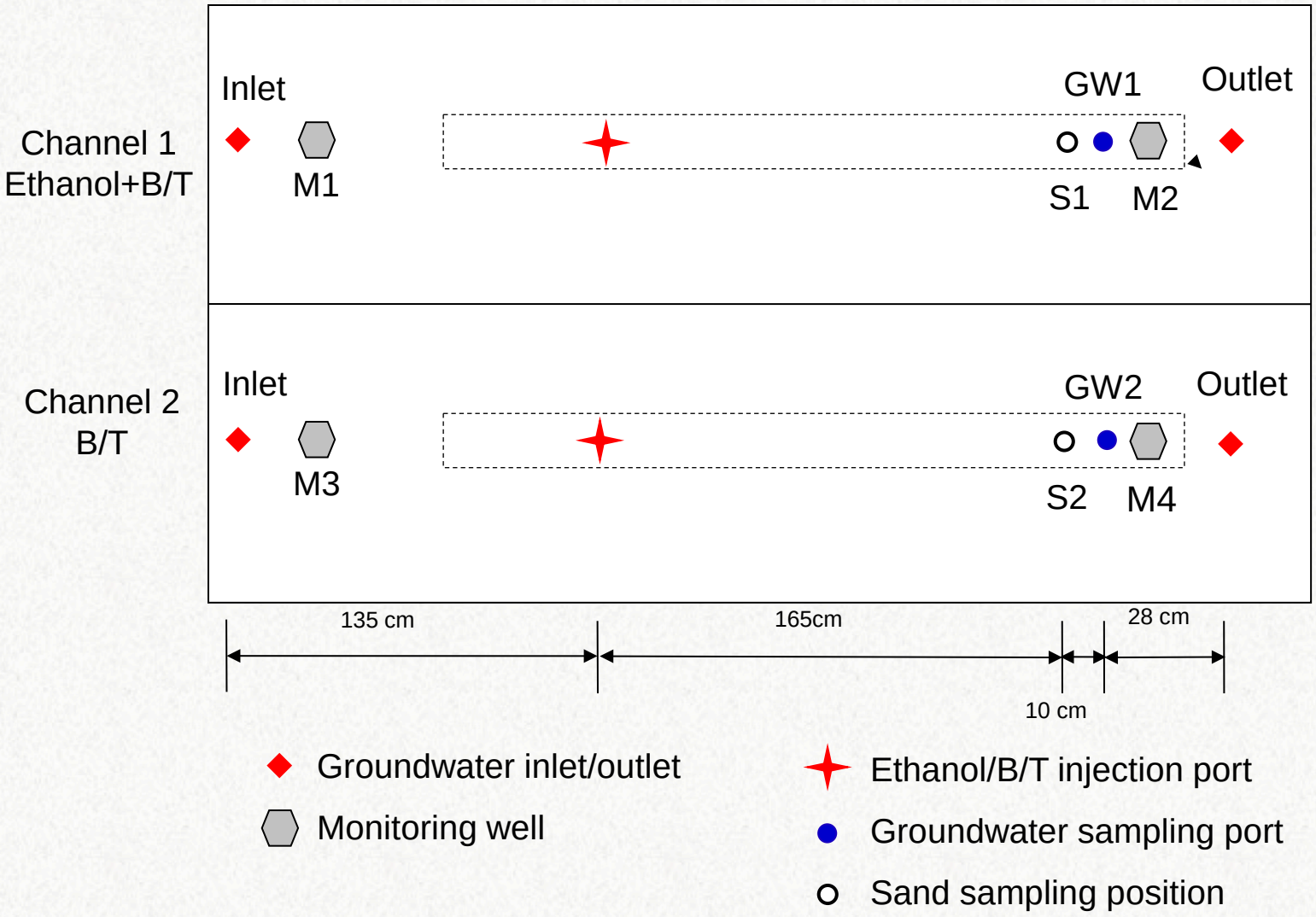


Continuous Release:



Continuous Release:

Tank plan view



Groundwater Impacts:

CH_4 concentration in groundwater

Sampling port	**Winter (February 2011)**	**Summer (June 2011)**
GW-1A	7.6	21.6
GW-1B	8.3	20.6
GW-1C	5.8	22.5

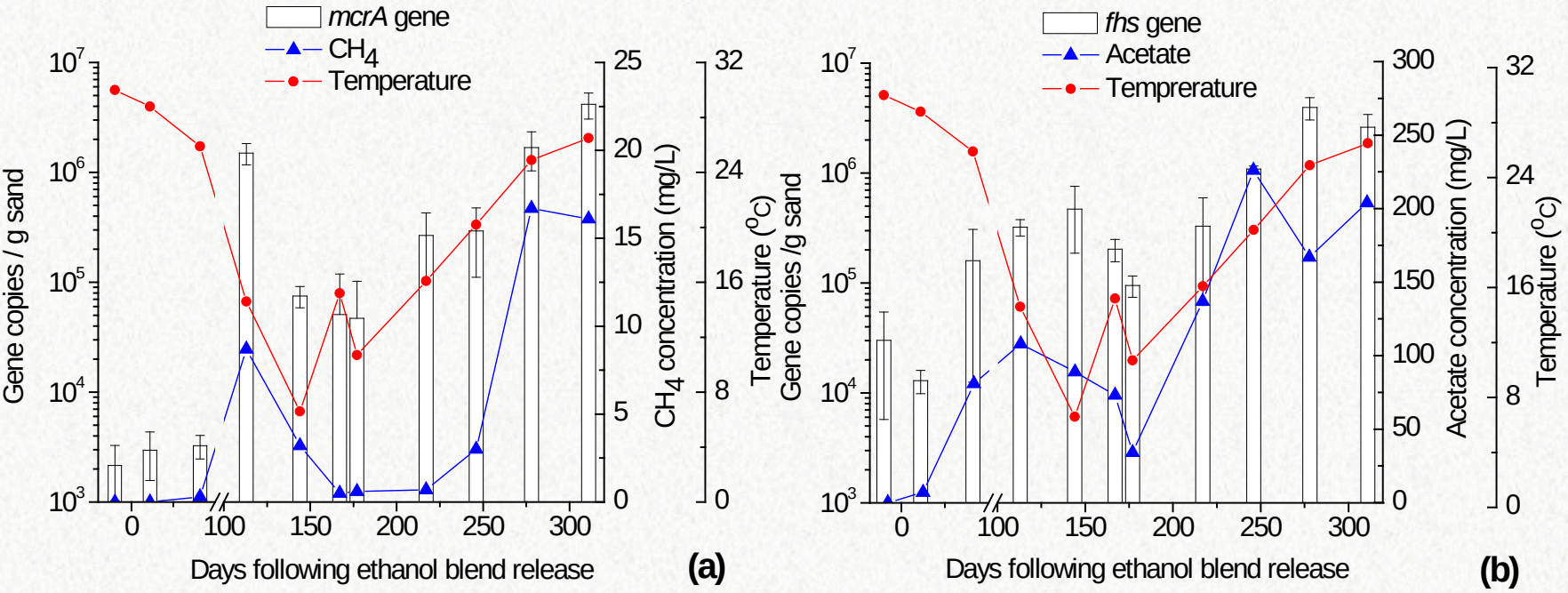
CH_4 solubility is 21.4 mg/L at 28 °C

In summer, the groundwater was **saturated** with CH_4

Ma, J., et al. ***Environ. Sci. & Tech.*** (2012)

Groundwater Impacts:

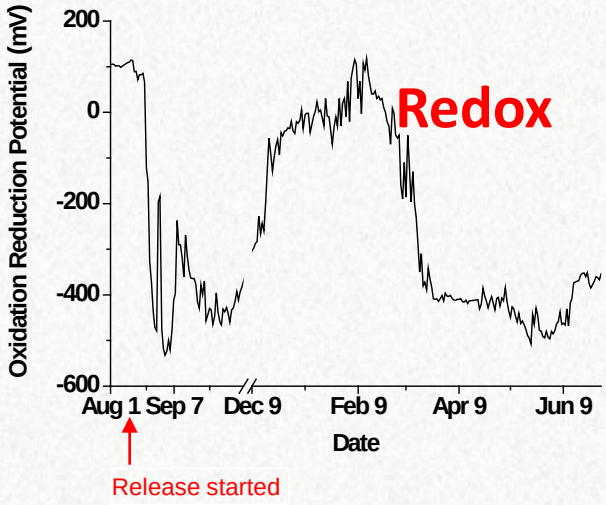
Metabolites concentration and functional genes abundance for methanogenesis (a) and acetogenesis (b)

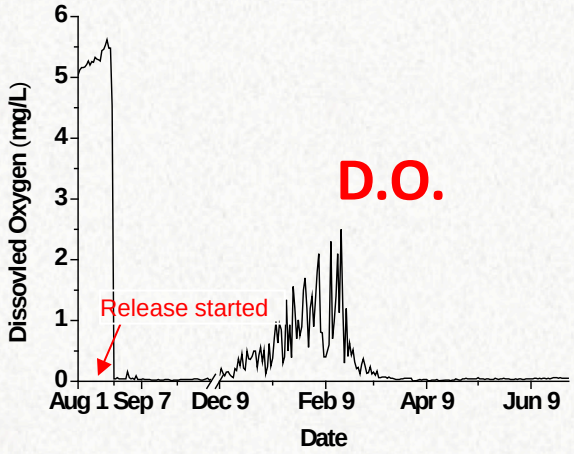


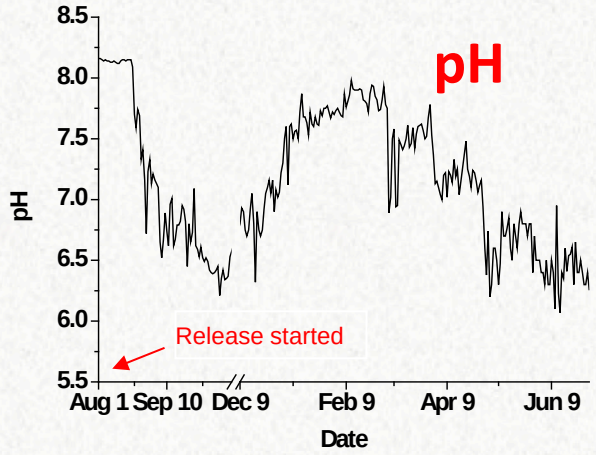
Ma, J. et al. ***Environmental Pollution*** (2013)

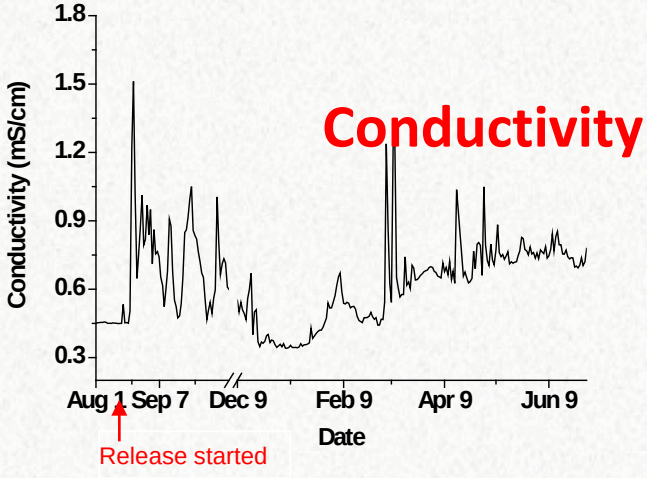
Groundwater Impacts:

Geochemical measurements





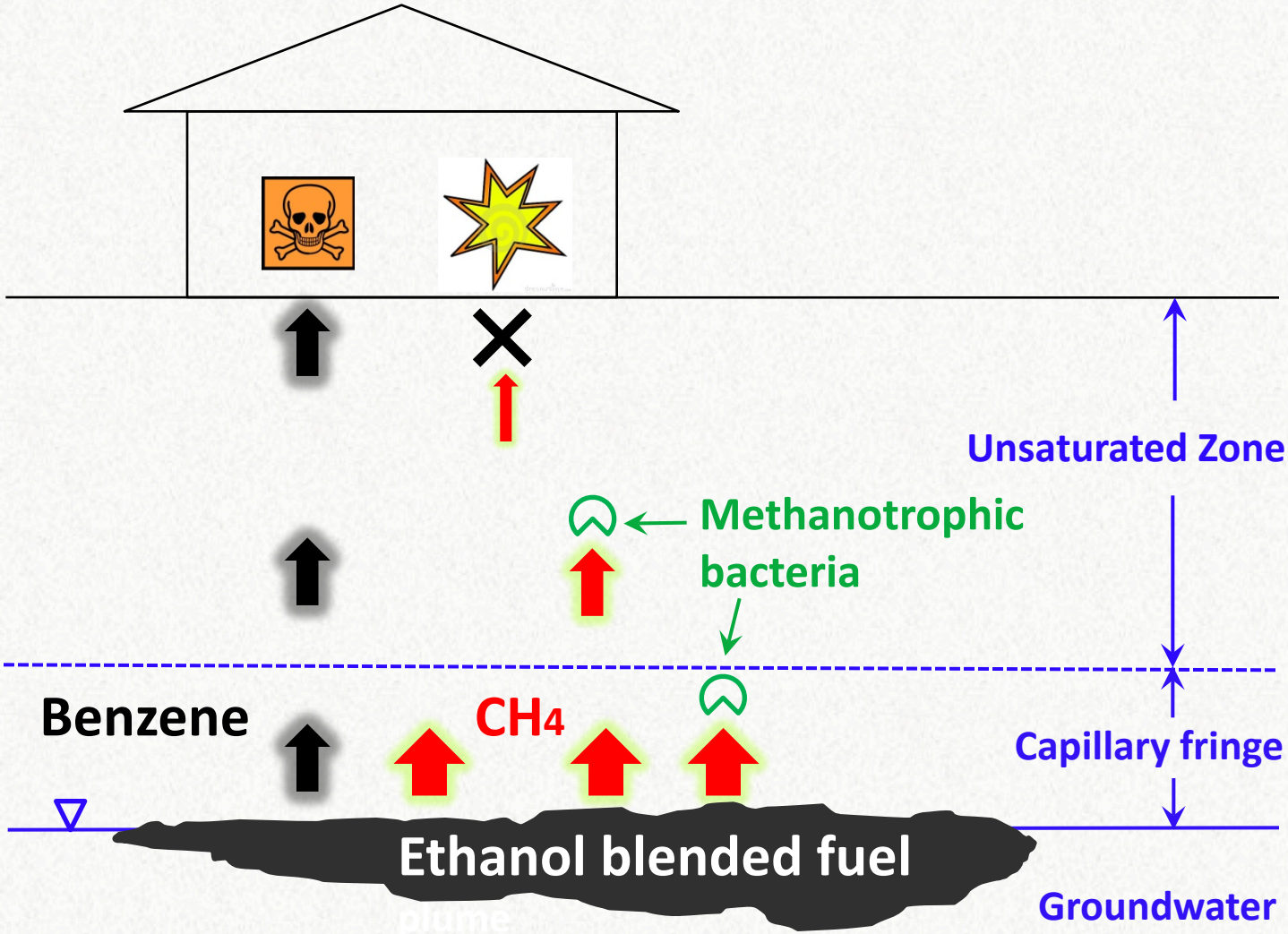




Consistent with methanogenesis and acetogenesis. In summer, gw tends to more anaerobic with lower pH

Ma, J. et al. ***Environmental Pollution,*** (2013)

Flux Measurements:



Ma, J., et al. ***Environ. Sci. & Tech.*** (2012)

Flux Measurements:

A pilot aquifer system

Channel 1:

10% (v:v) ethanol

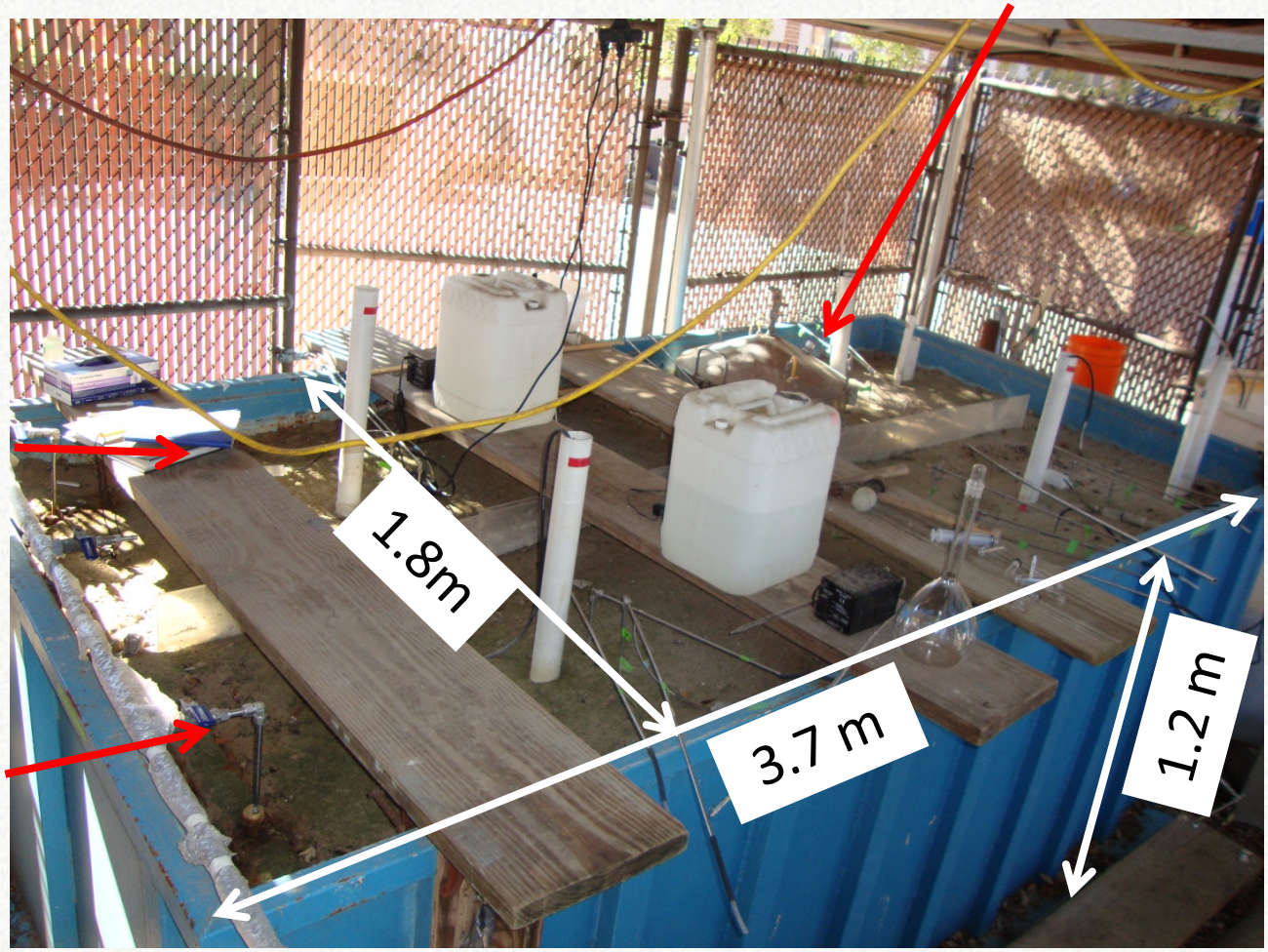
50 mg/L benzene

50 mg/L toluene

Channel 2:

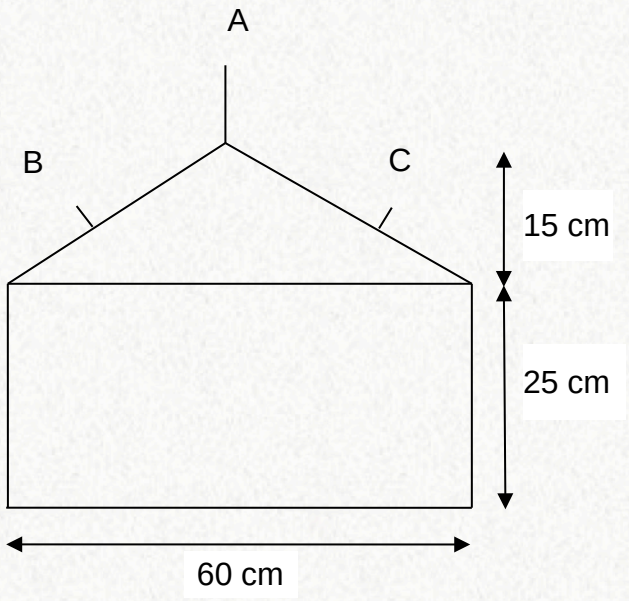
50 mg/L benzene

50 mg/L toluene



Flux Measurements:

Flux chamber



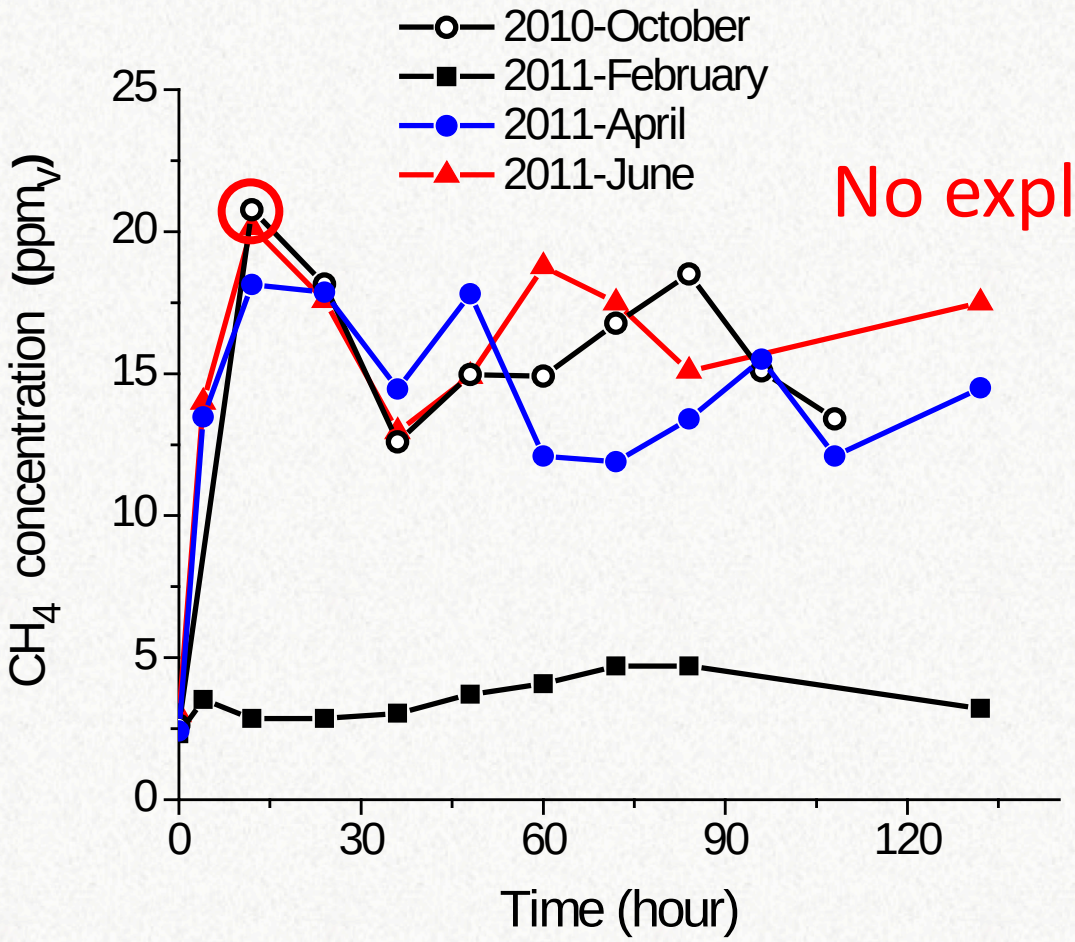
Structure schematic

Photo

Flux Measurements:

CH_4 accumulation inside the flux chamber

Explosion limit: 50,000 ppmv

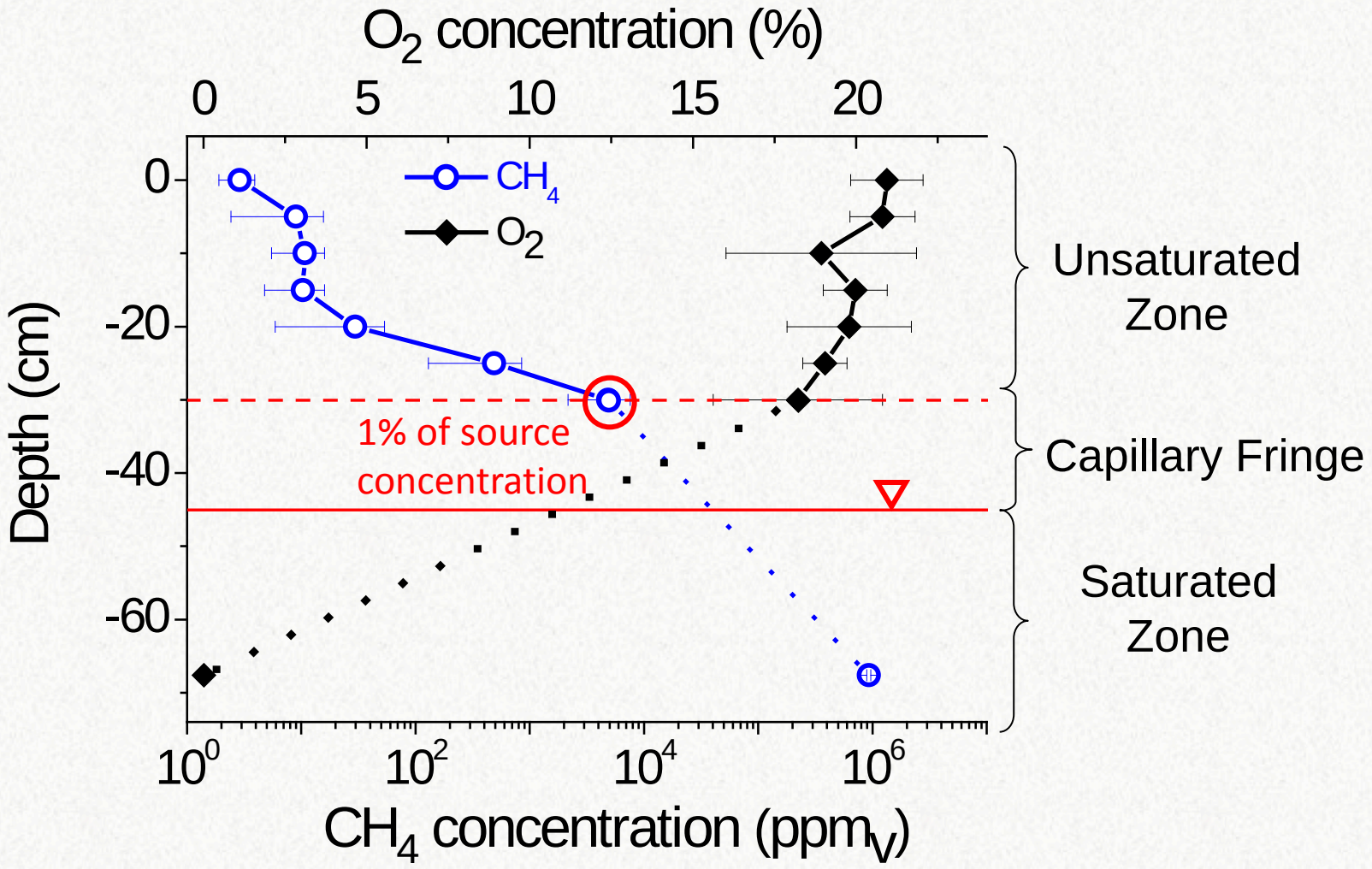


No explosion risk!

Ma, J., et al. ***Environ. Sci. & Tech.*** (2012)

Flux Measurements:

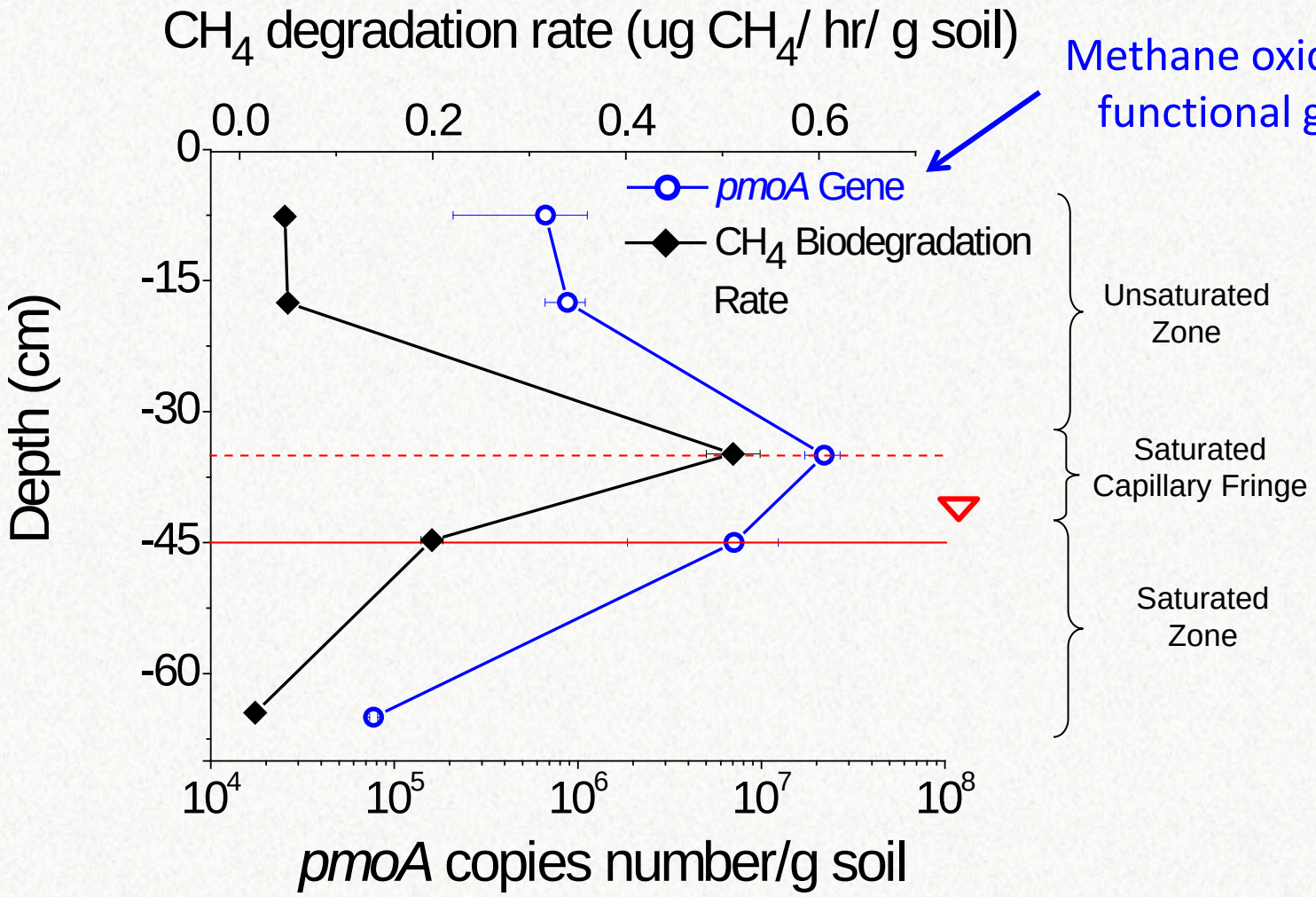
Most of CH_4 was attenuated in the capillary fringe and saturated zone



Ma, J., et al. ***Environ. Sci. & Tech.*** (2012)

Flux Measurements:

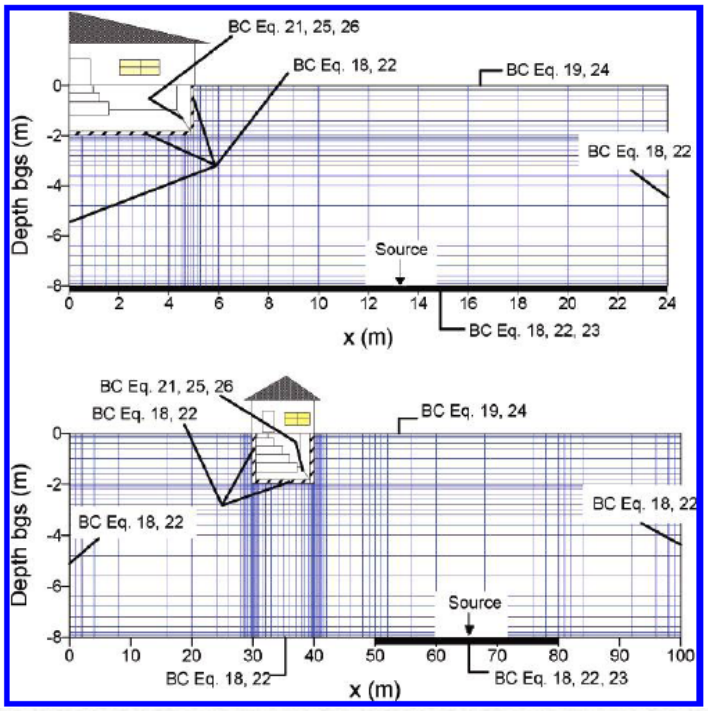
Capillary fringe and saturated zone near water table have strongest CH_4 degradation activities

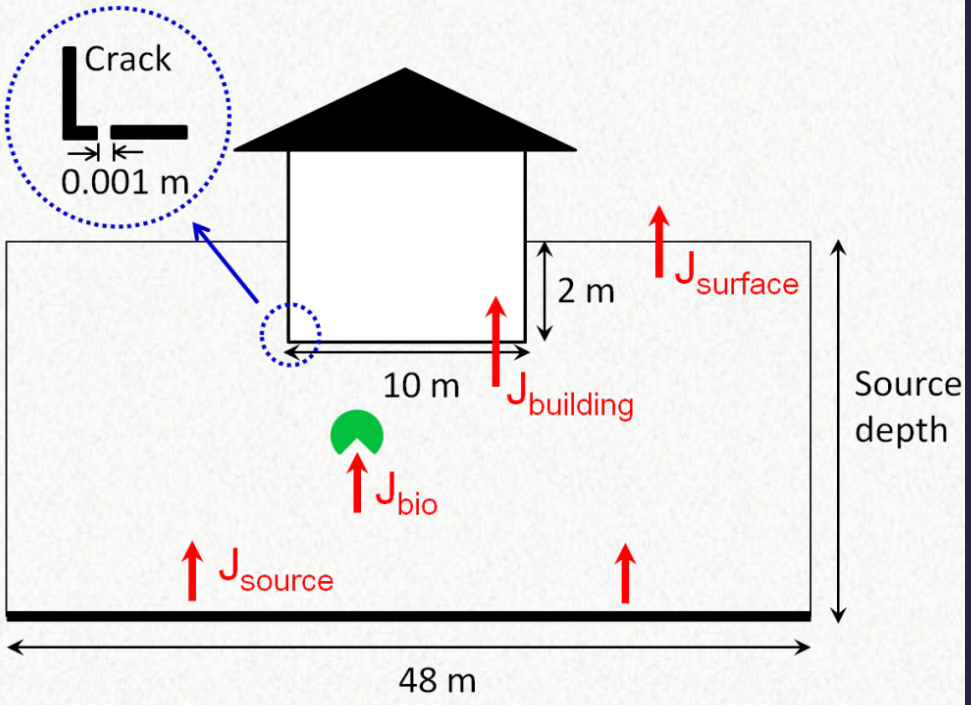


Ma, J., et al. ***Environ. Sci. & Tech.*** (2012)

Flux Modeling:

Abreu & Johnson 3-D numerical vapor intrusion model





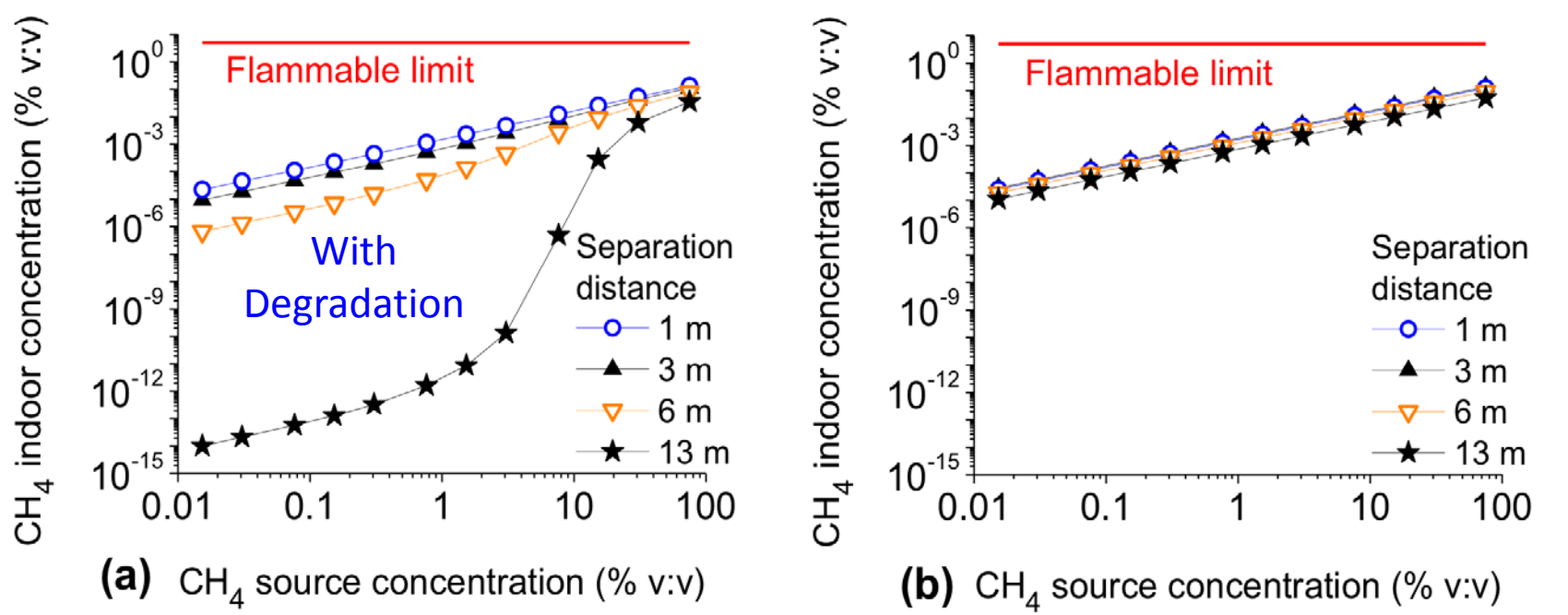
- A single-family house.
- Benzene and CH_4 coexisted in the source zone.

Abreu, L., et al. ***Environmental Science & Technology*** (2005)

Ma, J., et al. ***Environmental Science & Technology*** (2014)

Flux Modeling:

Simulated CH_4 indoor concentrations

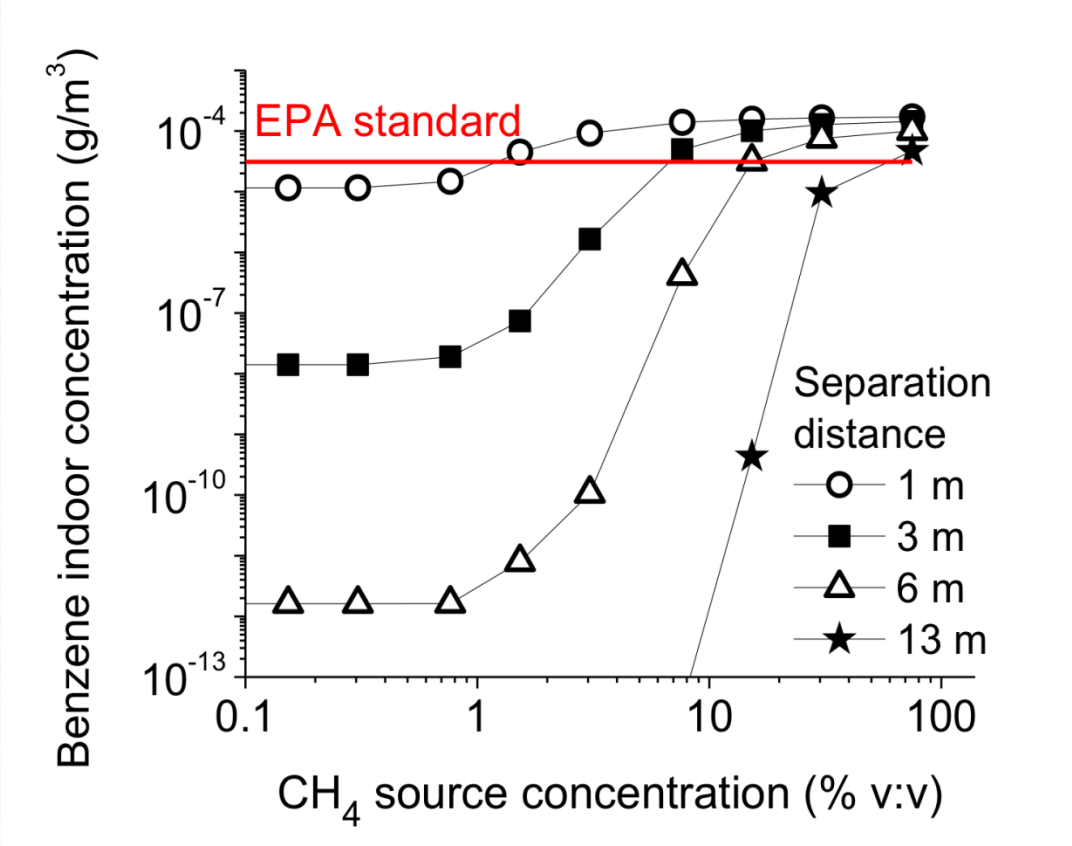


- Biodegradation significantly reduces CH_4 flux and alleviates the associated explosion risk.
- If diffusion is the major mass transport mechanism, CH_4 is unlikely to cause explosion risk.

Ma, J., et al. ***Environ. Sci. & Tech.*** (2014)

Flux Modeling:

Simulated benzene indoor concentrations

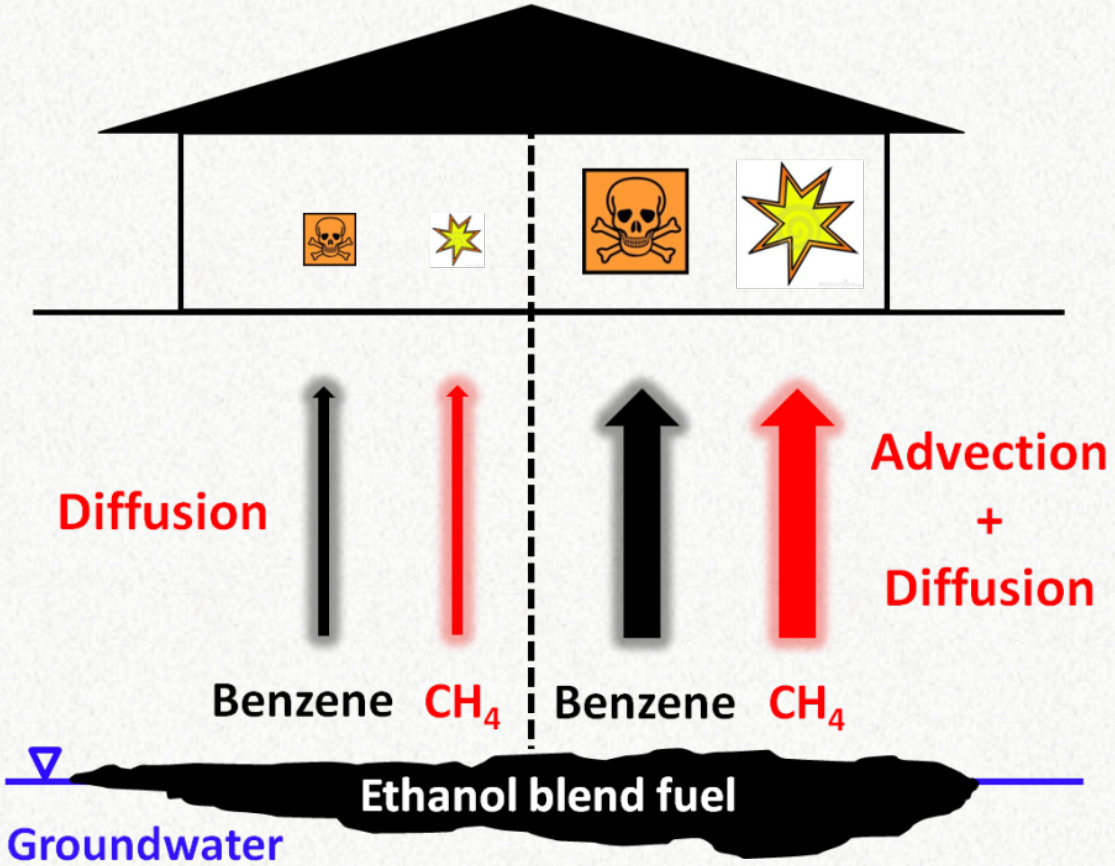


CH_4 degradation depletes O_2 that otherwise could be used for benzene biodegradation, thus increasing the vapor intrusion potential for benzene.

Ma, J., et al. ***Environ. Sci. & Tech.*** (2014)

Flux Modeling:

Impacts of advection

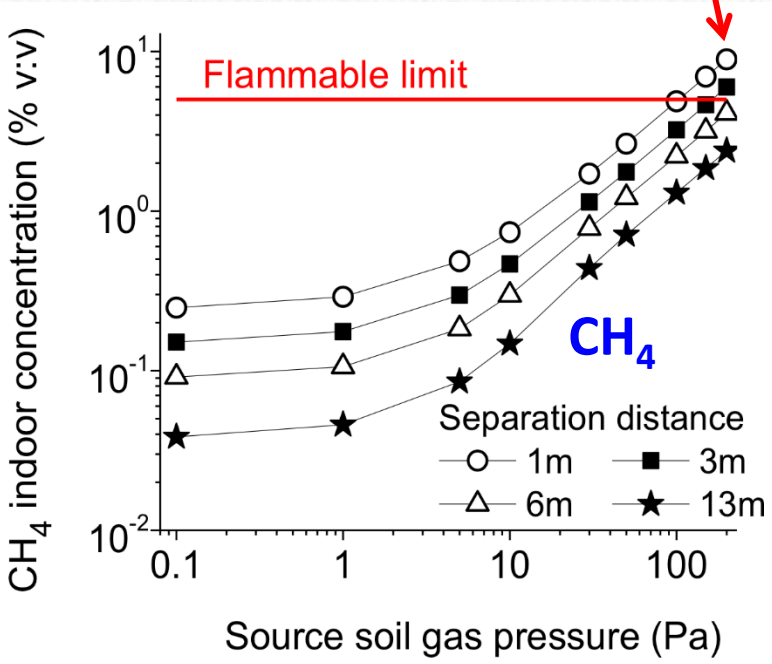


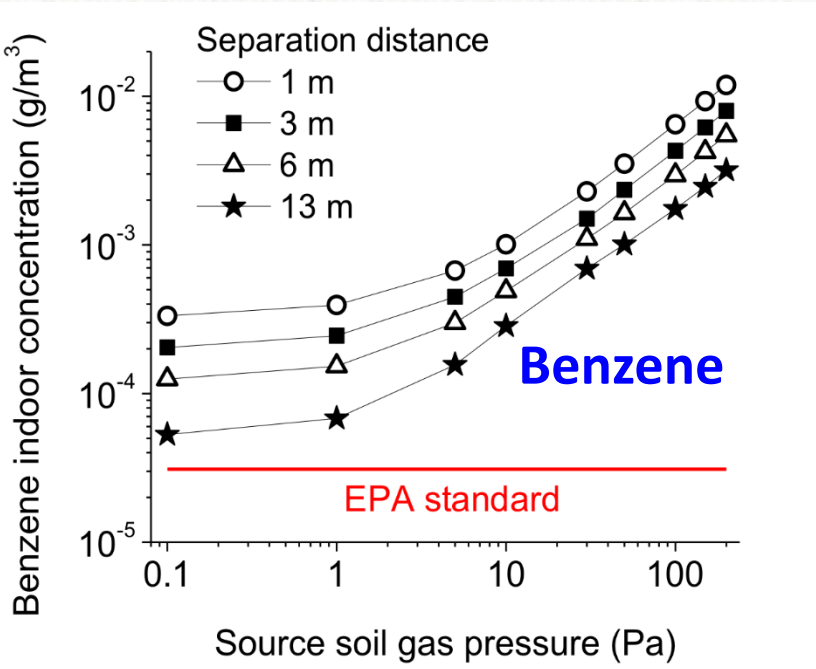
Ma, J., et al. ***Environ. Sci. & Tech.*** (2014)

Flux Modeling:

Simulated CH_4 and benzene indoor concentrations for different source pressures

Explosion may occur!

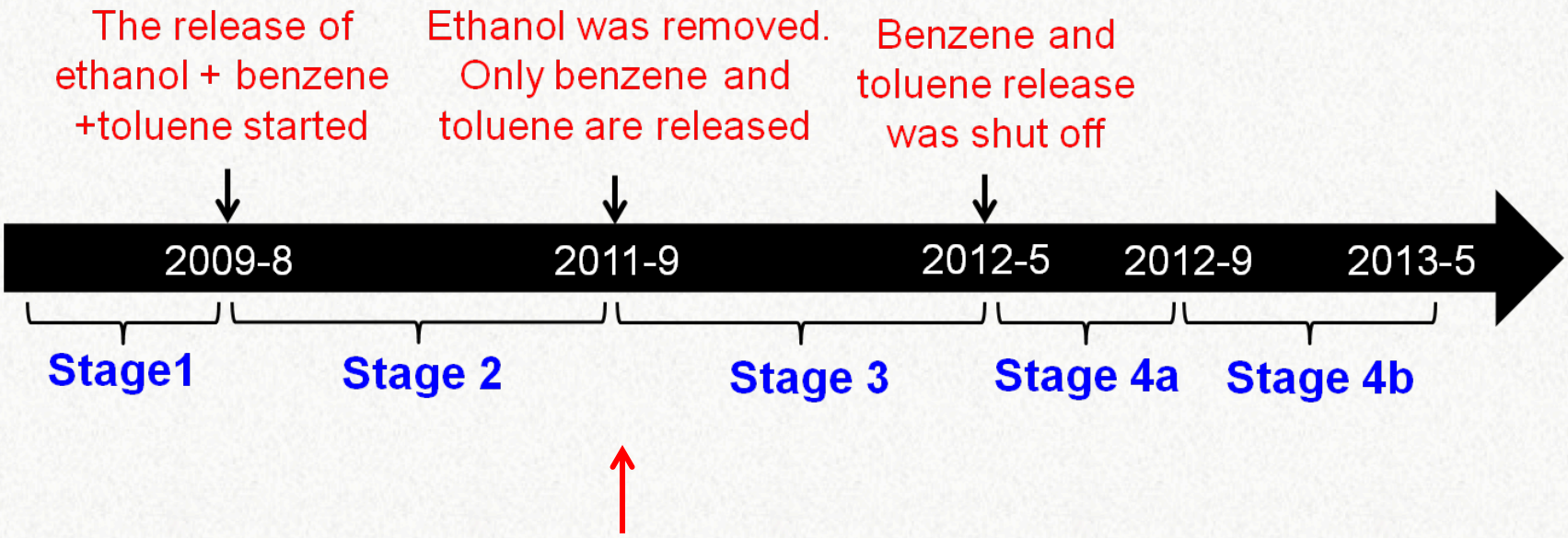




Advection-driven gas flow exacerbates the vapor intrusion risk of both CH_4 and benzene.

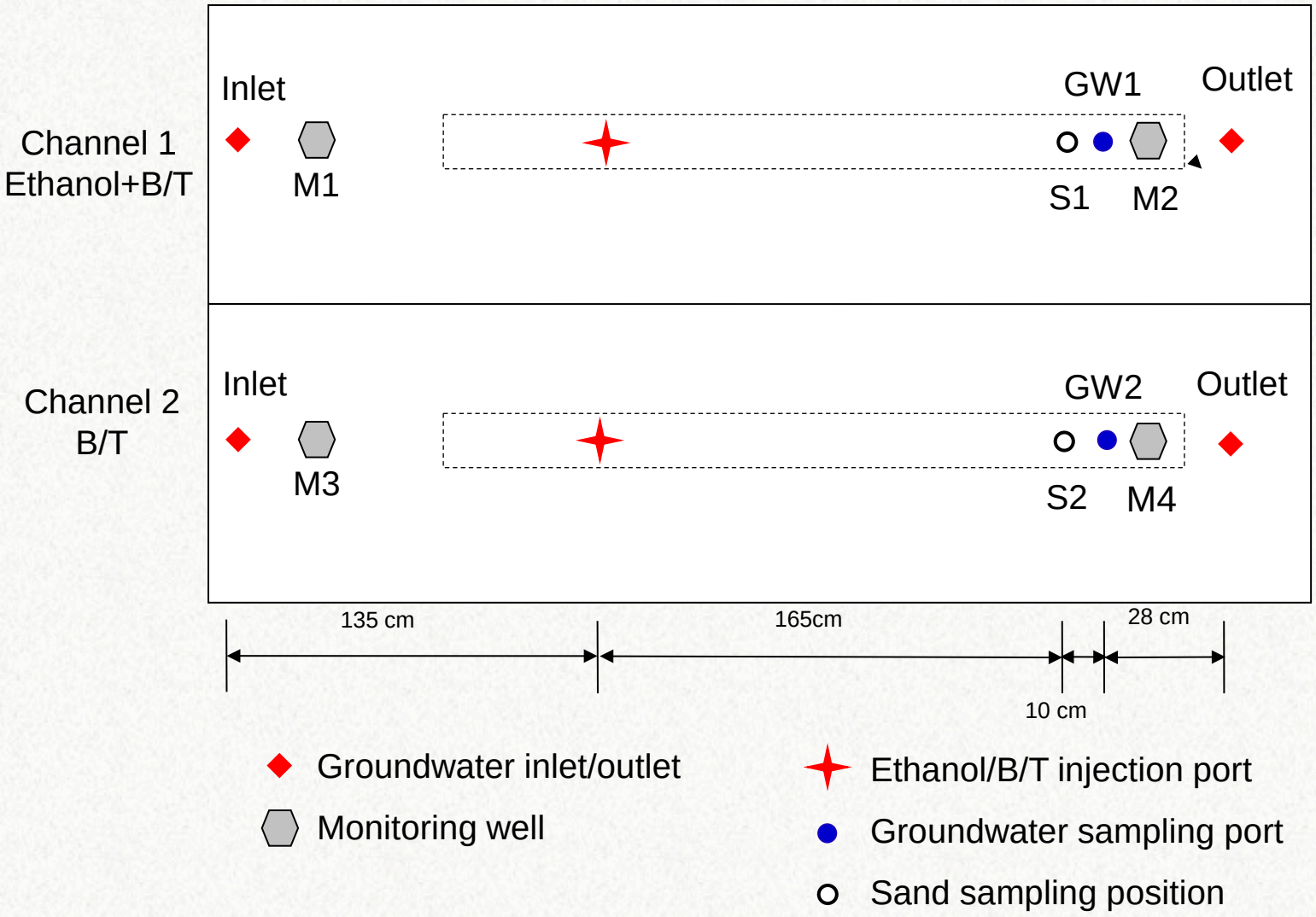
Ma, J., et al. ***Environ. Sci. & Tech.*** (2014)

Response to Source Removal:

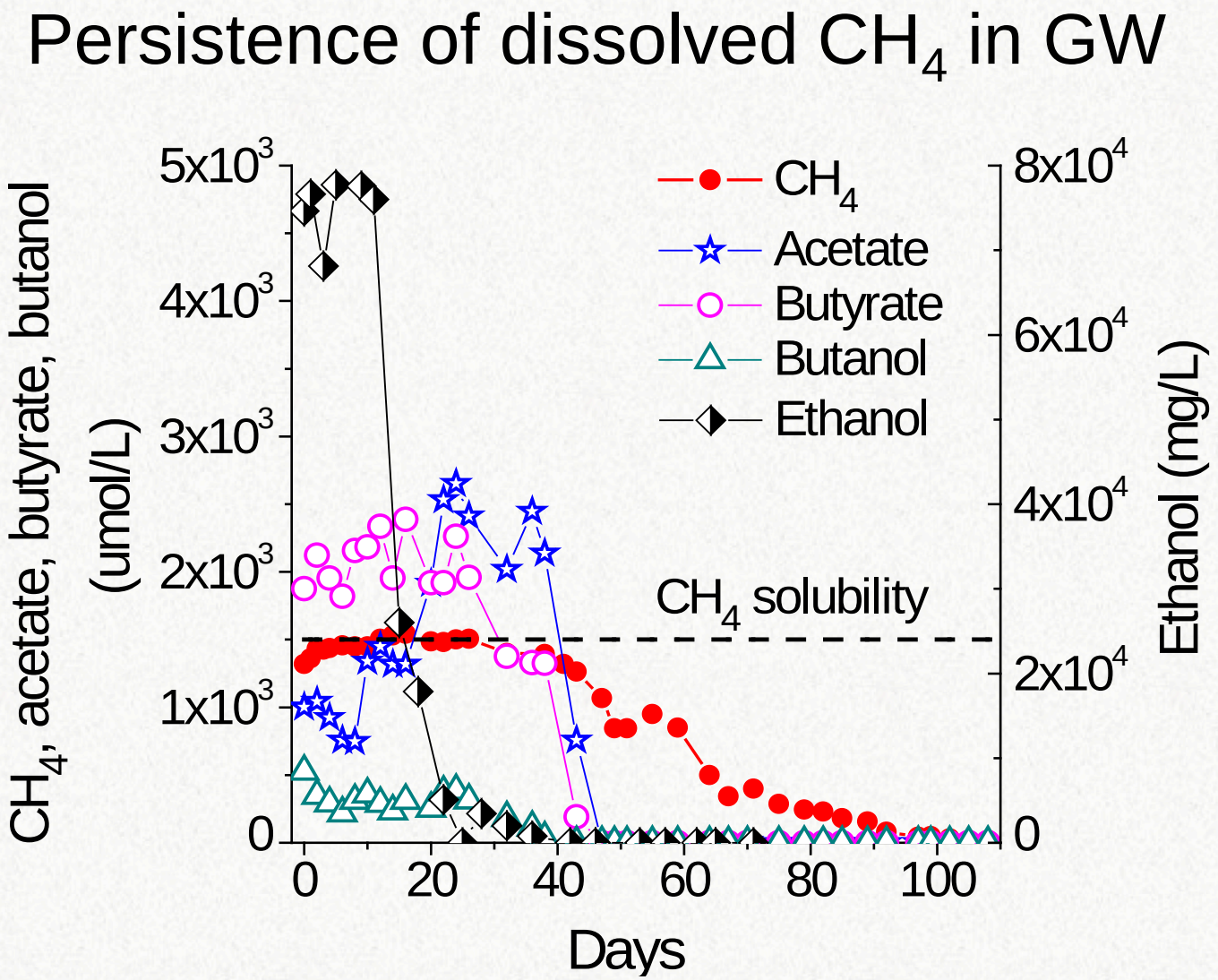


Response to Source Removal:

Tank plan view



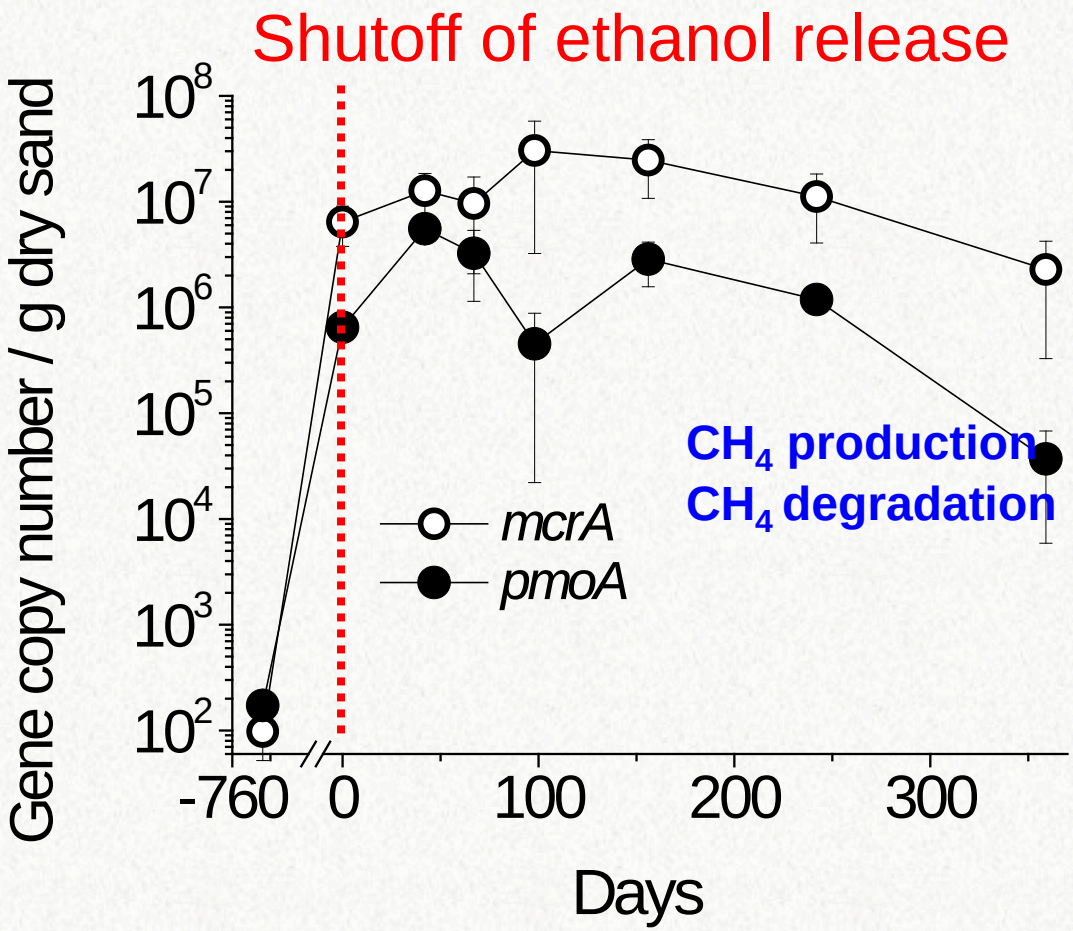
Response to Source Removal:



Ma, J. et al. ***in review*** (2014)

Response to Source Removal:

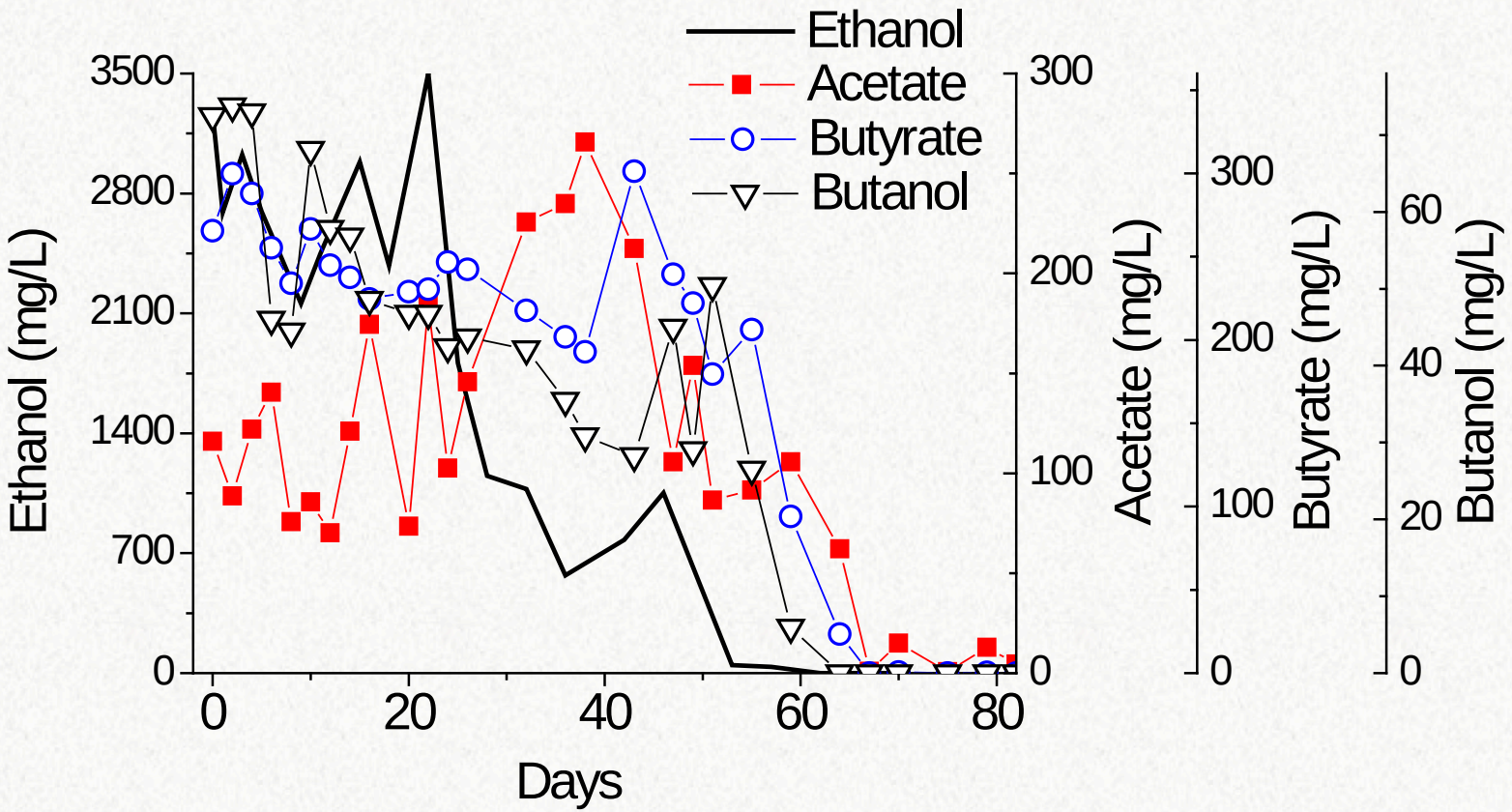
Persistence of methane metabolic genes



Ma, J. et al. ***in review*** (2014)

Response to Source Removal:

Unexpected stimulation of ethanol degradation



3,300-3,500 mg/L of ethanol is toxic and could partially inhibit ethanol degradation.

Ma, J. et al. ***in review*** (2014)

Summary

- Anaerobic biodegradation of fuel ethanol produces VFAs and methane.
- The accumulation of VFAs (e.g., butyric acid) may affect groundwater aesthetic quality.
- Methanotrophic activities reduce CH_4 flux and the explosion risk, but it may deplete O_2 and increase vapor intrusion potential for other hydrocarbons (e.g., benzene).
- Vapor intrusion would be enhanced if methanogenic activity is sufficient to cause advective transport in the unsaturated zone.

Summary (cont.)

- The fermentative degradation of ethanol may be temporarily stimulated when the ethanol concentration decreases below its toxicity threshold, thus leading to transient accumulation of ethanol degradation byproducts.
- CH_4 generation in the impacted aquifer may continue for a long time even after the disappearance of dissolved ethanol.
- Increases in microbial diversity and degradation rates suggest an adaptive response that increases the potential for natural attenuation of ethanol blend releases.

Ongoing work: determine the extent to which ethanol is converted to degradation byproducts, especially to methane, for various size releases and fuel types.

Acknowledgements

- American Petroleum Institute
- Pedro Alvarez (Rice)
- Jia Ma, Zongming Xiu, Amy Monier (Rice)
- Yi Zhang, Irina Mamonkina (UH)
- George DeVaull, Brent Stafford (Shell)

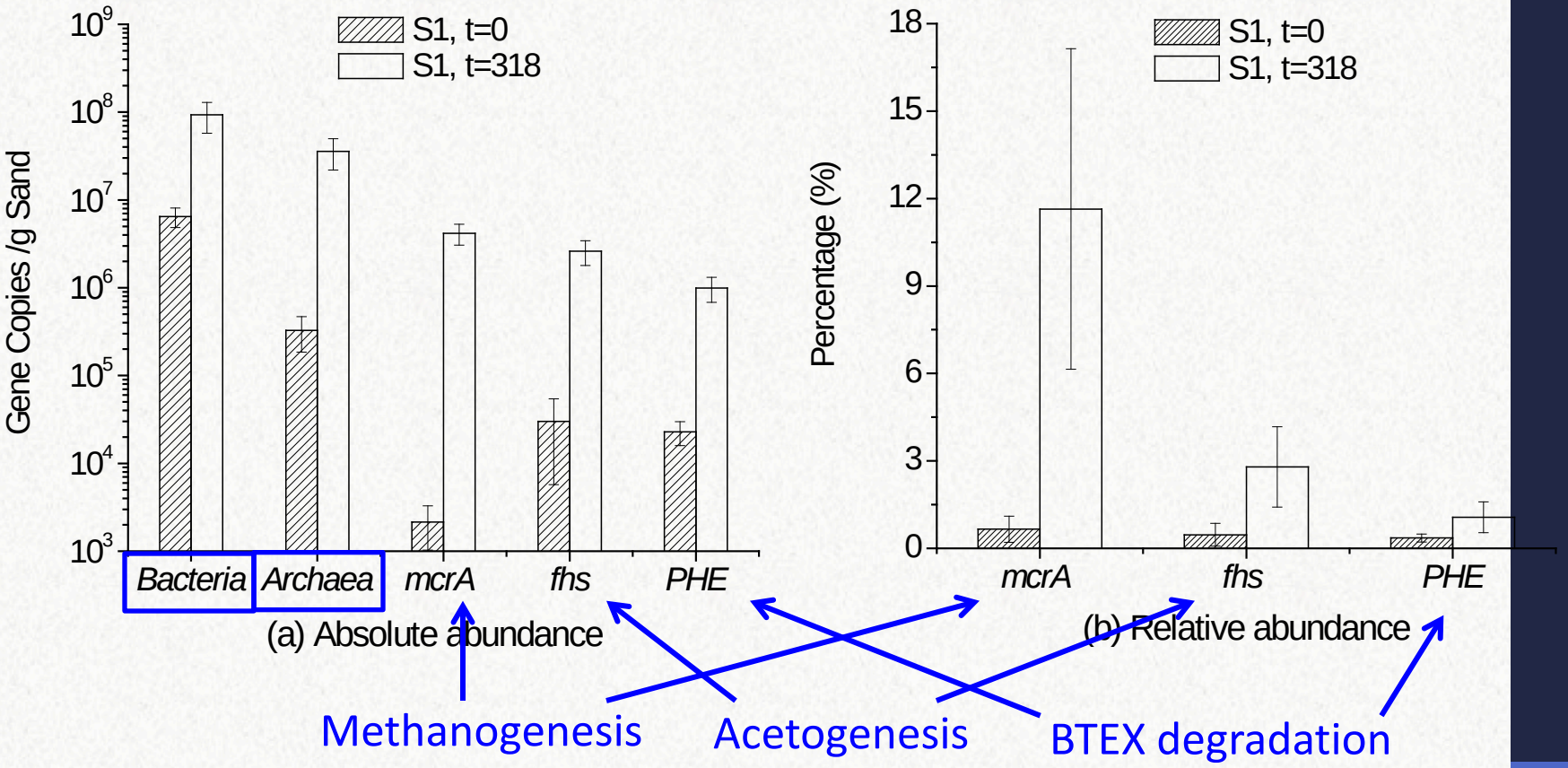
References

- Ma, J., Luo, H., DeVaull. G.E., Rixey, W.G., and Alvarez, P.J.J. (2014) Numerical Model Investigation for Potential Methane Explosion and Benzene Vapor Intrusion Associated with High-Ethanol Blend Releases. ***Environmental Science & Technology*** 48: 474-481.
- Ma, J., Rixey, W.G., and Alvarez, P.J.J. (2013) Microbial Processes Influencing the Transport, Fate, and Groundwater Impacts of Fuel Ethanol Releases. ***Current Opinion in Biotechnology*** 24: 457-466.
- Ma, J., Nossa, C.W., Xiu, Z.M., Rixey, W.G. and Alvarez, P.J.J. (2013) Adaptive Microbial Population Shifts in Response to a Continuous Ethanol Release Increases Natural Attenuation Potential. ***Environmental Pollution*** 178: 419-425.
- Ma, J., Rixey, W.G., DeVaull, G.E., Stafford, B.P. and Alvarez, P.J.J. (2012) Bioattenuation of Methane along the Groundwater to Soil Surface Pathway in a Pilot-Scale Aquifer above a Dissolved Ethanol Plume. ***Environmental Science & Technology*** 46 (11): 6013-6019.
- Ma, J., Xiu, Z., Monier, A., Mamonkina, I., Zhang, Y., He, Y., Stafford, B., Rixey, W. and Alvarez, P. (2011) Aesthetic Groundwater Quality Impacts from a Continuous Pilot-Scale Release of an Ethanol Blend. ***Ground Water Monitoring & Remediation*** 31(3), 47–54.

Additional Slides

Groundwater Impacts:

Changes of absolute (a) and relative (b) abundance of selective genes following 10 months release

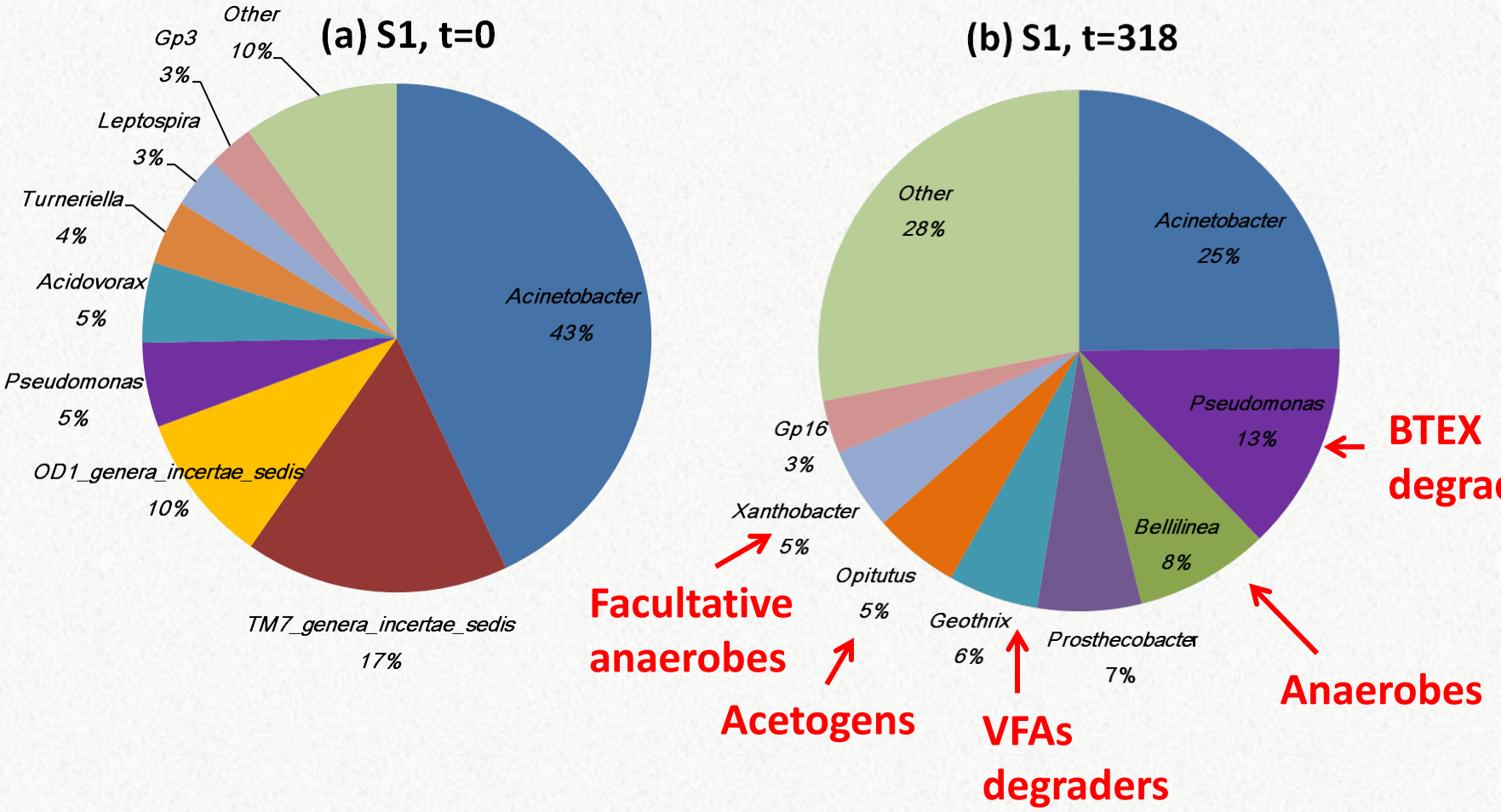


Ethanol blends stimulate microbial growth and enriched certain genotypes

Ma, J. et al. ***Environmental Pollution*** (2013)

Groundwater Impacts:

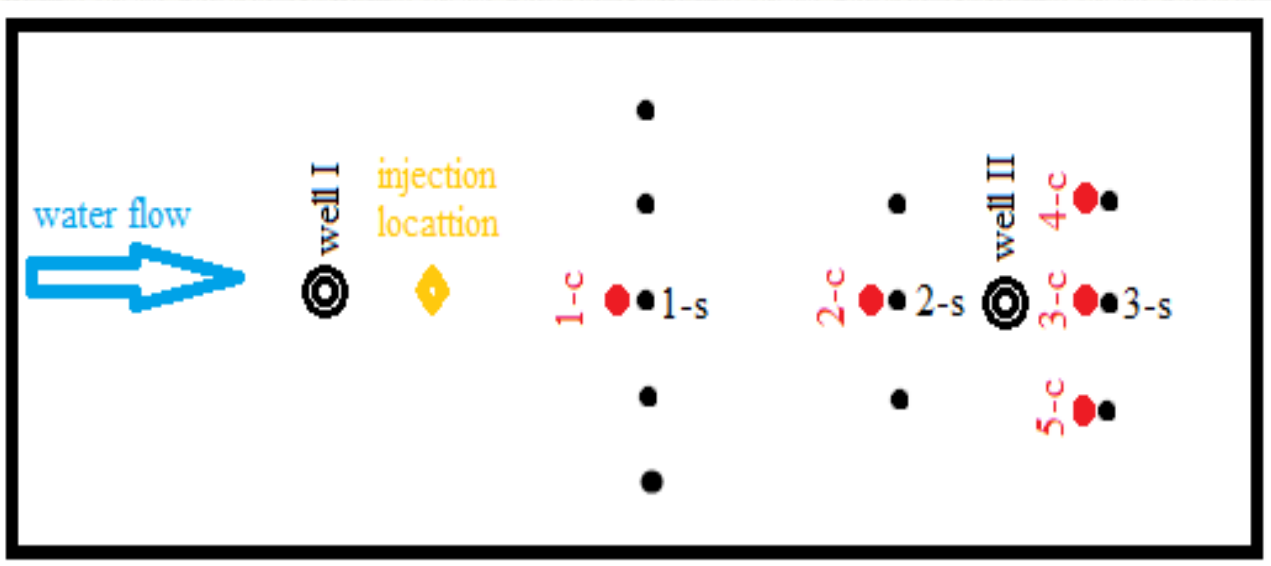
Impacts of ethanol blends on bacterial community structure (genus level)



Ma, J. et al. ***Environmental Pollution*** (2013)

Pilot-Scale Aquifer - Fixed Volume Spills

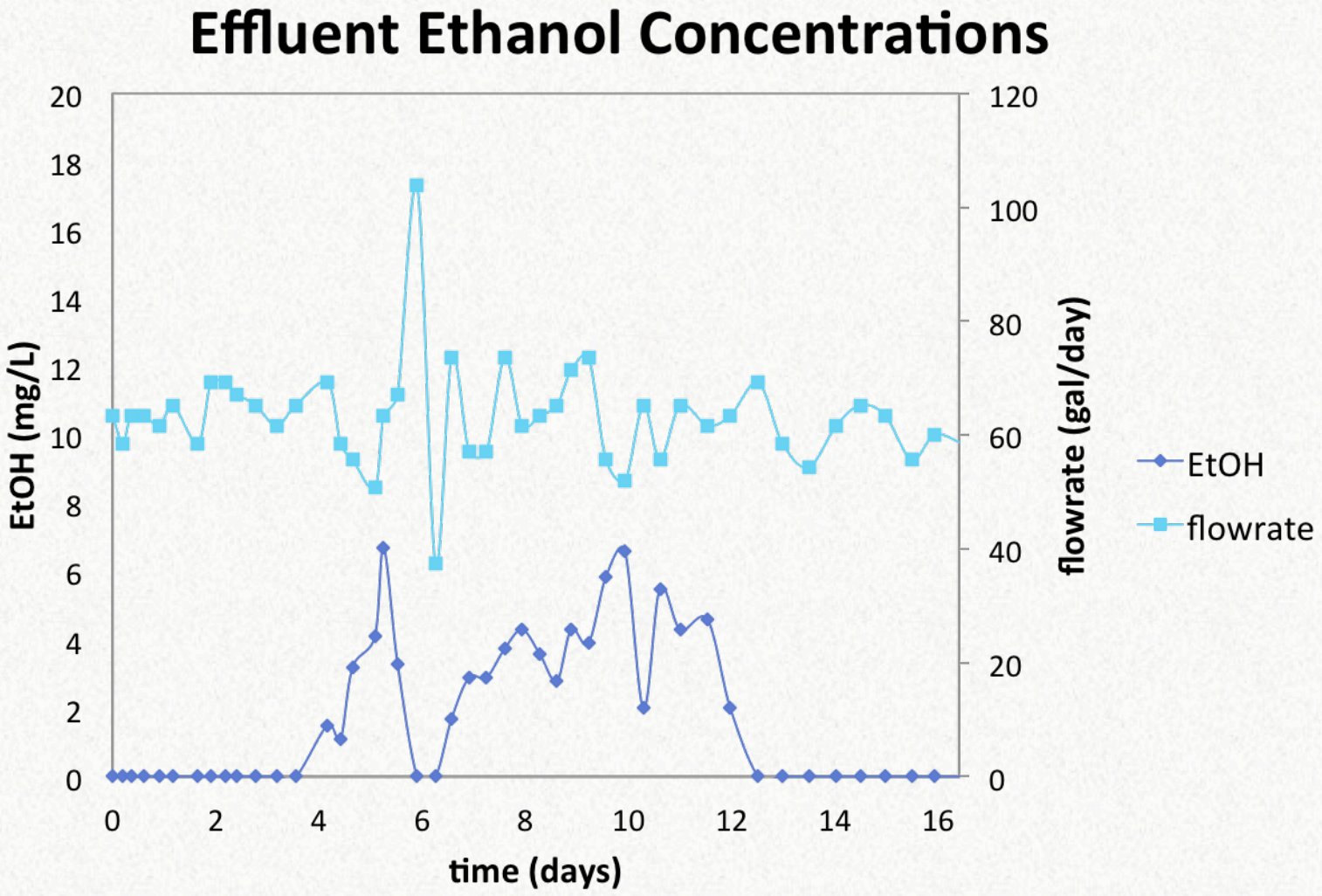
- 1-L E25 and 5-L E25 spills
- Q = 60 gpd
- Fuel Blend: 25% EtOH - 75% BTX, TMB, isooctane mixture
- 1-L and 5-L Bromide (5,000 mg/L) tracer



Channel 1 injection and sampling locations

Fixed Volume Releases:

5L E25 Release



Ethanol mass recovered = 0.6 %

Fixed Volume Releases:

Major Findings/Conclusions

- Ethanol highly attenuated for 1-L and 5-L releases - 99%+
- CH_4 production low (below detection limit) for these releases.
- Significant conversion to VFAs and CH_4 for the 1-L E25 release.
- We expect for higher spill volumes, higher rates of CH_4 generation, but lower fractional conversion of EtOH.

- **Ongoing work**: determine the extent to which ethanol is converted to degradation byproducts, especially to methane, for various size releases and fuel types.