

MTBE and TBA Biodegradation Assessment Under Natural and Engineered Conditions Using Compound-Specific Carbon Isotope Analysis at Port Hueneme , CA.

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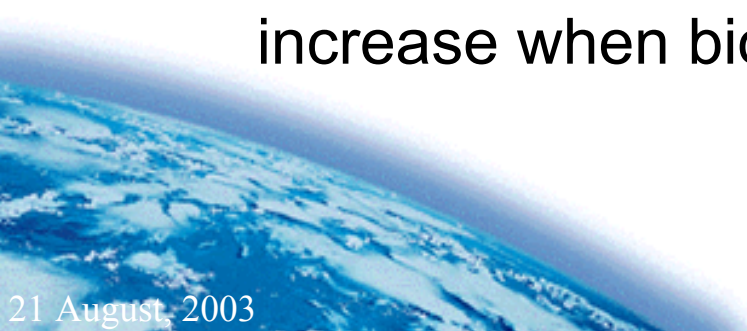
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Port Hueneme Field Study - Background

- Stable Isotope ($^{13}\text{C}/^{12}\text{C}$ and D/H) Tools are being proposed and to diagnose the observed attenuation of MTBE Plumes
- In most cases, site-specific mechanistic conclusions are being from the analyses of small numbers of samples
- Port Hueneme is a site that is relatively well-understood mechanistically... because of the abundance of data from biobarrier studies and historical plume characterization data.
- This site provides a unique opportunity to look at the results from field data sets relative to what is known mechanistically (previously only known for bench-top microcosm studies).



- Carbon has 2 stable isotopes: ^{13}C (abundance 1.11%) and ^{12}C , and one radioactive isotope: ^{14}C ($T_{1/2} = 5,730$ years)
- For kinetic reasons, there is a preference for microorganisms to break ^{12}C - ^{12}C bonds rather than ^{13}C - ^{12}C bonds during biodegradation
- Therefore the $^{13}\text{C}/^{12}\text{C}$ ratio of the reactant will increase when biodegradation occurs



- For carbon:

$$\delta^{13}\text{C} = \frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{VPDB}}} \times 1000\text{‰}$$

Yes—it IS an equation, however, there are NO differentials in it.

For the Geologically
Challenged (i.e., engineers)
This is a Belemnite



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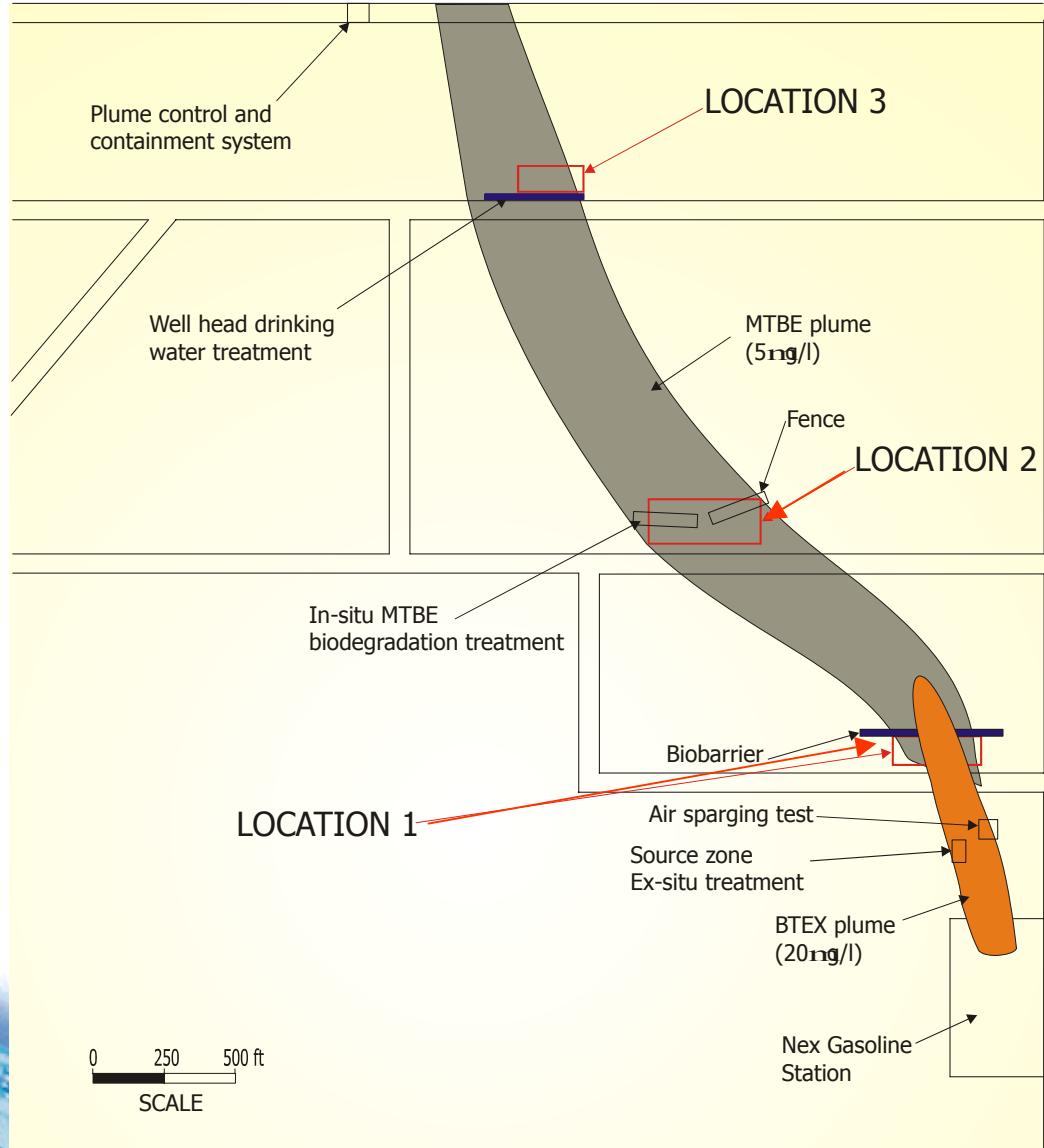
- Hunkeler et al. (2001) found that on microcosms experiments MTBE became enriched in ^{13}C during aerobic biodegradation by 5.1‰ to 6.9‰.
- Kolhatkar et al. (2002) report an increase in the MTBE- ^{13}C during anaerobic biodegradation from 31.0‰ to 33.4‰.
- Both studies show only lab results and no field

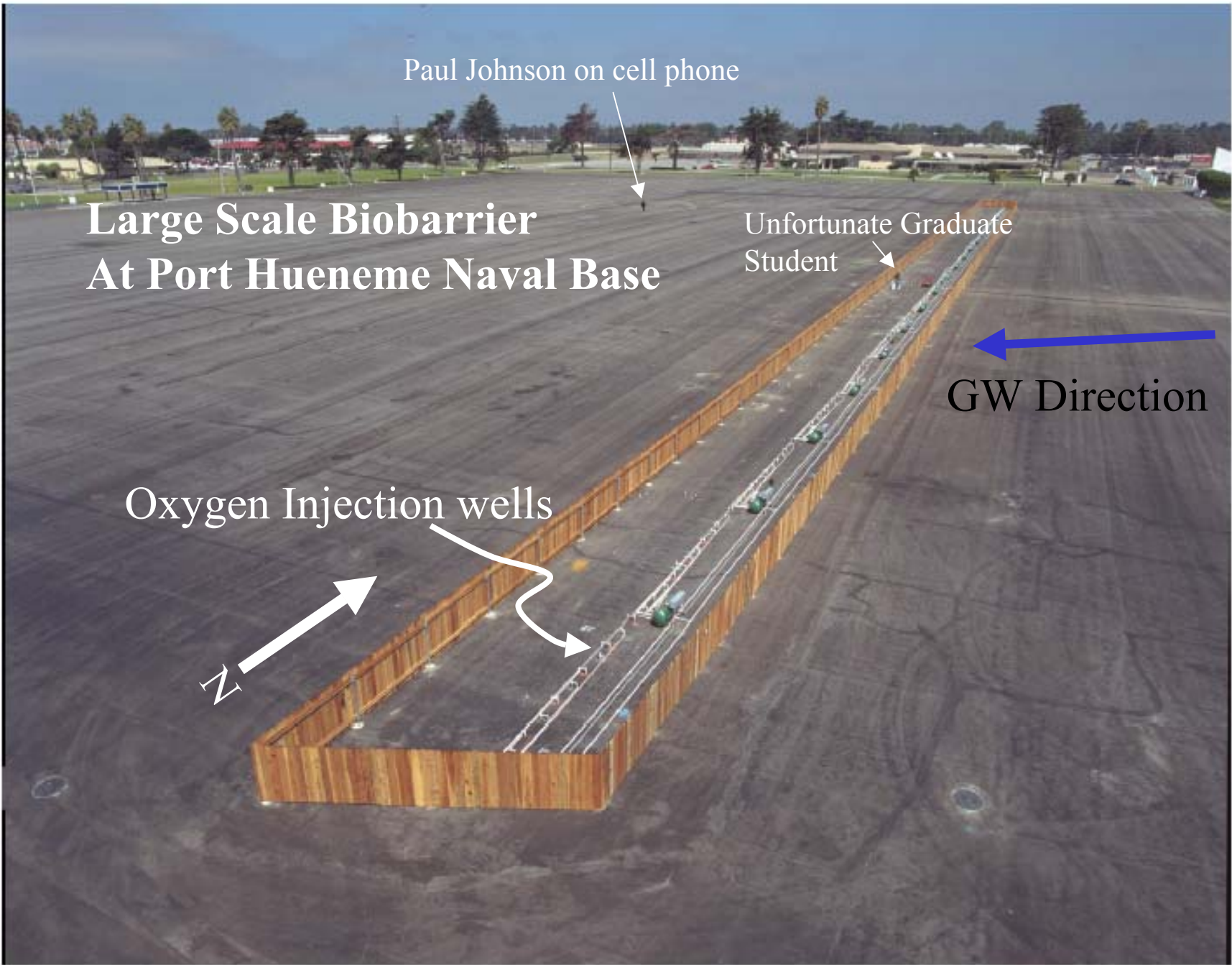
Port Hueneme Field Study - Overview

50 samples were collected in the plume with the purposes:

- Assess the isotopic fractionation in zones where biodegradation is known to occur
- Assess isotopic fractionation associated with dilution and spreading of the contaminant plume
- Assess isotopic fractionation along flowpaths biodegradation is not likely taking place
- Assess the variability of in field data sets..

Port Hueneme Field Study





Large Scale Biobarrier At Port Hueneme Naval Base

Paul Johnson on cell phone

Unfortunate Graduate Student

GW Direction

Oxygen Injection wells

N

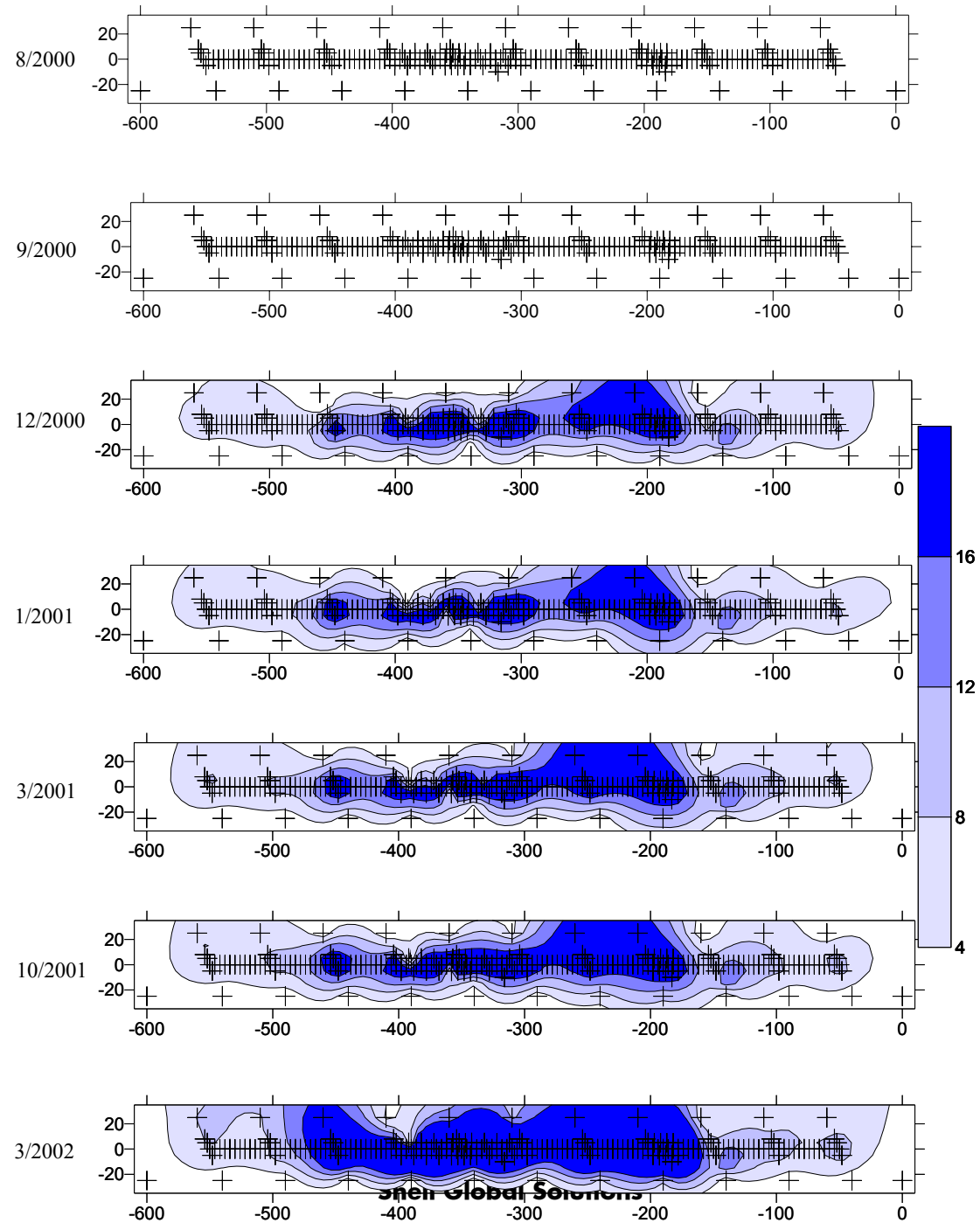


Paul Johnson on the cell phone

Approximate Location of the Bioactive Zone

GW Direction

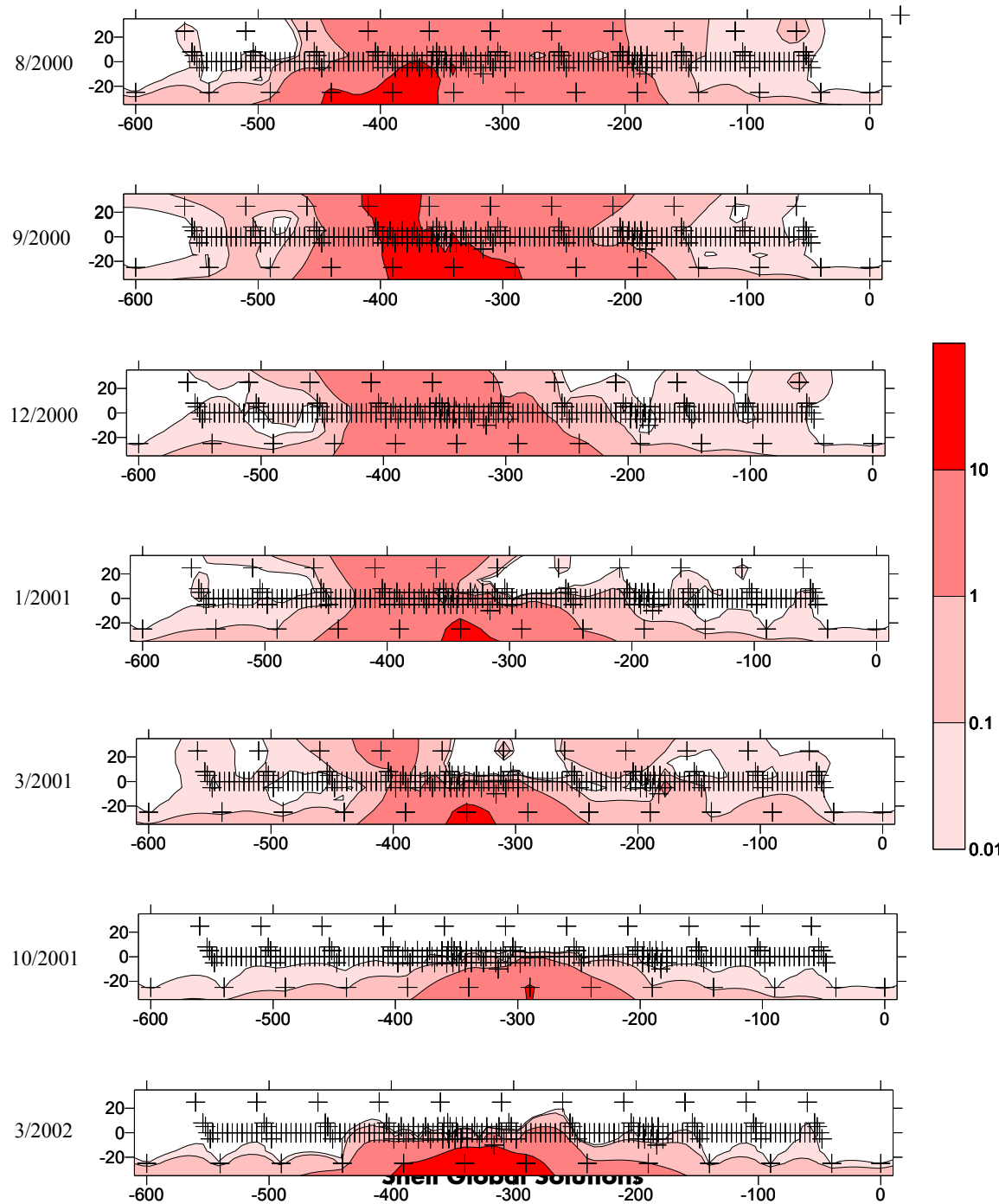
N



Dissolved Oxygen concentrations at Location 1 (15 ft below surface)



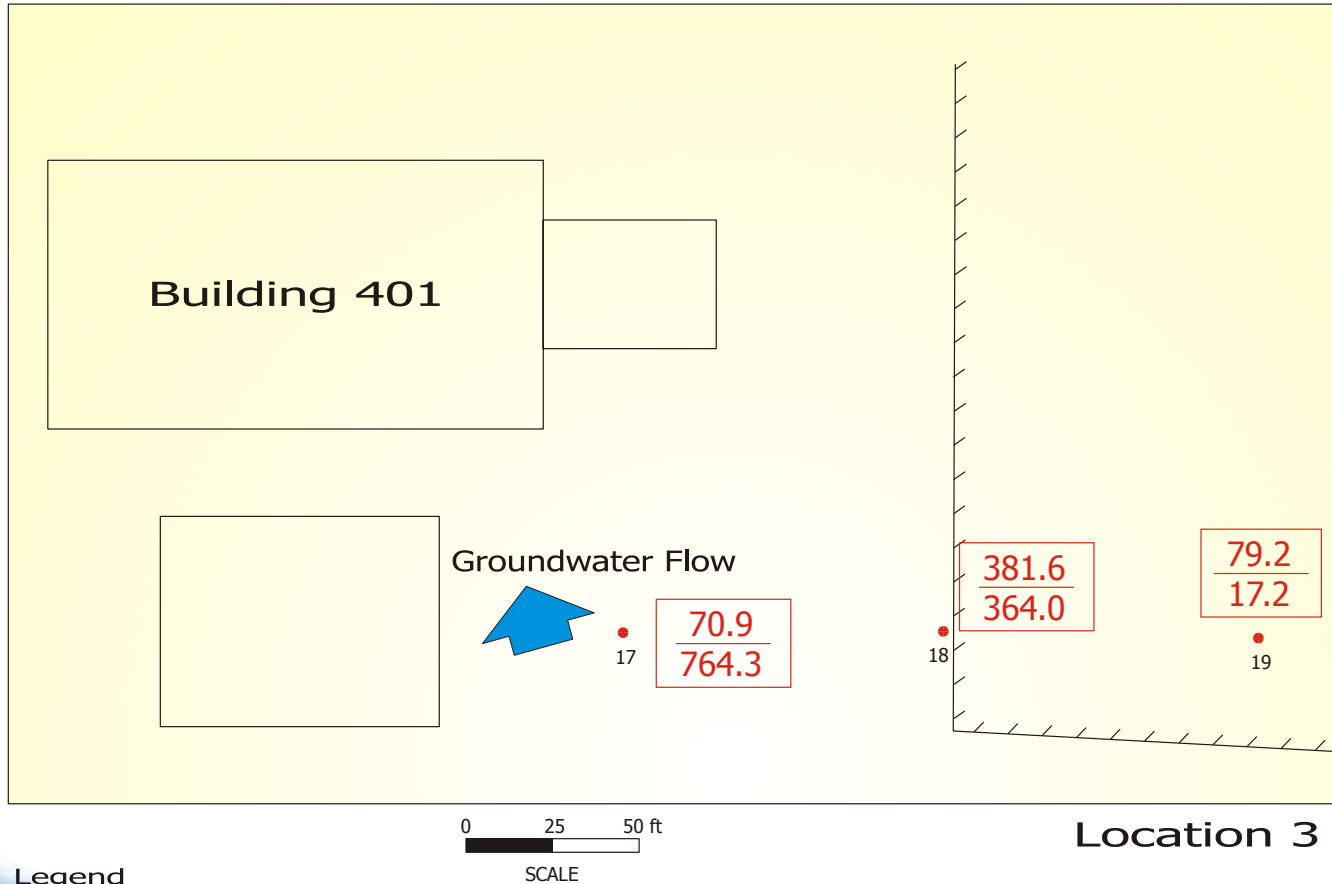
MTBE
concentrations at
Location 1
(15 ft below
surface)



And---what did we see????



Port Hueneme Field Study



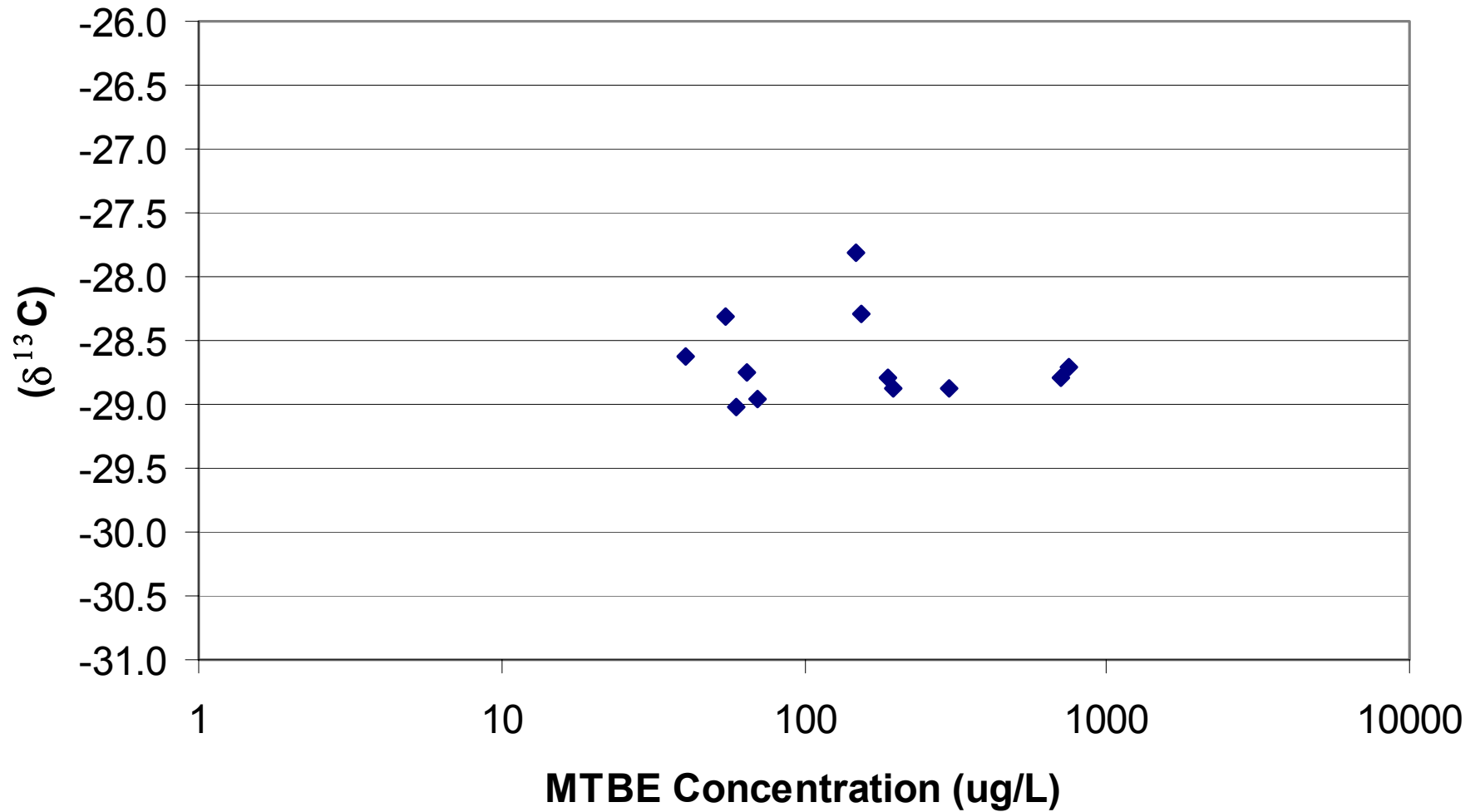
Legend

● Isotope sample
17

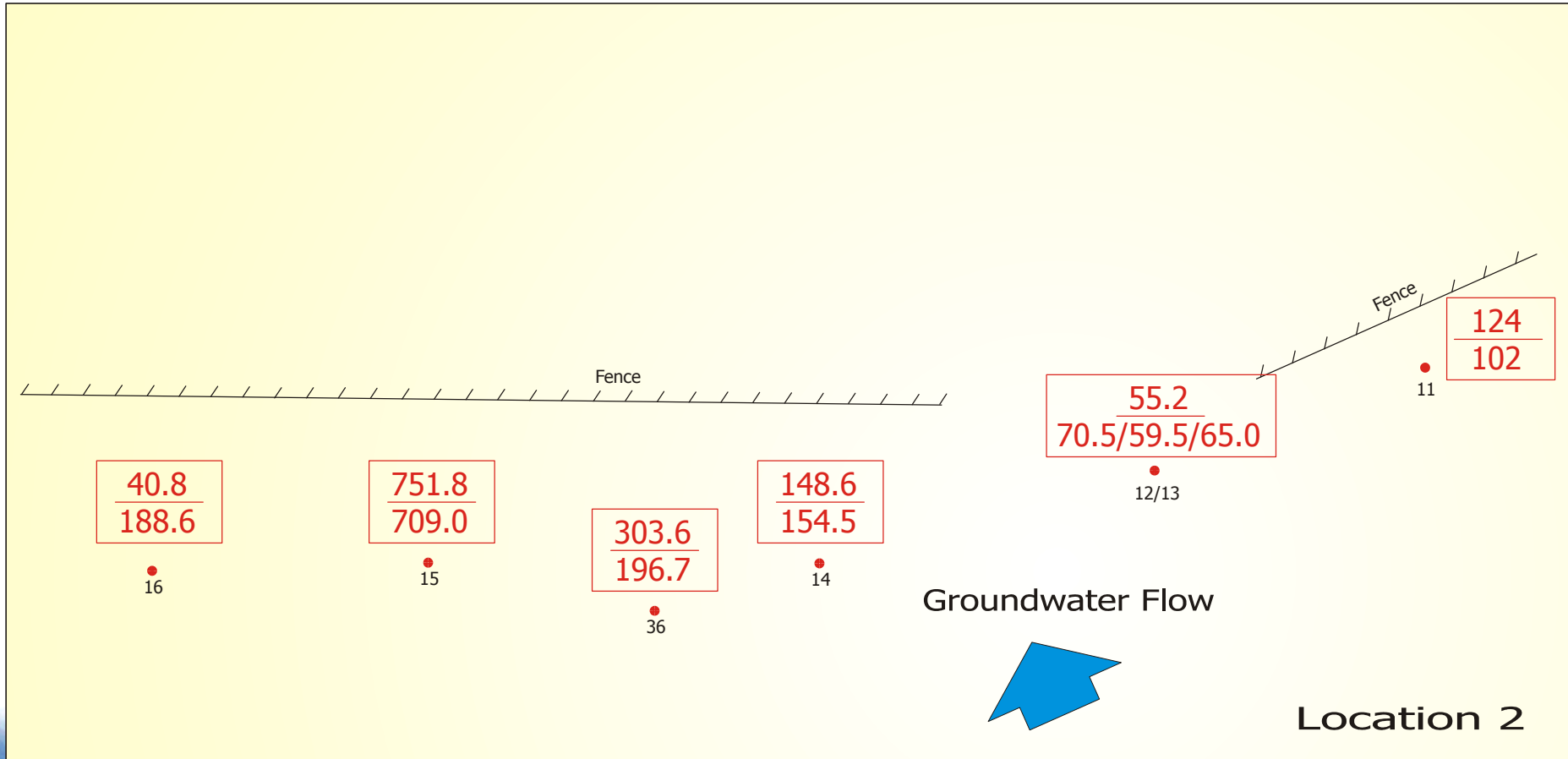
70.9	Mtbe concentration in ng/l
764.3	Shallow sample (10 to 12 ft deep)
●	Mtbe concentration in ng/l
17	Deep sample (18 to 20 ft deep)
●	Isotope location

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Carbon Isotope Results - Location 2

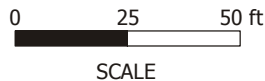


Port Hueneme Field Study



Legend

- Isotope sample
- 15
- 12/13 Triplicate isotope sample

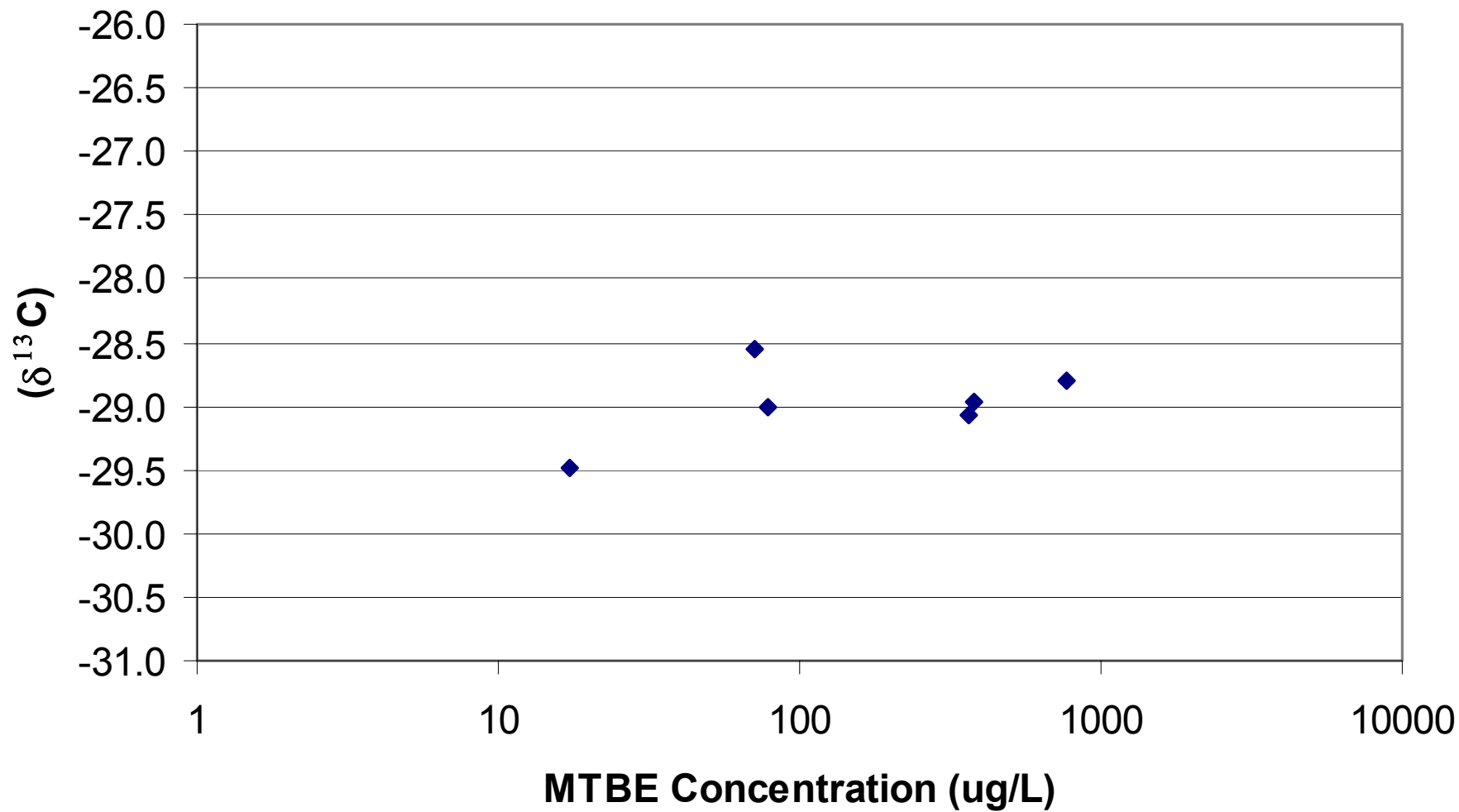


55.2 — Mtbe concentration in **ng/l**
Shallow sample (10 to 12 ft deep)

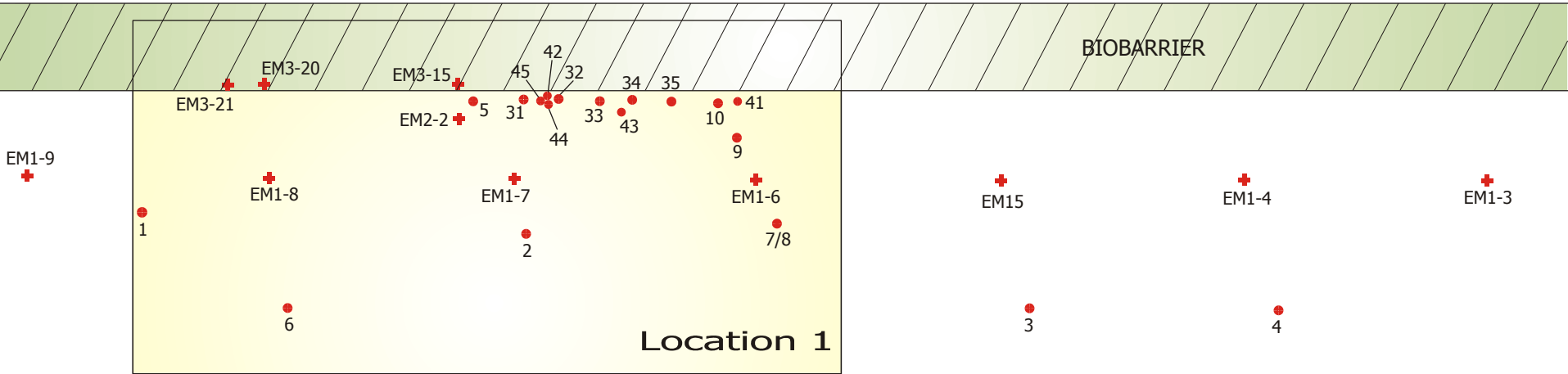
70.5/59.5/65.0 — Mtbe concentration in **ng/l**
Triplicate deep sample results (18 to 20 ft deep)

● 12/13 **Shell Global Solutions**
Isotope location

Carbon Isotope Results - Location 3



Port Hueneme Field Study

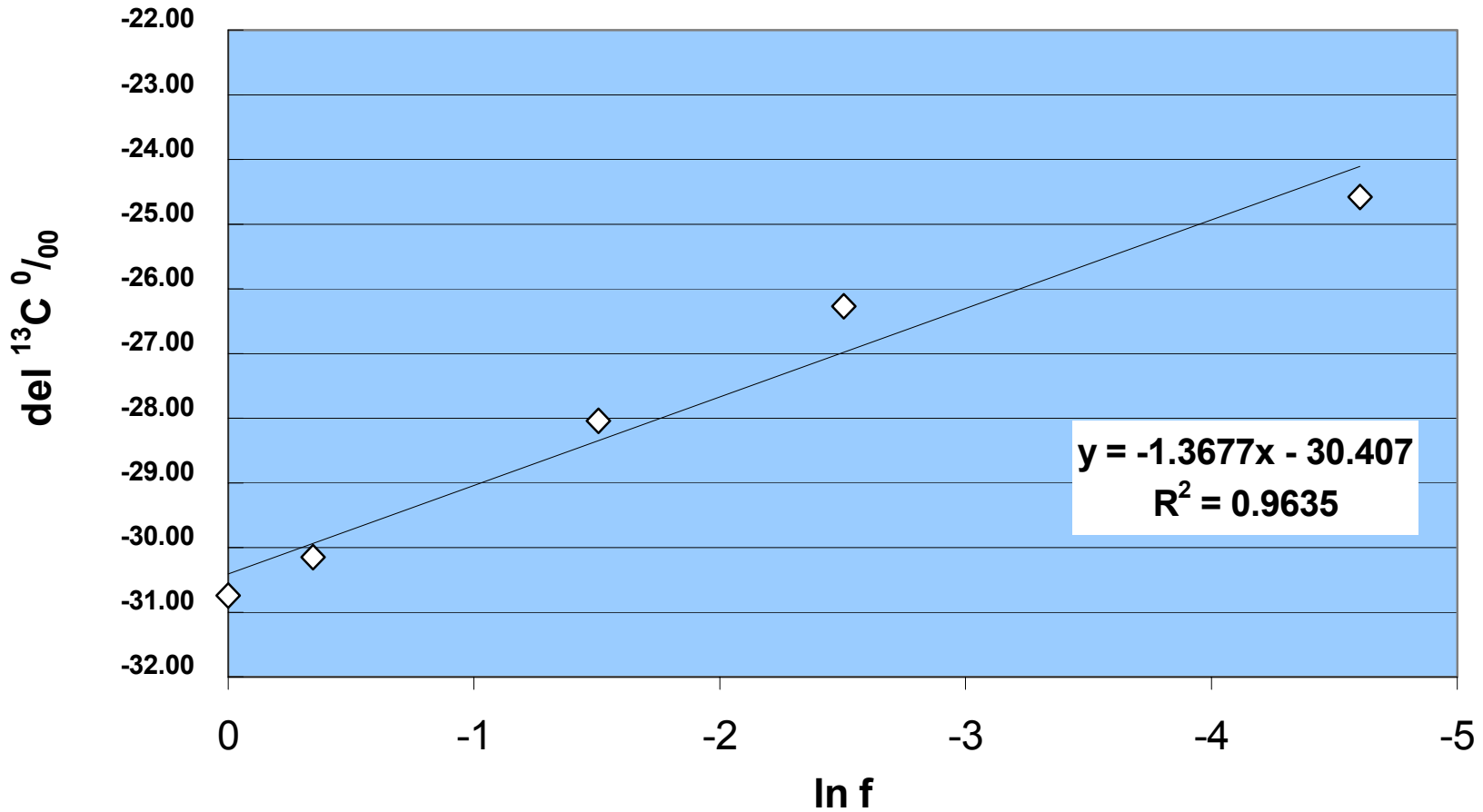


Legend

- Monitoring well
- EM1-9
- Isotope sample
- 2
- Triplicate isotope sample
- 7/8

Rayleigh-Type Plot

Port Hueneme microcosm data

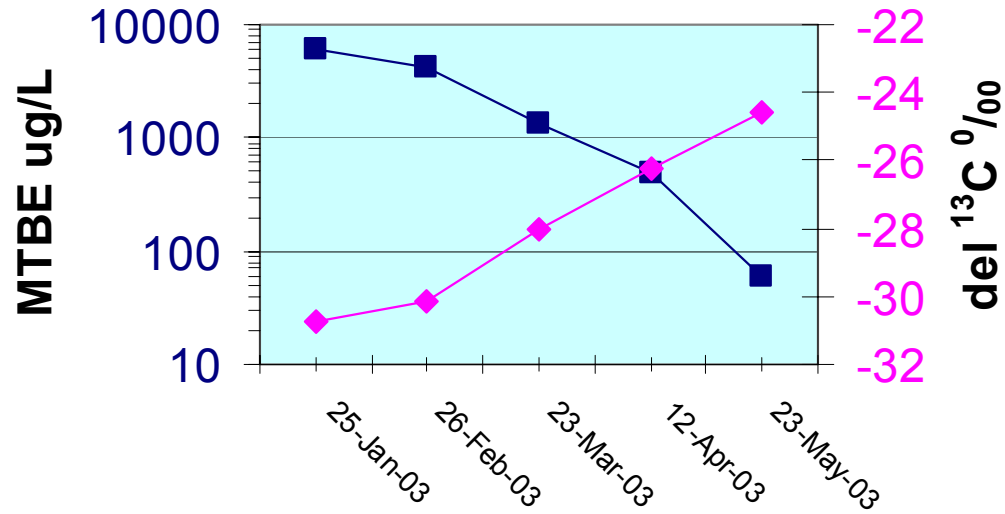


Microcosm del ^{13}C shift

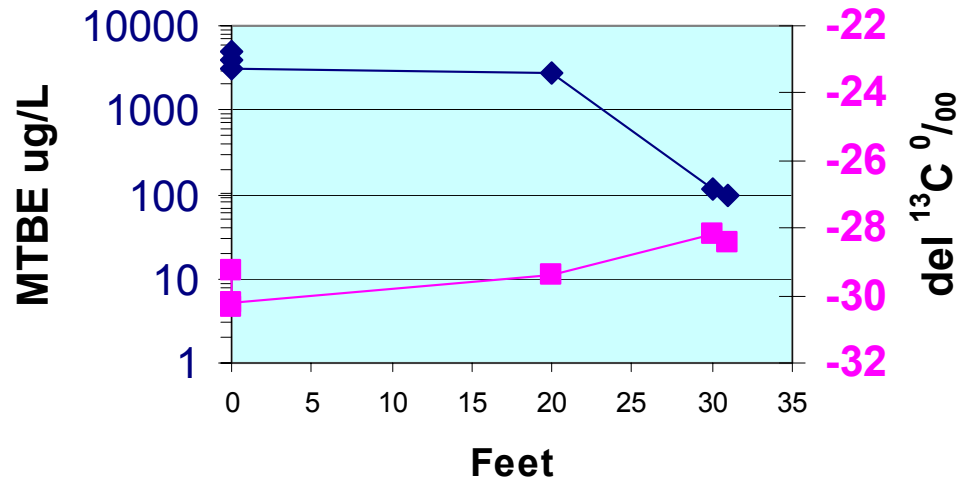
% Degraded	del ^{13}C shift
0	0.00
29	-0.59
78	-2.70
92	-4.47
99	-6.16



Microcosm

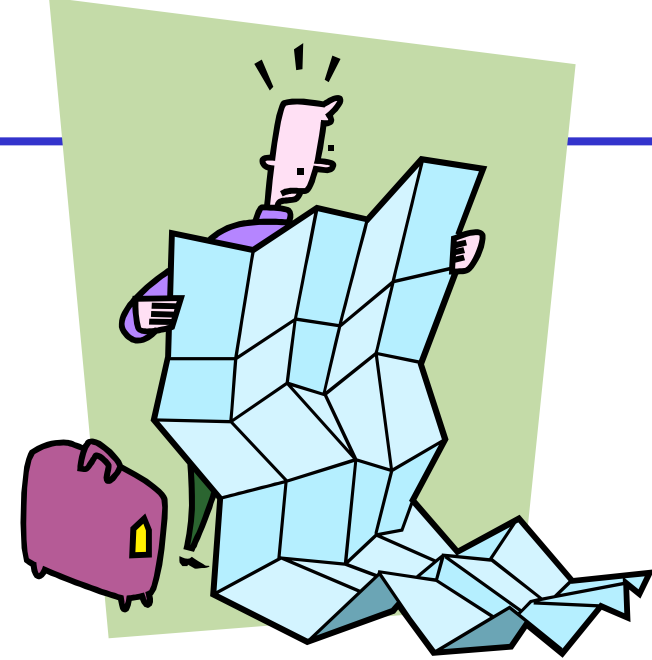


Field Data



What gives?

- If we know there is aerobic degradation
- If we know aerobic degradation results in fractionation
- Why don't we observe (significant) enrichment in the field samples?



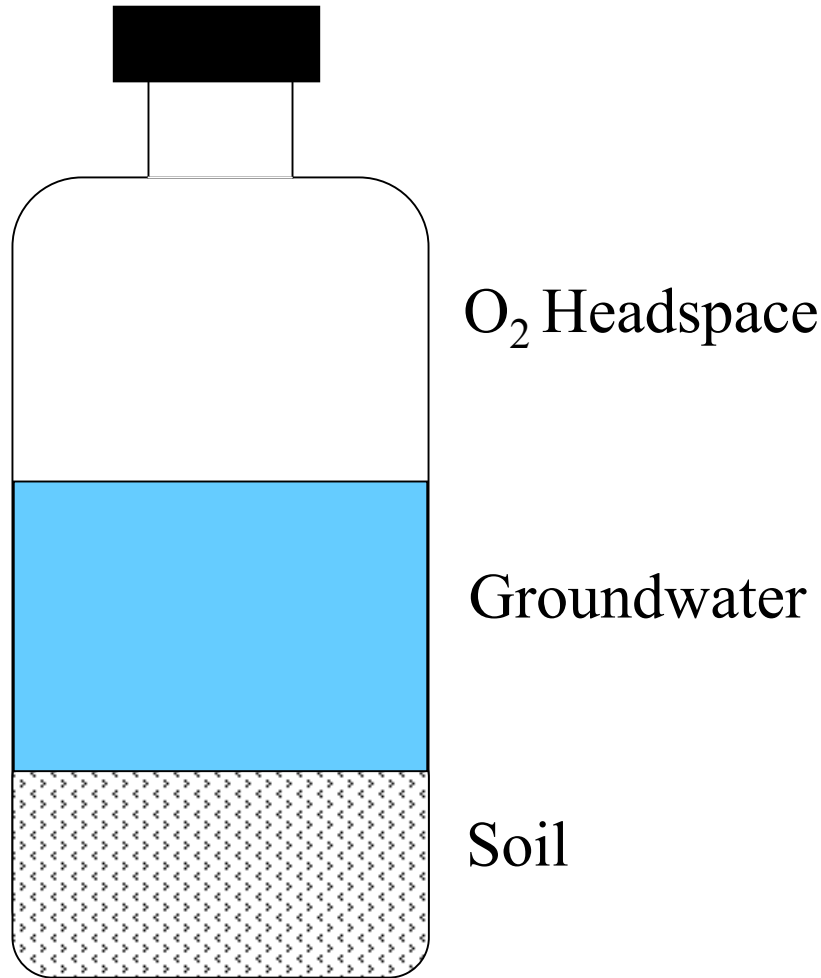
Luis

Shell Global Solutions

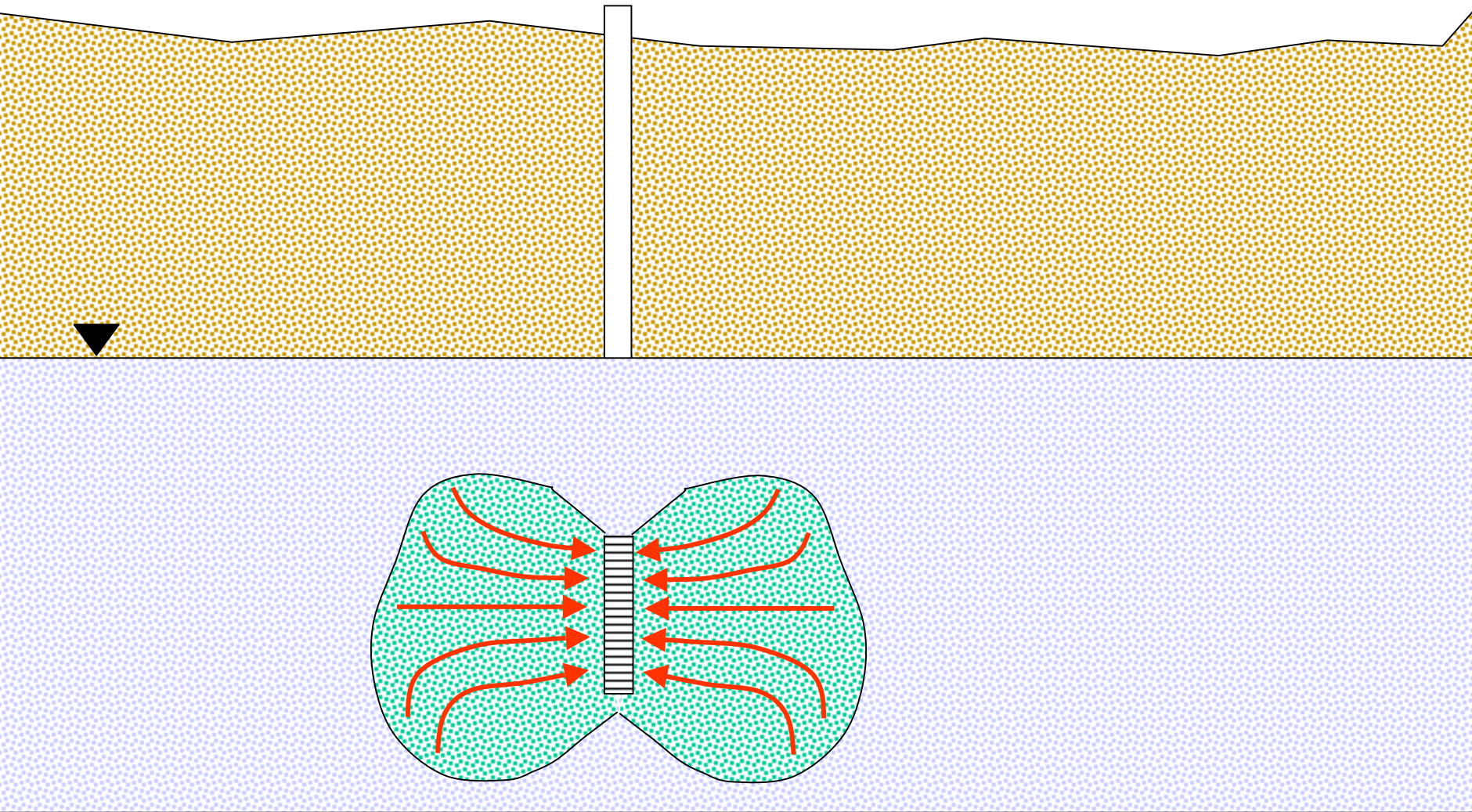
Soil Microcosm

MTBE Concentration Reduction

- Biodegradation
 - Soil Adsorption
 - Volatilization
- All Groundwater has the same experience
- “Leftover” GW enriched ^{13}C



Sample collection from a monitoring well



MTBE Concentration Reduction

- Microcosm
 - Biodegradation
 - $\delta^{13}\text{C}$ fractionation
- Field
 - Other concentration reduction methods are possible.
 - Mixing of "clean", i.e., biodegraded groundwater and contaminated water
 - $\delta^{13}\text{C}$ minor? Fractionation observed



Source Zone

High MTBE Conc

Low DO

Mean $\delta^{13}\text{C} = -29.8\text{‰}$

Biodegradation zone

Low MTBE Conc

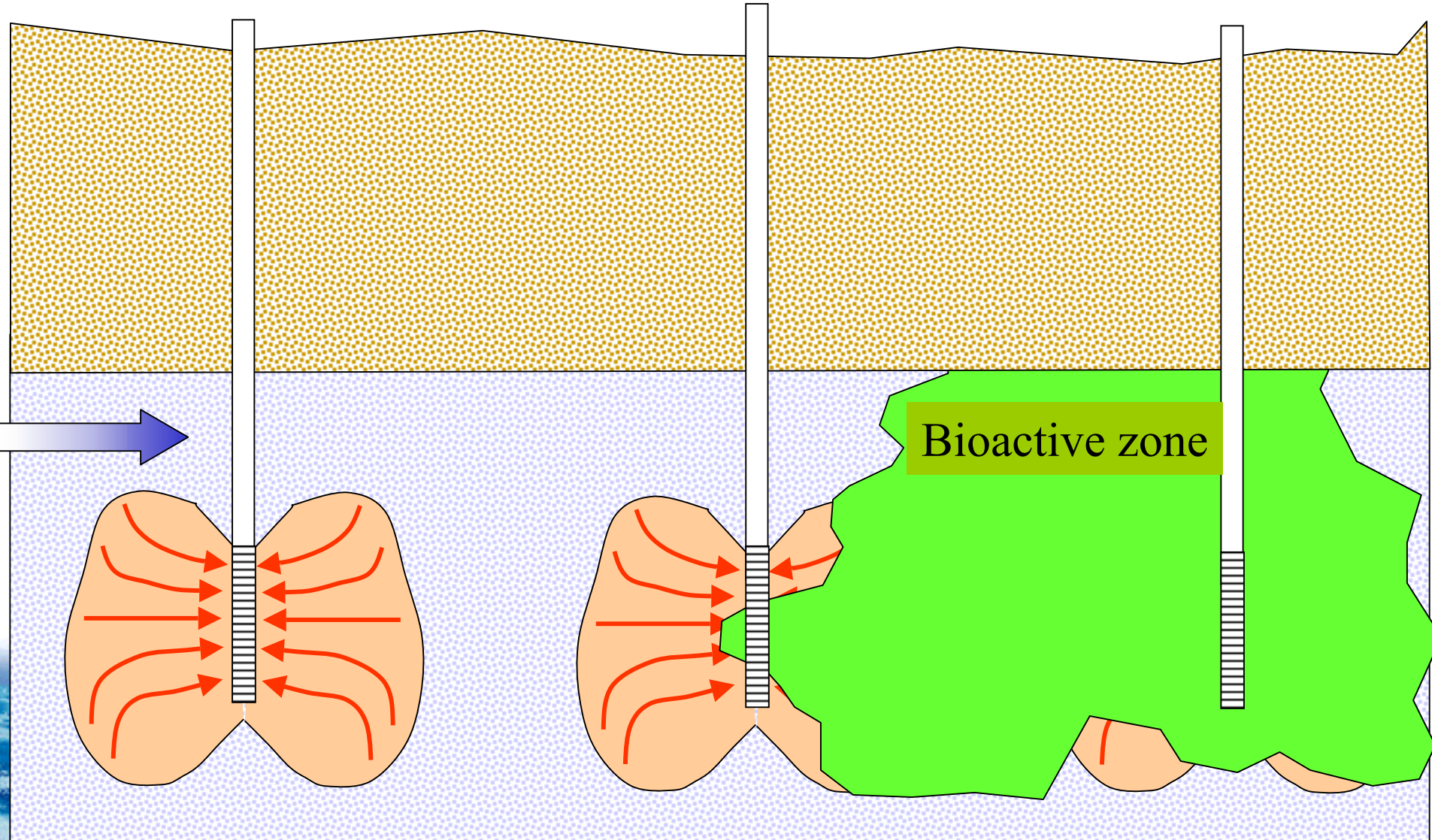
High DO

Mean $\delta^{13}\text{C} = -28.3\text{‰}$

ND MTBE Conc

High DO

Mean $\delta^{13}\text{C}$ unmeasurable



Tell me it ain't so.....

- MTBE concentration reduced by mixing with “Clean” (biodegraded) groundwater
- Biodegraded groundwater does not show enrichment since there is little to no residual MTBE
- Counterintuitive result: Because of biodegradation, no fractionation is observed!



Summary

- Compound specific ^{13}C isotope method showed little to no fractionation in Port Hueneme field samples
- The same technique showed fractionation with site microcosms
- Multi Path Mixing Model
- Large isotopic data set necessary to make any conclusions
- ^{13}C isotopic fractionation results must be interpreted with great care

