Field Pilot to Evaluate Feasibility of Enhanced LNAPL Depletion with Gypsum Land Application

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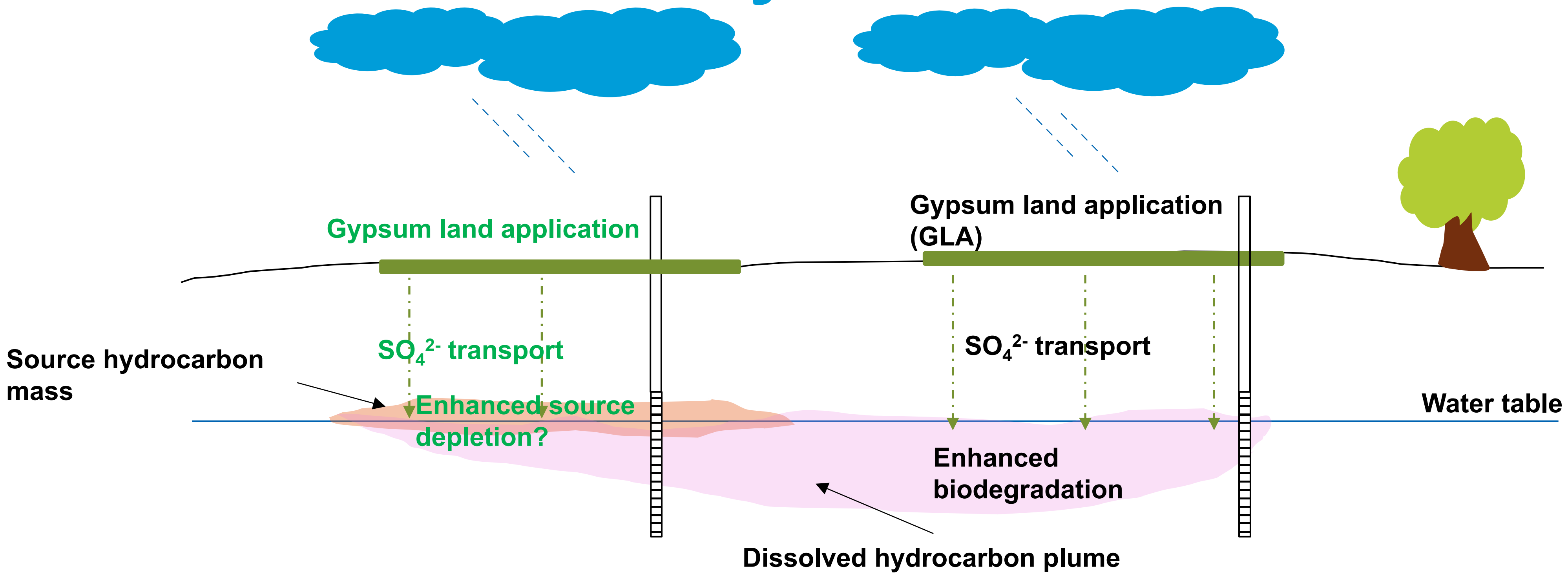
- John Wilson

Outline

- Motivation
- Hypothesis
- Field pilot setting
- Results
- Conclusions

Motivation – Extend Learnings from Sulfate Delivery to Dissolved Hydrocarbon Plumes



Field Pilot – wells with LNAPL*

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Sulfate Delivery Methods to Accelerate BTEX Biodegradation and Expedite Site Closure

By Kammy Sra, Ravi Kolhatkar, Daniel Segal (Chevron Technical Center), and John Wilson (Scissortail Environmental)

Deployments

1. 10 sites in multiple states (NJ, GA, IL, MS, MA, CA, AL and OH)
2. Different site types – former retail site, former terminal, former and active refinery sites, former oil field
3. Range of soil lithologies, depth to water and source concentration
4. Up to 10-fold decrease in estimated time for benzene clean-up in groundwater

*LNAPL – light non-aqueous phase liquid

Hypothesis

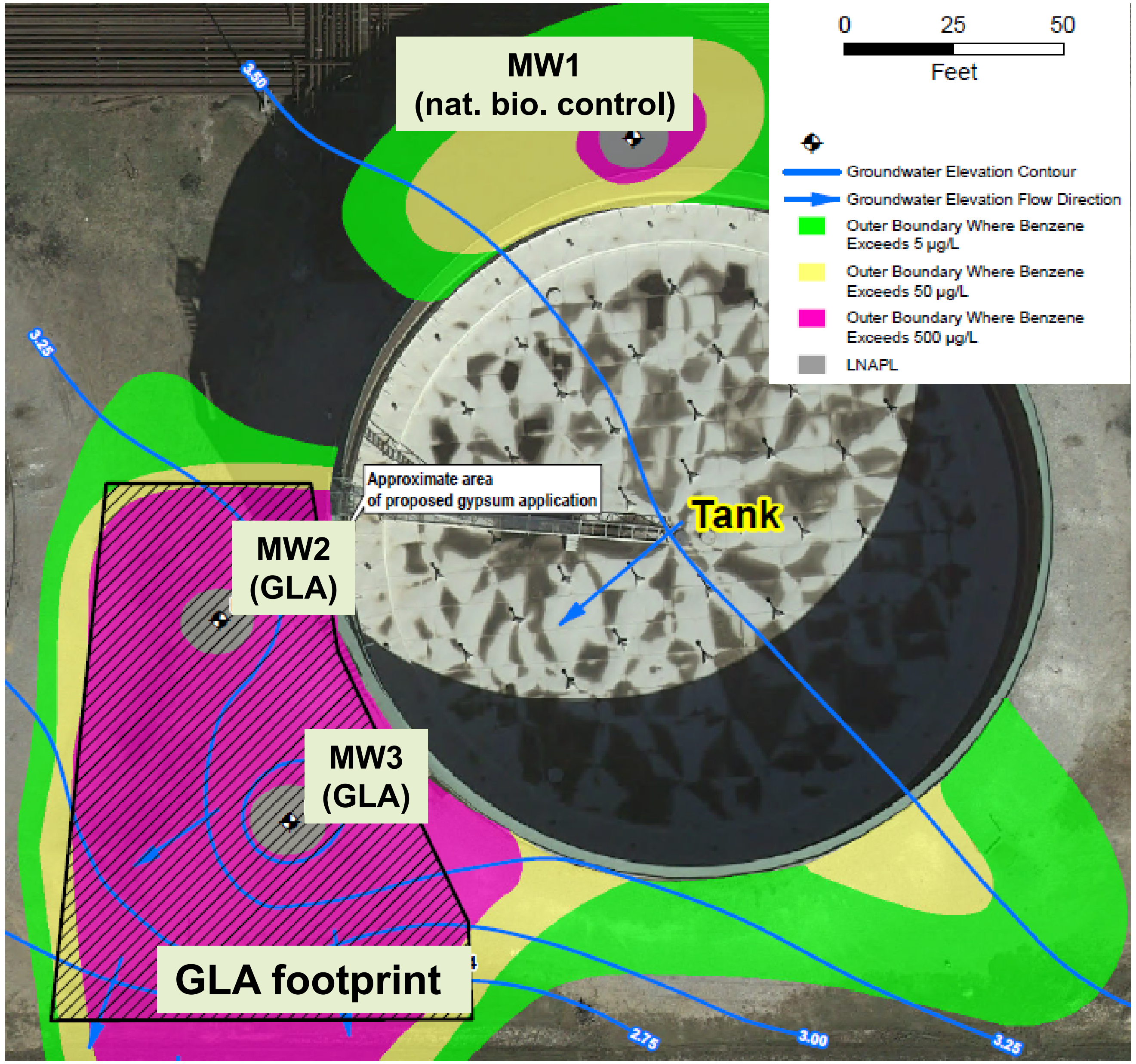
Sulfate-mediated biodegradation of LNAPL can significantly enhance LNAPL depletion

- sulfate as electron acceptor for anaerobic oxidation of hydrocarbons
- sulfate to improve syntrophic biodegradation of hydrocarbons

<u>Key questions for field pilot</u>

1. Can we demonstrate biodegradation in groundwater contacting LNAPL?
2. Is the LNAPL depletion different with addition of sulfate?
3. Are the differences in LNAPL signatures (in space and time) statistically significant?

Field Pilot to Evaluate Enhanced LNAPL Depletion with GLA



Site setting

- Release of gasoline range refinery intermediate
- Shallow groundwater (2 to 5 ft. below ground surface)
- Geology
  - MW1 and MW2 – interbedded silty sand and silty clay
  - MW3 – predominantly silty sand

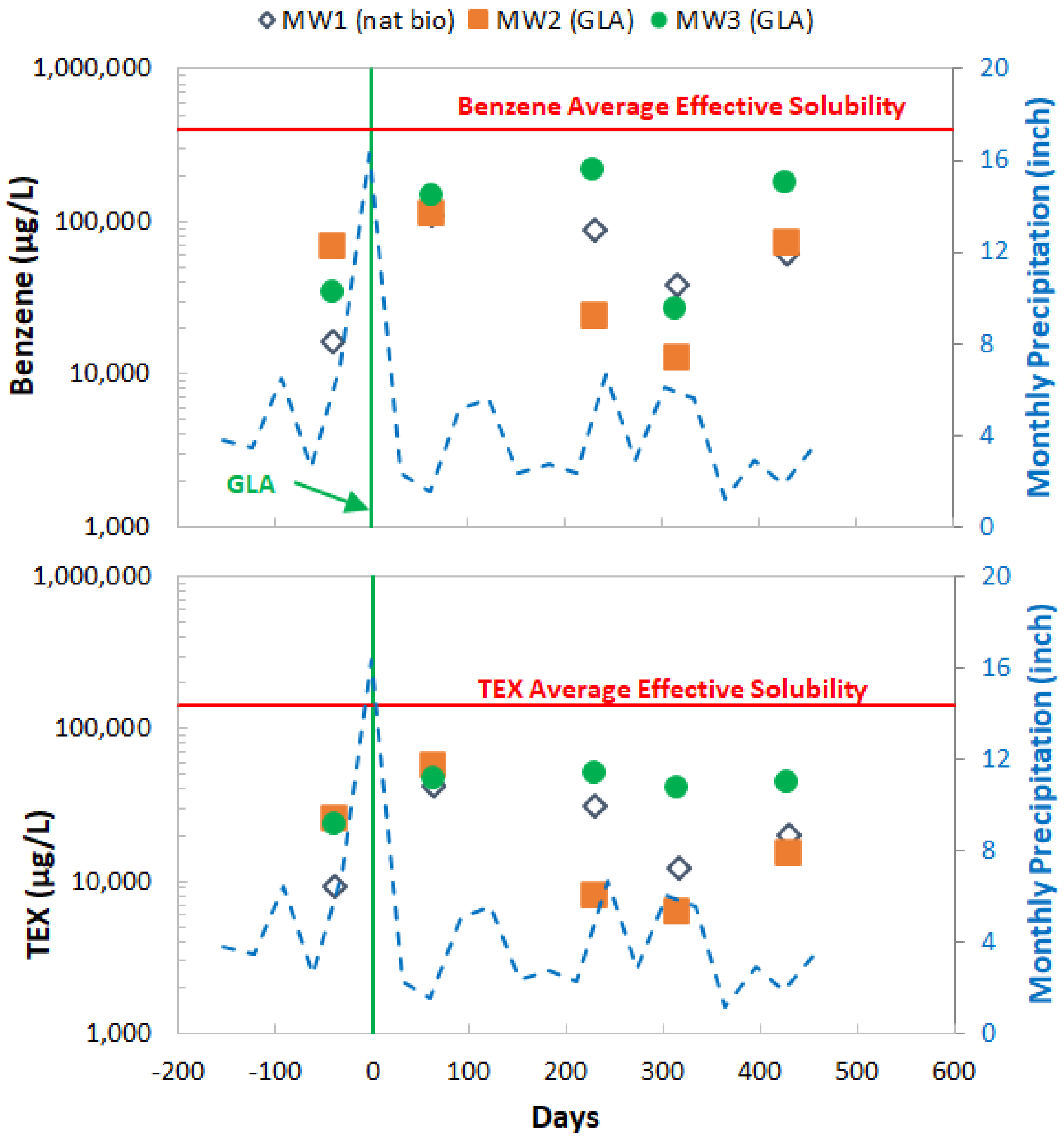
Sulfate delivery by gypsum land application (GLA)

- MW1 (natural biodegradation control), MW2 and MW3 (wells within GLA footprint)
- Loading - 0.9 lb. gypsum/ft^2 across entire footprint and 0.009 lb.$CaBr_2$/ft^2 over 20' × 20' area around wells
- No irrigation was necessary due to heavy rainfall

Performance Monitoring

- Baseline and 4 events post-GLA (over 430 days or 1.2 years)
- Analysis of groundwater contacting LNAPL
  - BTEX, sulfate, methane, δ^{13}C- & δ^{2}H-benzene, δ^{34}S-sulfate and δ^{13}C-Dissolved inorganic carbon (DIC)
- Detailed LNAPL composition over time

#1 – Preliminary Indication of B/TEX Attenuation in GW contacting LNAPL



For GW contacting LNAPL:

- B and TEX concentration trends over 3 events after GLA indicate signs of attenuation
  - For benzene in all 3 wells
  - For TEX in MW2 (well within GLA) and in MW1 (natural bio control)
  - Concentration changes likely to be masked by ongoing dissolution of BTEX from LNAPL

- BTEX concentrations are significantly lower than the estimated effective solubility

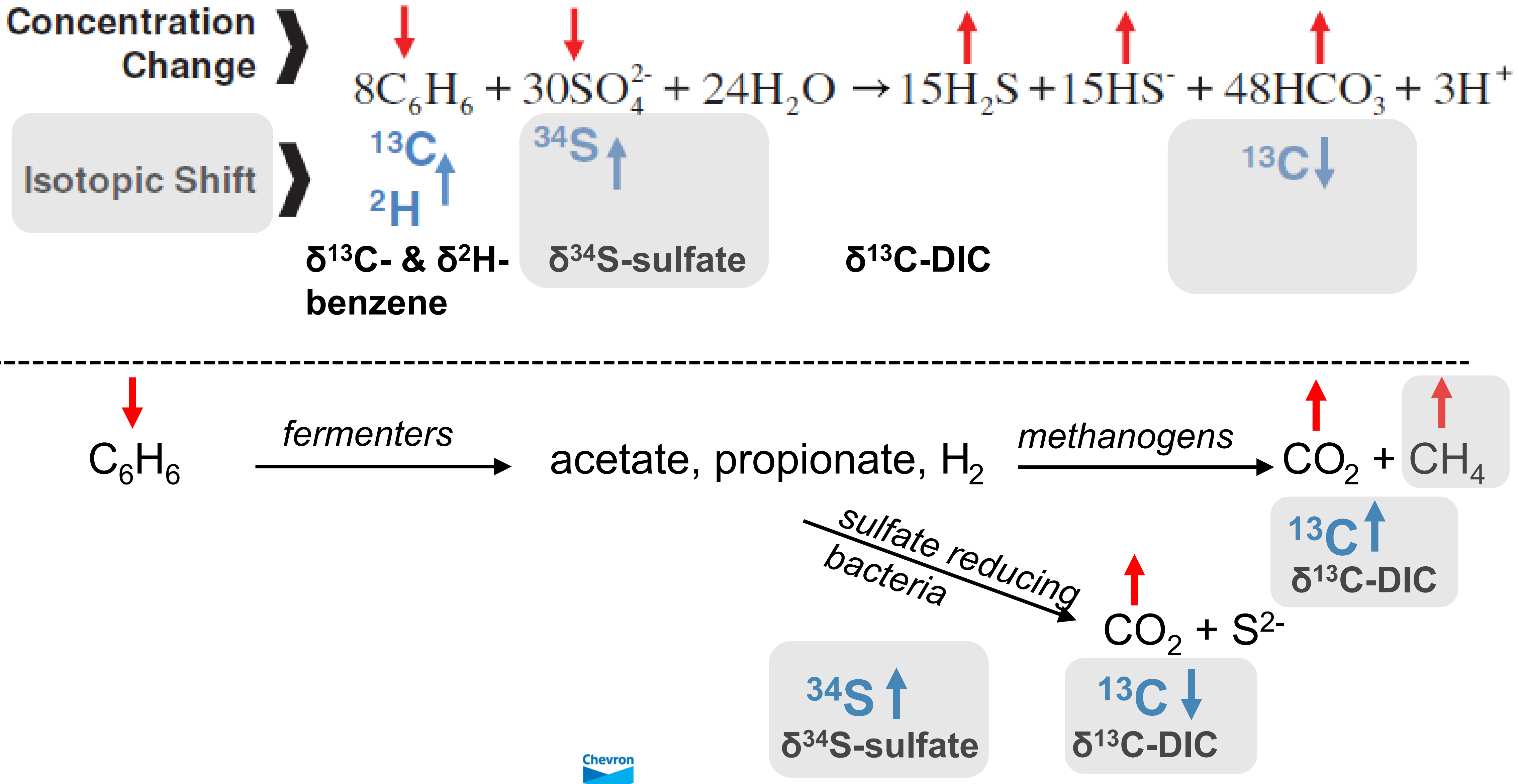
- Concentrations of TEX < B, however, are significant and will impact B longevity

What to expect in groundwater due to sulfate-mediated hydrocarbon biodegradation?

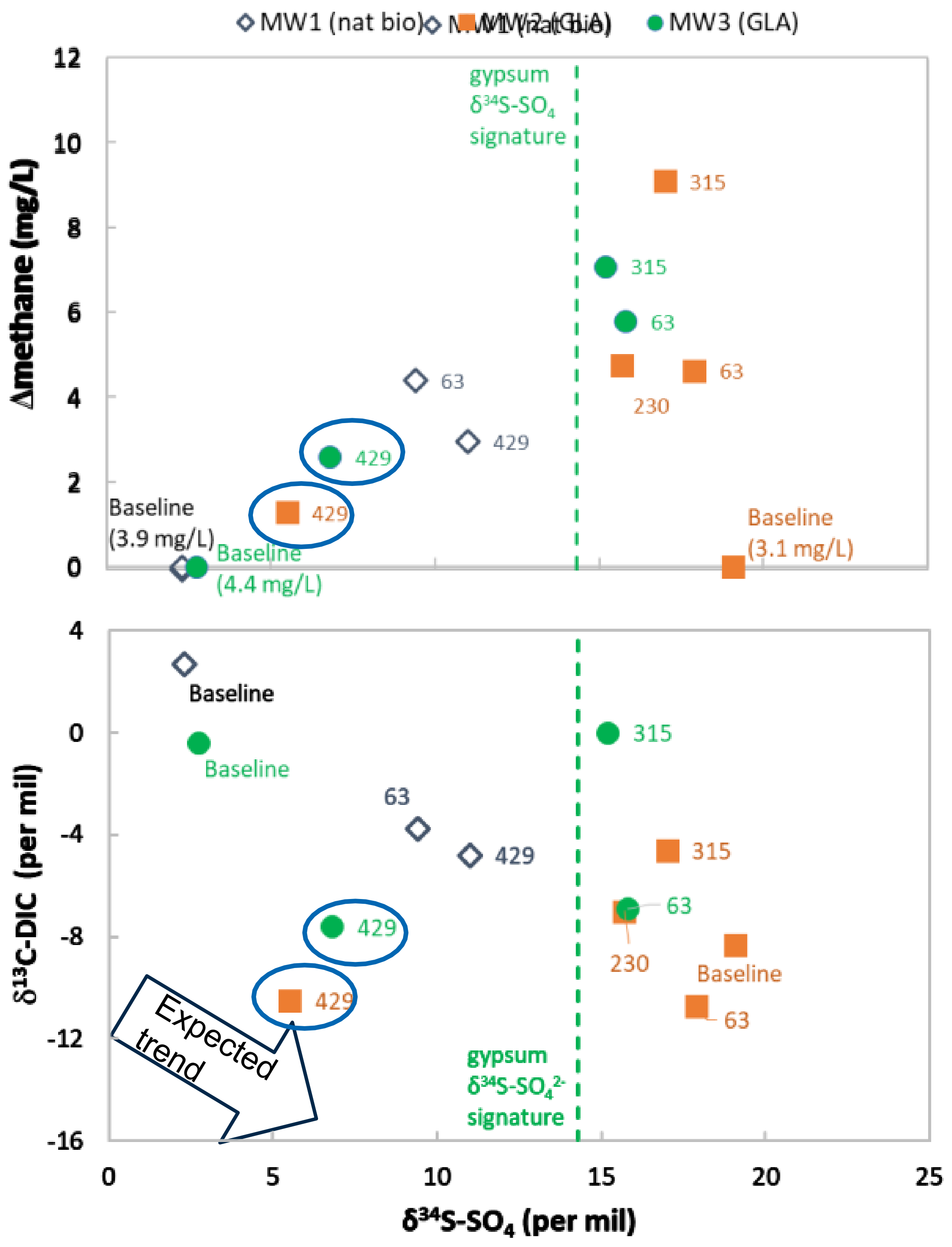
(Wei et al. 2018, Gieg et al. 2014)

Sulfate as electron acceptor

Sulfate to improve syntrophic biodegradation

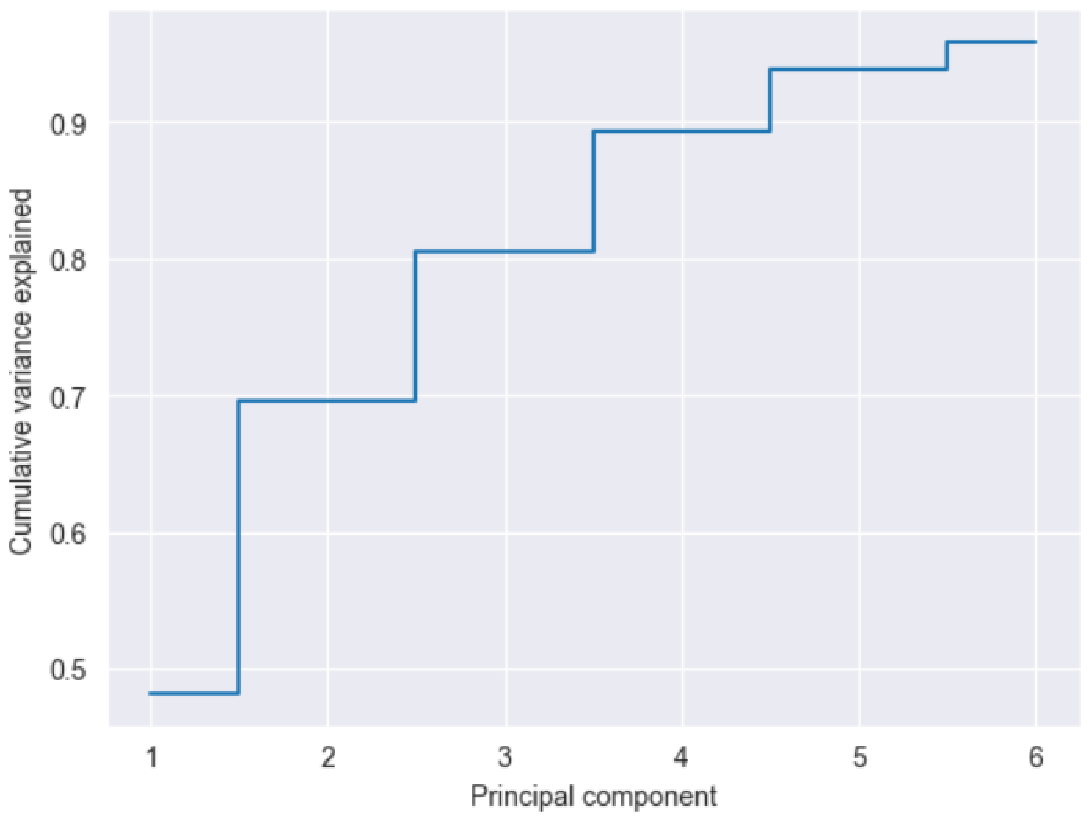


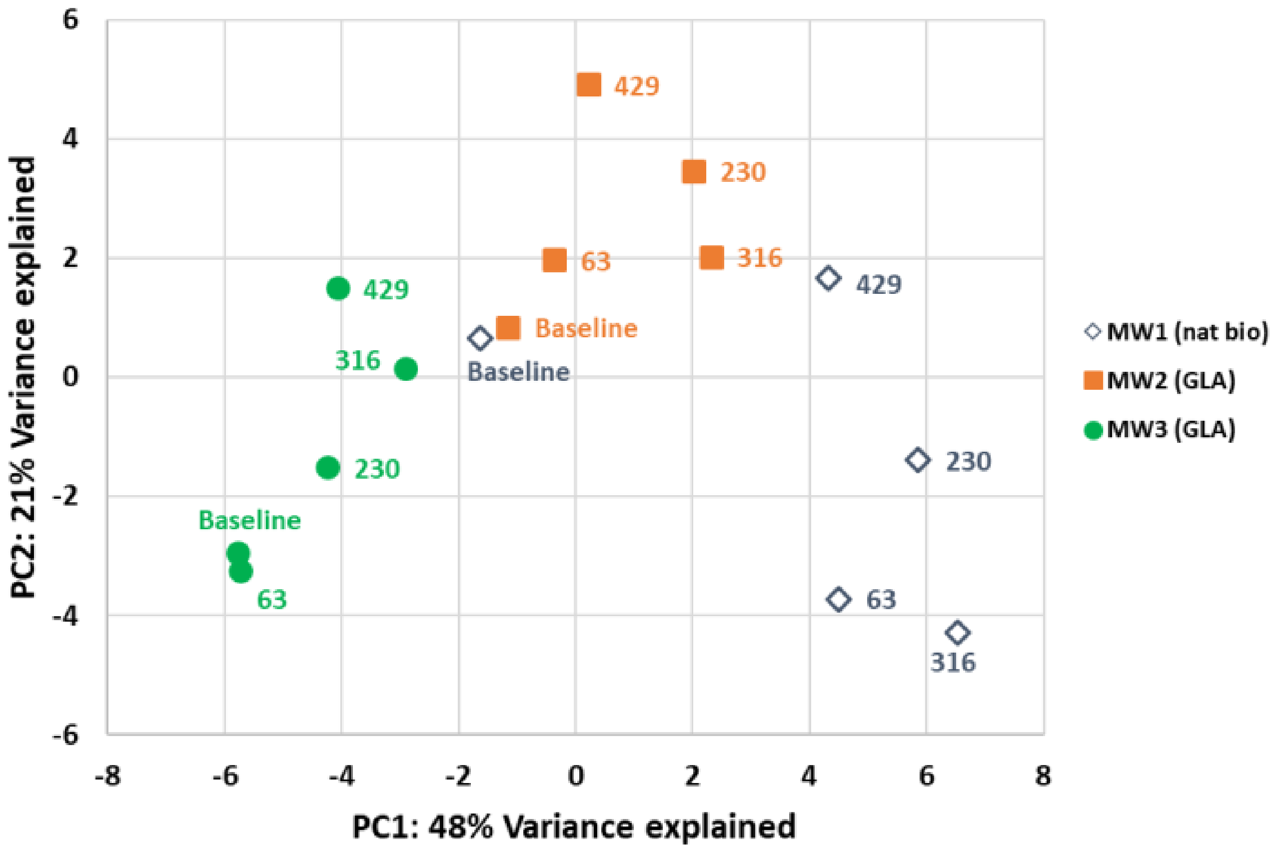
#1 – Indication of Sulfate-mediated Biodegradation in GW contacting LNAPL



- At MW3, strong indication of sulfate-mediated biodegradation suggested by increase in δ^{34}S-sulfate, along with:
  - significant increase in methane concentrations compared to baseline and natural bio control
- At MW3, generally decreasing trend for δ^{13}C-DIC suggesting evidence of complete mineralization
  - δ^{13}C-DIC trends can be confounded by methanogenesis
- δ^{34}S-sulfate and methane approaching baseline conditions by Day 429 for both MW2 and MW3 suggesting sulfate limitation

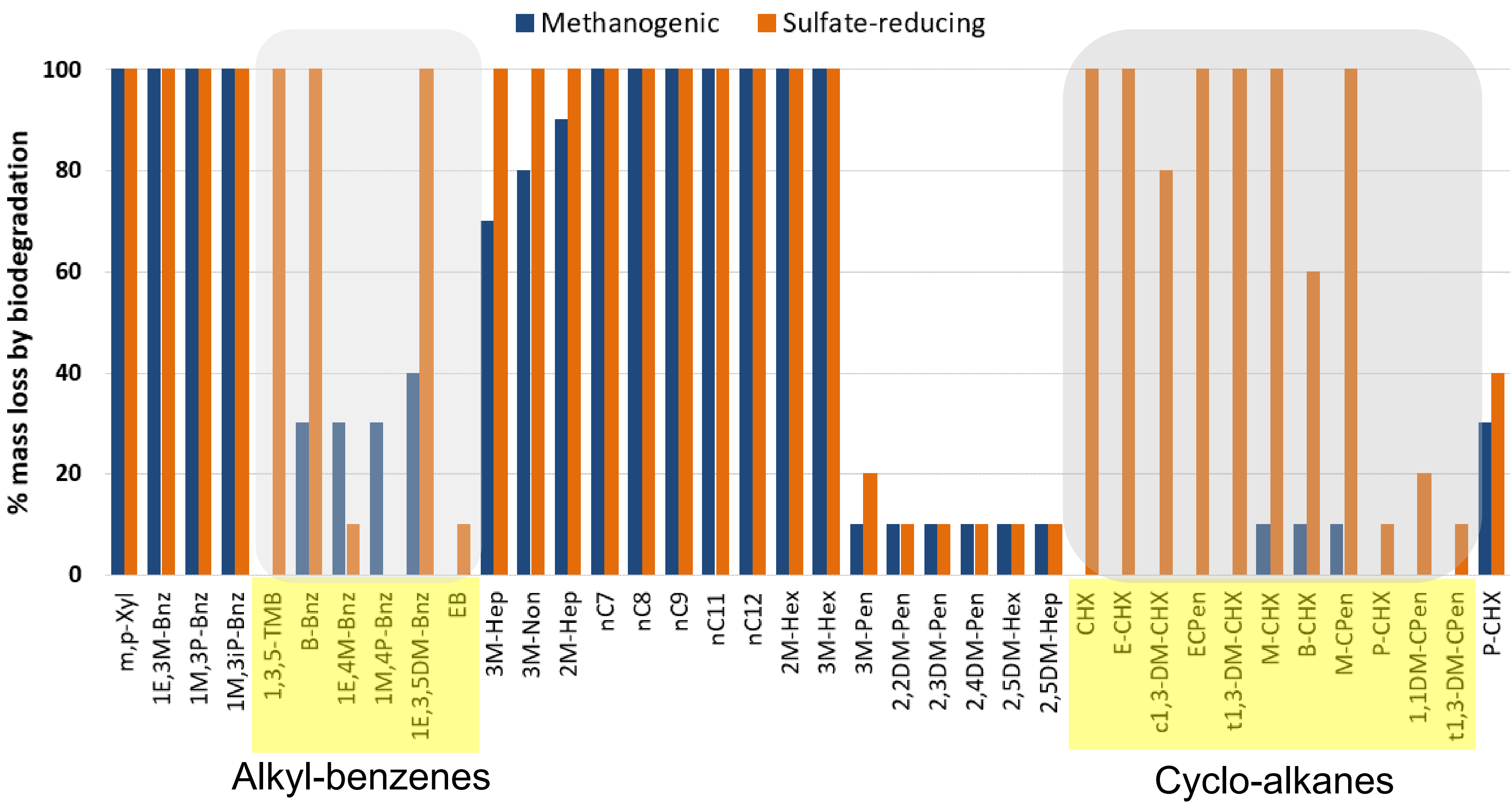
#2 - LNAPL Composition: Principal Component Analysis (PCA)





- Alternative data visualization using PCA simplifies illustration, yet explains majority of the data
- Clustering (Unsupervised ML approach) generally captures distinctness of MWs
- Plotting the top 2 principal components indicates that:
  – LNAPL data from wells generally clusters together and is heterogenous between locations
  – LNAPL samples from the same well indicate a distinct change in overall composition over time
  – MW2 and MW3 (sulfate-influenced) compositional changes track very similarly in the PCA space compared to MW1 (natural bio control)

Expected Differences in Anaerobic Biodegradation (209 days)
(Lab data from Prince and Suflita, 2007)

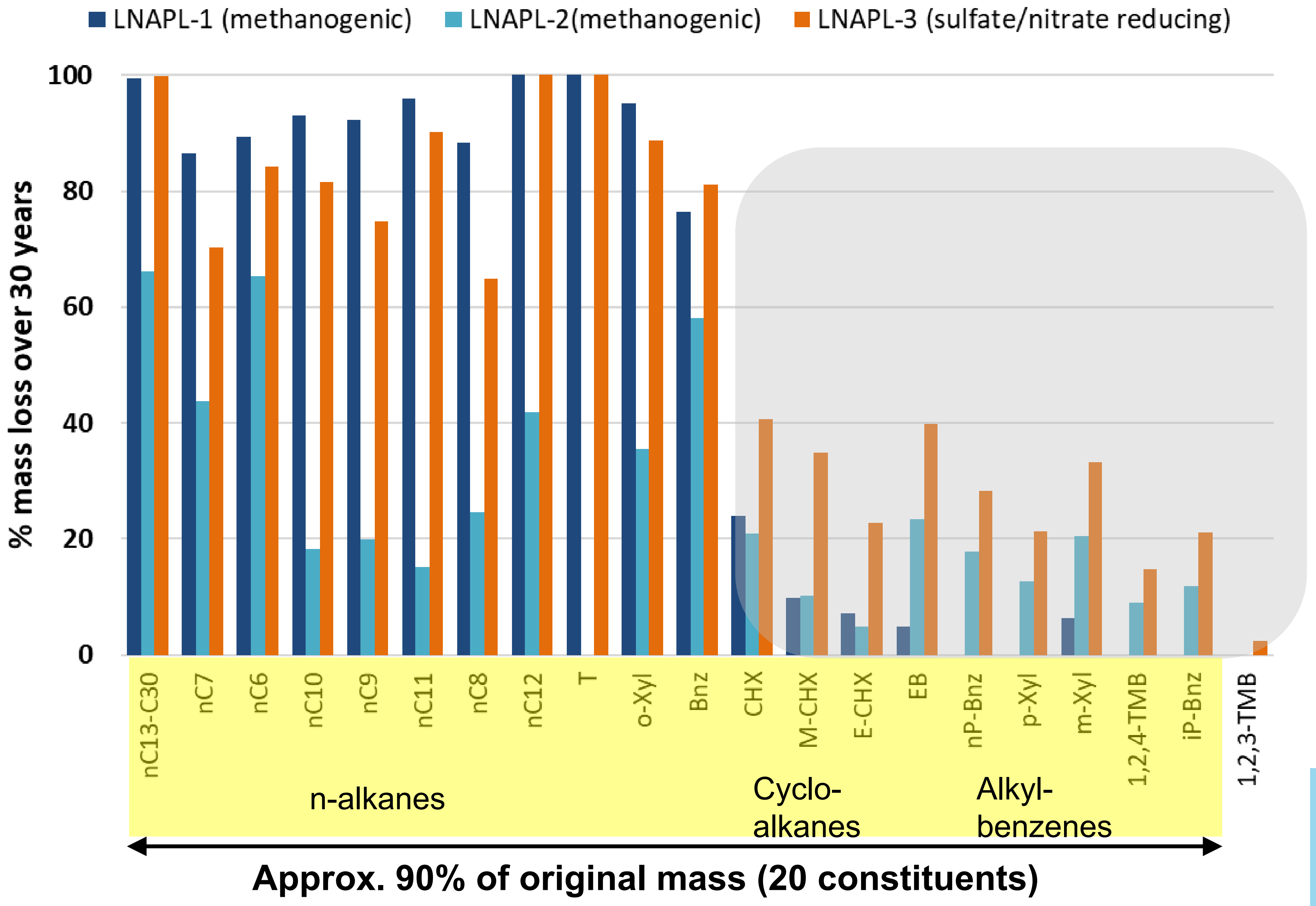


% mass loss by biodegradation at 209 days in laboratory incubations under methanogenic and sulfate reducing conditions

- Specific cyclo-alkanes, branched alkanes and alkyl-benzenes behaved differently under methanogenic and sulfate reducing conditions (highlighted yellow)
- Other n-alkanes, branched alkanes and alkylbenzenes either:
  - completely degraded or
  - did not degrade at all (potential 'conservative marker' constituents)

Expected Differences in Natural LNAPL Depletion (30 years)

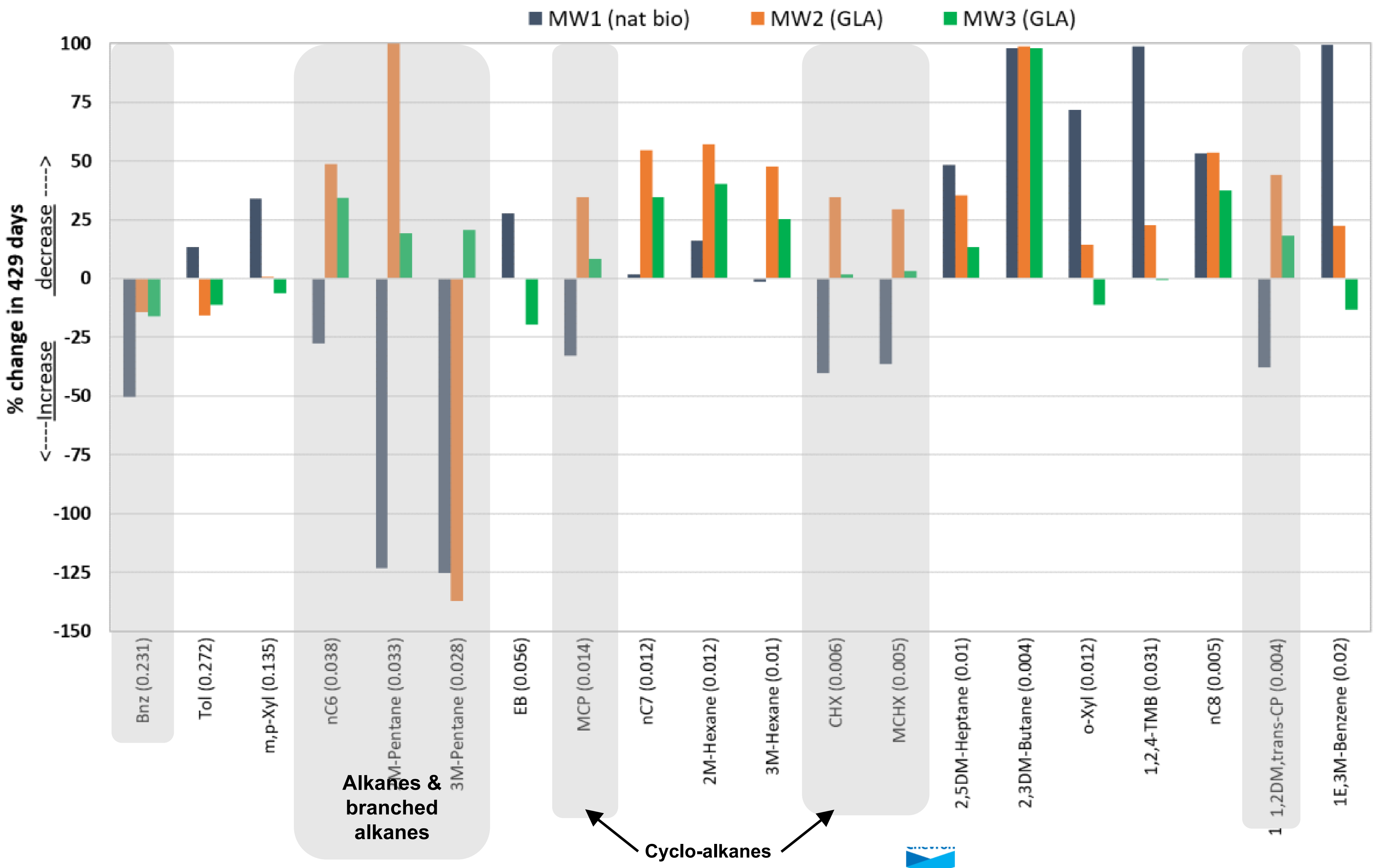
(Field data from Baedecker et al. 2018)



- Natural weathering of crude oil from 1979 pipeline release (Bemidji, MN; USGS field research site)
- Comparison of % depletion (vs. pipeline oil) after 30 years in three LNAPL bodies
  - LNAPL-3 (3 m below ground surface (bgs.)) has access to more recharge than LNAPL-1 (7 m bgs.) and LNAPL-2 (9 m bgs.)
  - Greater depletion of specific cyclo-alkanes and alkyl-benzenes in LNAPL-3 related to higher sulfate/nitrate (through greater recharge)
  - Rest behave as potential conserved markers (data not shown)

Suggests potential to enhance LNAPL/source zone depletion by sulfate delivery

#2 – Different Nature and Extent of Depletion of LNAPL Constituents
(Field Pilot Data)



- Focus is on the top 90% contributors to mass fraction
- Some constituents are relatively depleted (+ve y-axis) and some are enriched (-ve y-axis)
- Differences in nature and extent of depletion of LNAPL constituents is consistent with literature data
  - Cycloalkanes generally more depleted in MW2 and MW3 (sulfate-mediated bio) vs. MW1 (natural bio)
- Cycloalkanes and branched alkanes likely candidates as potential markers to analyze data using Devaull et al. 2020.

Conclusions

Encouraging results to date, but will need additional GLA and monitoring over time

1. Indication of sulfate-mediated biodegradation in GW contacting LNAPL
   – B and TEX attenuation (confounded by ongoing LNAPL dissolution)
   – enrichment of $\delta^{34}S$-sulfate concurrent with general decrease in $\delta^{13}C$-DIC and increase in methane concentrations (indication of sulfate limitation by ~ 1.2 years)

2. Nature and extent of depletion of LNAPL constituents between sulfate-mediated and natural biodegradation control are different
   – LNAPL compositional changes can be visualized in PCA space
   – Differences are consistent with literature

3. Too early to estimate LNAPL constituent depletion rates using Devaull et al. 2020 (~1.2 years since GLA)

References

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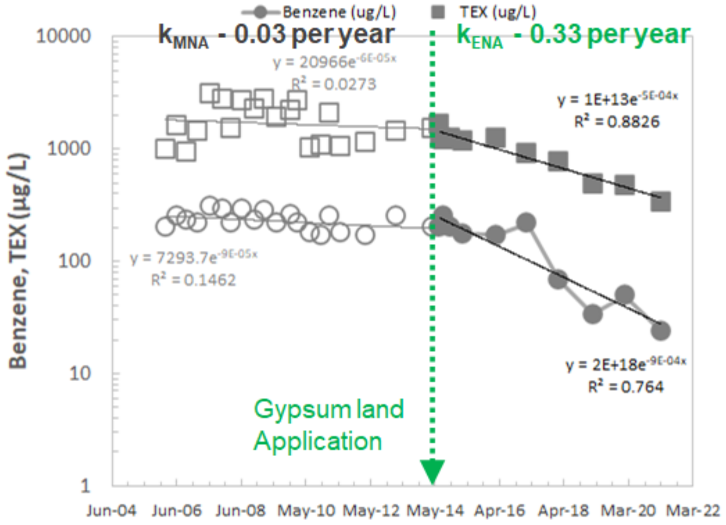
Backup

Significant Reduction in Monitoring Timeframes After Sulfate Addition

Single Well - estimate attenuation rate constants (k_{MNA} and k_{ENA})

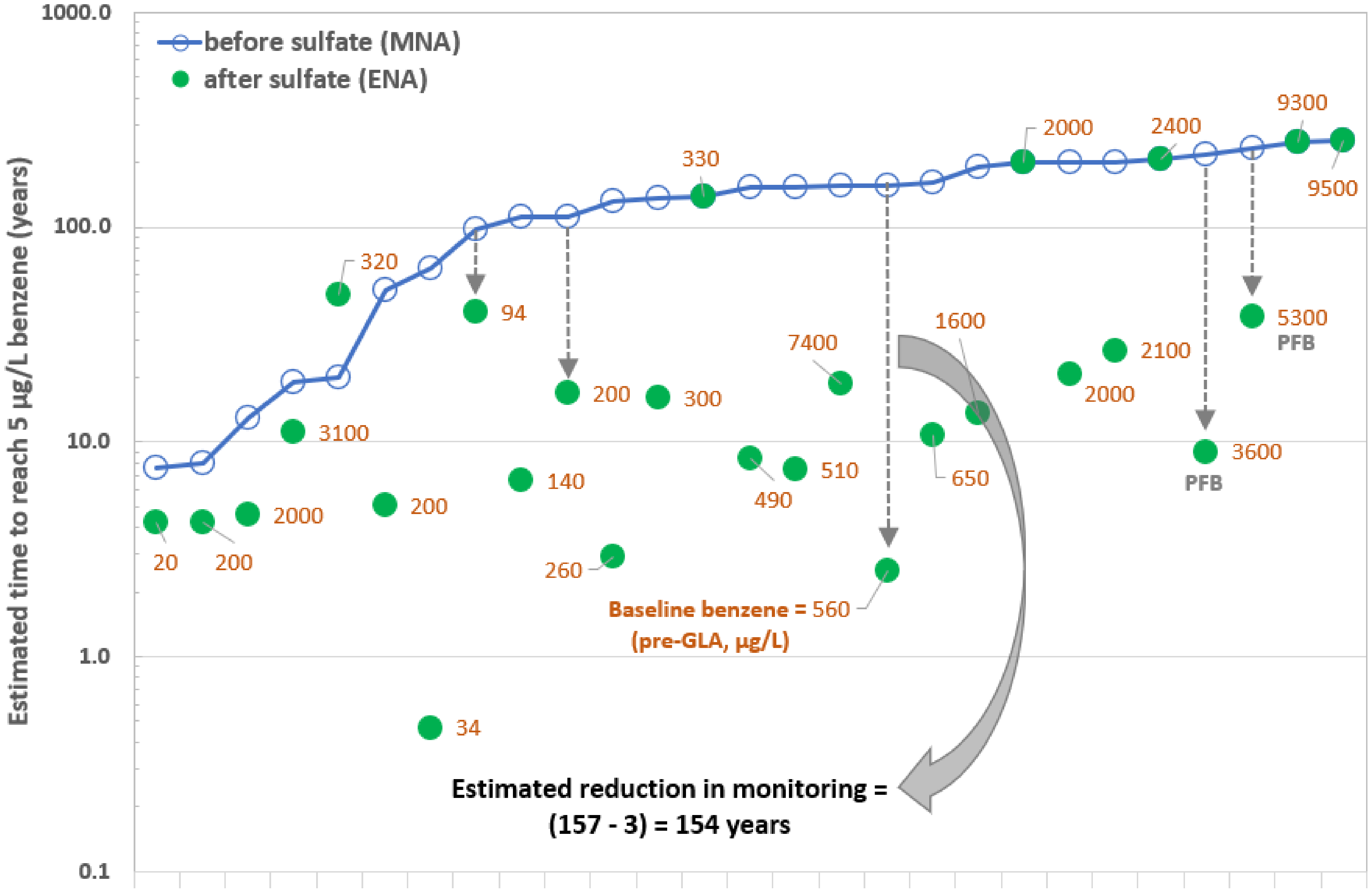


For each well

- Estimate years to achieve 5 µg/L benzene starting from baseline benzene concentration using
  1. k_{MNA} and
  2. k_{ENA}
- For wells where k_{MNA} is 0, used 0.03 per year

repeat

27 wells from 8 sites (2 gypsum permeable filled borings (PFB), rest GLA)



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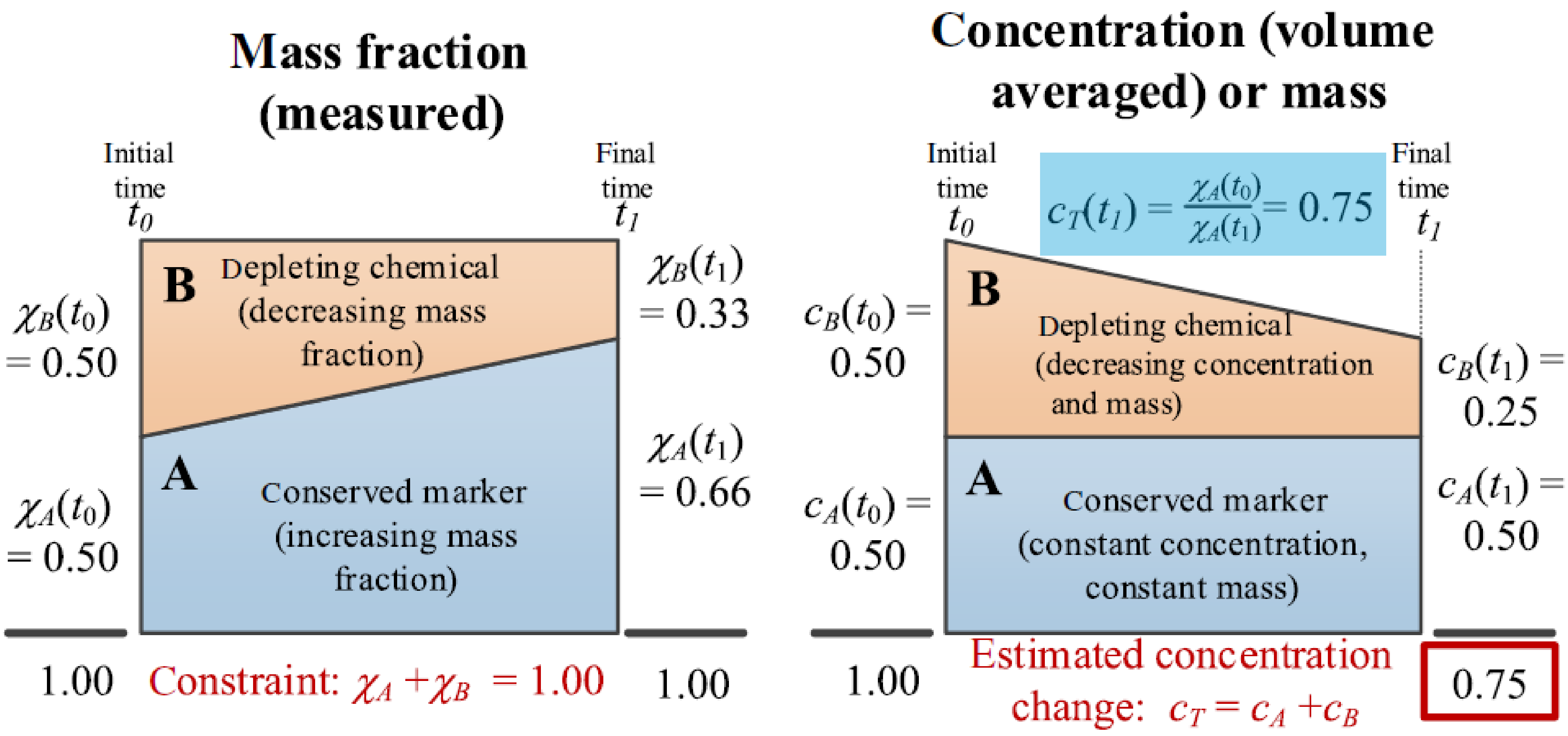
#3 – Is the difference in LNAPL depletion statistically significant?



DeVaull et al. 2020, ASTM 2022.

- Devaull et al. 2020 method to evaluate differences in LNAPL depletion between control (MW-1) and sulfate-influenced wells (MW-2 and MW-3)
- Early days to see differences (half life for refined product ~ 8 years)
-

Estimated Depletion Rate (per year) at 429 days

Constituent	MW1	MW2	MW3
2M-Pentane		5.51	
Octane	0.72	0.64	0.4
2M-Octane	1.68		
1E, 3M-Benzene	3.52		
1,3-DE-Benzene		3.56	
1E, 4M-Benzene			4.57
2E, 1,3-DM-Benzene		3.04	
1,2,3,4-TMB		3.09	

No entry (blank cell) – depletion not significant at 95% CL