Feasibility Evaluation of Enhanced LNAPL Depletion in a Gypsum Land Application Field Pilot

Kammy Sra & Ravi Kolhatkar

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Chevron

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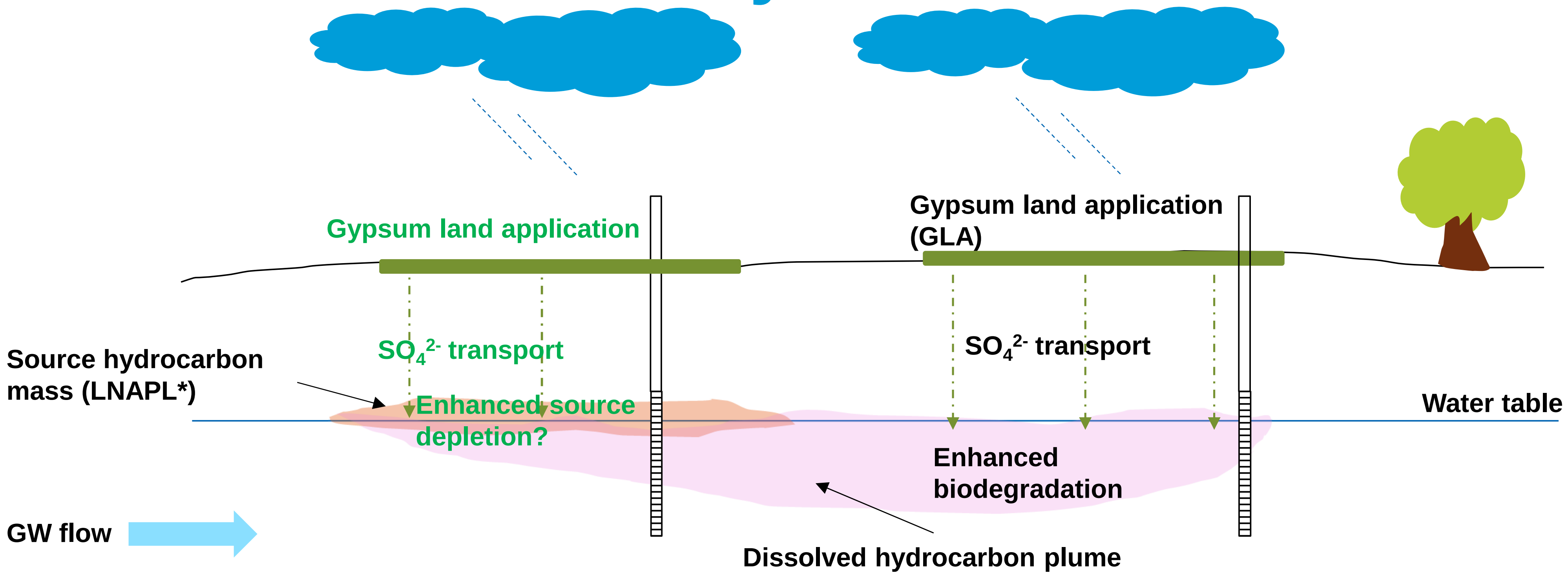
Outline

- Motivation
- Field pilot setting
- Results
- Conclusions

Motivation – Extend Learnings from Sulfate Delivery to Dissolved Hydrocarbon Plumes



Field Pilot – wells with LNAPL

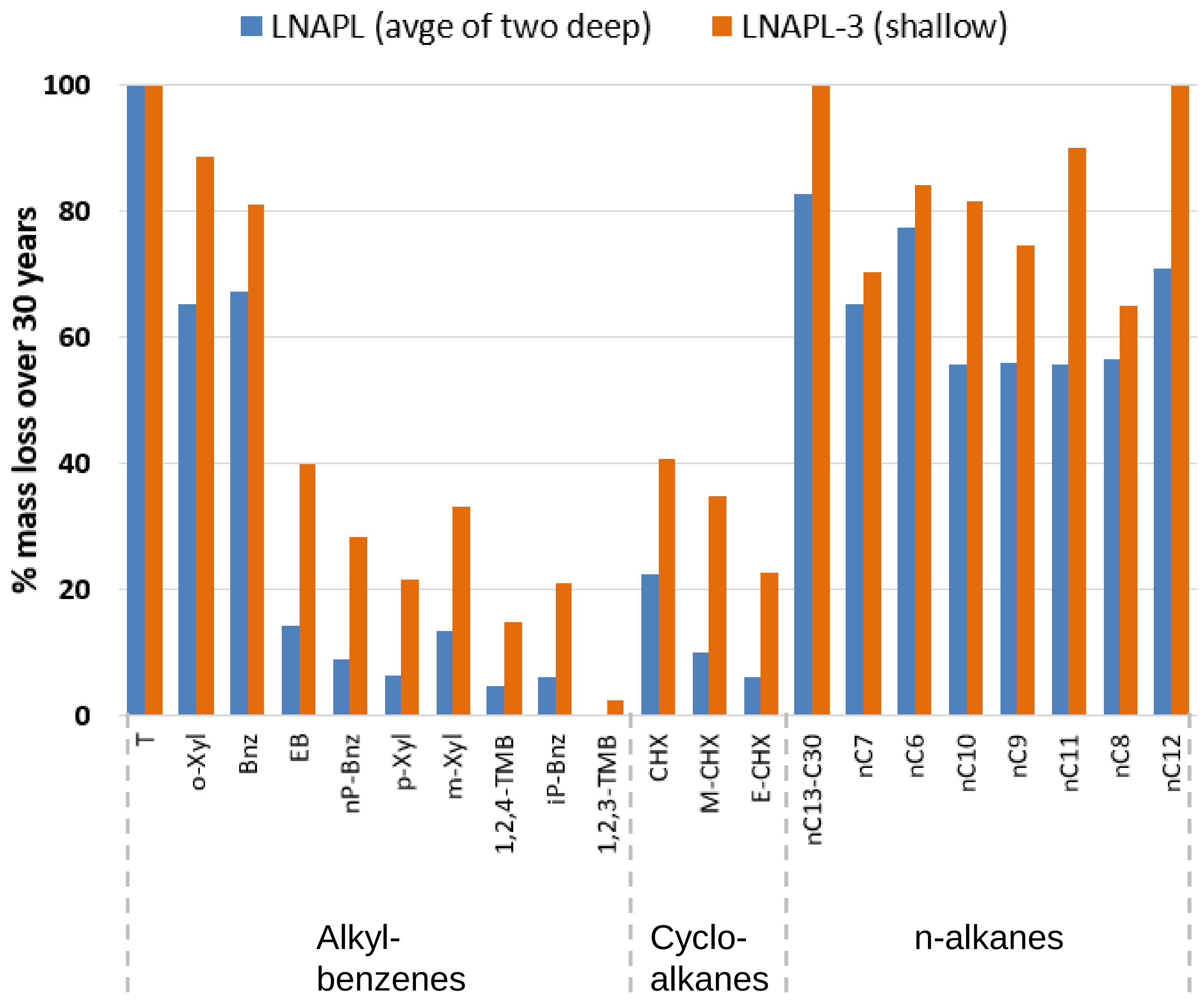
Deployments to date

1. 45 sites in 14 states (AL, CA, CO, GA, IL, MA, MS, NJ, NC, OH, TX, UT, WA and WY)
2. **Up to 10-fold decrease in estimated time for benzene clean-up in groundwater**
3. Different site types – former retail site, former terminal, former and active refinery sites, former oil field
4. Range of soil lithologies, depth to water and source concentration

*LNAPL – light non-aqueous phase liquid

Motivation - Natural Depletion in LNAPL Over 30 Years

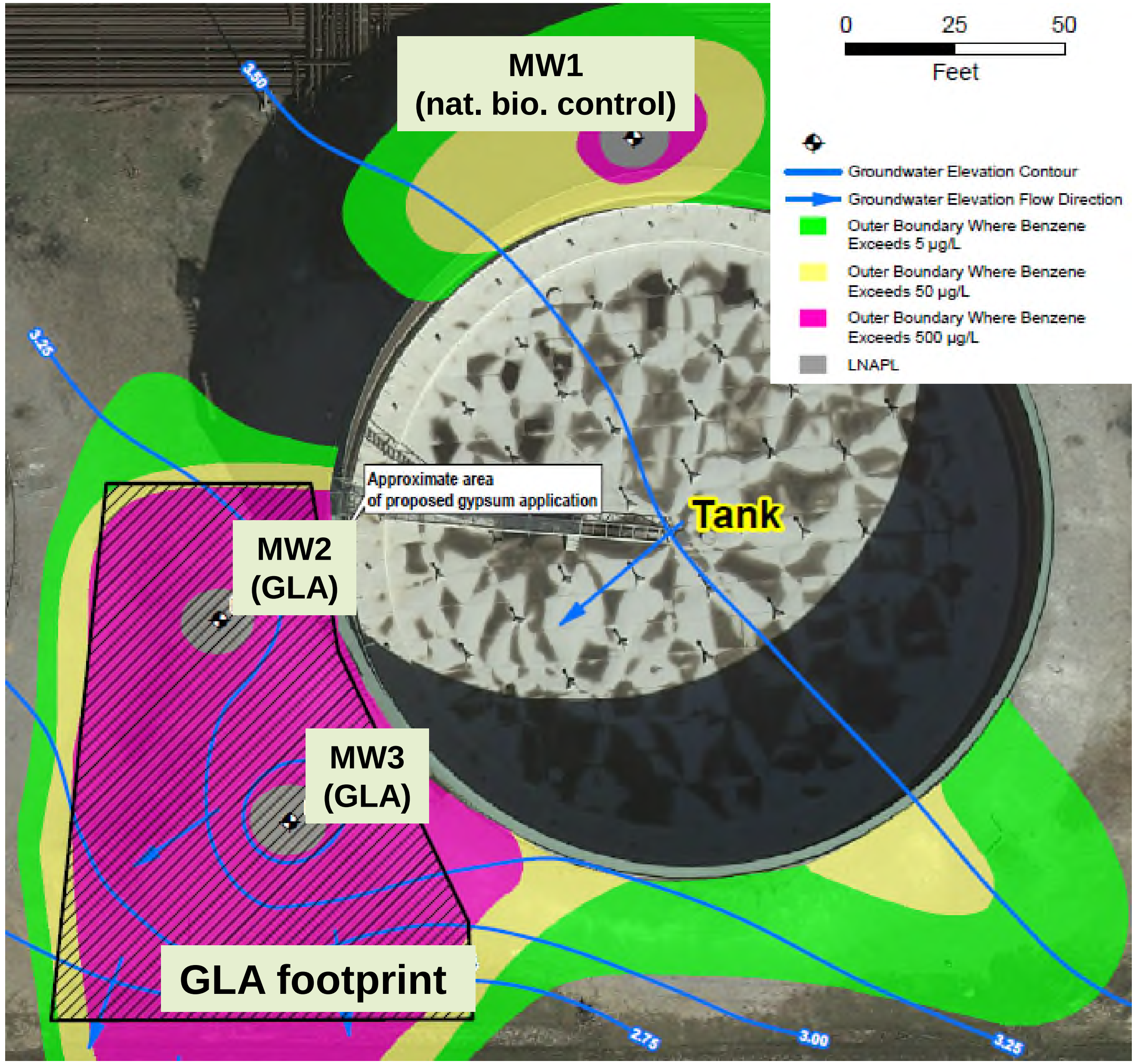
(Field data from Baedecker et al. 2018)



- 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 majority of constituents in LNAPL-3 related to higher sulfate/nitrate (through greater recharge) vs. average of two deeper LNAPL bodies
  - Rest behave as potential conserved markers (data not shown)

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

Field Pilot Setting



Site

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

Sulfate delivery by gypsum land application (GLA – August 2022 and March 2024)

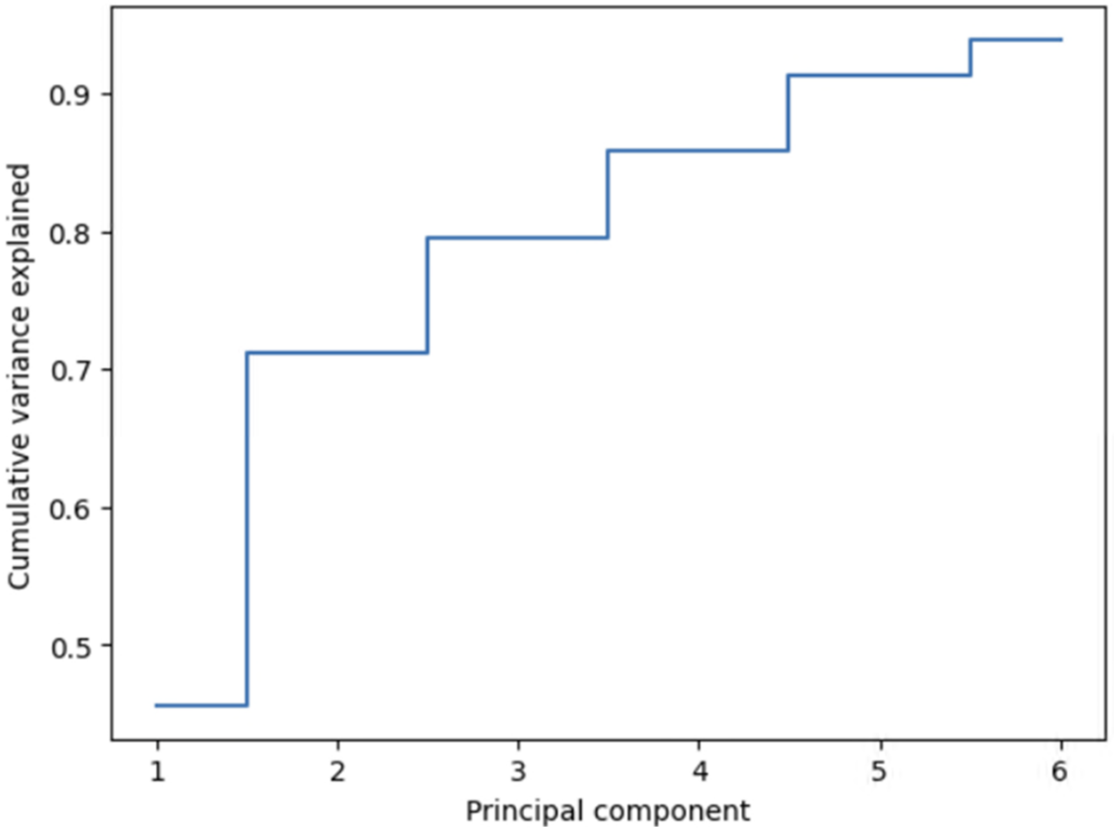
- MW1 (natural biodegradation control), MW2 and MW3 (wells within GLA footprint)
- Loading - 0.9 lb. gypsum/ft^2 across entire footprint and 0.009 lb.$CaBr_2$/ft^2 over 20' × 20' area around wells
- No irrigation was necessary due to heavy rainfall

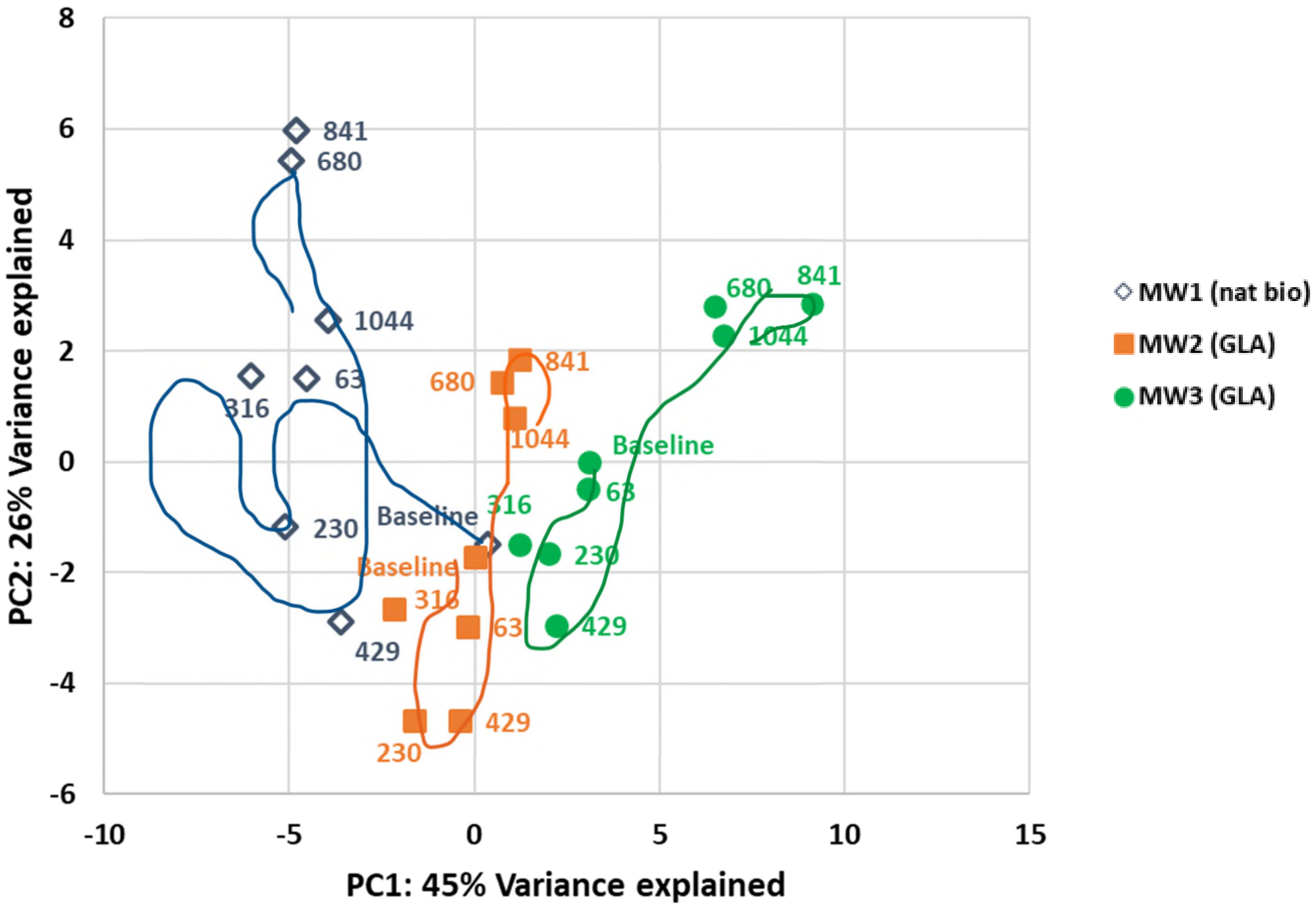
Performance Monitoring

Baseline and 7 events post-GLA (over ~1044 days)

- 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 (8 events over 1044 days)

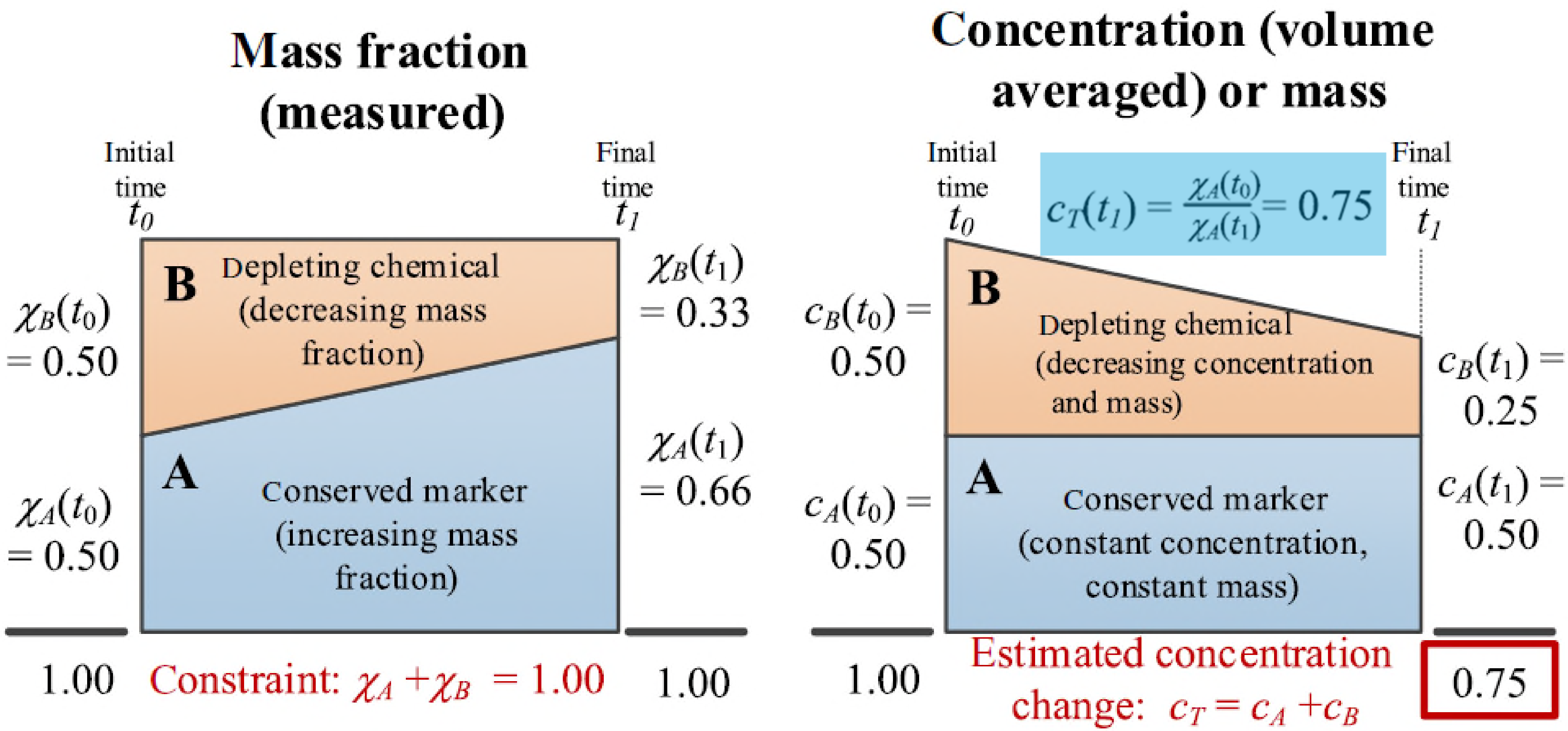
LNAPL Composition: Principal Component Analysis (PCA)





- Clustering (Unsupervised ML approach) generally captures distinctness of temporal trend of LNAPL composition in MWs
- MW2 and MW3 (sulfate-influenced) compositional changes track very similarly in the PCA space compared to MW1 (natural bio control)

Is the difference in LNAPL depletion statistically significant?

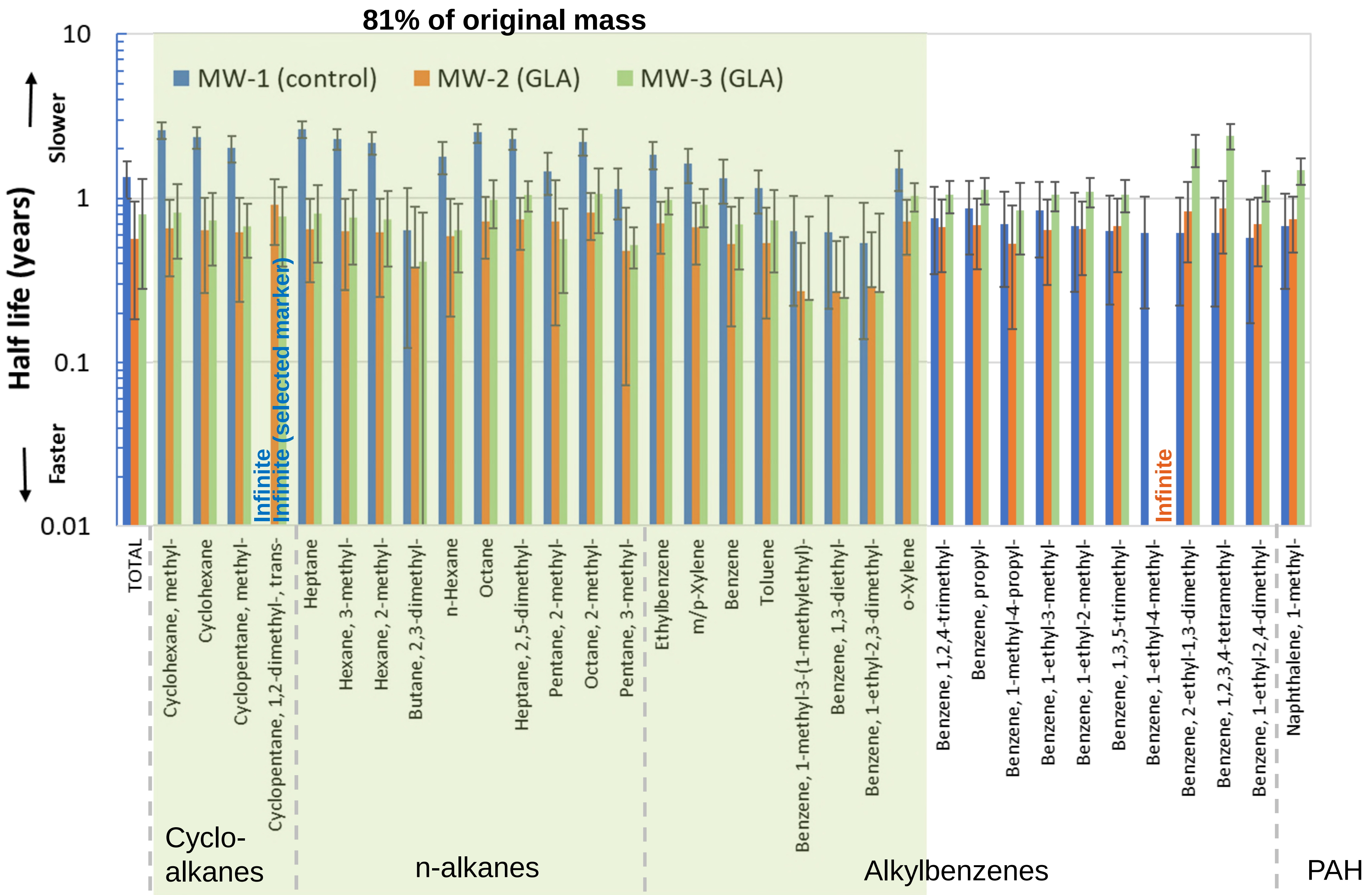


- DeVaull et al. 2020 method to evaluate differences in LNAPL depletion between control (MW-1) and sulfate-influenced wells (or GLA wells MW-2 and MW-3).
- Identify 'tracer' (constituent A) for each well to estimate bulk and constituent depletion half lives.

DeVaull et al. 2020, ASTM 2022.

Half Lives for Hydrocarbon Depletion in LNAPL

(1044 days after first GLA)



- 81% of original mass in LNAPL shows clear evidence of faster depletion with GLA
- Two times faster depletion for bulk LNAPL in GLA wells compared to MW-1 (control)

Using method in DeVaull et al. 2020 and ASTM 2022.

Conclusions

Encouraging results to date, as we continue to monitor past 1044 days.

1. 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

2. 81% of original mass in LNAPL shows clear evidence of <u>faster</u> depletion with sulfate-mediated biodegradation
   – This includes BTEX, cycloalkanes and n-alkanes
   – Bulk depletion rate of LNAPL is two times higher under sulfate-mediated biodegradation than under natural biodegradation control conditions

3. Evidence of sulfate-mediated biodegradation in GW contacting LNAPL (data not shown)

References

1. ASTM 2022. Standard Guide for Estimating Natural Attenuation Rates for Non-Aqueous Phase Liquids in the Subsurface, E3361-22.
2. Baedecker, M.J., Eganhouse, R.P., Qi, H., Cozzarelli, I.M., Trost, J.J. and Bekins, B.A., 2018. Weathering of Oil in a Surficial Aquifer. Groundwater, 56: 797-809. (Open Access). https://doi.org/10.1111/gwat.12619
3. DeVaull, G.E., Rhodes, I.A.L., Hinojosa, E. and Bruce, C.L. (2020), Petroleum NAPL Depletion Estimates and Selection of Marker Constituents from Compositional Analysis. Groundwater Monitoring & Remediation, 40: 44-53. (Open Access). https://ngwa.onlinelibrary.wiley.com/doi/epdf/10.1111/gwmr.12410
4. Sra, K., Kolhatkar, R., Segal, D., and Wilson, J. (2023). Sulfate Delivery Methods to Accelerate BTEX Biodegradation and Expedite Site Closure, LUSTLine Bulletin 93, 15-21. LUST-line-Issue-93-Final.pdf (neiwpcc.org)

Backup

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?

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

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

Sulfate as electron acceptor

Concentration Change

$$8C_6H_6 + 30SO_4^{2-} + 24H_2O \rightarrow 15H_2S + 15HS^- + 48HCO_3^- + 3H^+$$

Isotopic Shift

^{13}C ↑ ^{2}H ↑ — **$\delta^{13}C$- & $\delta^{2}H$-benzene**

^{34}S ↑ — **$\delta^{34}S$-sulfate**

^{13}C ↓ — **$\delta^{13}C$-DIC**

Sulfate to improve syntrophic biodegradation

$$C_6H_6 \xrightarrow{\textit{fermenters}} \text{acetate, propionate, } H_2 \xrightarrow{\textit{methanogens}} CO_2 + CH_4$$

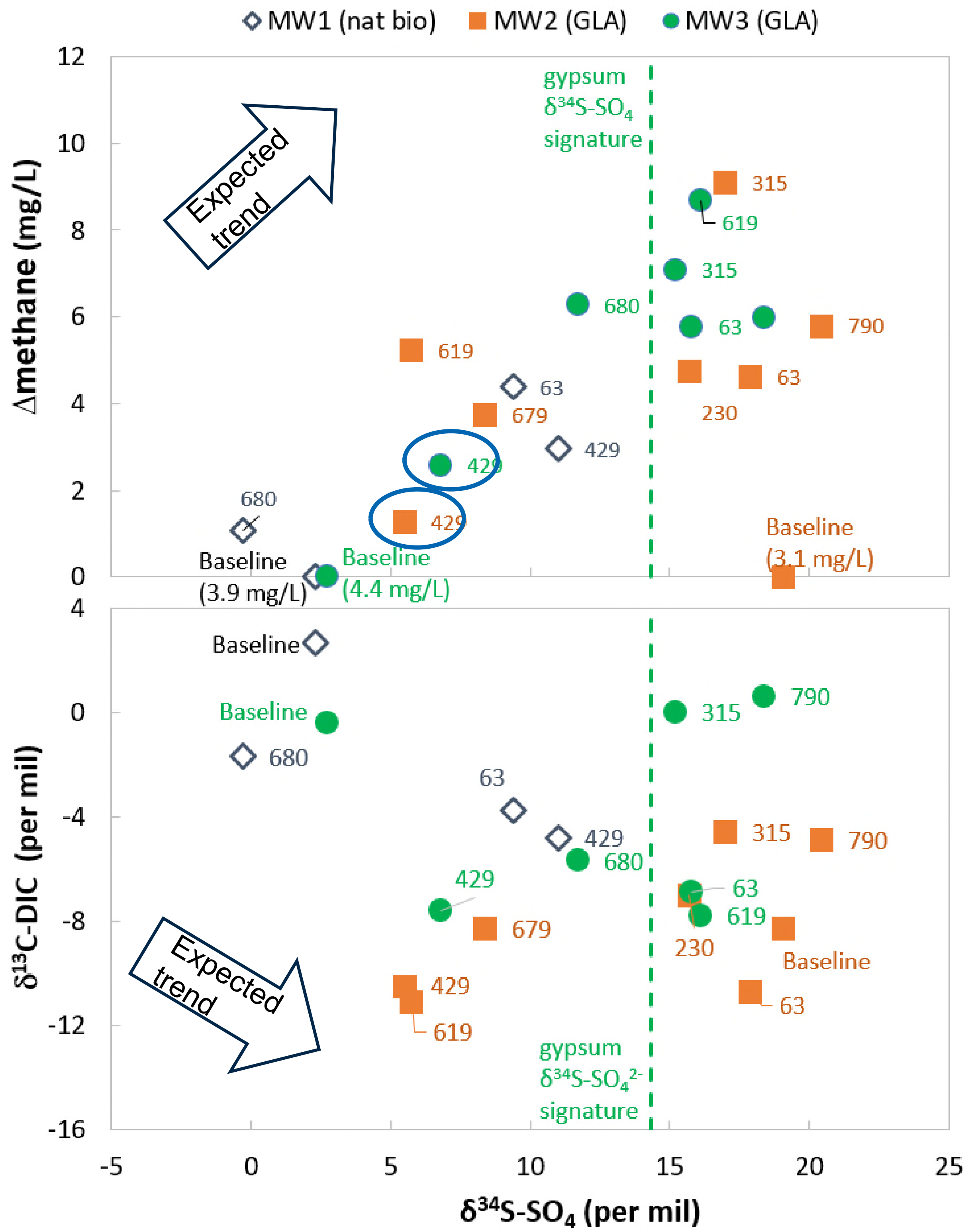
^{13}C ↑ **$\delta^{13}C$-DIC**

$$\text{acetate, propionate, } H_2 \xrightarrow{\textit{sulfate reducing bacteria}} CO_2 + S^{2-}$$

^{34}S ↑ **$\delta^{34}S$-sulfate**

^{13}C ↓ **$\delta^{13}C$-DIC**

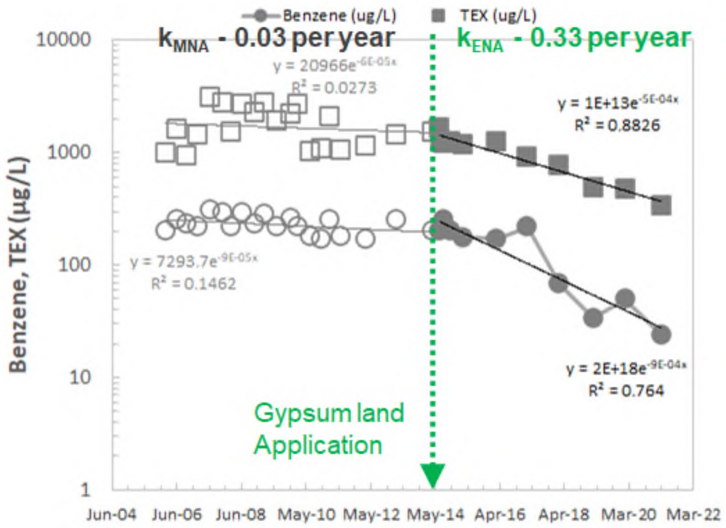
Evidence of Sulfate-mediated Biodegradation in GW contacting LNAPL



- At MW3, strong indication of sulfate-mediated biodegradation suggested by increase in $\delta^{34}S$-sulfate, along with:
  - significant increase in methane concentrations compared to baseline and natural bio control
- At MW3, generally decreasing trend for $\delta^{13}C$-DIC suggesting evidence of complete mineralization
  - $\delta^{13}C$-DIC trends can be confounded by methanogenesis
- $\delta^{34}S$-sulfate and methane approached baseline conditions by Day 429 for both MW2 and MW3 suggesting sulfate limitation
  - second round of GLA done on Day 575

Significant Reduction in Monitoring Timeframes After Sulfate Addition

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

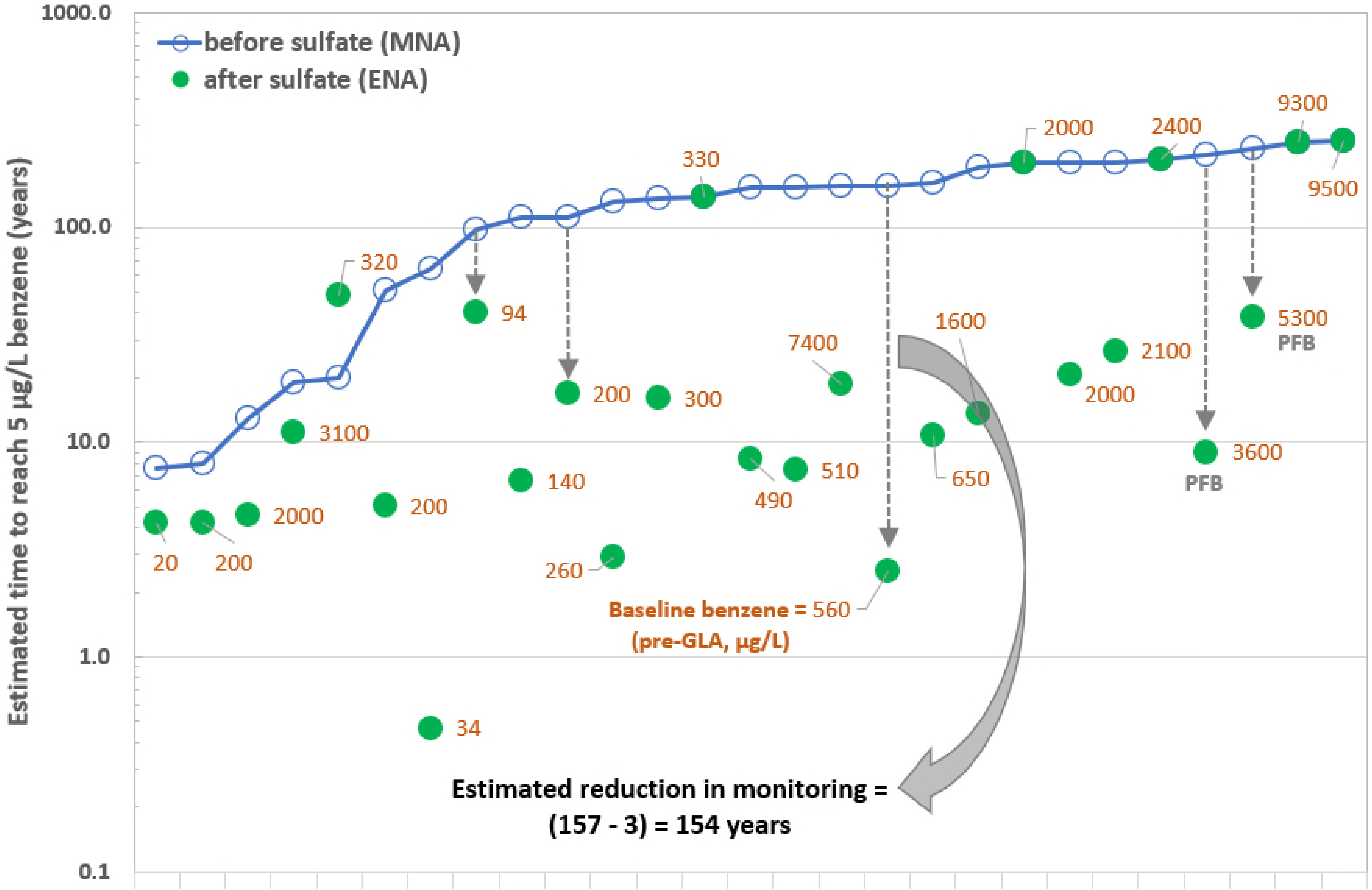


For each well

- 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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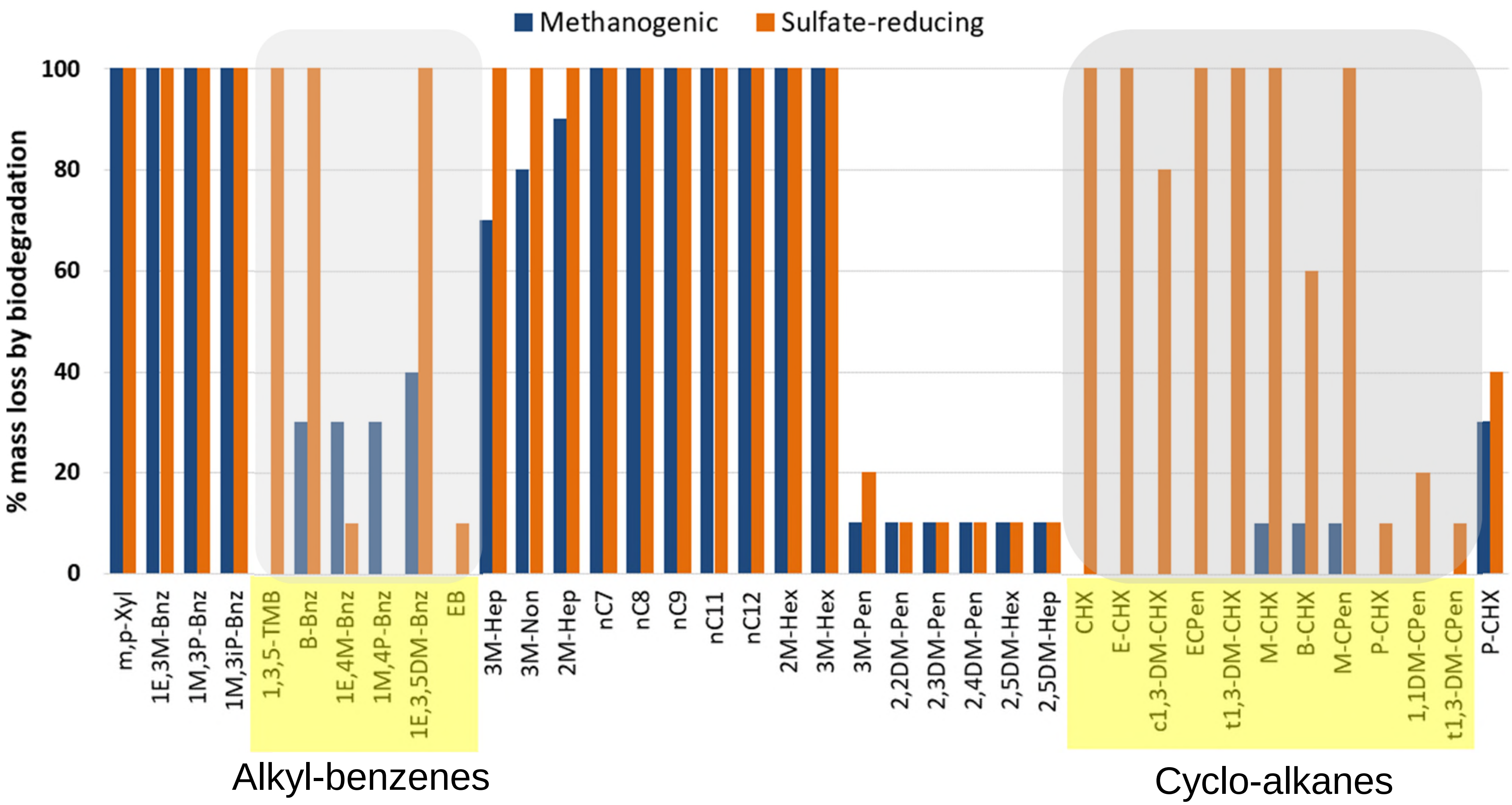
Expected Differences in Anaerobic Biodegradation (209 days)

(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:
  - o completely degraded or
  - o did not degrade at all (potential ‘conservative marker’ constituents)