Sulfate Delivery Methods for Enhancing Biodegradation of Petroleum Hydrocarbons

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1. Context – Why Sulfate?

- **Active electron acceptor** in degradation of petroleum hydrocarbons (PHCs) → sites are generally anaerobic and depleted in sulfate,
- **Higher potential capacity** to degrade (e.g., 55 mg-C_6H_6/L), due to **higher solubility** or another limit, (than oxygen, ferric iron or nitrate) and comparable degradation efficiency,
- **Higher persistence** and **lower non-target demand** (than oxygen or nitrate),
- Low potential for biofouling or clogging (than oxygen or iron).

Summary of Electron Acceptor Advantages and Concerns (adapted from Cunningham et al. 2001)

Reaction	Reactant	Product	Maximum Concentration in Water (mg/L)	Benzene Consumed (mg/L)	Notes / Likely Issues
Aerobic	O_2		9	3.0	• Limited solubility • Numerous other oxygen sinks • Potential aquifer clogging • Biofouling near injection point
Nitrate reduction	NO_3^-		45	9.5	• Drinking water concern • Primary MCL 10 mg/L NO_3^--N (or 45 mg/L NO_3^-) • Expensive
Iron (III) reduction		Fe^{2+}	≈50	1.2	• Oxidation of Fe^{+2} leads to aquifer clogging
Sulfate reduction	SO_4^{2-}		250	55	• Hydrogen sulfide; rarely an issue due to precipitation with iron in soil • Secondary MCL for sulfate – 250 mg/L • Much cheaper than nitrate
Methanogenesis		CH_4	≈16	21	• At concentrations ≈16 mg/L, methane leaves the groundwater as bubbles. Hydrocarbon degradation may be greater than estimated.

References:

J.A. Cunningham et al., 2001/ Environmental Science & Technology 35, no. 8: 1663-1670

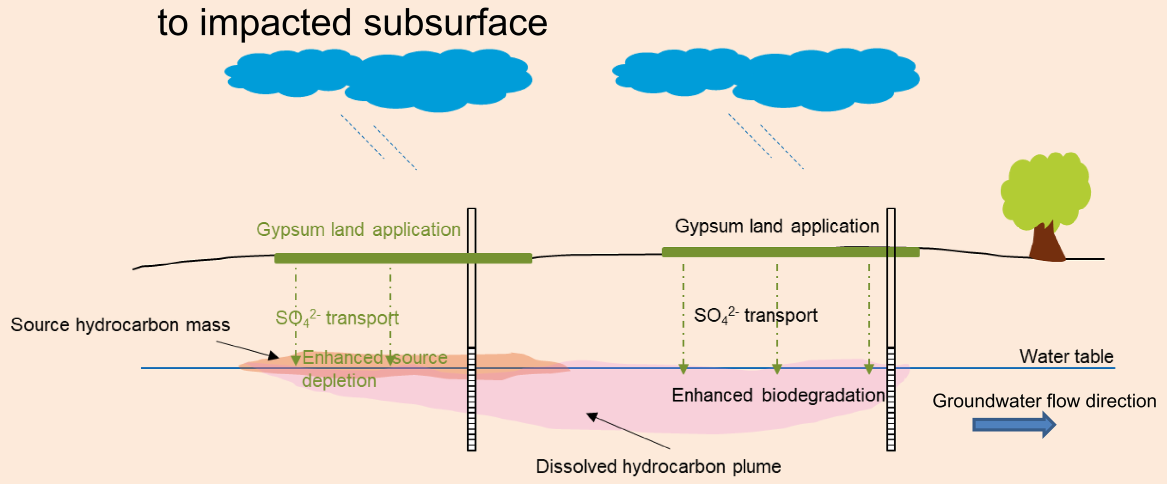
R. Kolhatkar and M. Schnobrich, 2017/Ground Water Monitoring & Remediation 37, no. 2, 43-57,
Open Access: https://doi.org/10.1111/gwmr.12209

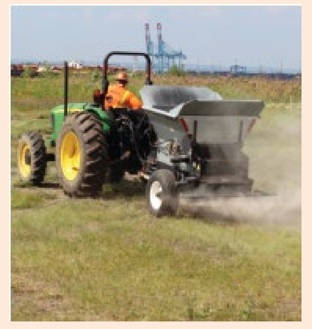
Buscheck et al., 2019/Ground Water Monitoring & Remediation 39, no. 3, 48-60, **Open Access:** https://doi.org/10.1111/gwmr.12346

K.S. Sra et al., 2022/Ground Water Monitoring & Remediation 43, no. 1, 44-59, **Open Access:** https://doi.org/10.1111/gwmr.12547

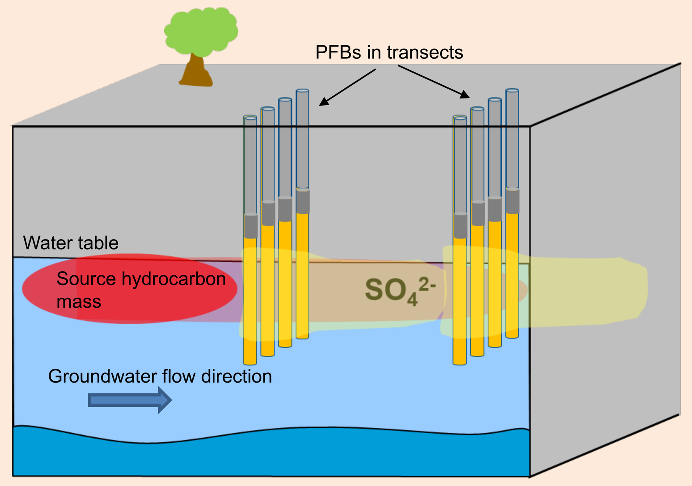
2. Sulfate Delivery Approaches

- **Gypsum Land Application (GLA)**
  - Gypsum spread on land surface
  - Precipitation or irrigation results in sulfate dissolution and infiltration to impacted subsurface





- **Permeable Filled Borings (PFBs)**
  - Vertical borings advanced in a transect to below impacted groundwater depth and filled with gypsum to top of smear zone
  - Lateral groundwater flow dissolves sulfate and transport it to impacted groundwater



- **Successful Applications**
  - Completed at 8 sites
    - 1 former terminal site; 4 former retail sites; 1 former chemical storage facility; 1 former refinery and 1 operating refinery
  - Evaluation/remedial action underway at 4 sites
    - 2 oil field sites and 2 refinery sites
  - Sulfate addition to impacted subsurface with depleted sulfate has enhanced the rate of BTEX biodegradation and improved site outcomes (e.g., optimize excavation footprint, expedite site closure) (See Conclusions Section)

Not Recommended

- Periodic Liquid Sulfate Injection
  - Sulfate preferentially migrates to deeper zones through density driven effects
  - Leads to inadequate contact with smear zone mass

3. Results: GLA (Sra et al., 2022)

Conceptual model of sulfate land application and expected changes in groundwater geochemistry and other performance indicators.

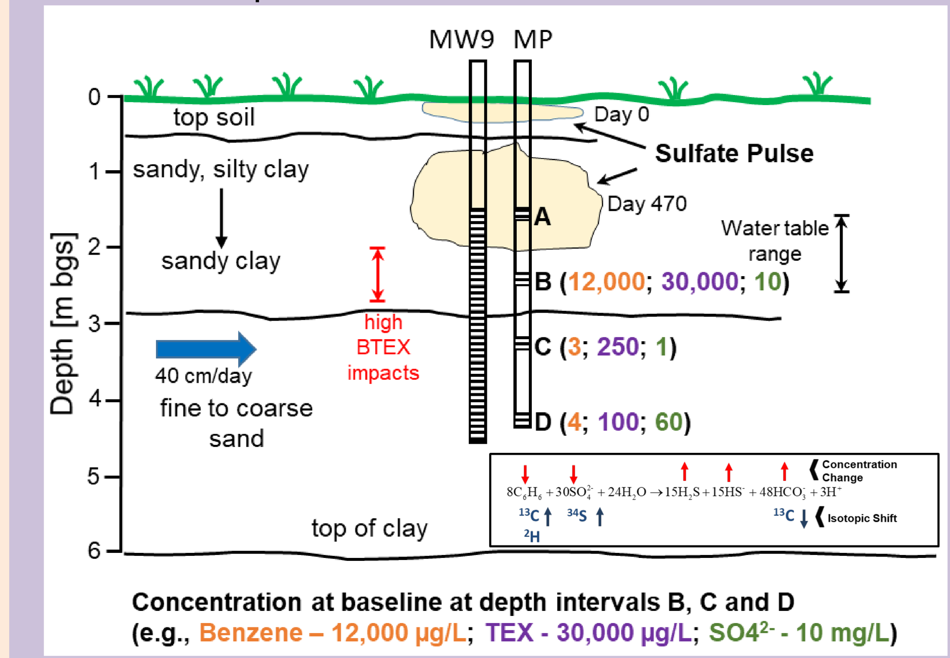
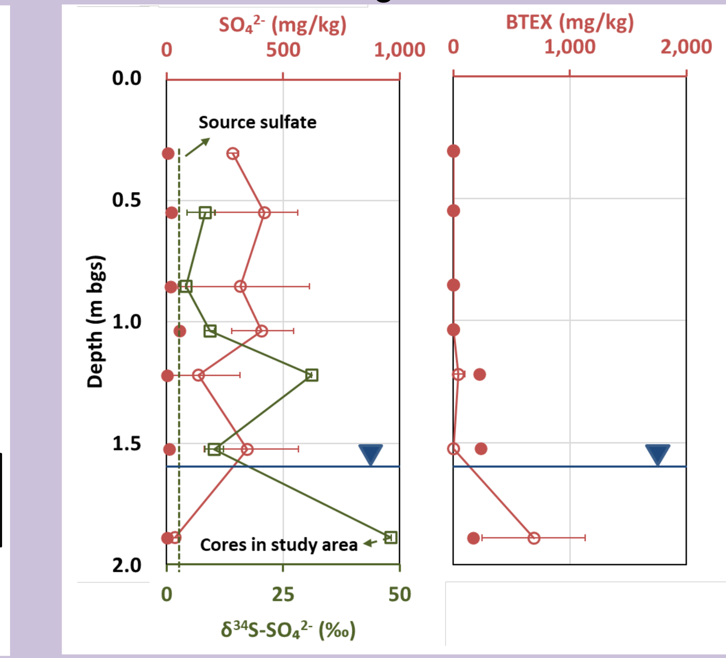
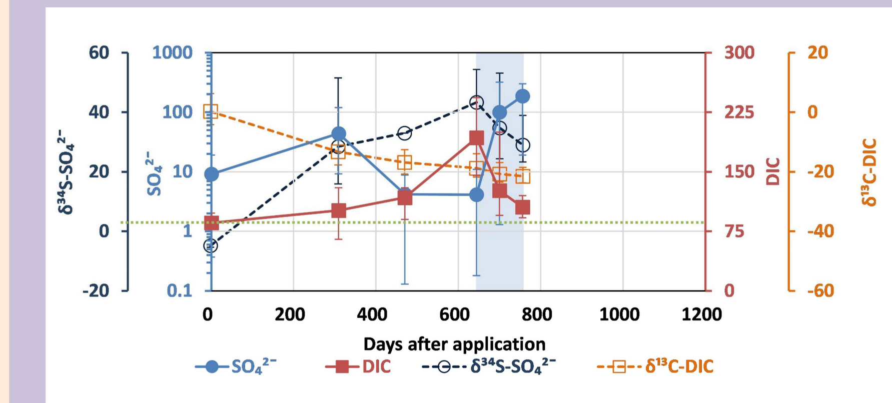


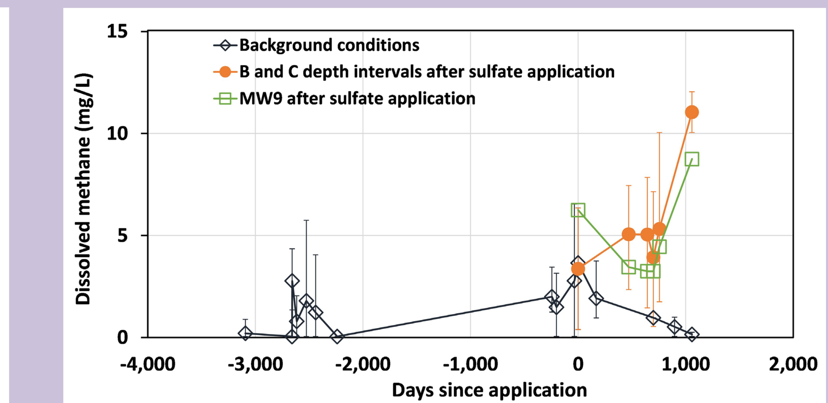
Illustration of significant sulfate breakthrough and ^{34}S-SO_4^{2-} enrichment in vadose zone during interaction with BTEX

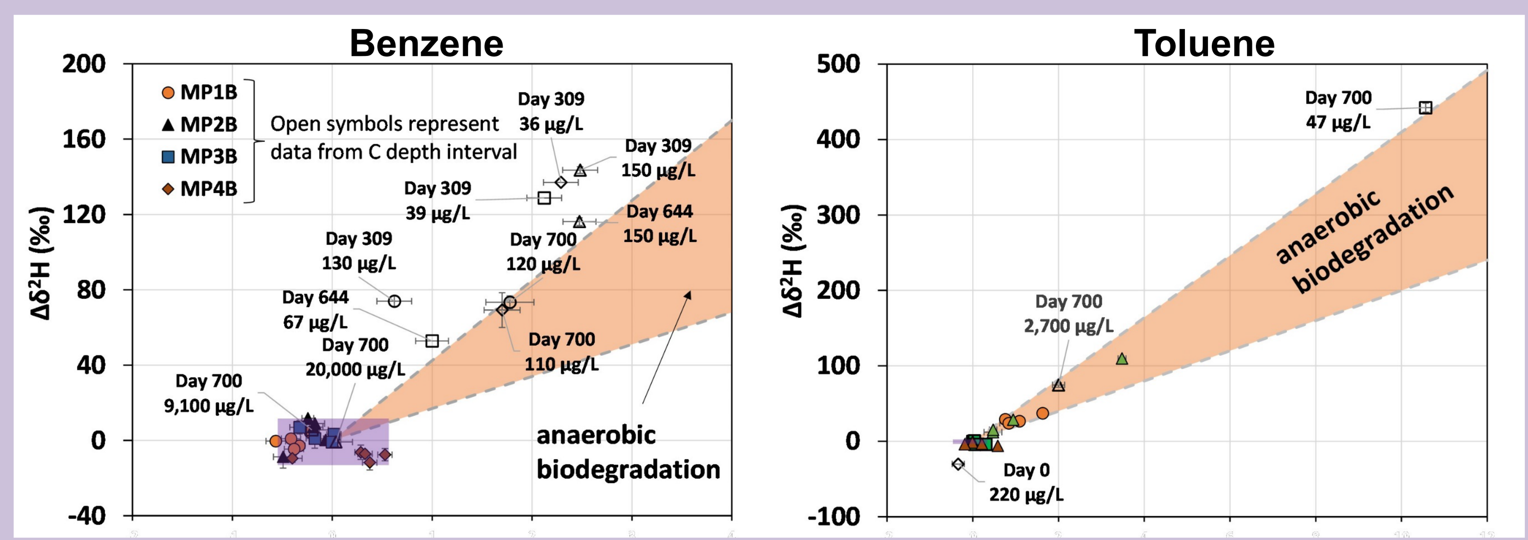


- Significant breakthrough of sulfate in groundwater
- Enrichment of ^{34}S-SO_4^{2-} indicating active sulfate reduction
- Depletion of ^{13}C-DIC indicating complete mineralization of petroleum hydrocarbons

- Significant increase in dissolved methane following sulfate depletion
- Indicates syntrophic benefit of adding sulfate to methanogenic or sulfate reducing systems





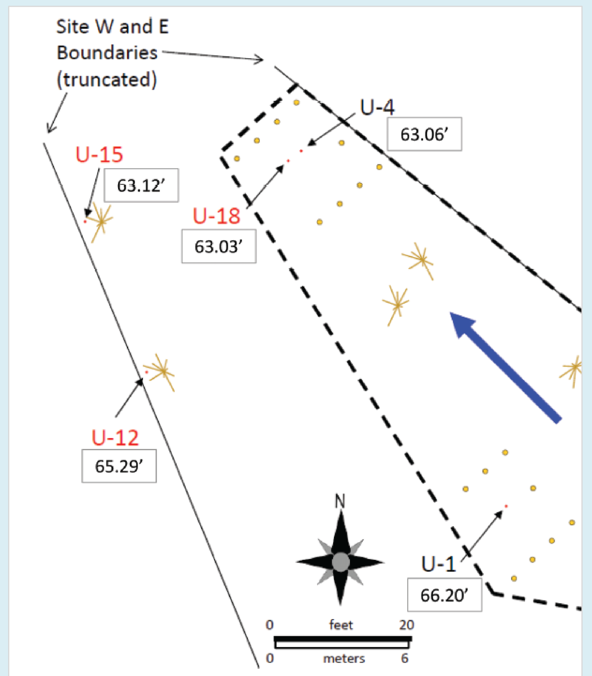


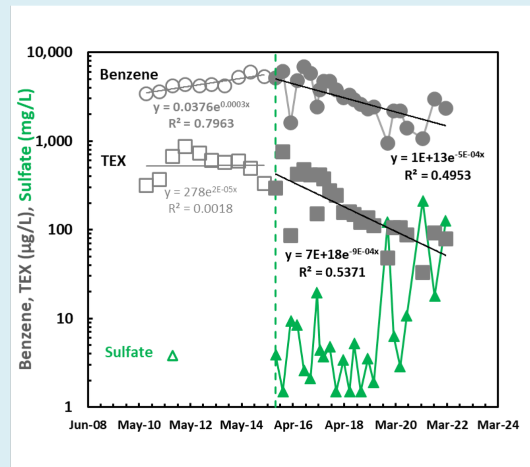
- Significant ^2H and ^{13}C enrichment in remaining benzene (in C depth interval) indicating degradation of benzene co-occurring with sulfate reduction
- Significant ^2H and ^{13}C enrichment in remaining toluene (at B depth interval) indicating expeditious removal of inhibitory competition to eventually support enhanced biodegradation of benzene

4. Results: PFBs (Buscheck et al., 2019)

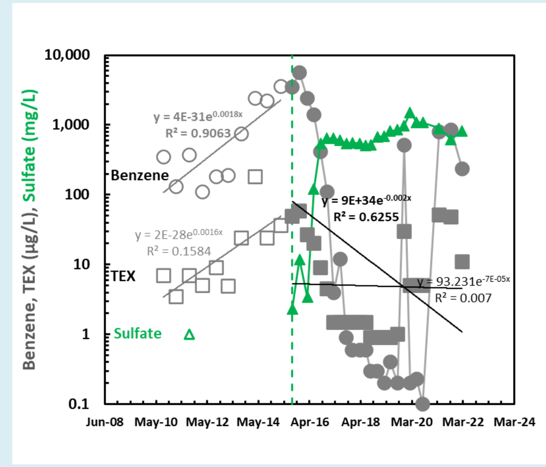
PFBs were installed to depth of around 60' below ground surface around monitoring wells U-4, U-18 and U-1.

- Sulfate breakthrough occurred with sulfate reaching up to 100 mg/L
- Benzene and TEX attenuation was enhanced after sulfate delivery





U-18 (high BTEX)

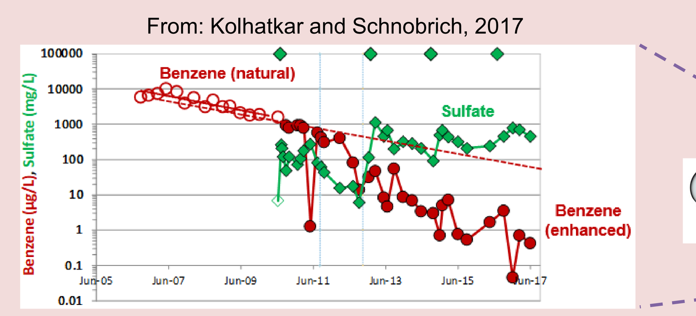


U-4 (low BTEX)

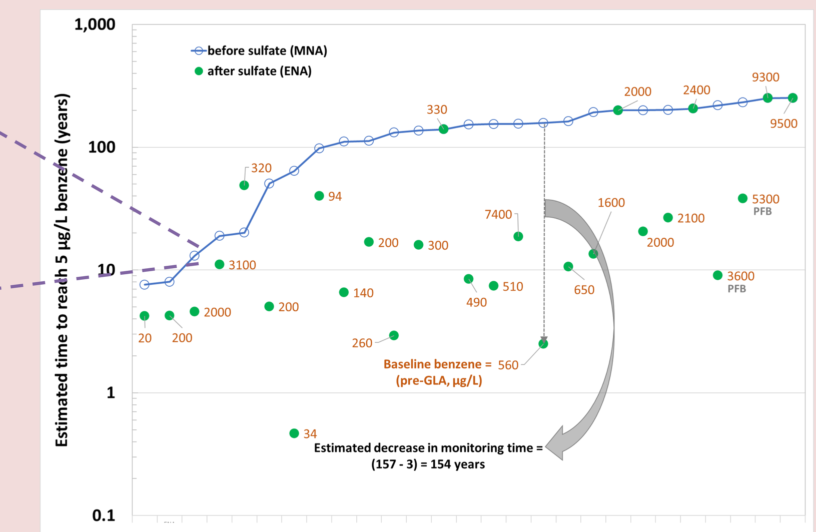
- Sulfate breakthrough occurred with sulfate reaching up to 1,000 mg/L
- Benzene and TEX attenuation was enhanced after sulfate delivery
- Sulfate reduction stimulated: median ^{34}S-SO_4^{2-} in U-18 (24‰) & U-4 (22‰) >> ^{34}S-SO_4 in gypsum (12.4 ‰)

5. Conclusions

- Natural biodegradation of PHCs in the presence of sulfate is commonplace and, therefore, sulfate is a commonly depleted electron acceptor at PHC impacted sites
- GLA and PFBs resulted in sustained sulfate breakthrough, induced sulfate-reducing conditions and enhanced degradation of BTEX (monitored through ^{13}C, ^2H on benzene, ^{34}S-SO_4^{2-} & ^{13}C-DIC) in groundwater which was otherwise depleted in sulfate
- Overall, sulfate addition at sites depleted with sulfate significantly improved timeframe to benzene cleanup in groundwater from a median of 150 years (for MNA) to 15 years (for ENA)



- Rate of sulfate-enhanced benzene attenuation (ENA) increased ~3 fold from baseline (MNA) rate
- Reflected in change in estimated time to reach 5 µg/L benzene from 13 years to 4.6 years



Data from 8 sites (27 wells): 25 GLA, 2 PFB
Pre-GLA benzene: 20 to 9,500 µg/L (median – 560 µg/L)