Sulfate Delivery Methods for Enhancing Biodegradation of Petroleum Hydrocarbons

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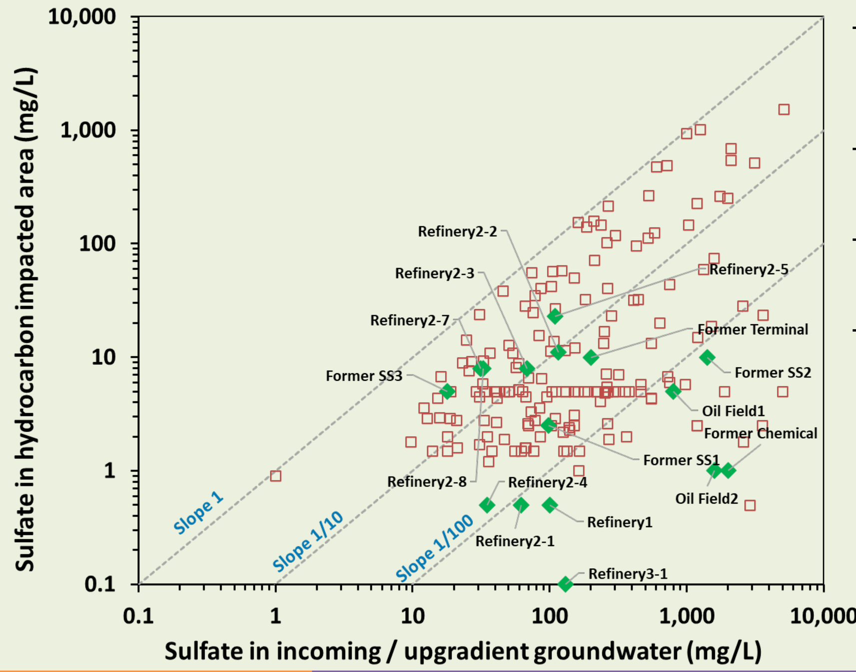
1. Context – Why Sulfate?

- **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).

Illustration of Active Sulfate Participation and Depletion at 164 Gasoline Release Sites (modified from Kolhatkar and Schnobrich, 2017)



- Sulfate in the hydrocarbon impacted area for each of the 164 sites is depleted compared to incoming sulfate concentration at the site
- Sulfate at 56% of sites is more than 10 times lower than the incoming sulfate concentration
- Sulfate at 11% of sites is more than 100 times lower than the incoming sulfate concentration
- 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)
  Completed at 7 sites:
  1 former terminal site; 3 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

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

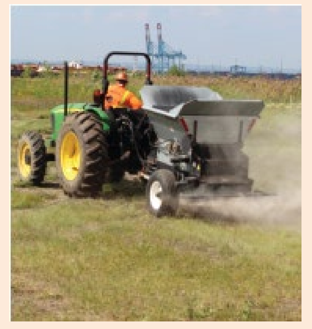
Buscheck et al., 2019/Ground Water Monitoring & Remediation 39, no. 3, 48-60
Open Access: https://doi.org/10.1111/gwmr.12346

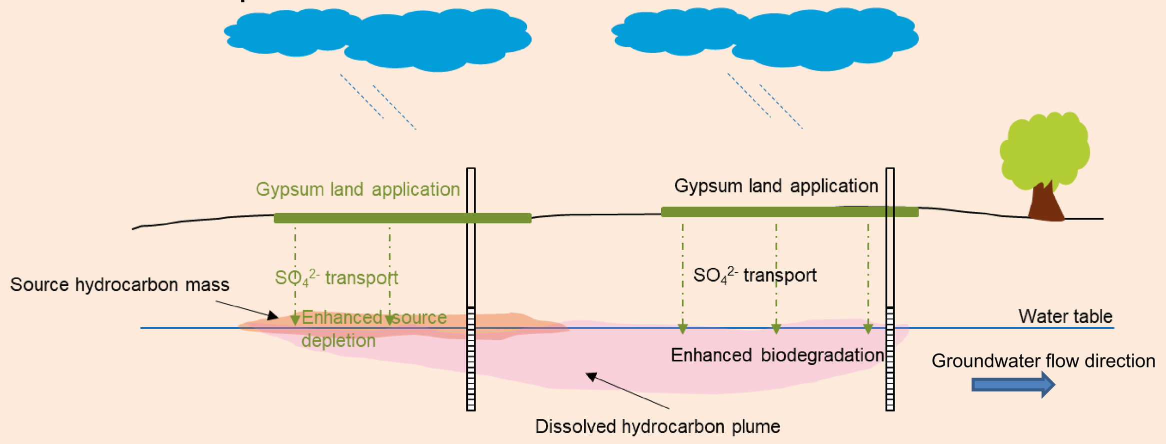
R. Kolhatkar and M. Schnobrich, 2017/Ground Water Monitoring & Remediation 37, no. 2, 43-57
Open Access: https://doi.org/10.1111/gwmr.12209

K.S. Sra et al., 2022/Ground Water Monitoring & Remediation, DOI: 10.1111/gwmr.12547
Open Access: https://doi.org/10.1111/gwmr.12547

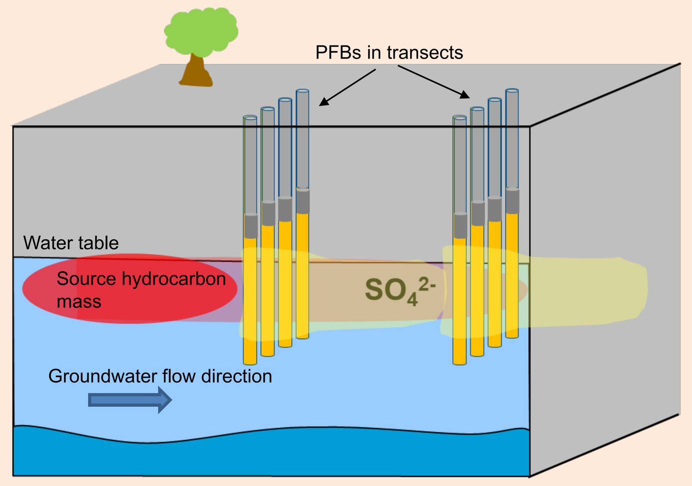
2. Sulfate Delivery Approaches

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

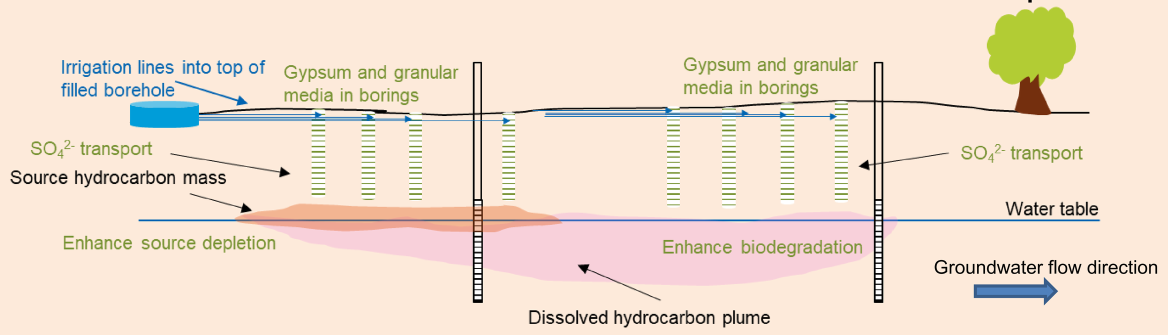




- **Permeable Filled Borings (PFBs)**
  - Vertical borings advanced in a transect to below impacted groundwater depth and filled with gypsum to top of smear zone
  - Lateral groundwater flow dissolves sulfate and transport it to impacted groundwater



- **Permeable Filled Conduits (currently being piloted)**
  - Vertical boreholes advanced to top of impacted subsurface and filled with gypsum
  - Irrigation induces dissolution and trickle flow of dissolved sulfate to impacted subsurface

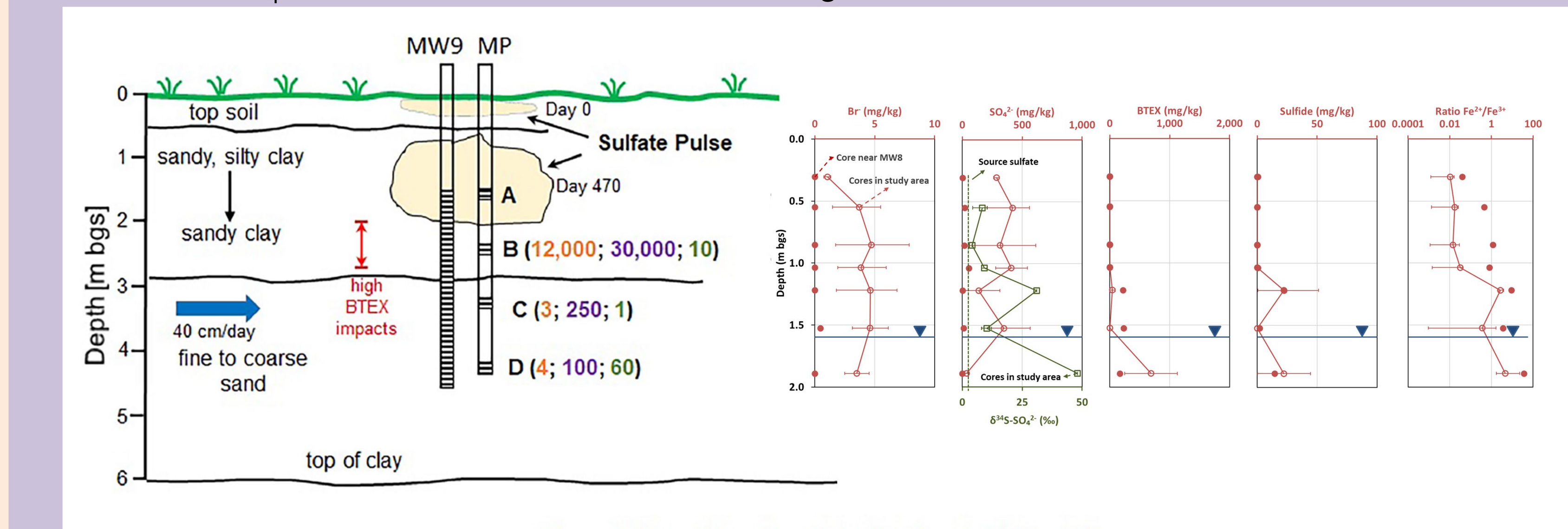


Not Recommended

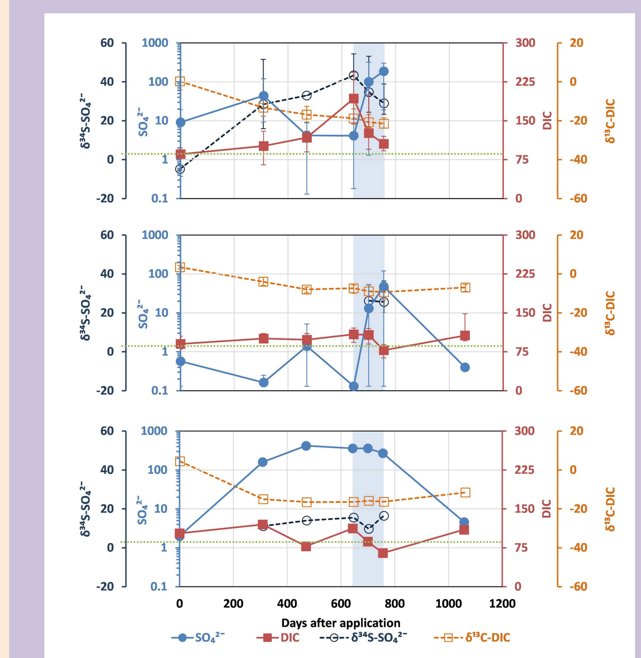
- Periodic Liquid Sulfate Injection
  - Sulfate preferentially migrates to deeper zones through density driven effects
  - Leads to inadequate contact with smear zone mass

3. Results: Sulfate Land Application (Sra et al., 2022)

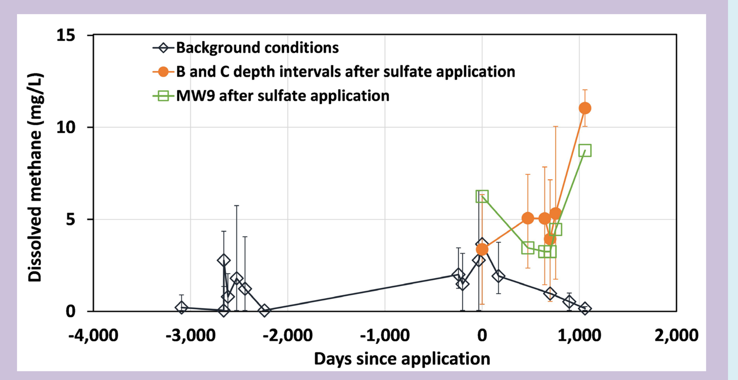
Conceptual model of sulfate land application and expected changes in groundwater geochemistry and other performance indicators. Panel on right illustrates sulfate breakthrough and ^{34}S-SO_4^{2-} enrichment in vadose zone during interaction with BTEX



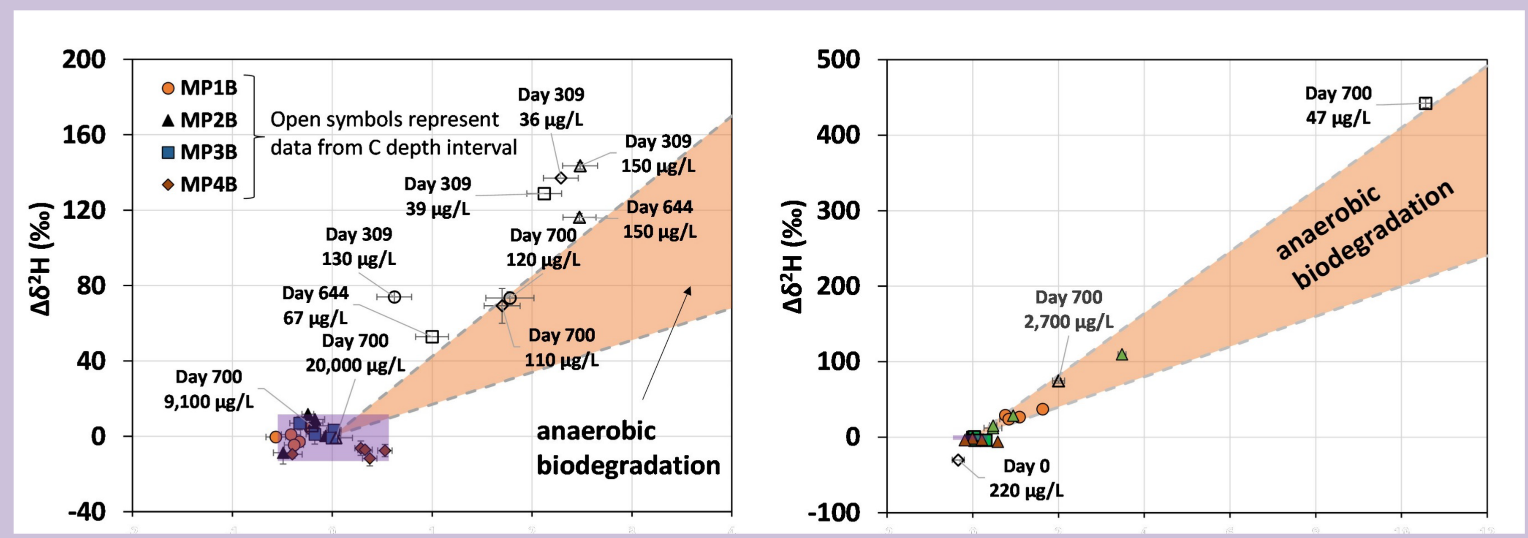
Concentration at baseline at depth intervals B, C and D
(e.g., Benzene – 12,000 µg/L; TEX - 30,000 µg/L; SO4²⁻ - 10 mg/L)



Significant breakthrough of sulfate
Enrichment of ^{34}S-SO_4^{2-} indicating active sulfate reduction
Depletion of ^{13}C-DIC indicating hydrocarbon mineralization



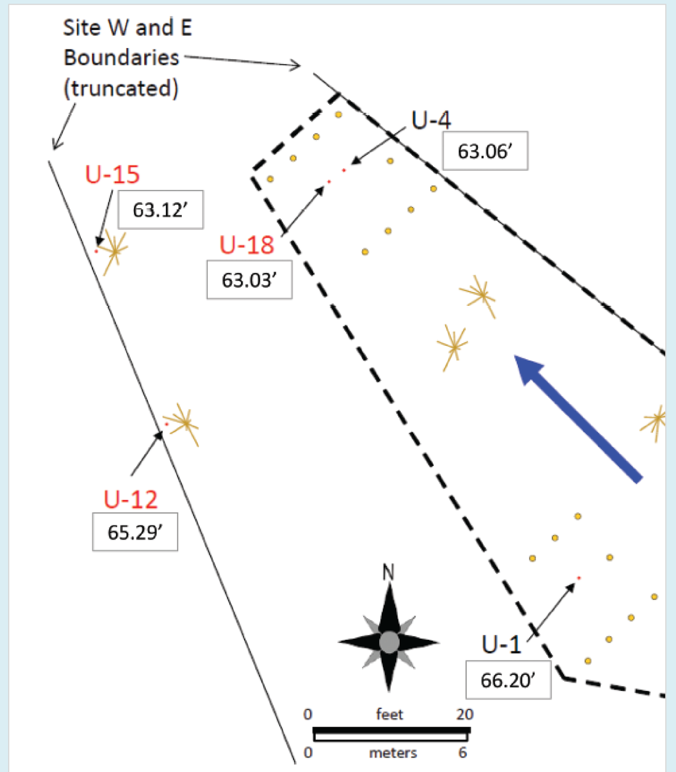
Significant increase in dissolved methane following sulfate depletion indicating syntrophic benefit of adding sulfate to methanogenic or sulfate reducing systems



- 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 removal of inhibitory competition to eventual degradation of benzene

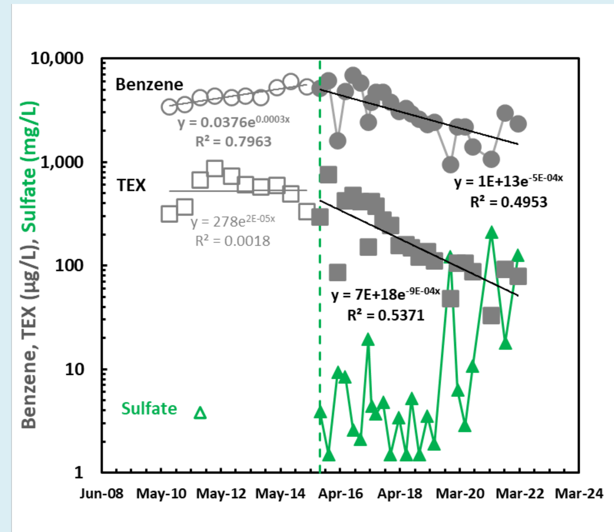
4. Results: PFBs (Buscheck et al., 2019)

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

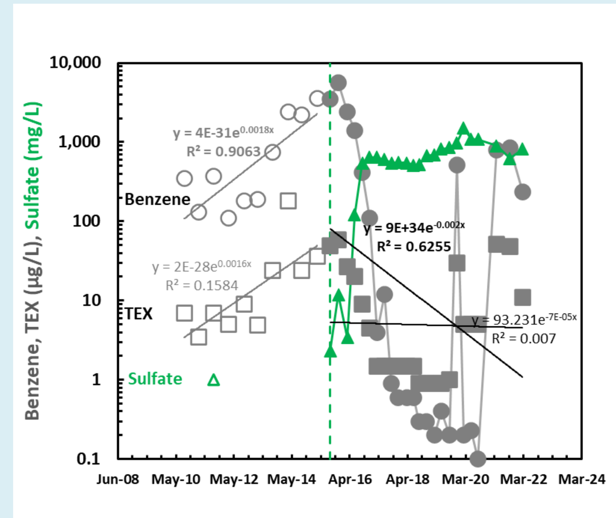


- Sulfate breakthrough occurred with sulfate reaching up to 1,000 mg/L
- Benzene and TEX attenuation was enhanced after sulfate delivery
- Sulfate reduction stimulated: median ^{34}S-SO_4^{2-} in U-18 (24‰) & U-4 (22‰) >> ^{34}S-SO_4 in gypsum (12.4 ‰)

- 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)

5. Conclusions

- Sulfate is a commonly depleted electron acceptor at PHC impacted sites and delivery of sulfate in a sustained manner results in enhanced degradation rates of PHCs
- Addition of sulfate induced sulfate reducing conditions which resulted in
  - Sustained sulfate breakthrough at monitoring points,
  - Enriched ^{34}S-SO_4^{2-} indicating sulfate reduction
  - Depleted ^{13}C-DIC indicating PHC mineralization
  - Enhanced degradation of BTEX in groundwater
  - Enriched ^{13}C and ^2H in benzene and toluene
- Enhanced methanogenesis after sulfate was consumed suggesting syntrophic benefit from sulfate addition and enrichment of the microbial ecosystem
- Gypsum in excavation backfill and permeable filled trenches are other viable approaches for sulfate delivery
- Overall, sulfate addition at sites depleted in the electron acceptor can result in enhanced biodegradation of the PHC source zone and result in expedited timeframes for cleanup of environmental sites