

ENHANCED IN SITU BIOREMEDIATION AT A FORMER REFINERY SITE DUE TO RECYCLING OF AEROSOL SULFATE IN THE GROUNDWATER FLUCTUATION ZONE

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FORMER REFINERY SITE IN NORTH CENTRAL US

1970–1981: 450,000 gal product recovered

- Seepage into creek 1 mile downgradient eliminated
- 1976 - Detailed chemical analyses of product

1991: Additional 108,000 gal product recovered

- Site assessment studies from 1993 – 1997
- MNA proposed for most of site
- 500 year cleanup projection is too long – potential lawsuit

1998: Forensic study of residual LNAPL

- Biodegradation of LNAPL is 10 times model projection
- 5 year MNA pilot study made to evaluate ‘methanogenesis’ and ‘vertical dispersion’ to explain high rate of MNA
- Second 5 year MNA study made to evaluate methods for monitoring MNA/in situ bioremediation



Objective of Study

Quantify rates of vertical transport processes

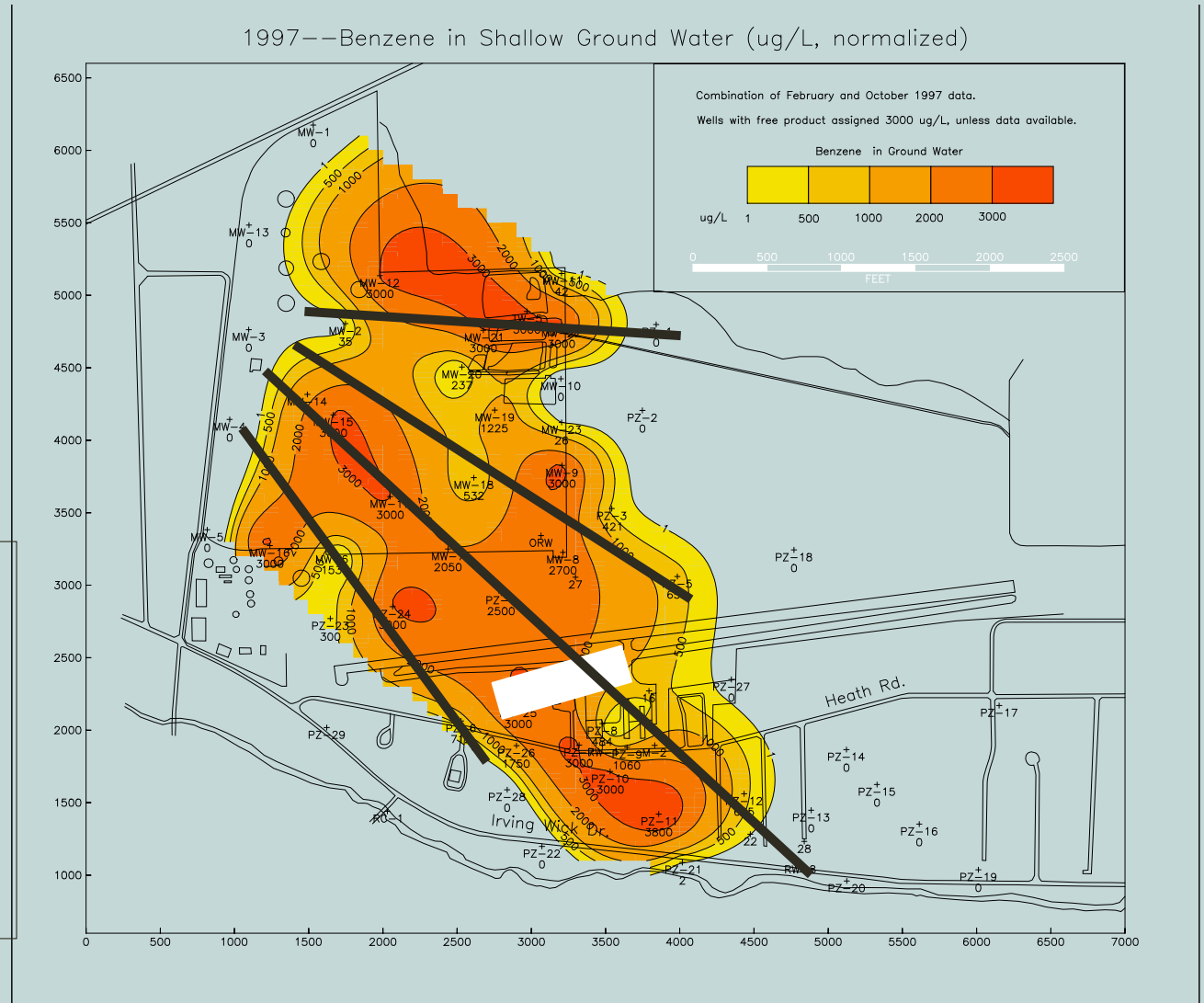
- Methane loss via transport to vadose zone
- Vertical dispersion of EA/ED with GW below smear zone

Field Approach

Vertical sampling at 19 locations (GW/vapor) along 4 trends

- MNA parameters
- Above/below/within smear zone

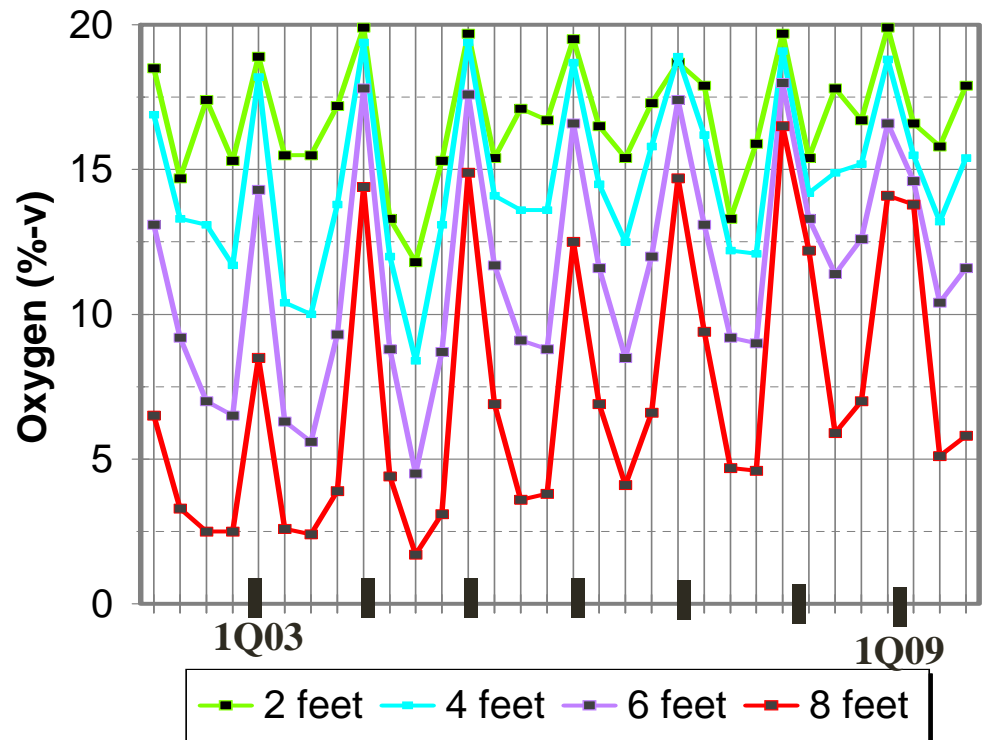
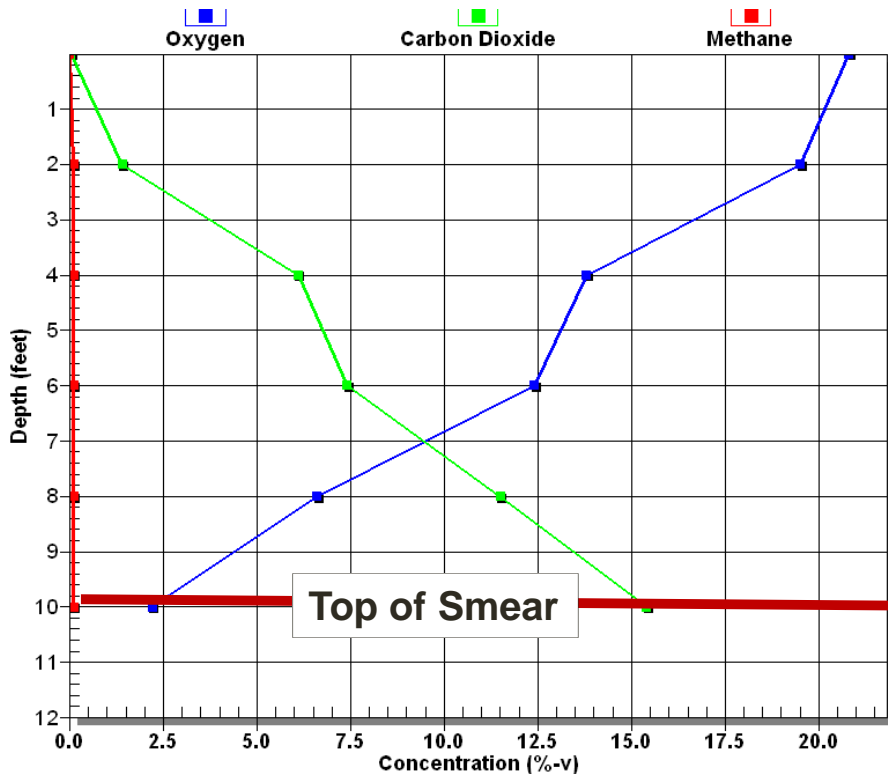
Second study - added ferrous iron and reduced sulfur in soil



Only Local Indication of Methane Transport into Vadose Zone

15 of 19 MNA Locations - CH₄ at base of vadose zone generally low

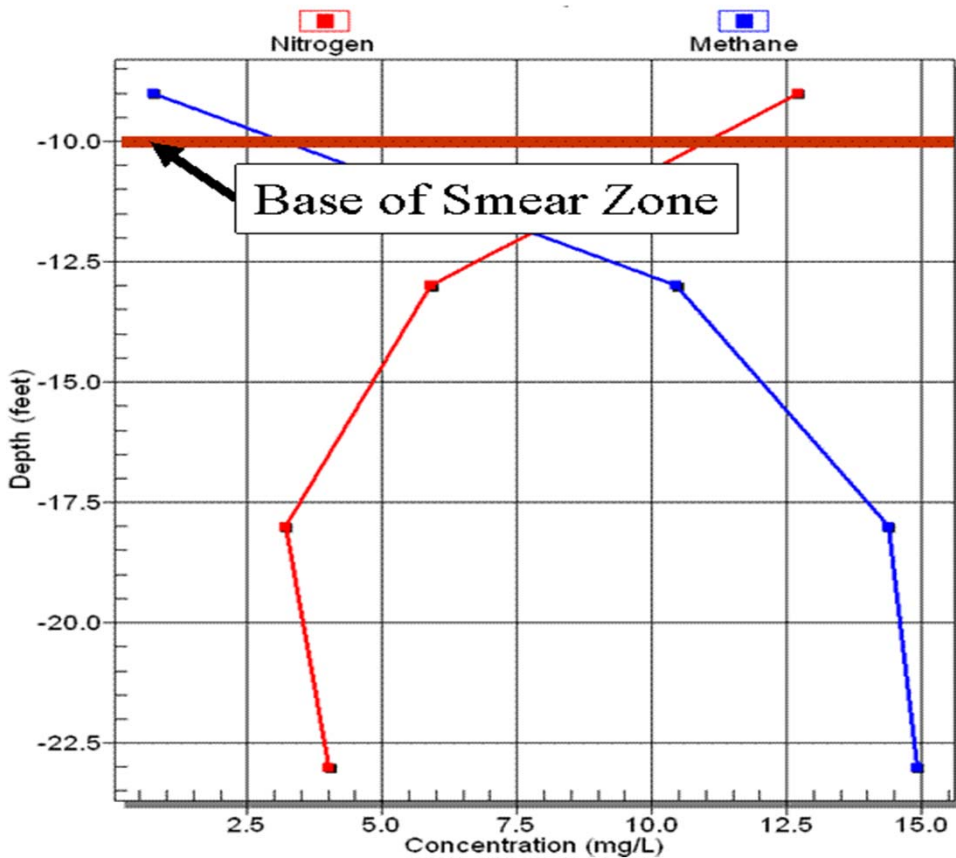
- O₂ seasonally < 5% - corresponding with high groundwater



Lack of Evidence for Methane Release from Groundwater

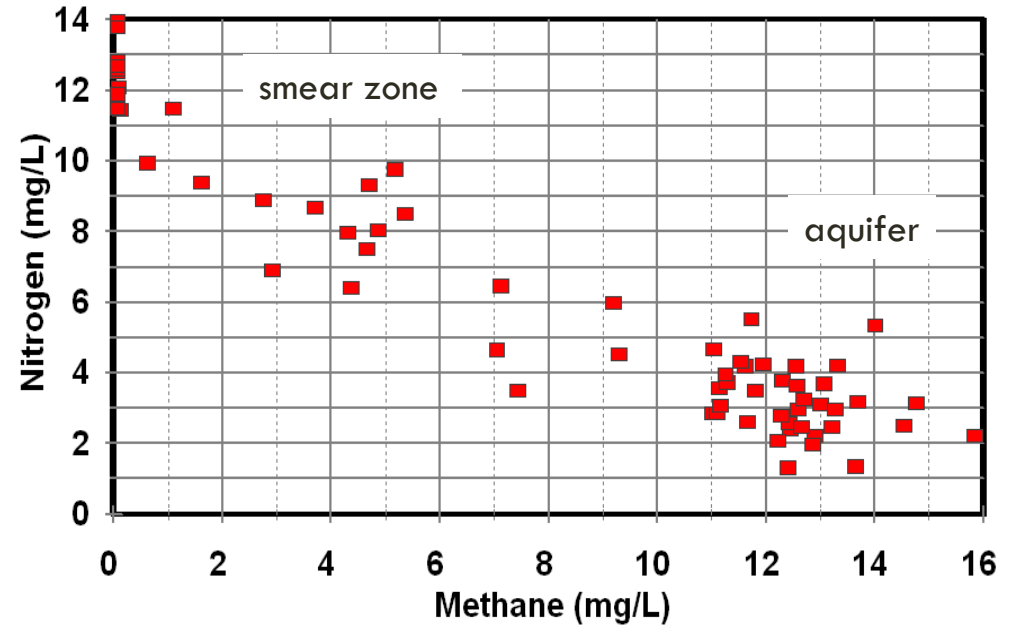
Methane is undersaturated (<22 mg/L) in smear zone groundwater

- Vertical Dispersion and N₂ fixation accounted for 5 X model MNA rate



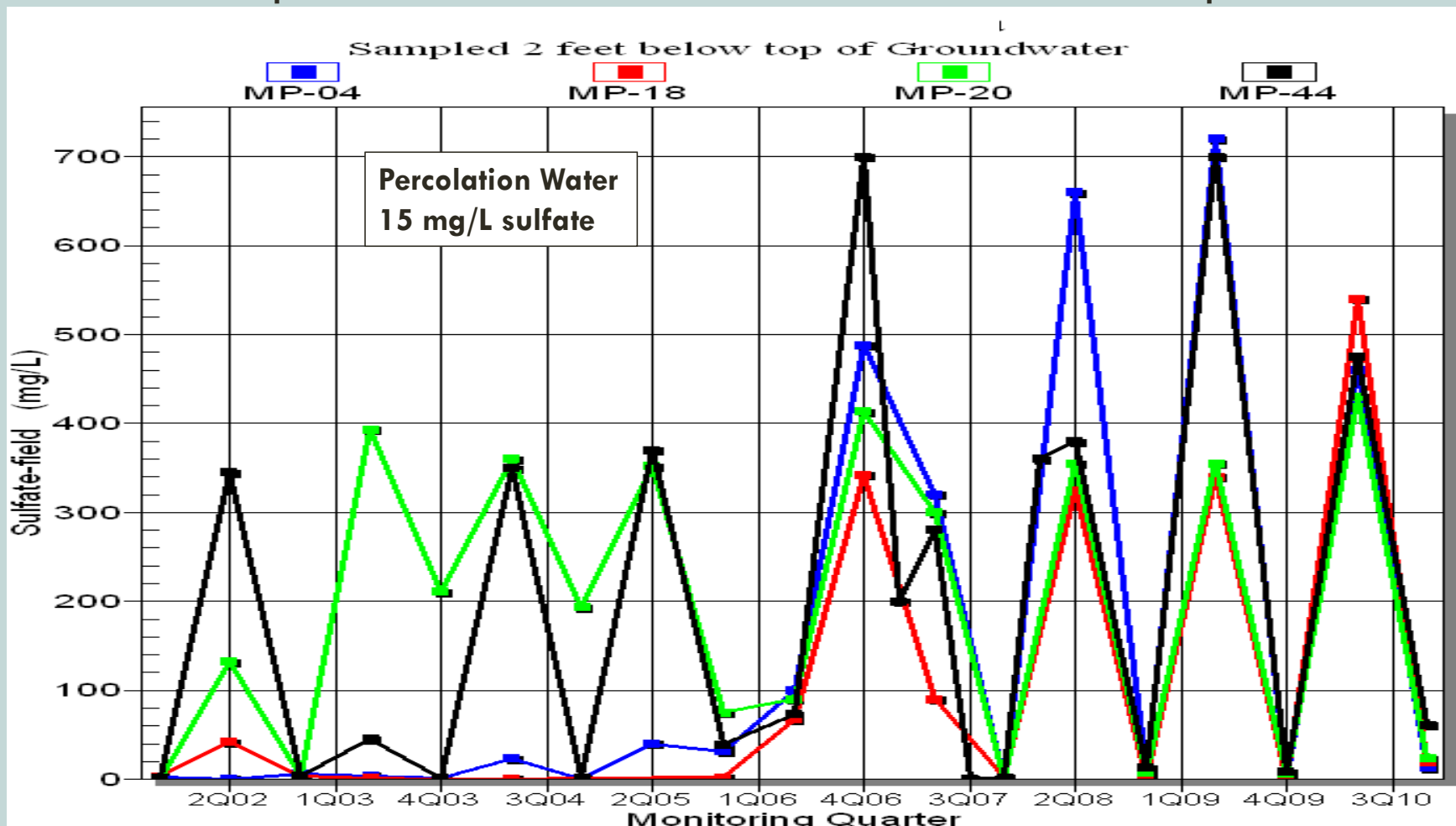
Vertical Biogeochemical Zonation

- Needed addition Anaerobic EA from above



Groundwater Evidence Suggesting Addition of Aerosol Sulfate

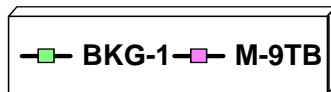
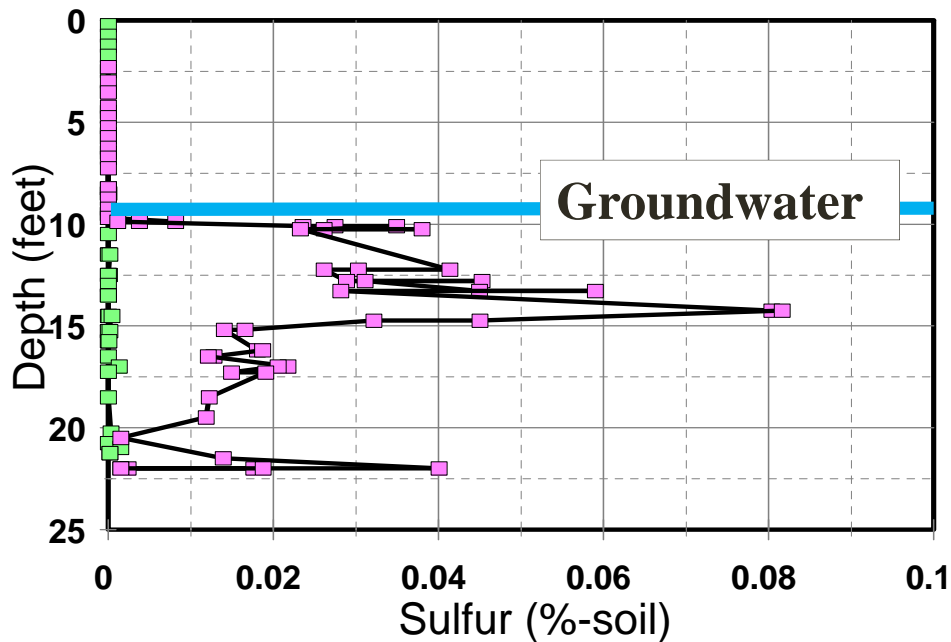
Need process to enhance sulfate concentration multiple times



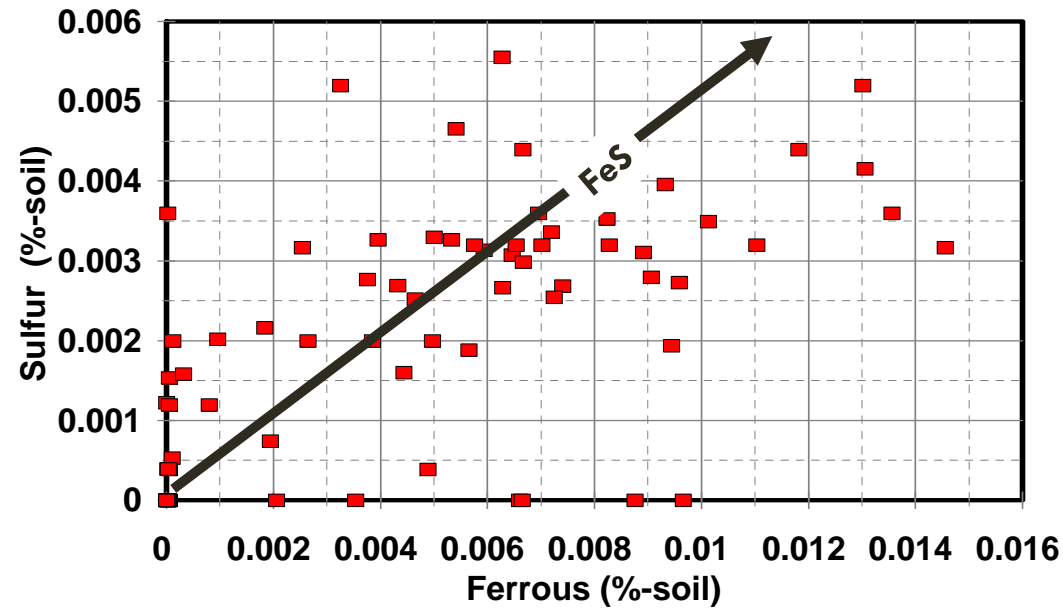
Evidence Indicating Mineralization of Aerosol Sulfate

Elevated concentrations of sulfur and iron in soil at downgradient locations

- 'air' oxidized sulfur/ferrous contents in soil indicative reactive iron sulfide

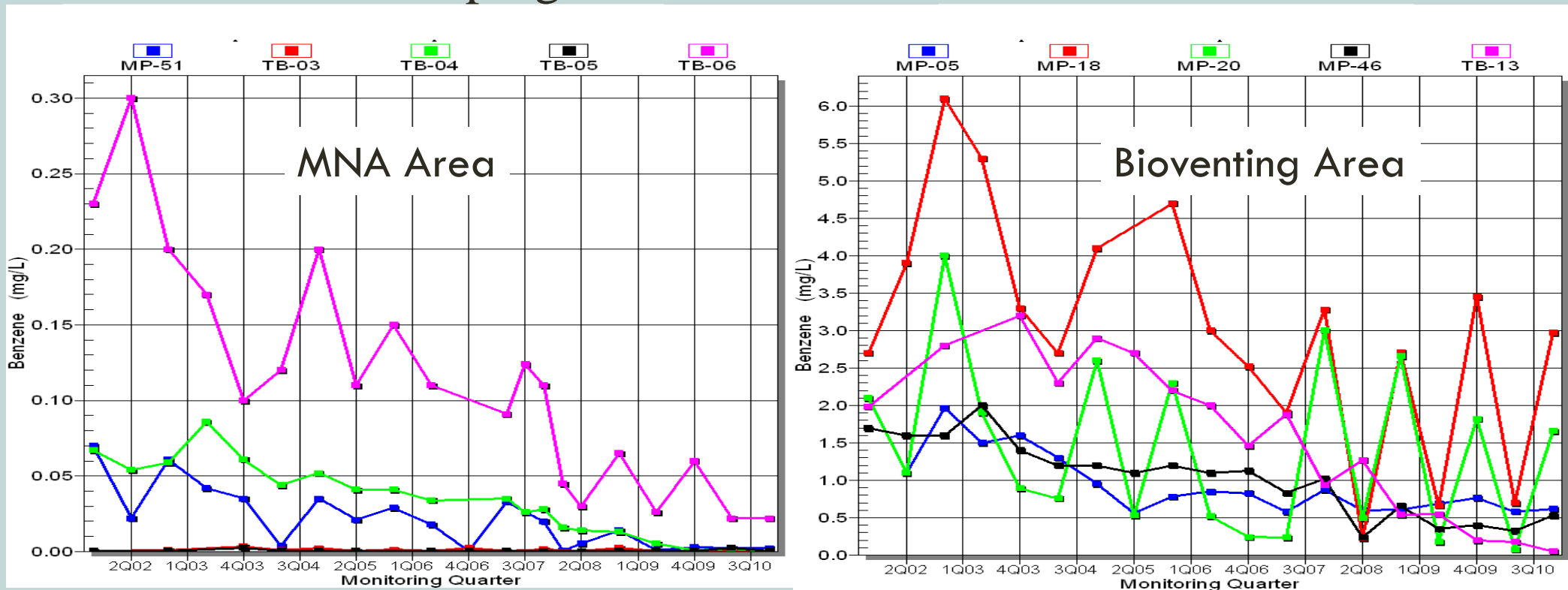


Sulfate Addition Area Soil Profile Chemistry



Evidence for Enhanced Biodegradation of Benzene

- Samples collected 2 feet below top of groundwater
- Small purge method



SUMMARY AND CONCLUSION

Vertical transport and biogeochemical zonation at the site resulted in an enhanced rate of BTEX removal from smear zone.

- Vertical Dispersion in Groundwater Important for Upgradient Portion of Site
- Recycling of Aerosol Sulfate Predominant Process for Downgradient Portion of site

Enhanced bioremediation based on 'recycling of sulfate'

- Sulfate needs to be added to vadose zone not directly to anaerobic groundwater
- Needs to be a significant seasonal fluctuation in groundwater elevation
- May work well in conjunction with bioventing