Spatial and Temporal Trends in Groundwater Chemistry and Precipitate Formation at the Elizabeth City Permeable Reactive Barrier

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US EPA Office of Research and Development

United States Environmental Protection Agency

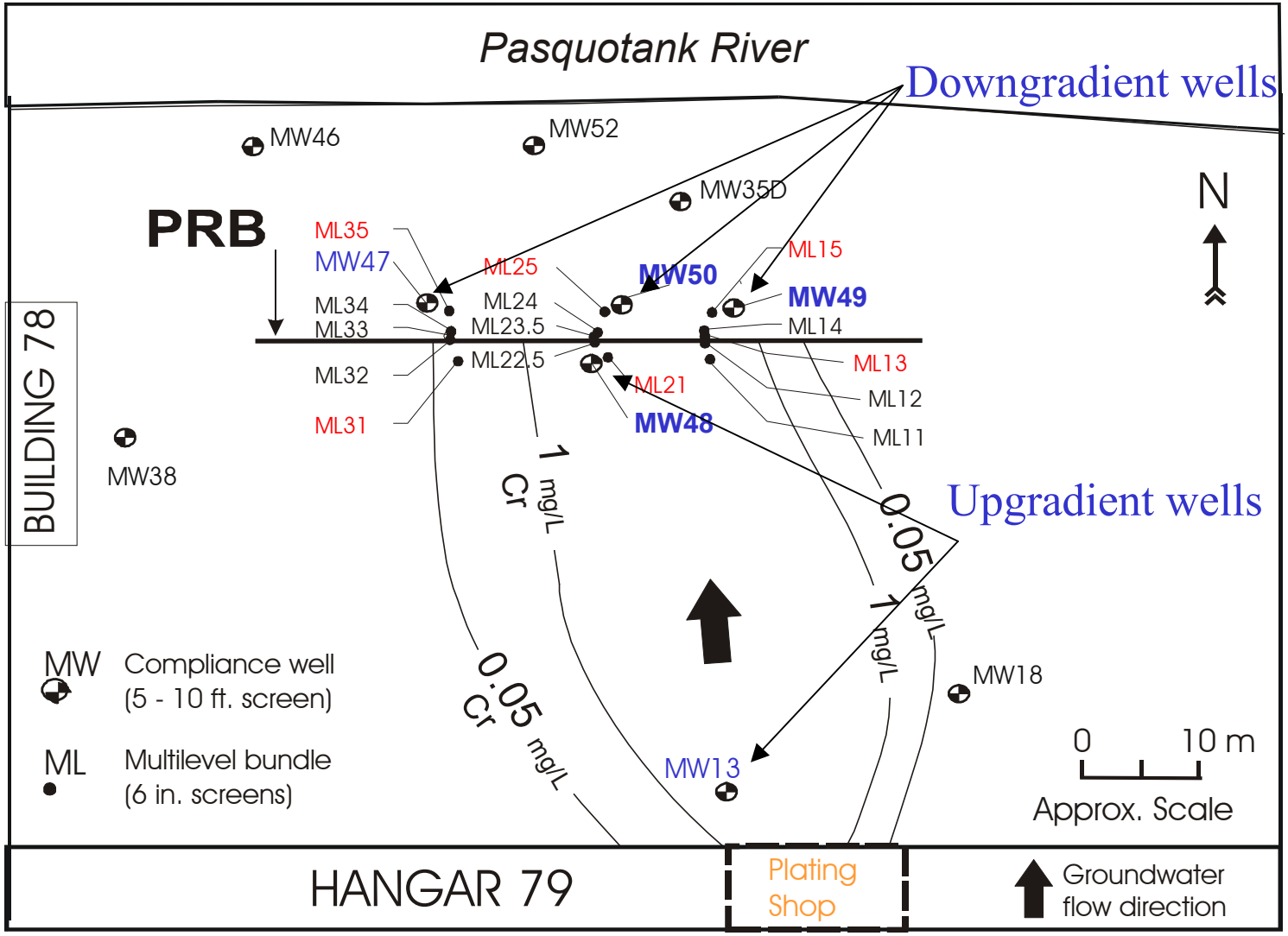
Long-Term Performance Monitoring of Zero-valent Iron PRBs

- U.S. Coast Guard Support Center, Elizabeth City, NC
  (June 96; Peerless iron, Continuous Wall; Cr+VOCs)
- Denver Federal Center, Lakewood, CO
  (Nov 96; Peerless iron, Funnel-and-Gate; VOCs)

Evaluate:

- Contaminant behavior
- Groundwater geochemistry
- Mineral precipitates
- Microbial community characterization
- Hydraulic performance

Elizabeth City USCG Site



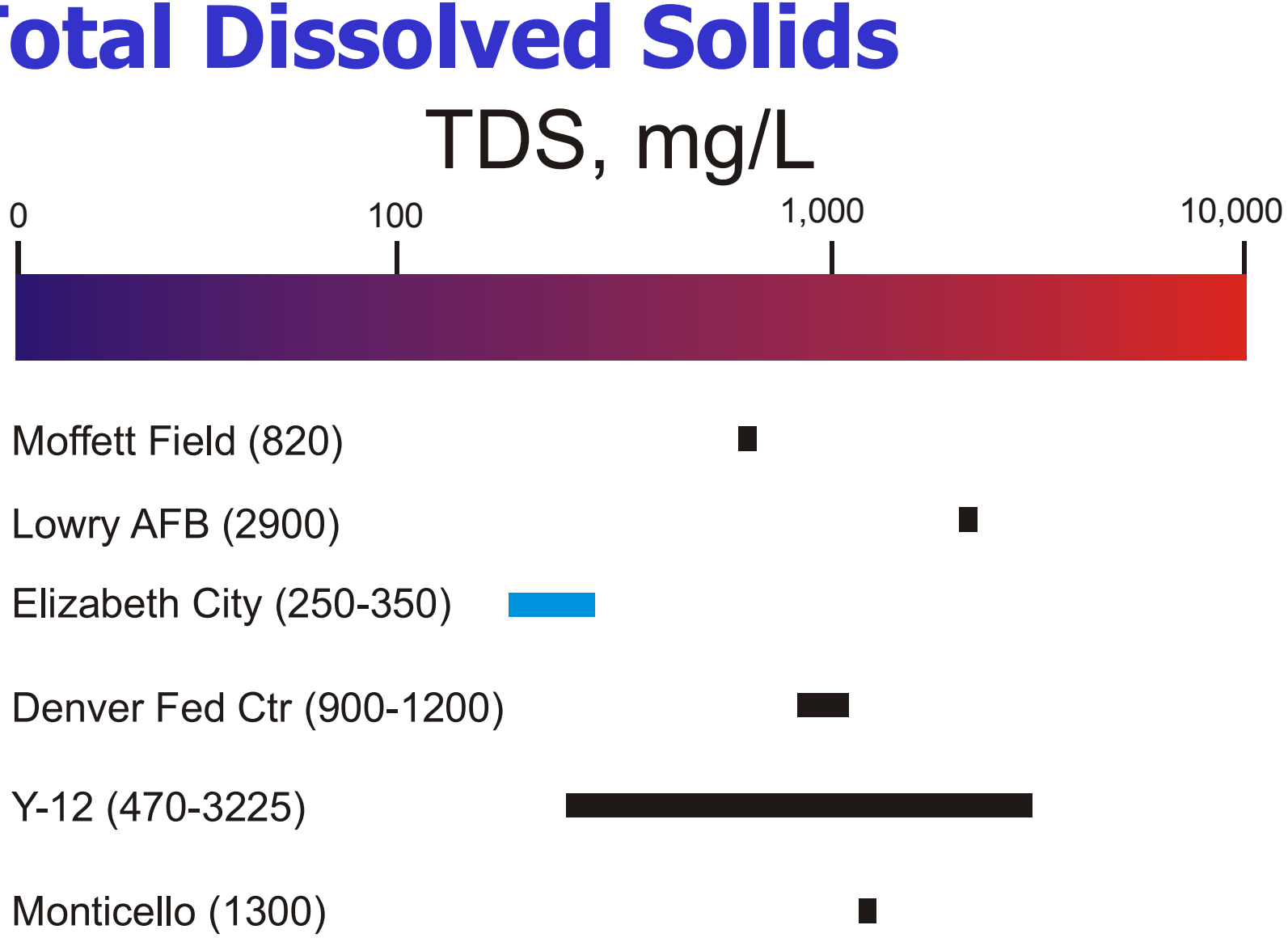
Performance Summary

- Consistent degradation of contaminants over 6+ y
- Cr completely removed, never above MCL in any downgradient sampling points
- The PRB has achieved containment of chrome plating shop plume (source area now being addressed)
- Organic compounds removed to less than MCL in most sampling points most of the time
- Multiple sources of chlorinated organic compounds at the site

Groundwater sampling

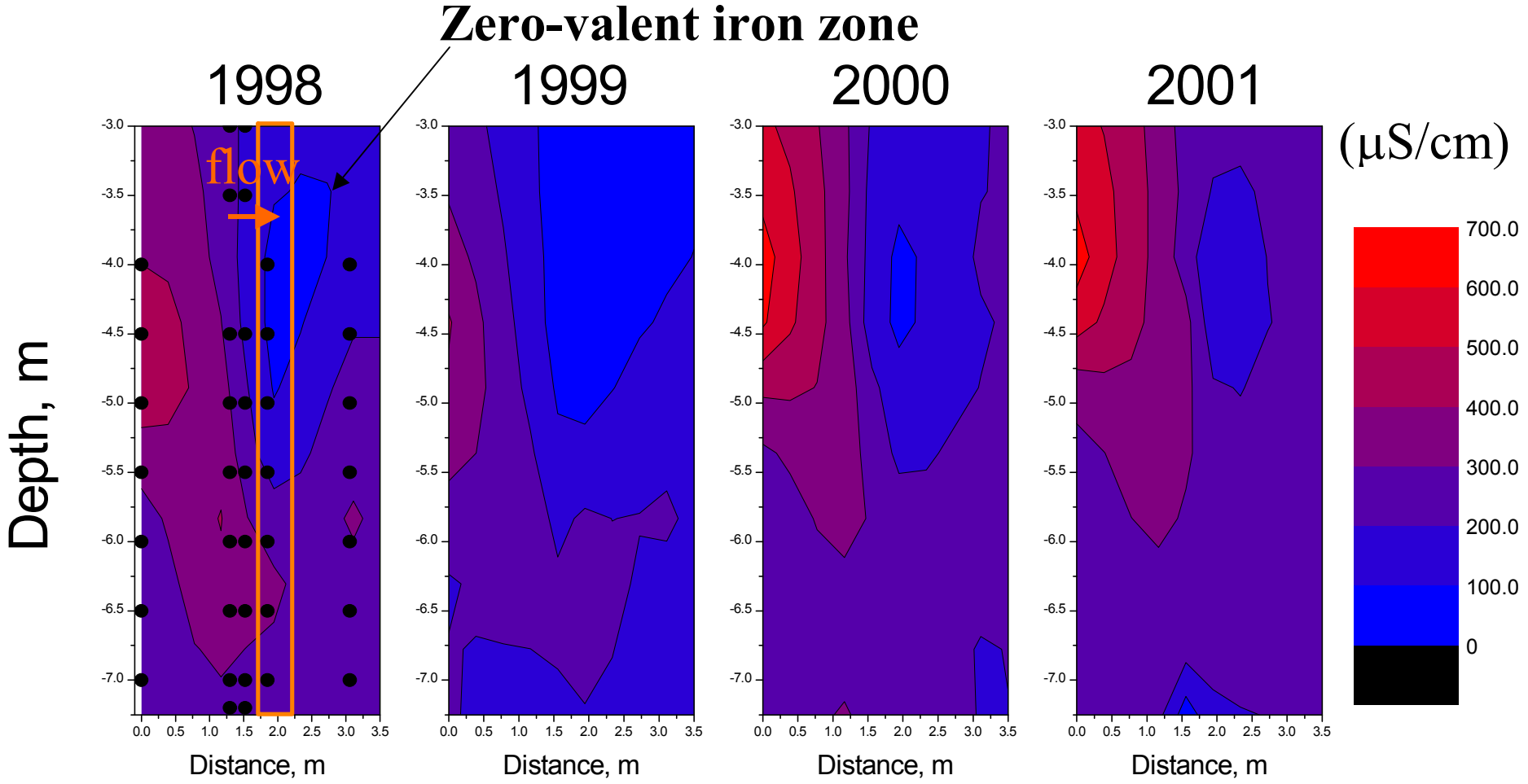
Soil core sampling

Total Dissolved Solids



Data source: Tri-Agency PRB Initiative, Combined report

Elizabeth City – Spec. Cond.



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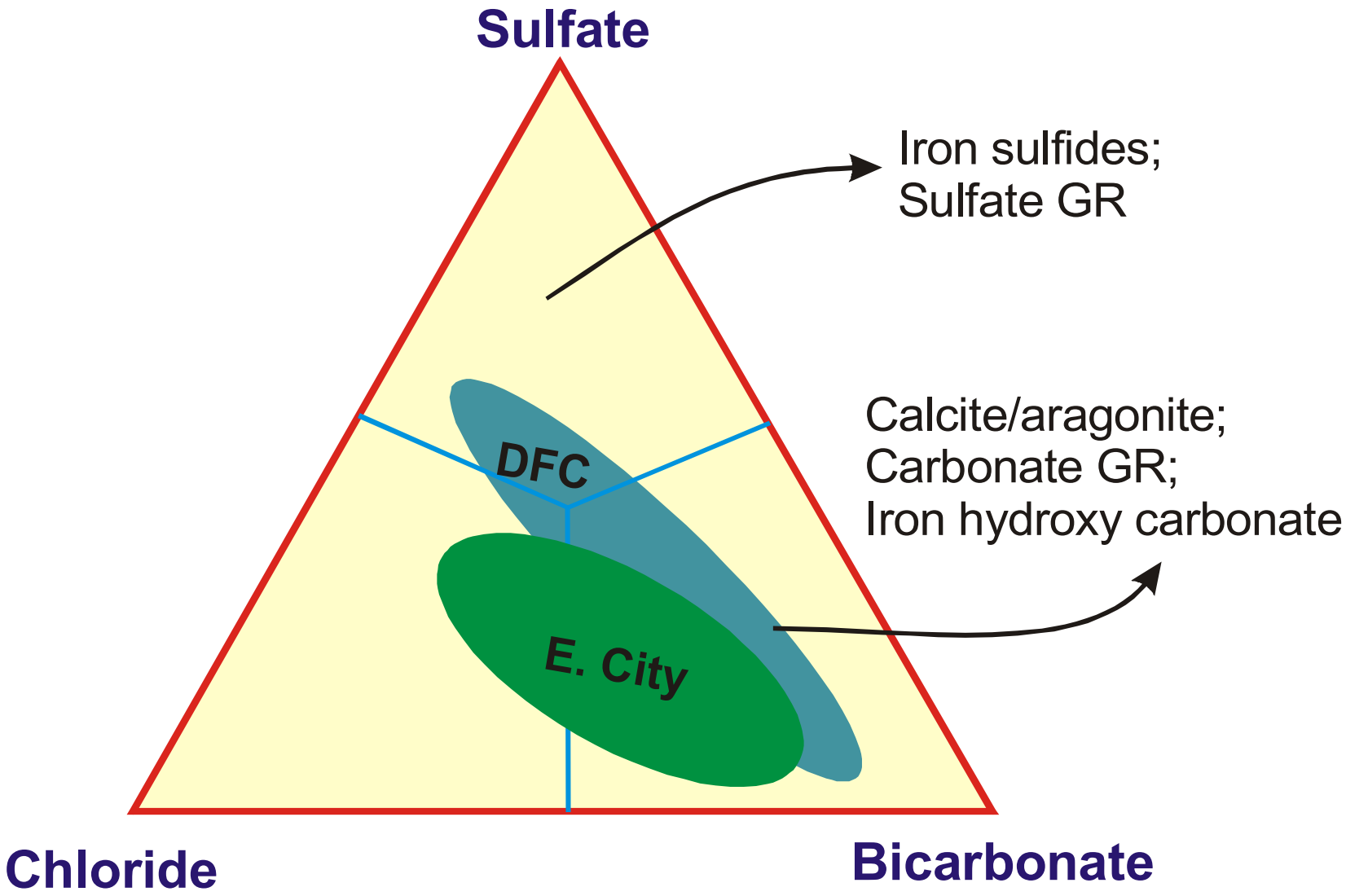
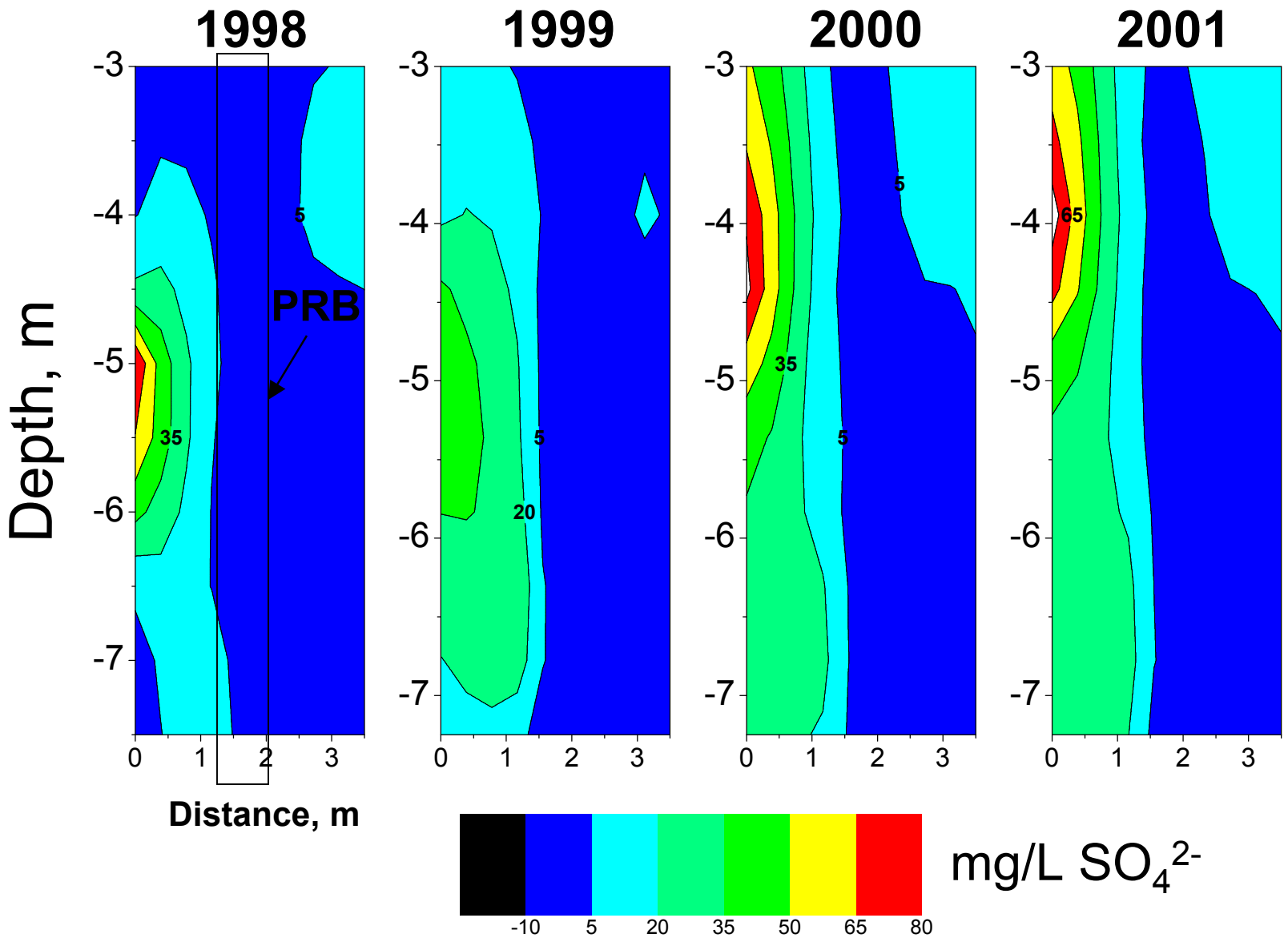
Anionic composition



Sulfate



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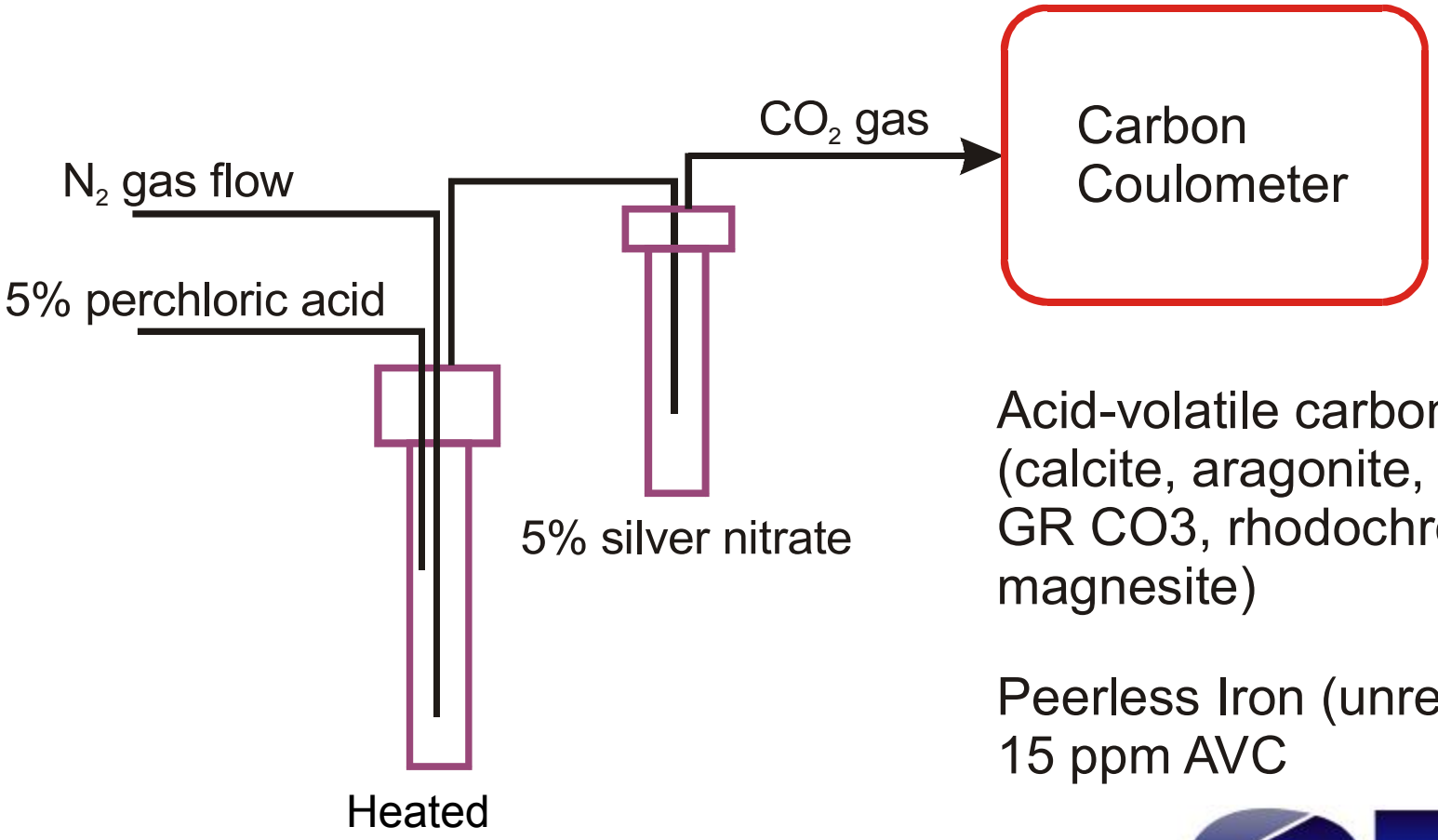
Core Analysis Methods

❖Tools

- SEM-EDS
- Reflected-light microscopy
- Transmission Electron microscopy (TEM)
- XPS (x-ray photoelectron spectroscopy)
- XRD (x-ray diffraction)
- Inorganic carbon analysis/Sulfur analysis/$\delta^{34}S$
- Microbial assays

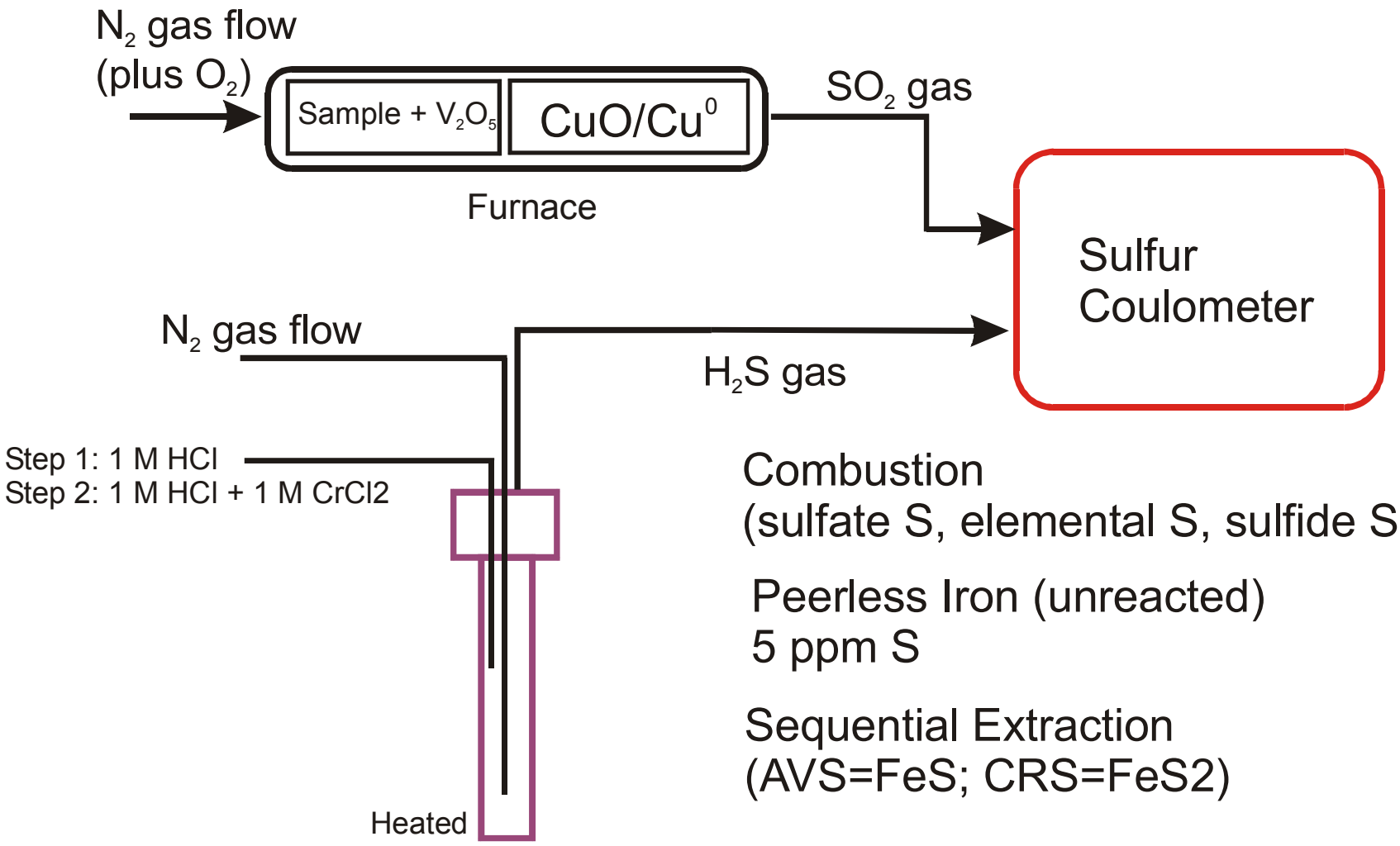
Inorganic Carbon Analysis



Acid-volatile carbon (calcite, aragonite, siderite, GR CO3, rhodochrosite, magnesite)

Peerless Iron (unreacted) 15 ppm AVC

Sulfur Analysis

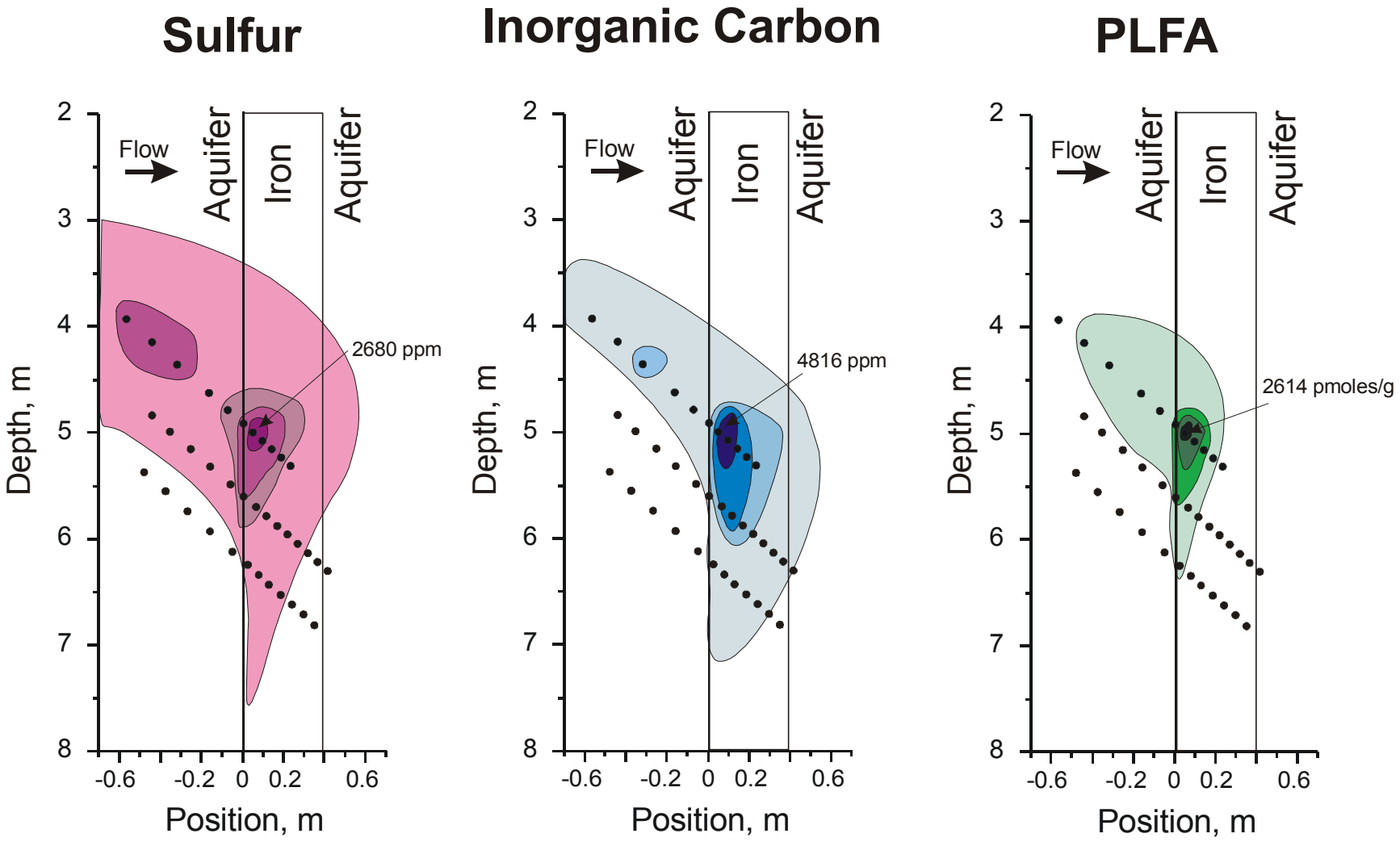


Combustion
(sulfate S, elemental S, sulfide S)

Peerless Iron (unreacted)
5 ppm S

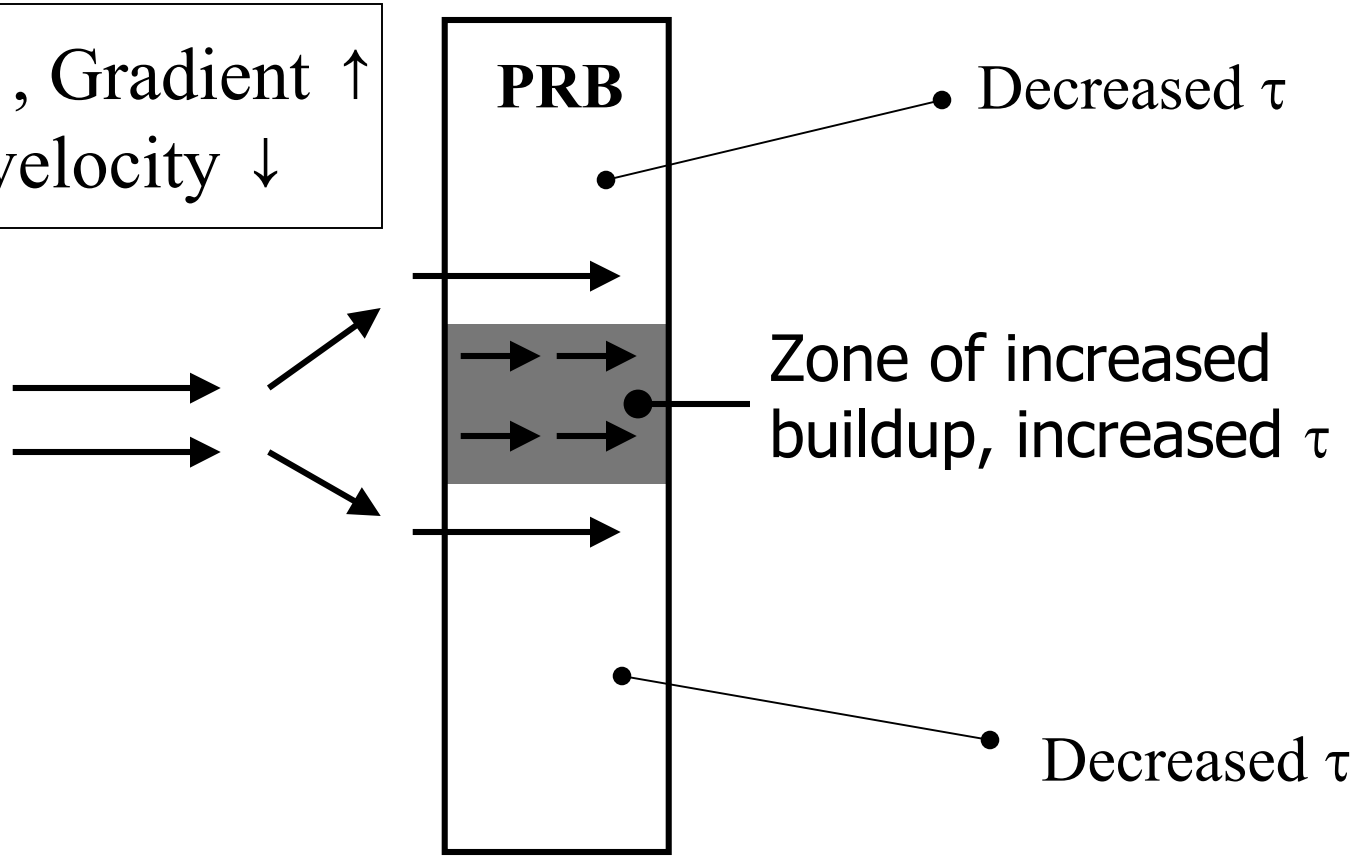
Sequential Extraction
(AVS=FeS; CRS=FeS2)

Mineral/Biomass Accumulation – E. City

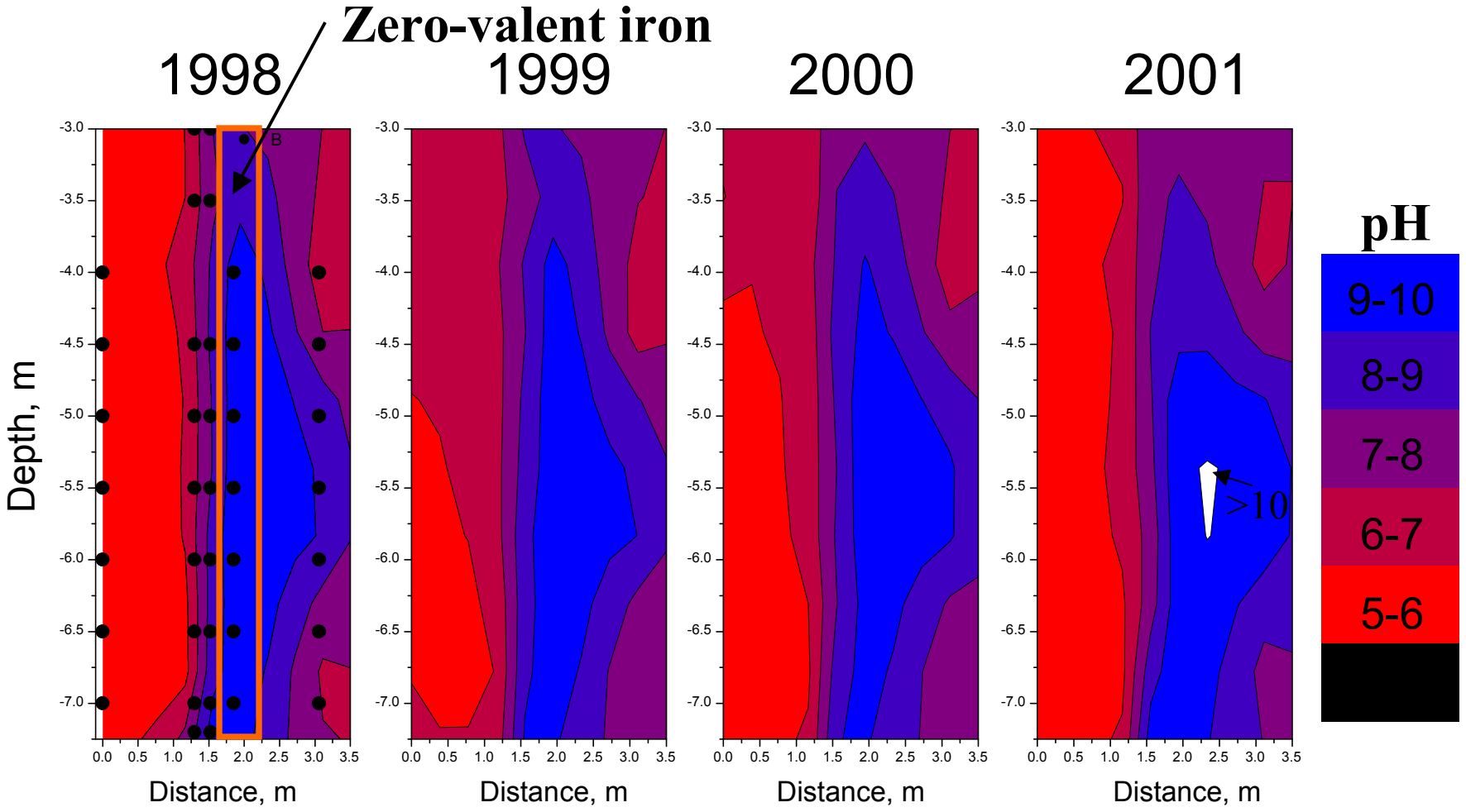


Impact of Mineral and Biomass Accumulation: Hydrology and Contaminant Residence Time

$\rho_e \downarrow$, K $\downarrow$, Gradient $\uparrow$
Seepage velocity $\downarrow$



Elizabeth City – pH



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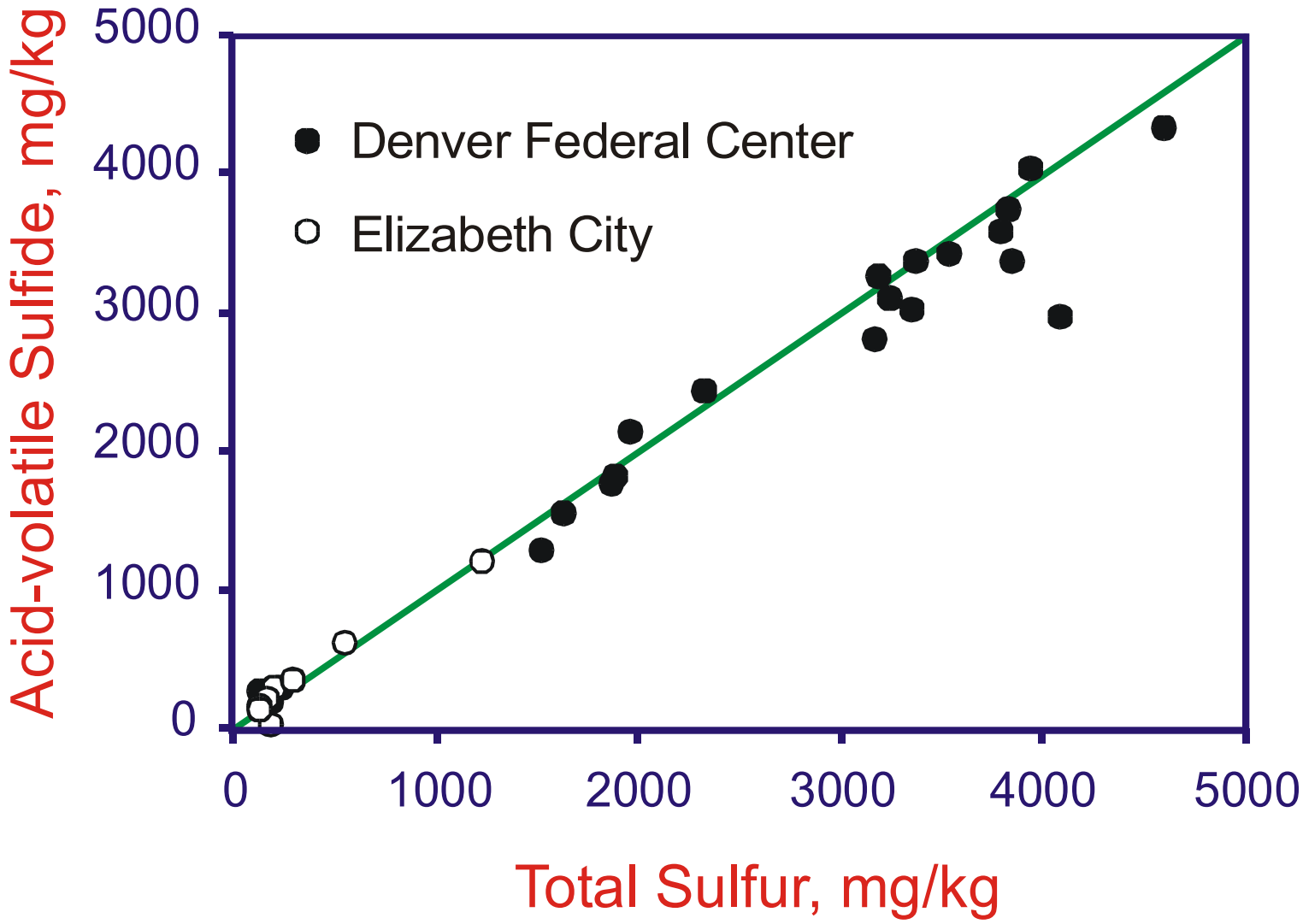
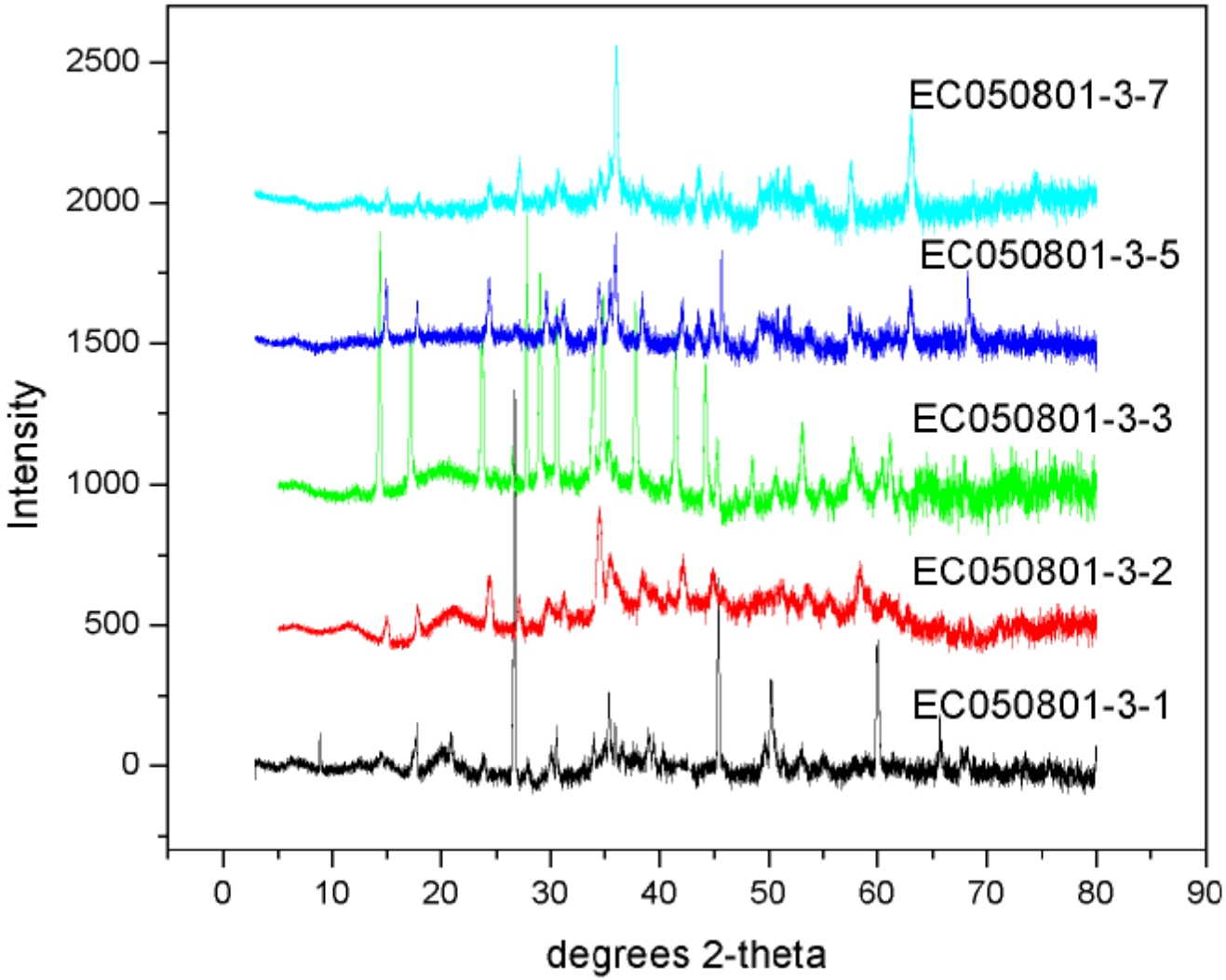
Total S vs AVS



X-Ray Diffraction



FeS weak

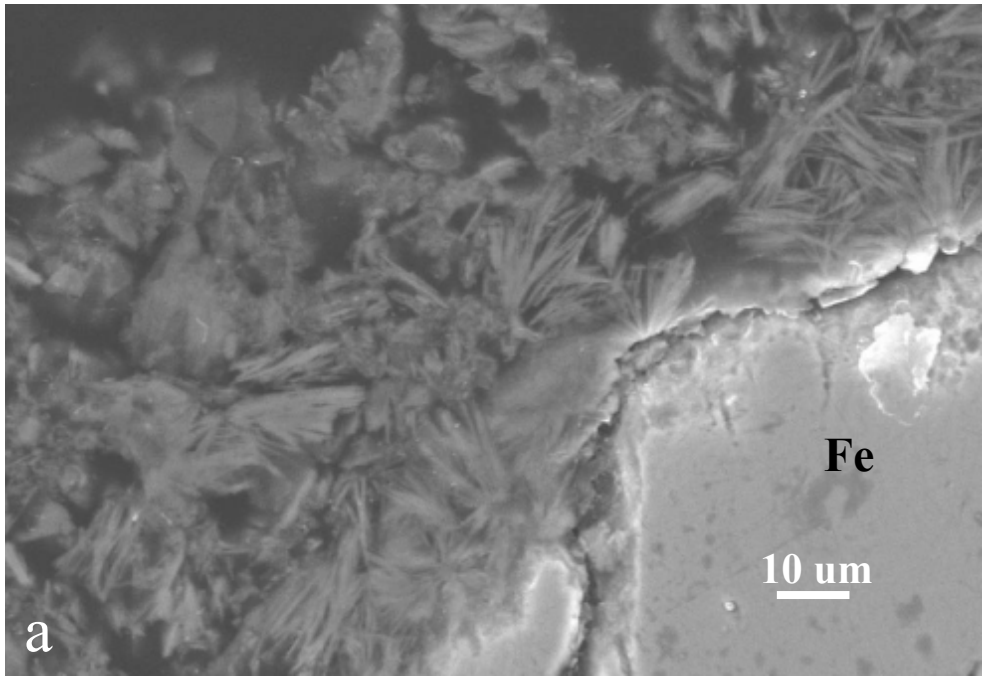
Aragonite weak

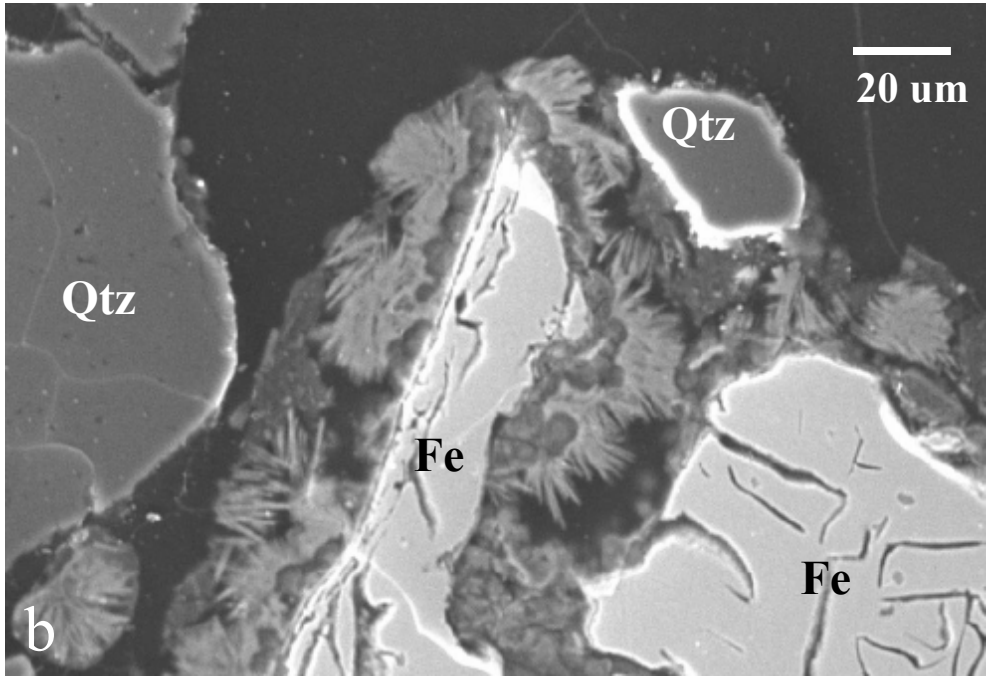
Magnetite strong

Siderite absent

Fe-OH-CO3 strong

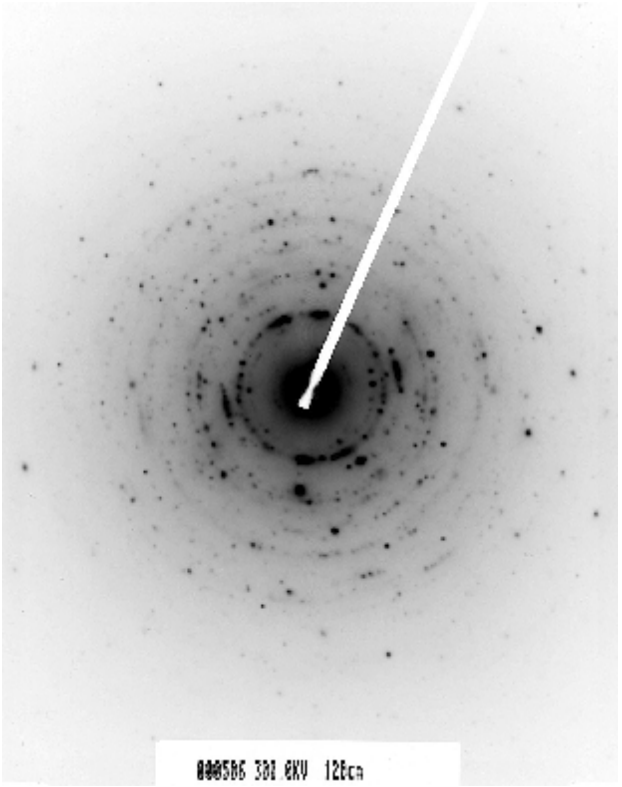
GRCO3 present



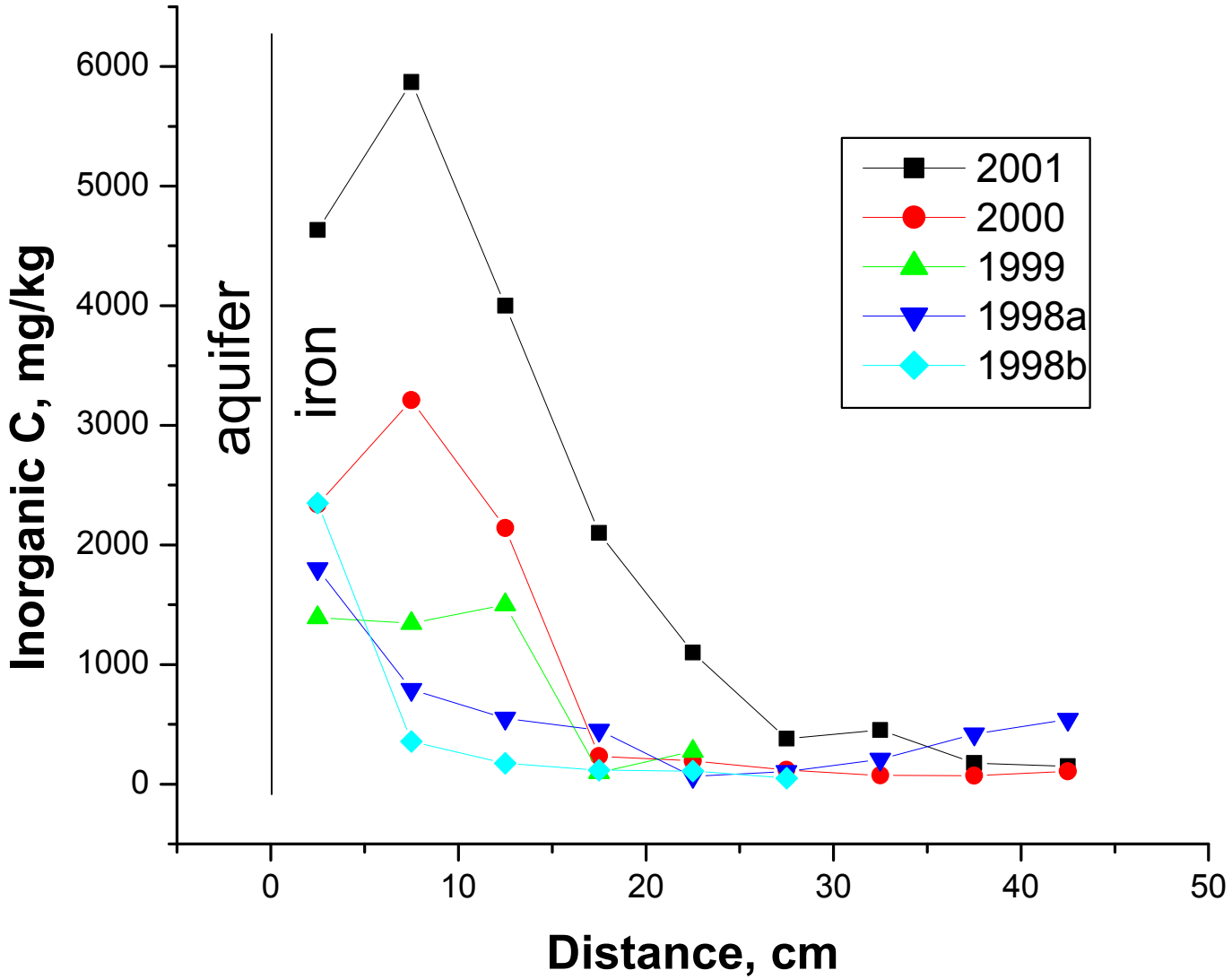


SEM/TEM

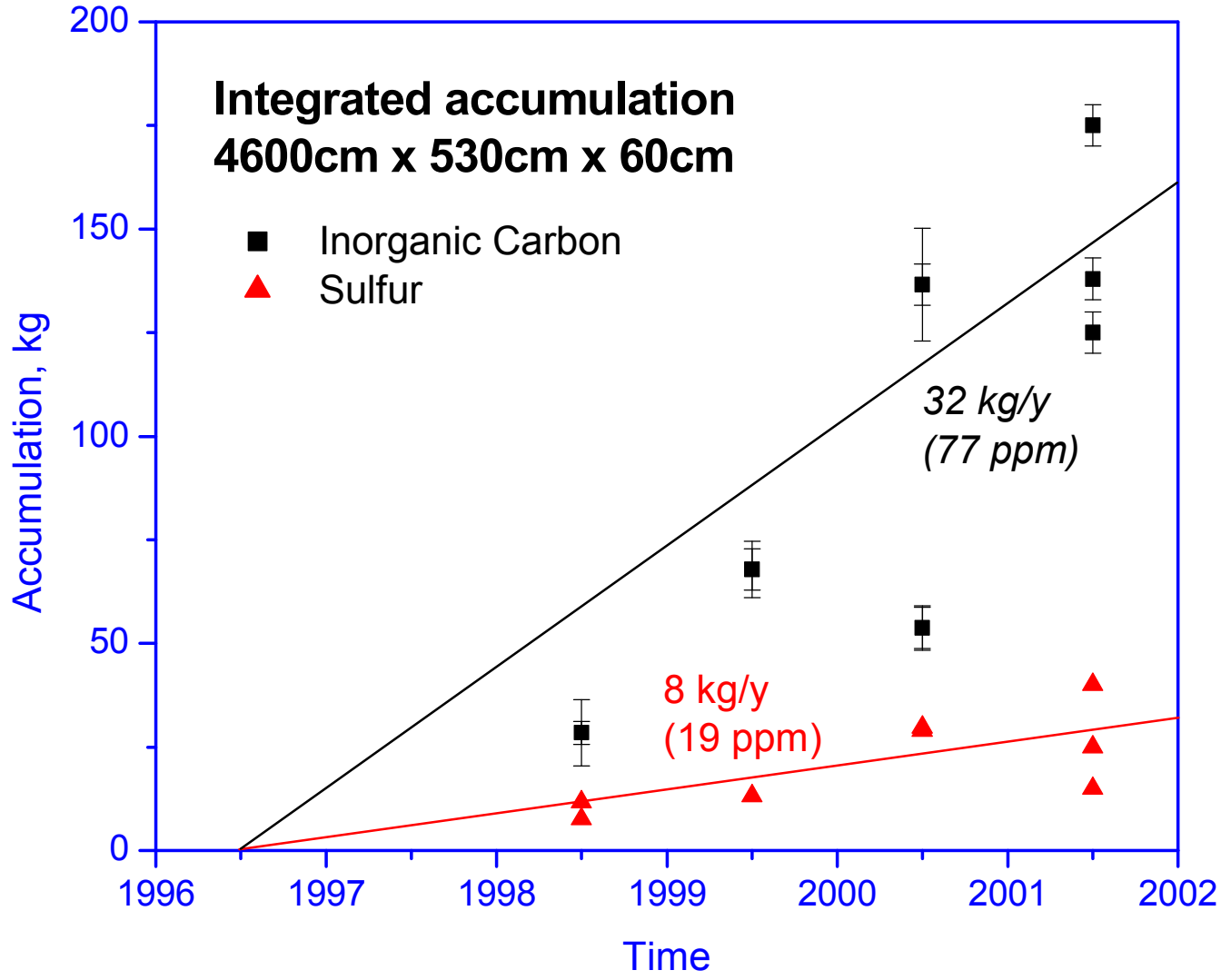
Furukawa and Wilkin (2002) ES&T, in press



Inorganic C with time

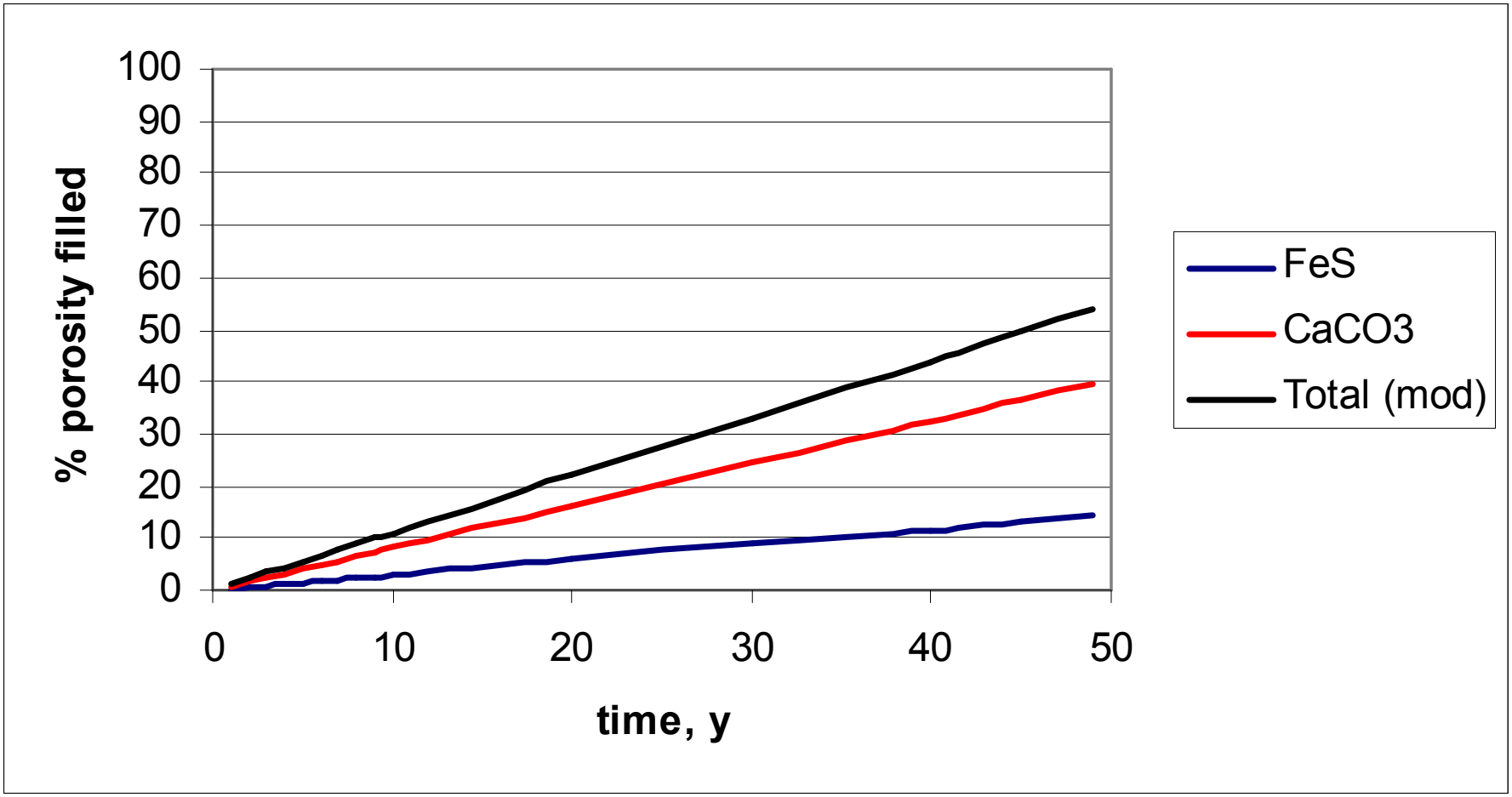


Mass Accumulation – E. City



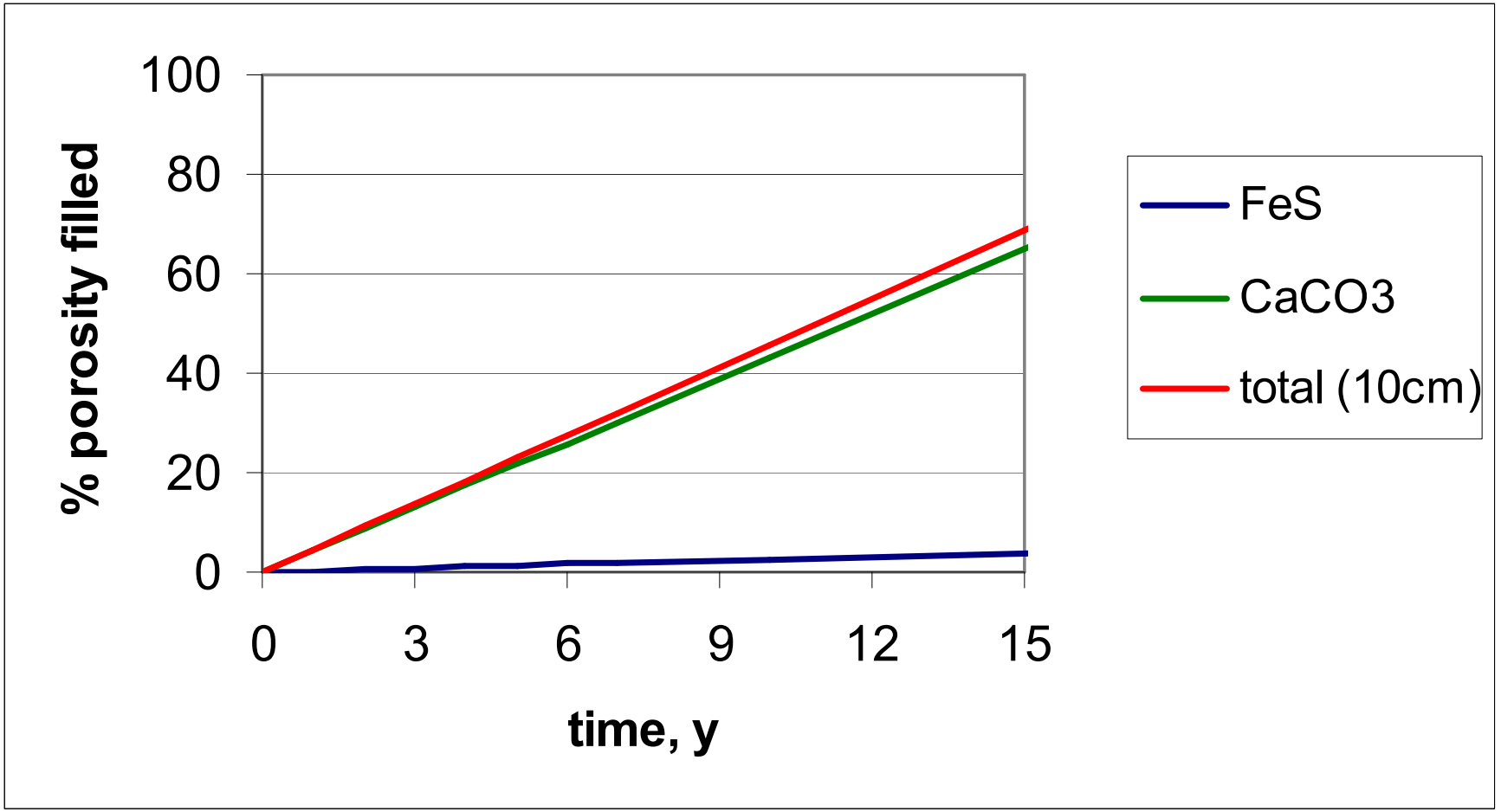
Porosity loss – Elizabeth City

Assume all ppt in front 10 cm, initial porosity = 50%



Porosity loss - DFC

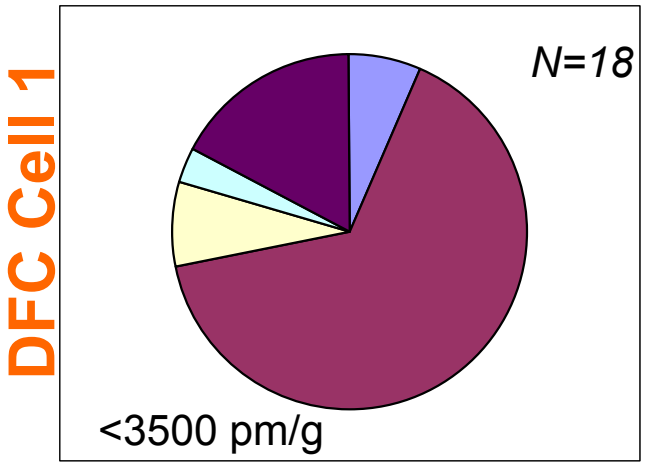
Assume all ppt in front 10 cm, initial porosity = 50%

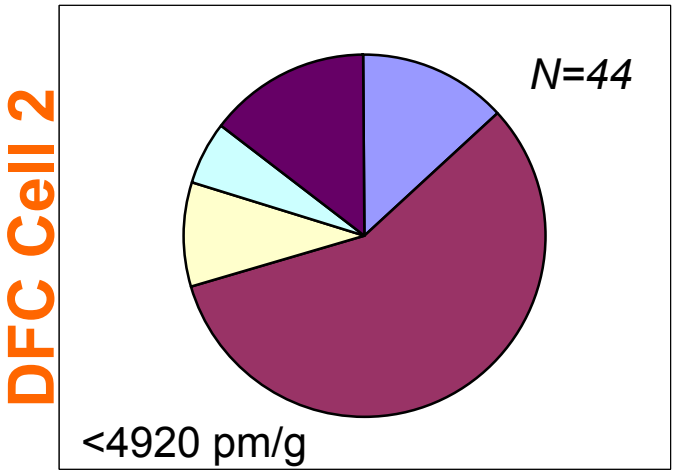


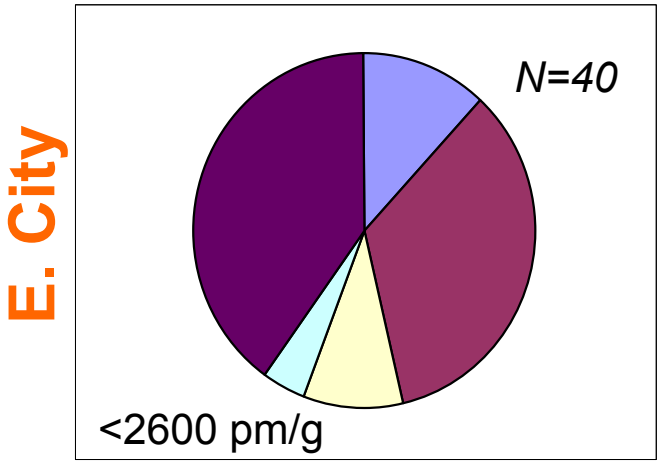
Pore loss estimations

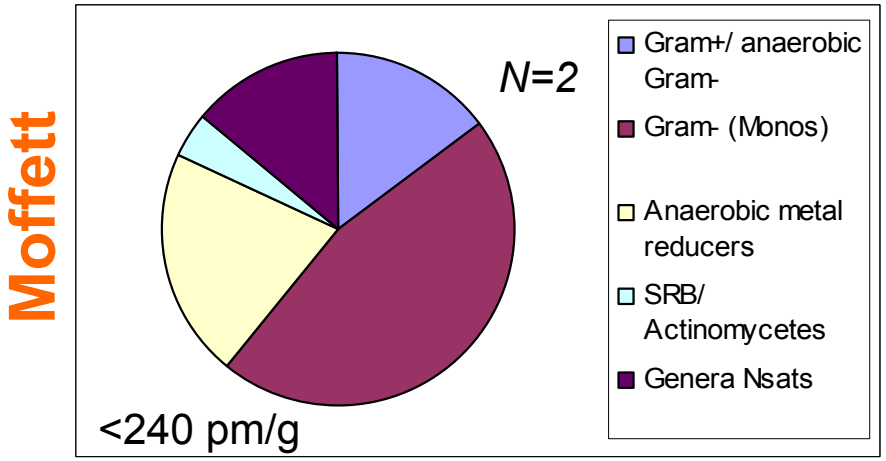
- Flow rate (flux in)
- Sulfate concentration/removal efficiency
- Bicarbonate concentration/removal efficiency
- Initial PRB porosity
- Iron corrosion (pore volume gain), oxidation (loss)
- Mineral molar volumes

Microbial Biomass – PLFA Dist.









From Gavaskar et al., 2002

Long-term performance: Overview

- Consistent degradation of contaminants over 6 y
- Spatial heterogeneity of mineral and biomass accumulation
- Buildup correlated to GW chemistry (TDS) and flow rate
- Fe^0 is long-term sink for C, S, Ca, Si, N, Mg, +/- Mn
  (mass balance on C & S)
- Porosity loss rate from 1 to 4% per y of original available V

Long-term performance: Overview - cont

- Reactive transport codes – data gaps
- Vertically resolved hydro/geochem data needed during site characterization
- Correlation between declining performance and changing geochemical parameters not evident after 6 y