Evaluating Effects of Mineral Fouling on the Long-Term Performance of Permeable Reactive Barriers

by

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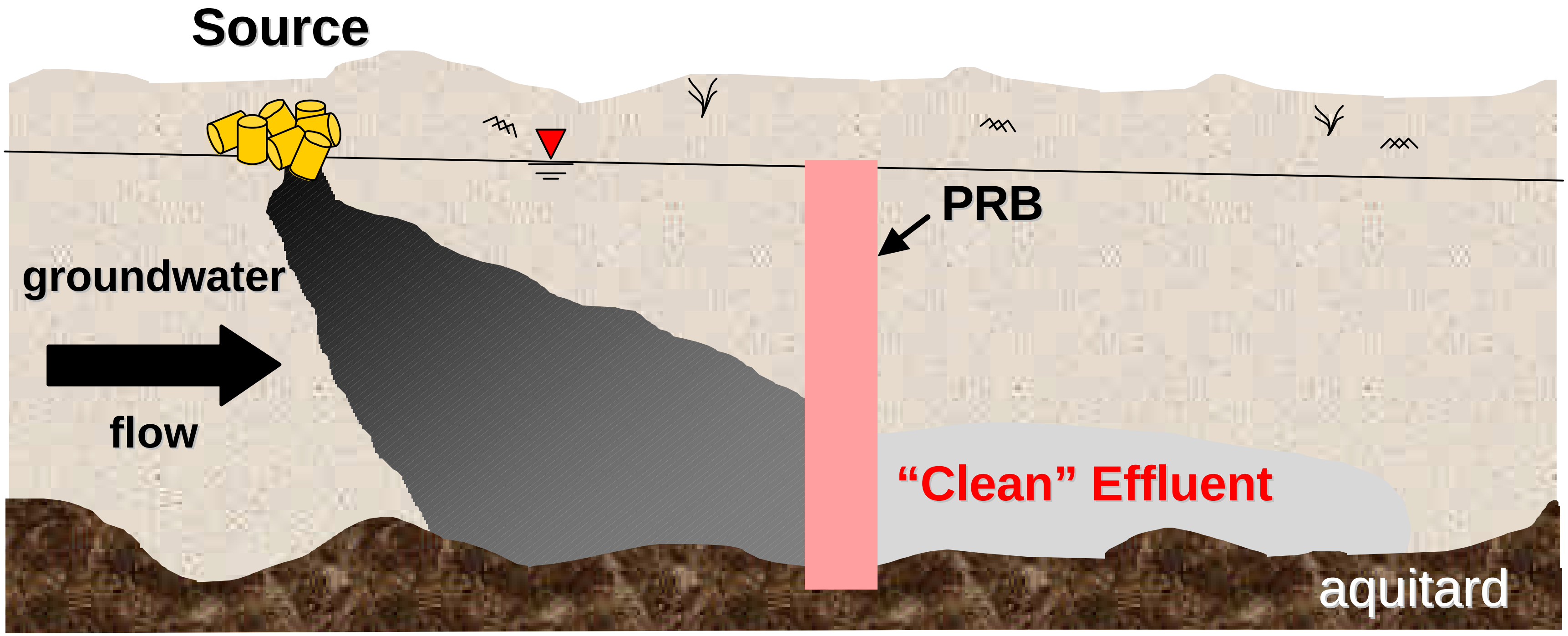


Effectiveness of PRB depends on:

- ability for water to flow through the wall
- adequate reactivity
- adequate residence time

Issues

- **Mineral fouling is a key concern in long-term performance of PRBs**
  - Mineral precipitation occurring as a result of changes in geochemistry due to iron corrosion
  - Reduces porosity, reactivity, and hydraulic conductivity of iron media in PRBs
  - Alters hydraulic characteristics, treatment ability, and life time of PRBs
- **Flow heterogeneity causes unpredictable fouling in PRBs**

Objectives

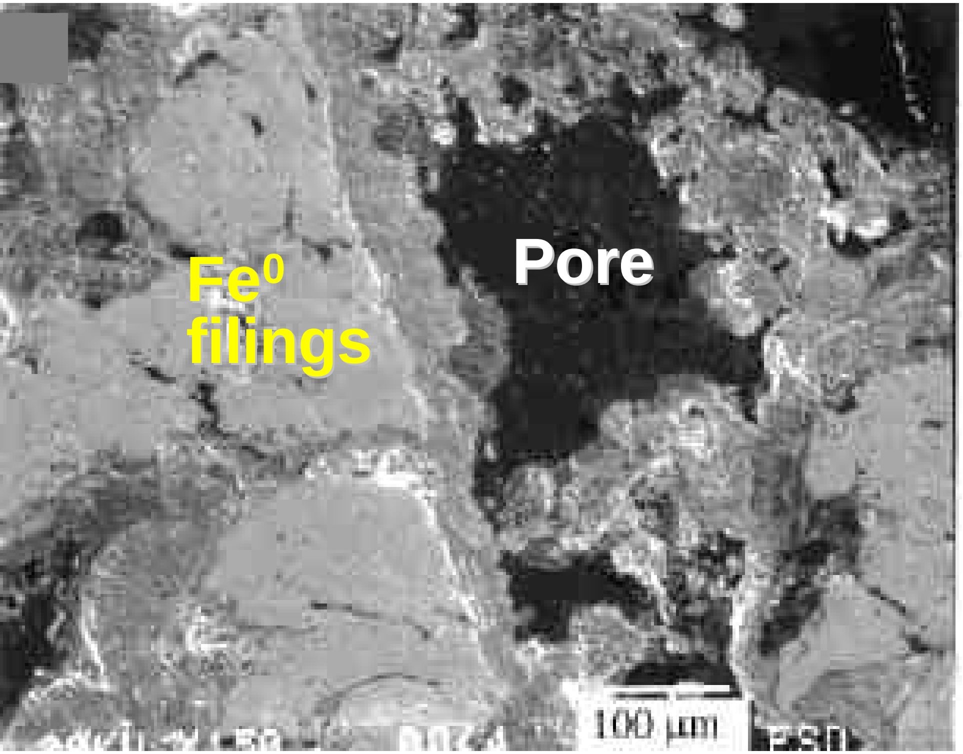
- Estimate the degree of fouling that will occur in PRBs located in realistic heterogeneous aquifers
- Evaluate how fouling is influenced by flow heterogeneity
- Evaluate impact of fouling on long-term hydraulic performance of PRBs

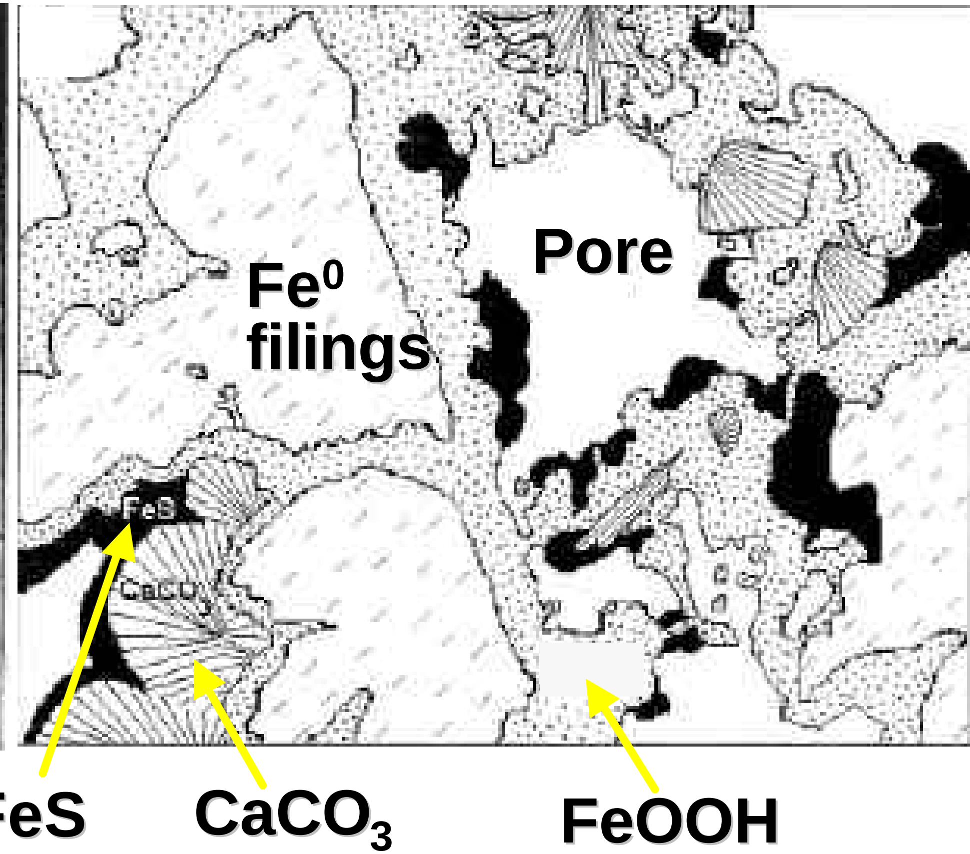
Mineral Precipitates

- **Minerals typically found in PRBs**
  - Iron oxyhydroxides: **FeOOH**
  - Iron oxides: **magnetite (Fe_3O_4), ferrous hydroxide ($Fe(OH)_2$), ferric hydroxide ($Fe(OH)_3$)**
  - Carbonates: **aragonite ($CaCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$), dolomite ($CaMg(CO_3)_2$)**
  - Others: **ferrous sulfide (FeS), brucite ($Mg(OH)_2$), green rust**
- **Crystalline & amorphous mineral formation**

Mineral Precipitates in PRB at Oak Ridge, TN

After 15 mos. operation, as reported Philips et al. (2000)

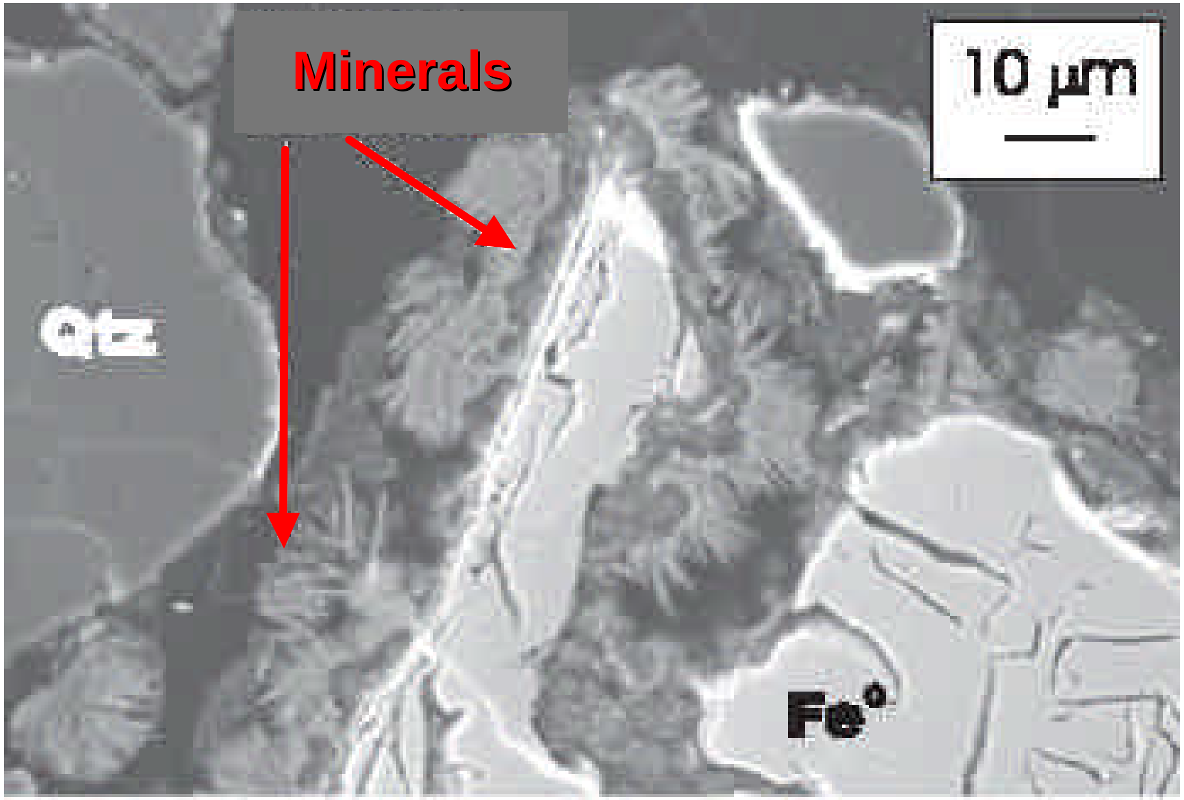




Porosity reduction of 0.02-0.20 per year (Sarr 2001)

Mineral Precipitates in Iron Media:

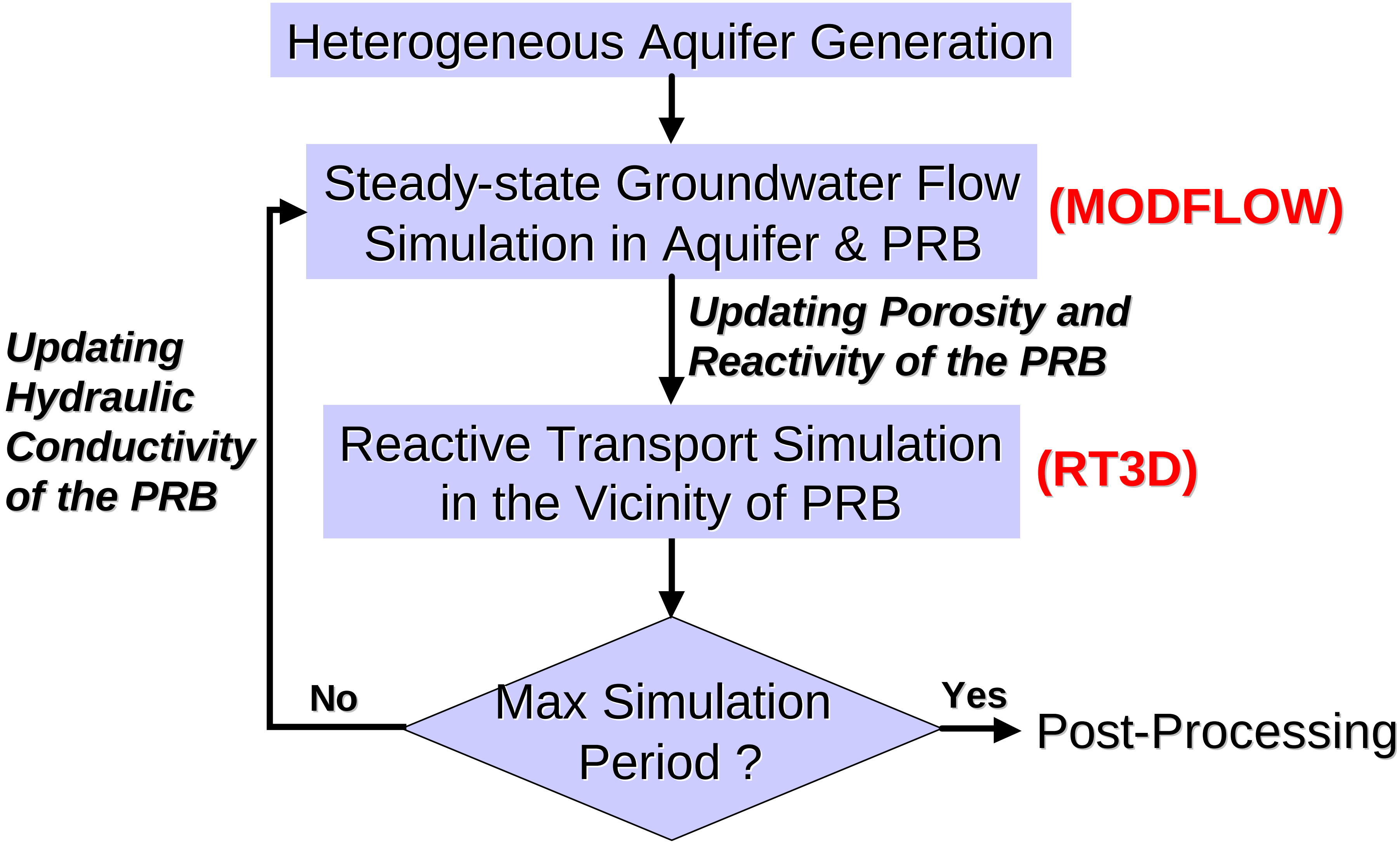
After 4 years of operation - PRB at Elizabeth City, NC,
Wilkin et al. (2002)



Approach

- Simulate flow, transport, & geochemical reactions in realistic heterogeneous aquifers using numerical models
- MODFLOW – groundwater flow
- RT3D – advection, dispersion, and reactive transport (custom geochemical algorithm)

Modeling Scheme



Iron Reactions

Contaminant reduction **(ignored)**

Fe^0

Corroded by

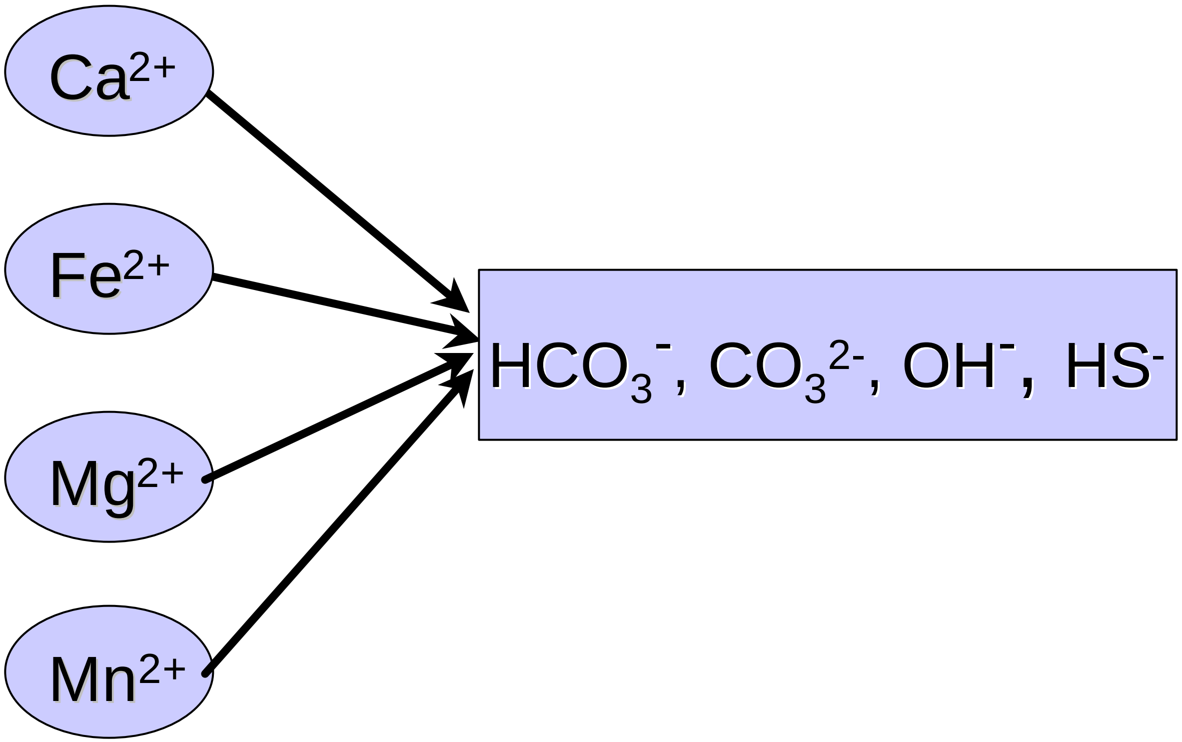
- DO
- Nitrate
- Sulfate
- Water

$OH^- \rightarrow$ pH increase

$Fe^{2+} \rightarrow$ iron precipitates

$$\mathbf{Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2(aq) + 2OH^-}$$

Mineral Precipitates



<u>9 Minerals:</u>

$CaCO_3$

$MgCO_3$

$FeCO_3$

$CaMg(CO_3)_2$

$MnCO_3$

$Fe(OH)_2$

$Mg(OH)_2$

$Mn(OH)_2$

FeS

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\,(s)$

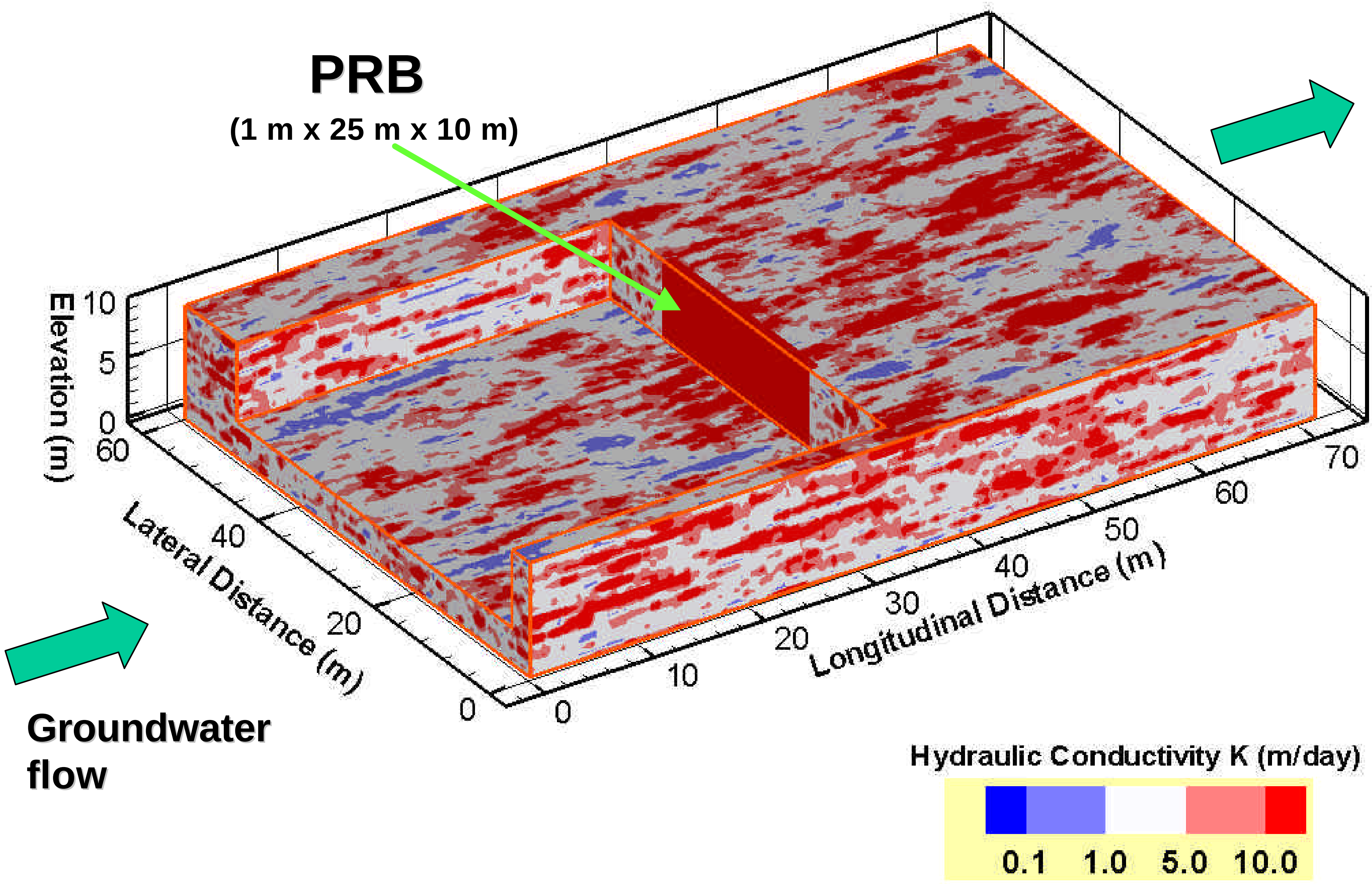
$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2\,(s)$

Reaction Kinetics

- **Iron Corrosion Rate**
  - Pseudo first-order rate law for iron corrosion by DO and NO_3^- (Mayer et al. 2001)
  - Zero-order rate law for iron corrosion by water under anaerobic conditions (Reardon 1995)
- **Mineral Precipitation Rate**
  - Reversible rate law based on transition state theory (Lasaga 1998)
- **Microbial Sulfate Reduction Rate**
  - Monod equation (Gu et al. 2002)

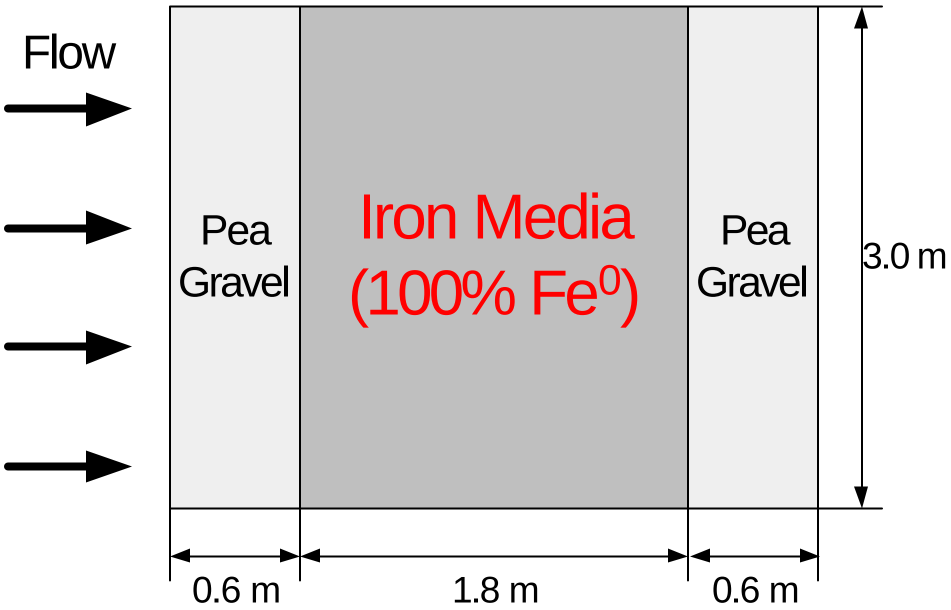
Heterogeneous Hydraulic Conductivity Field

(m_{lnK} = -10 m/s, s_{lnK} = 1, l_x = 3 m, l_y = 1 m)

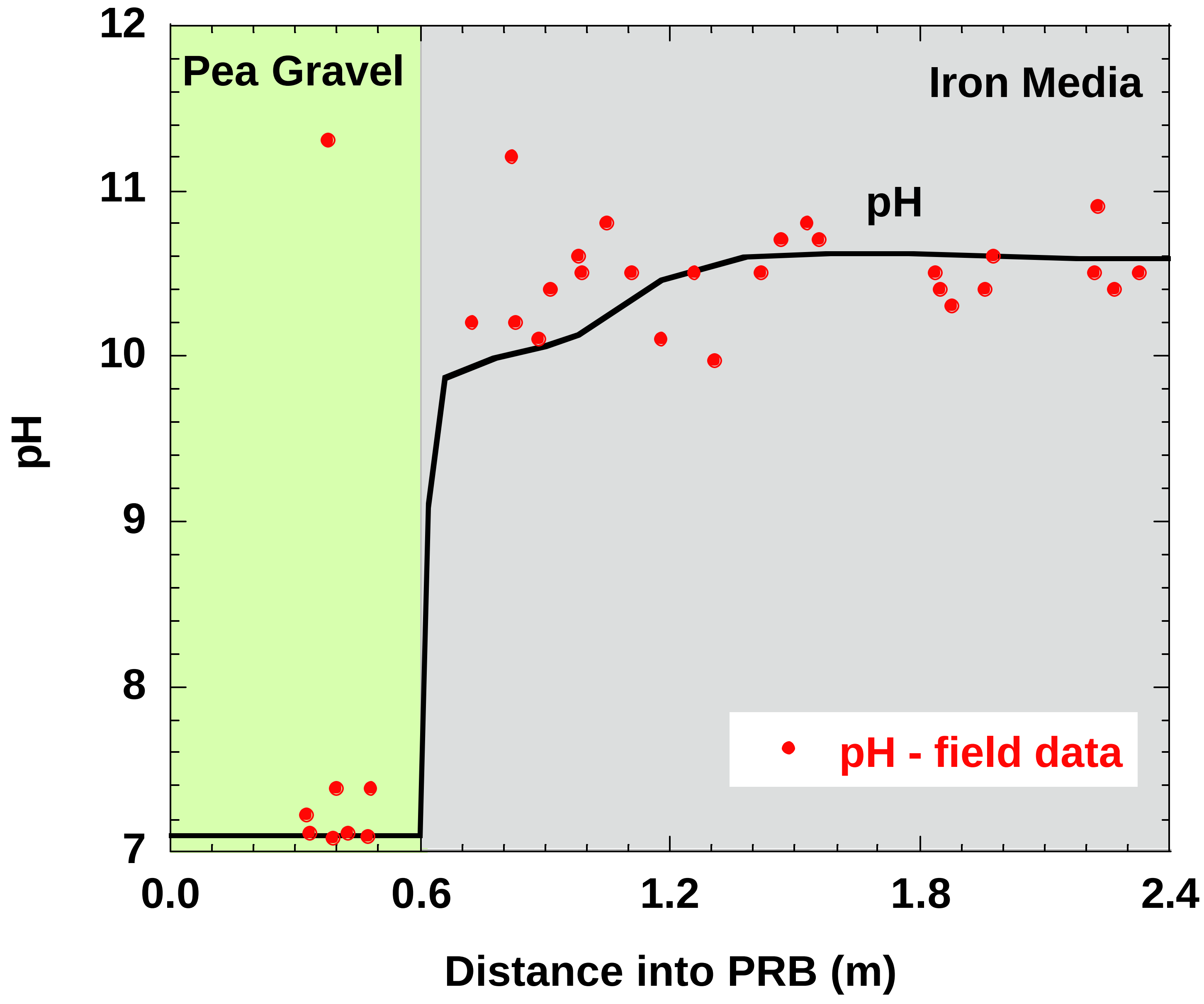


Model Validation: Moffett Field PRB

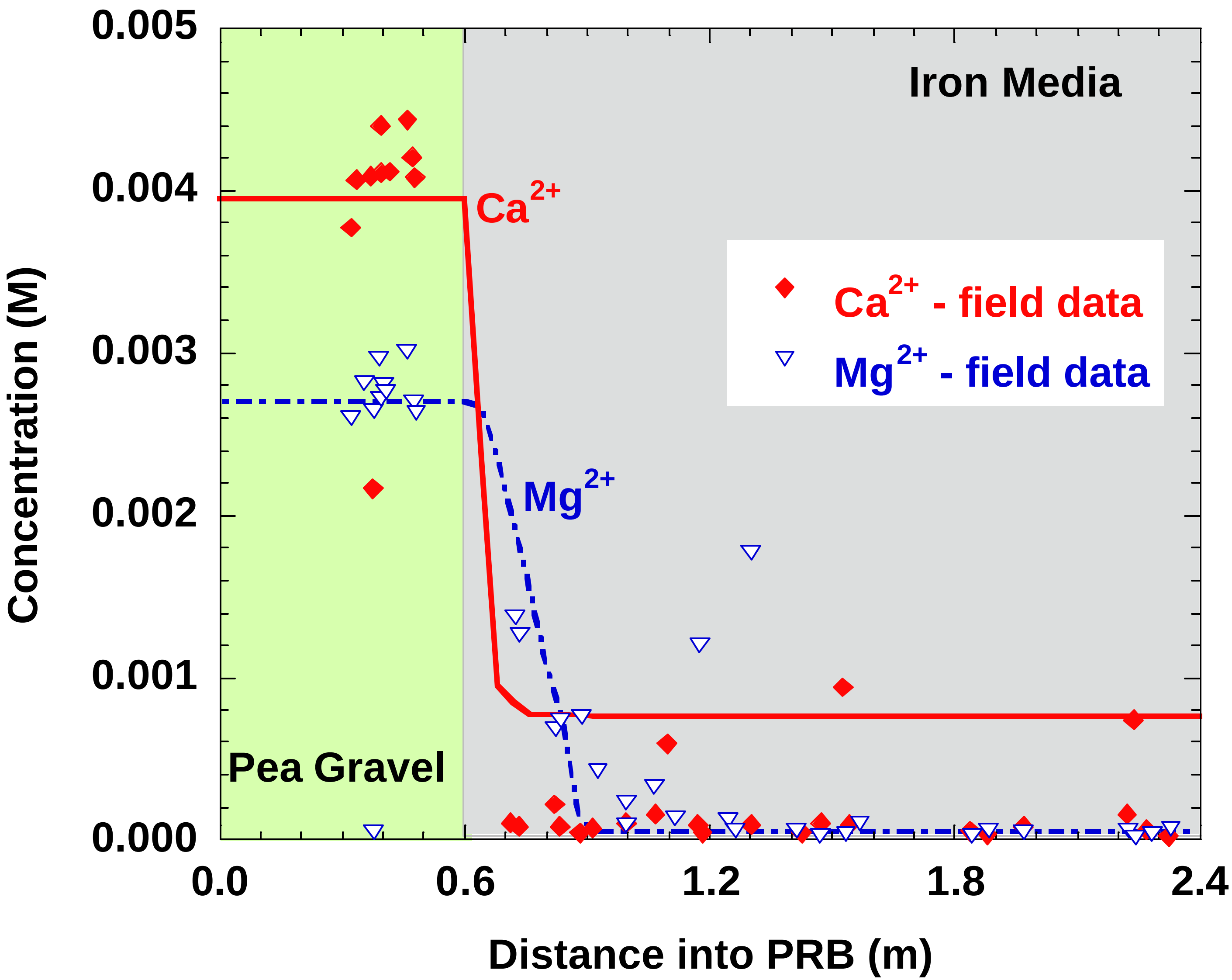
- Data from Yabusaki et al. (2001)
- PRB 3 m x 3 m x 5.5 m used to remove chlorinated solvents from groundwater
- 1D Model
- Uniform flow rate
- Geochemical modeling with OS3D by Yabusaki et al. 2001



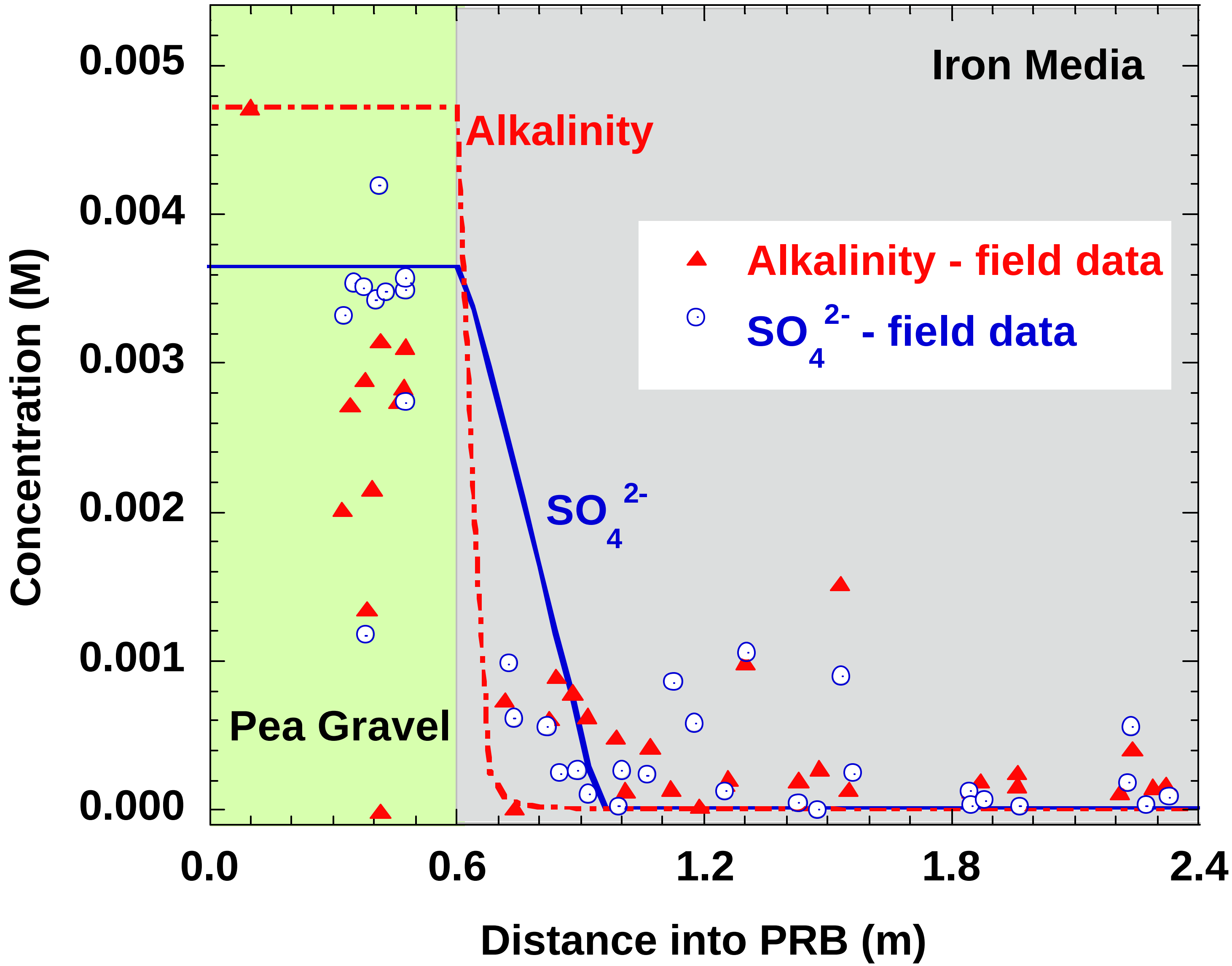
Predicted and Measured pH - Moffett Field PRB



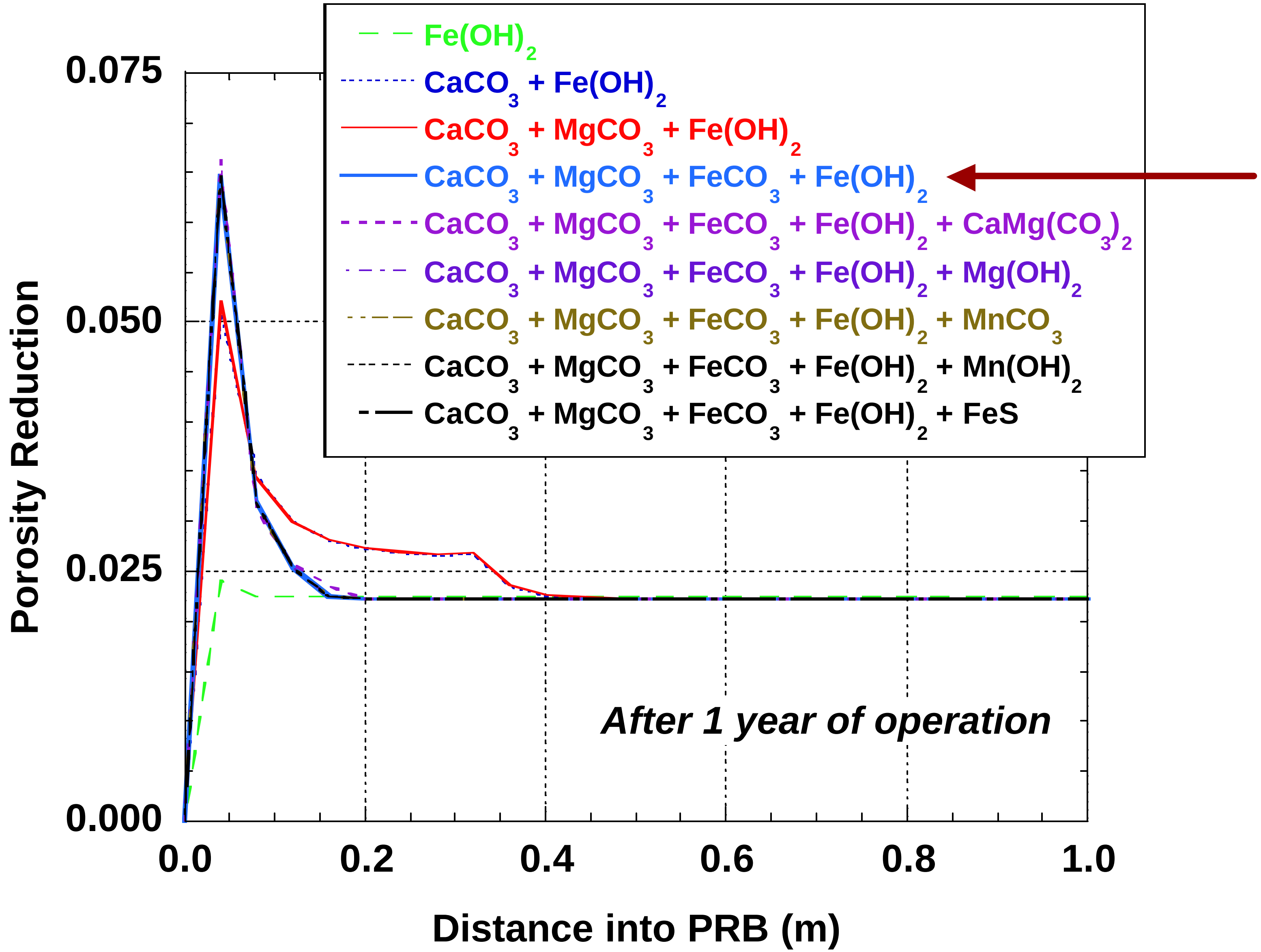
Predicted and Measured [Ca^{2+}], [Mg^{2+}] Moffett Field PRB



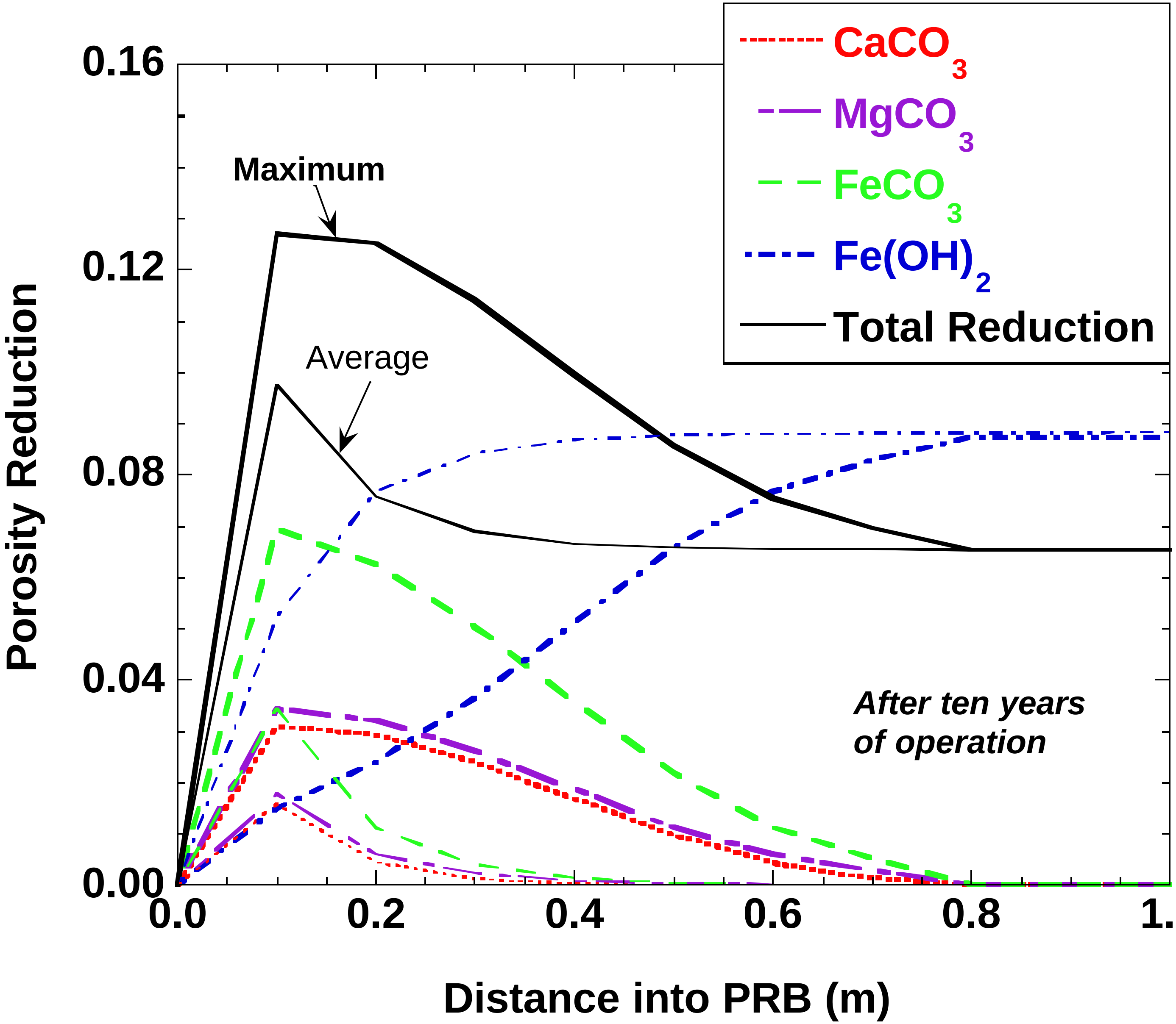
Predicted and Measured Alkalinity, [SO42-] Moffett Field PRB



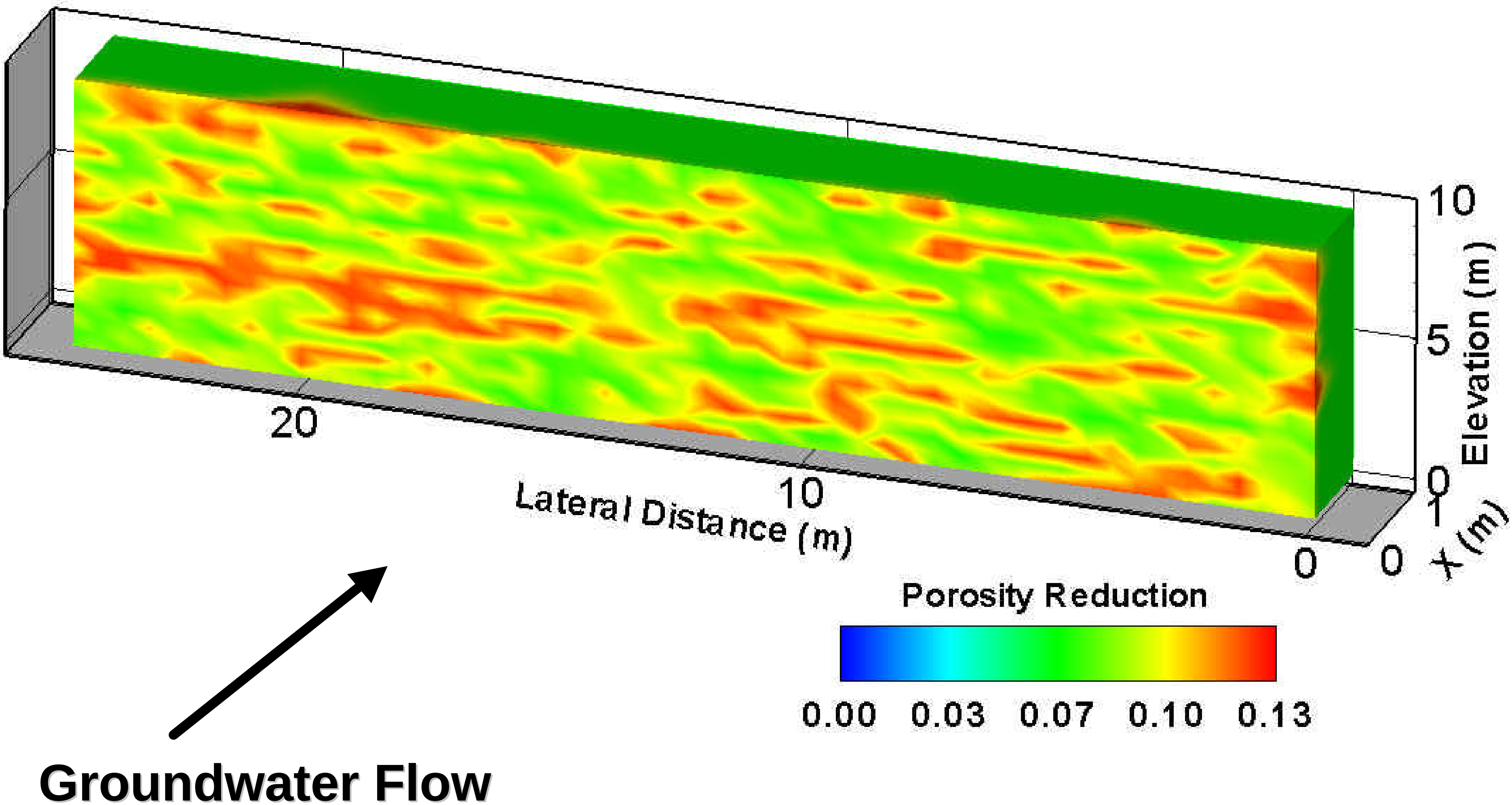
Sensitivity Analysis - Key Minerals



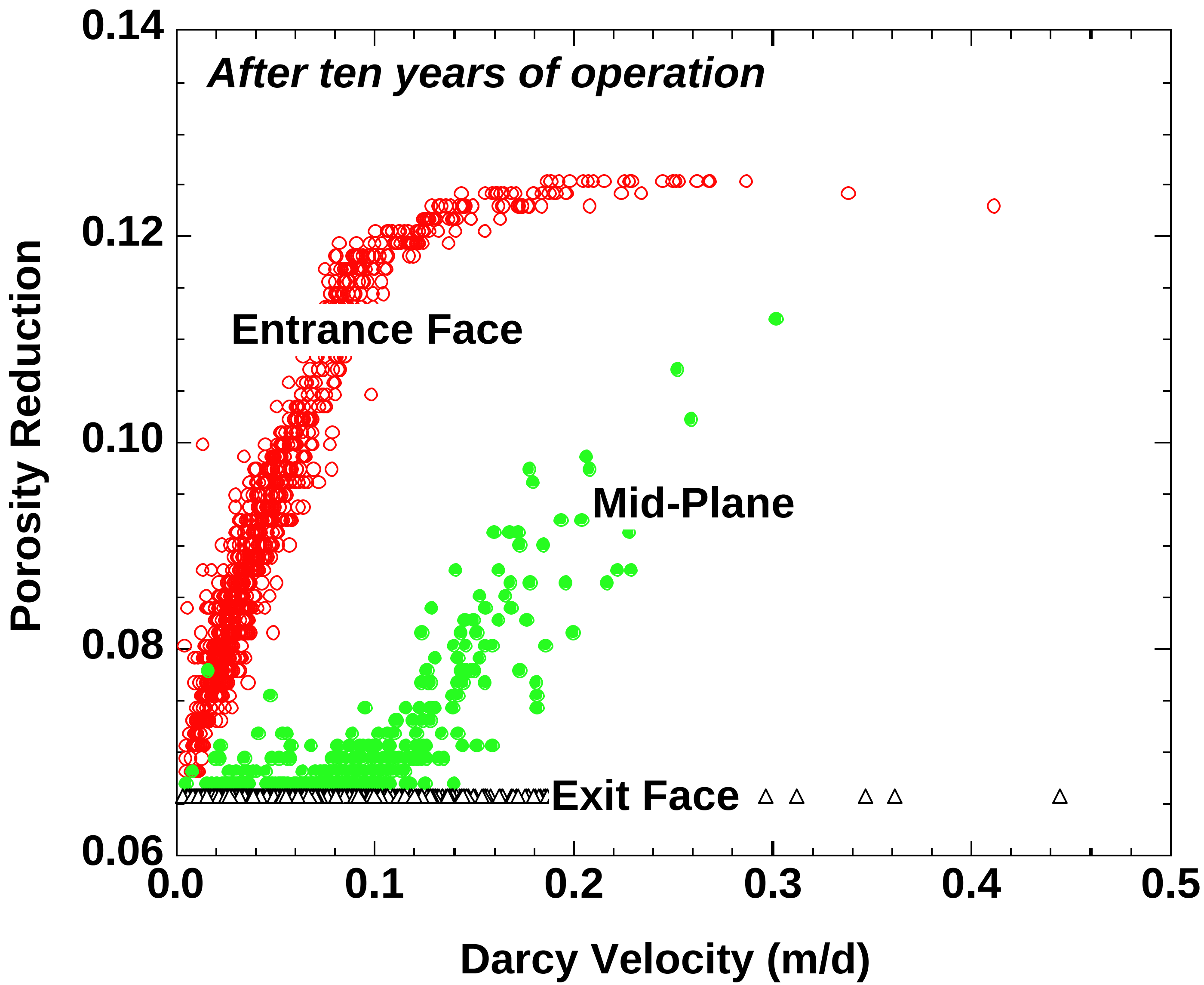
Porosity Reductions: Averages and Maxima



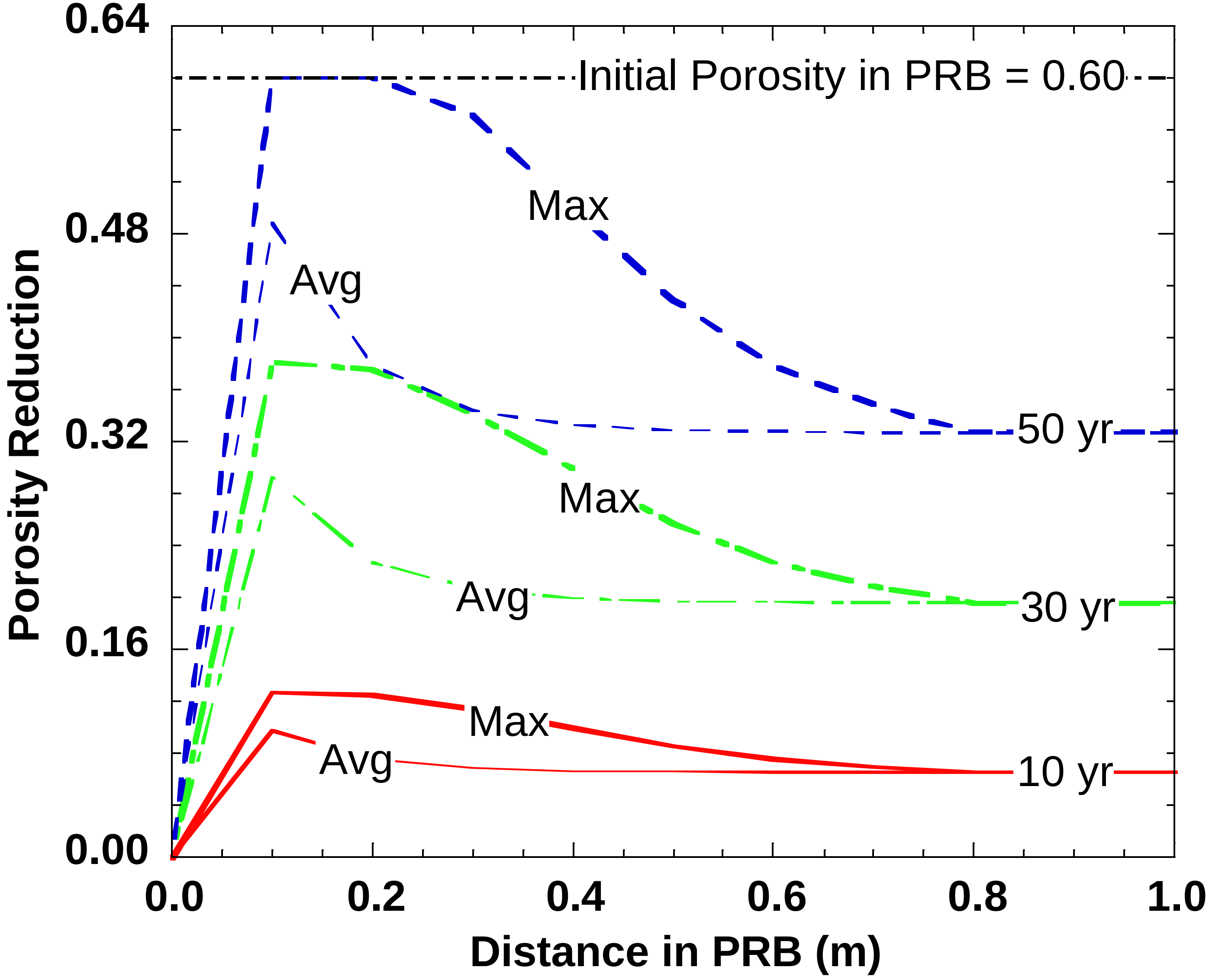
Porosity Reduction After 10 Years of Operation



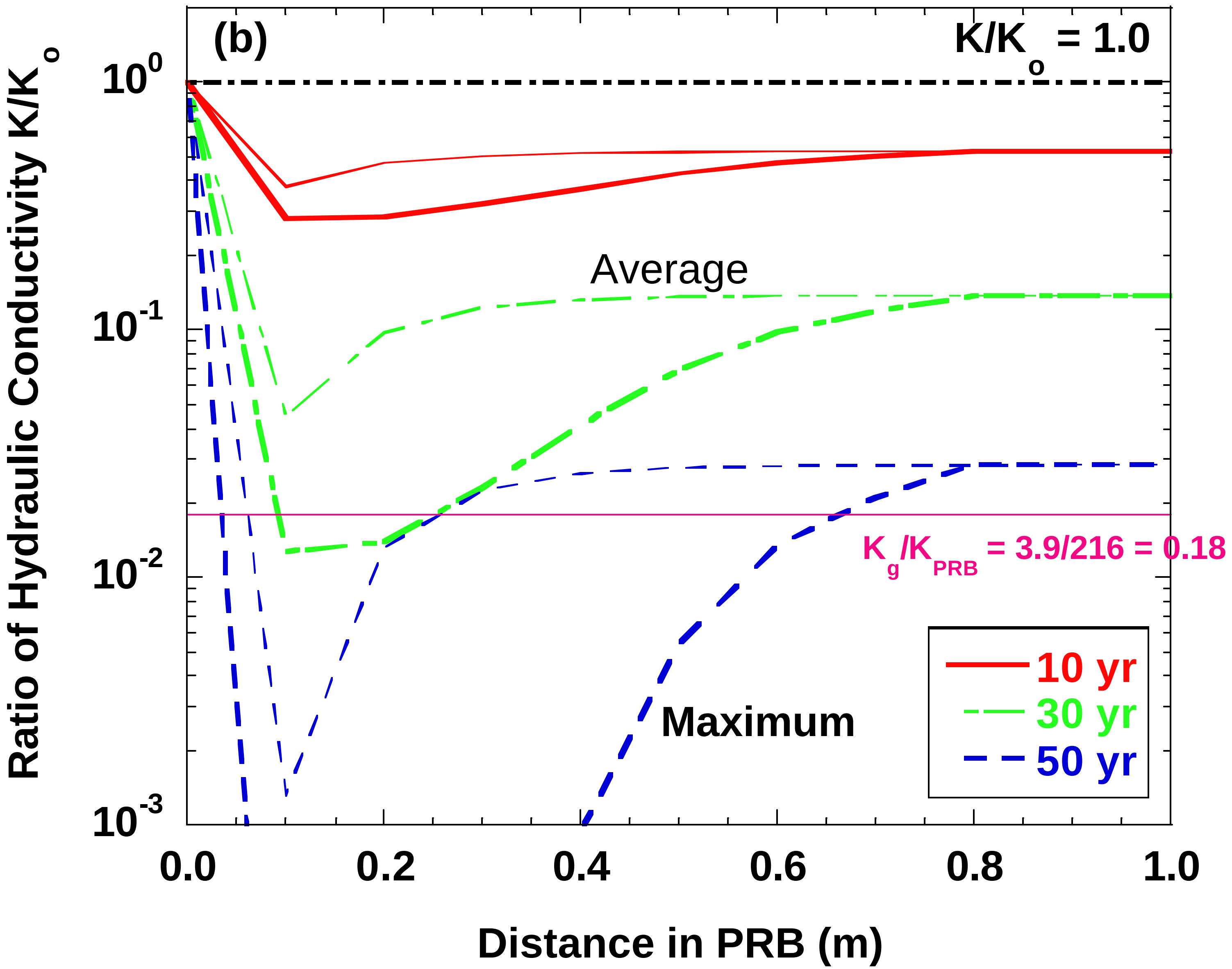
Porosity Reduction Related to Balance Between Seepage Velocity and Reaction Rate



Average and Maximum Porosity Reduction at 10, 30, 50 yr

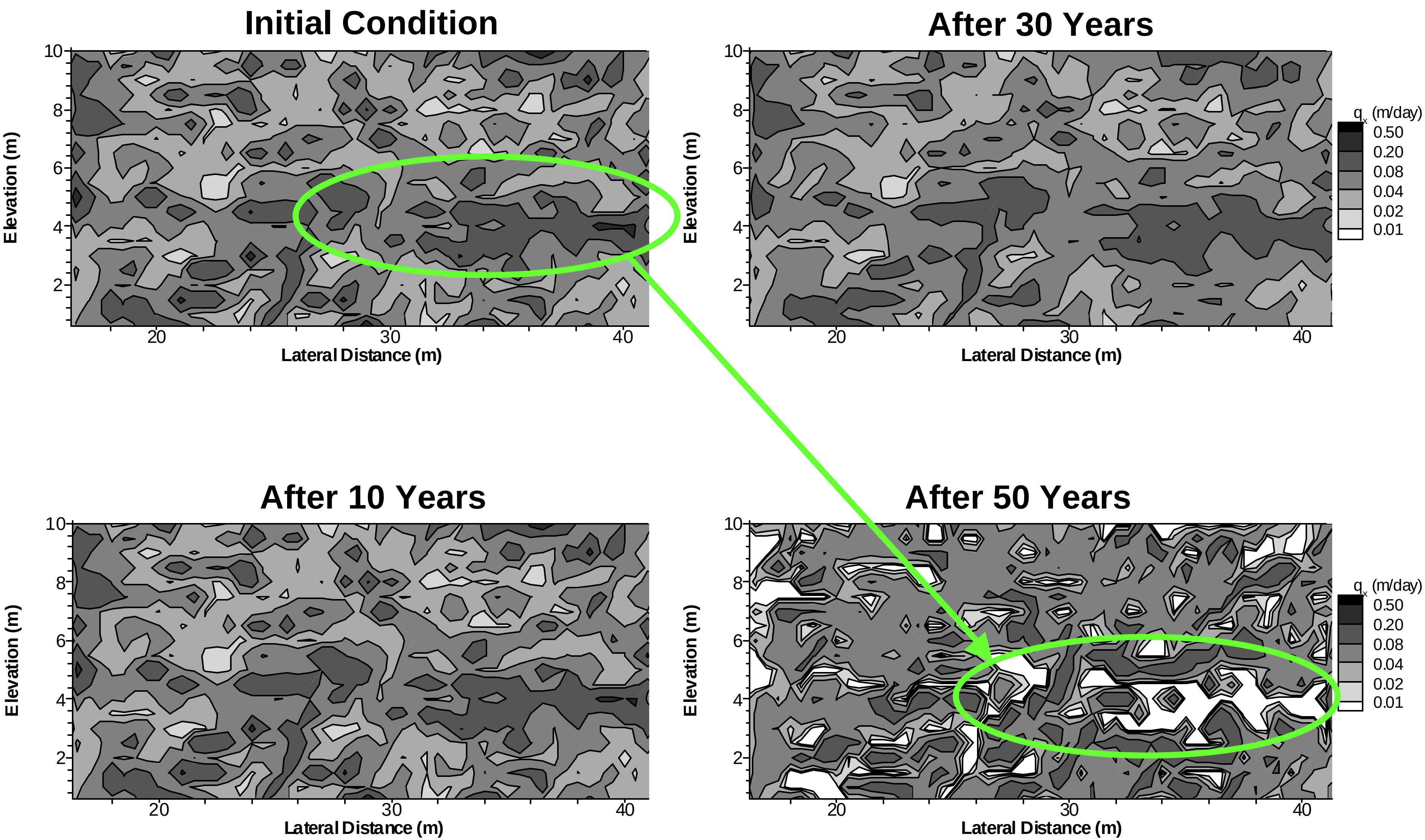


Average and Maximum Conductivity Reduction at 10, 30, 50 yr

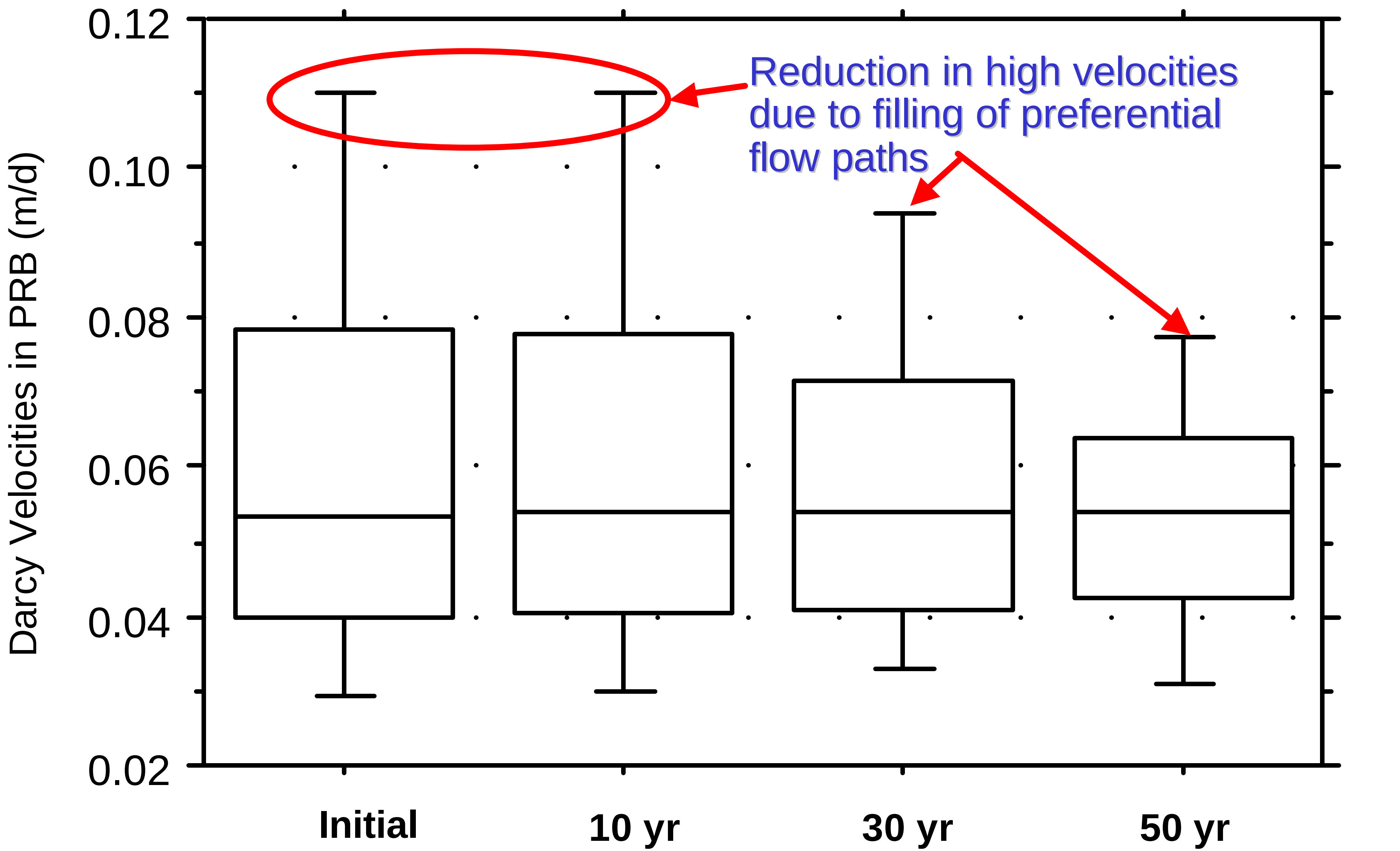


Inflow Darcy Velocity Over Time

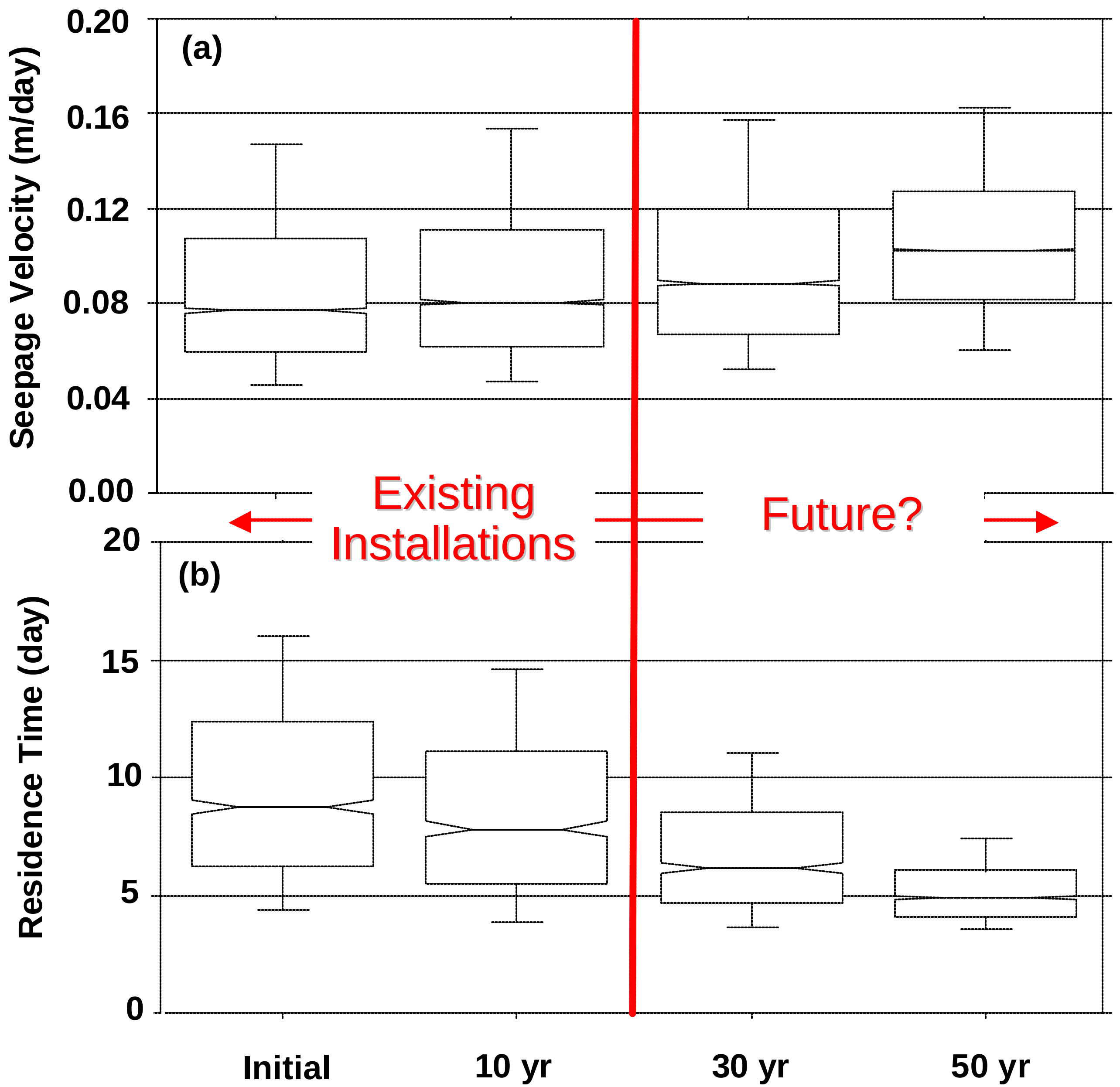
light-low velocity, dark high velocity



Darcy Velocities in PRB Over Time



Seepage Velocities and Residence Times

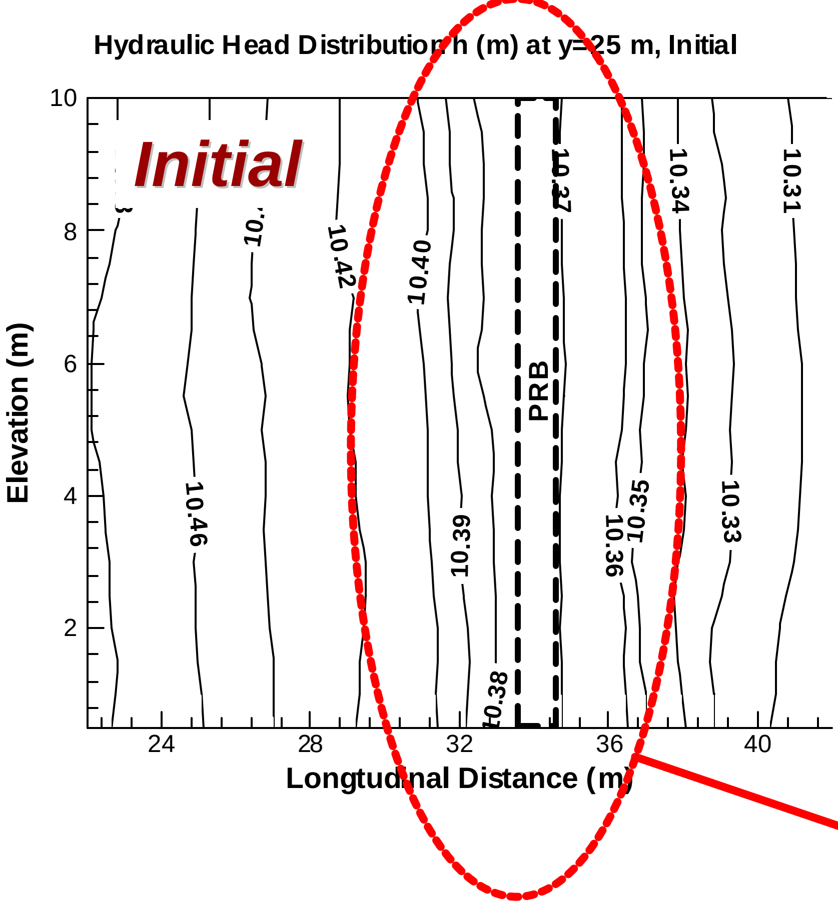


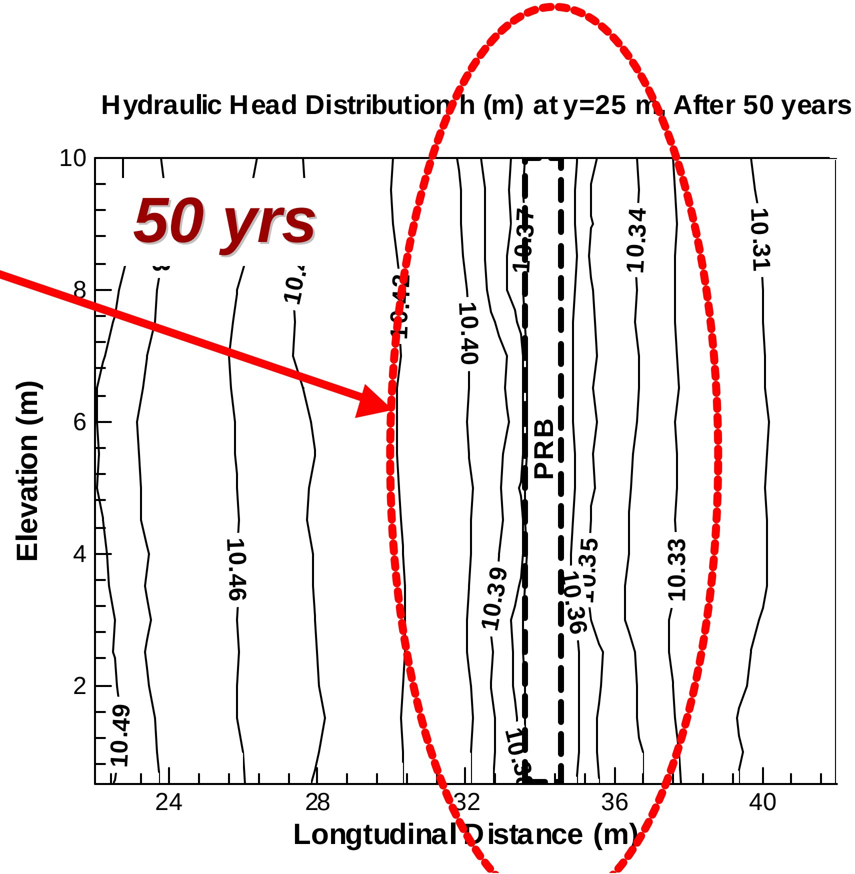
Darcy velocity (q) largely controlled by facies in aquifer, Elder et al. 2002

Seepage velocity (v_s) increases because porosity decreases ($v_s = q/n$)

Residence decreases as porosity fills because seepage velocity is increasing

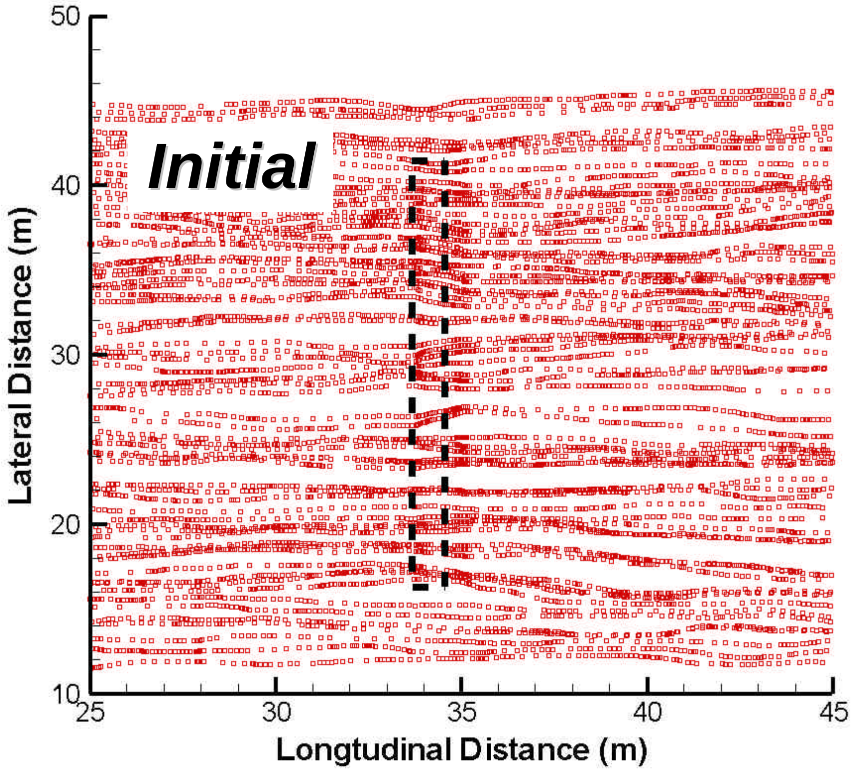
Head Distributions Initially and at 50 Yrs



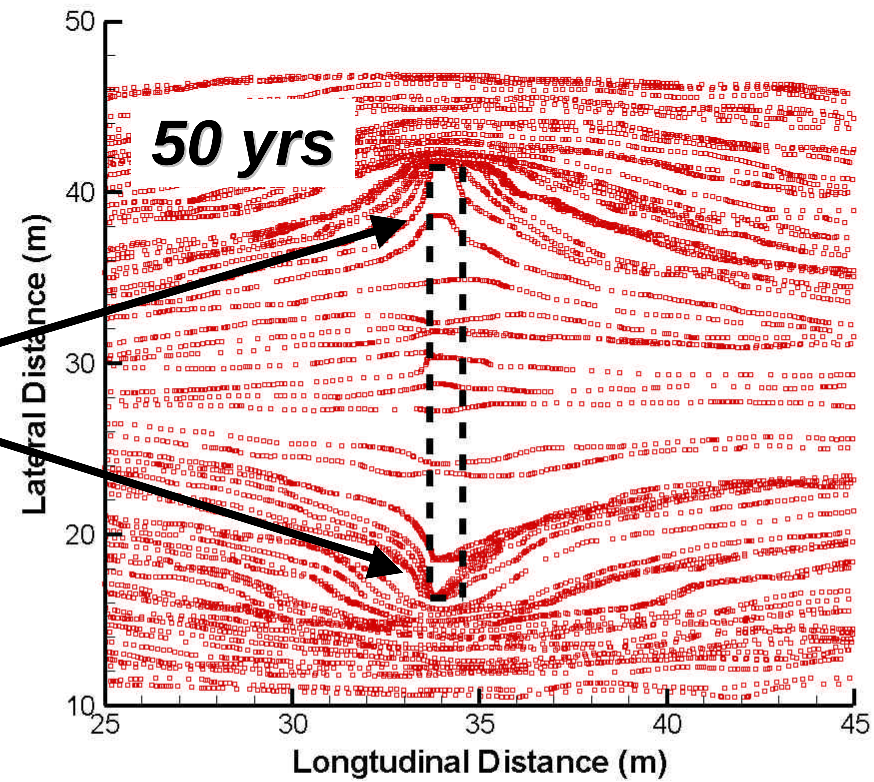


Gradient becomes steeper, but dramatic head changes not apparent

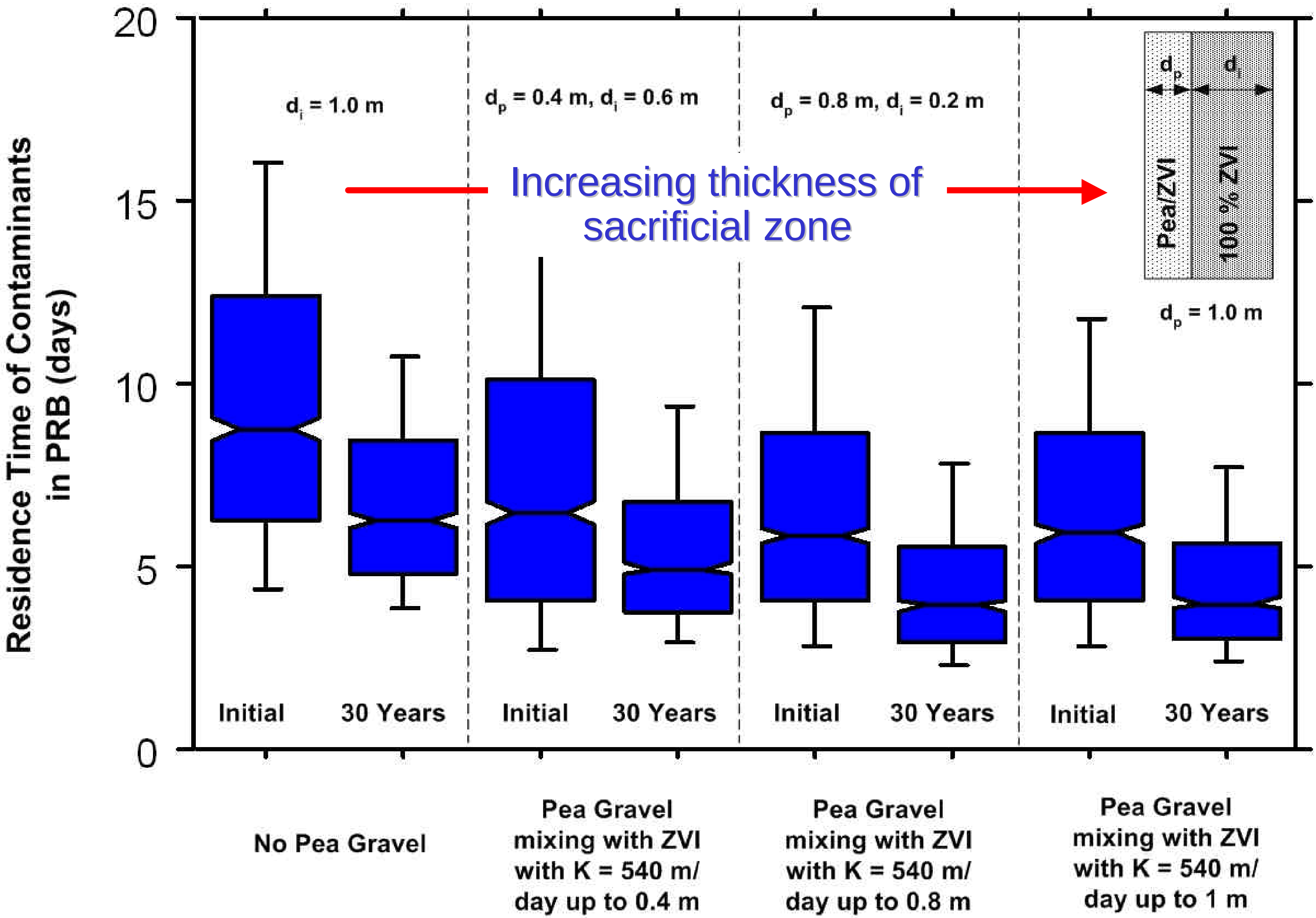
Effect on Flow Paths



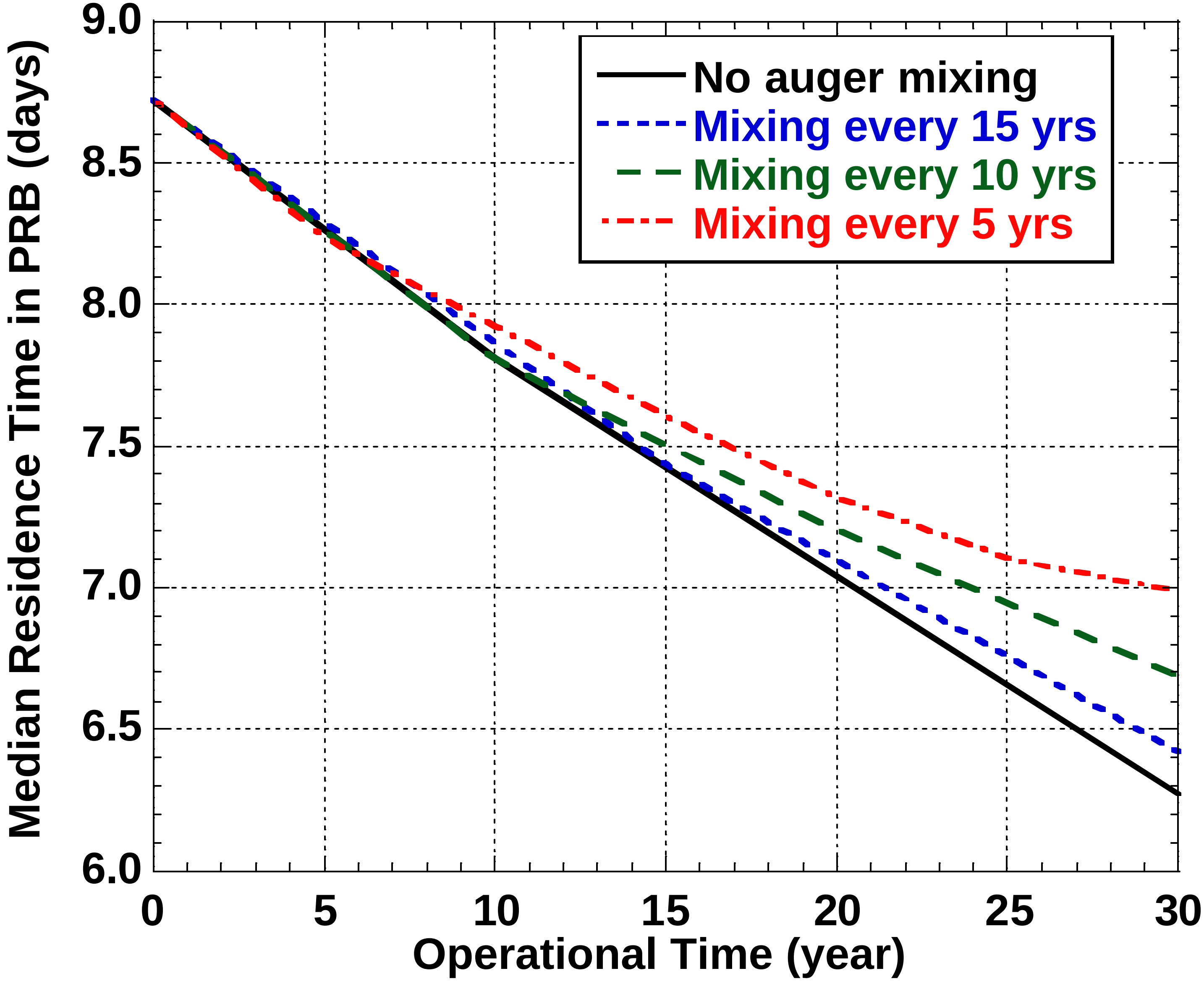
Flow bypassing!



Use of Sacrificial Upgradient Zone



Effect of Auger Mixing on Residence Time



Summary

- Mineral fouling causes porosity reductions
- Reductions are spatially variable due to flow heterogeneities (larger reductions where flow rates are higher)
- Impacts on hydraulic performance:
  - Re-distribution of flow paths
  - Reductions in residence time, largely after 10 yrs
  - Flow bypassing, largely after 10 yrs
  - Hydraulic gradient build-up, but subtle
- Auger mixing and sacrificial iron/gravel zones have modest effect on porosity reductions and changes in hydraulics