Reaction-Based Reactive Transport Modeling of Biological Iron(III) Reduction

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Mathematical Models

Reaction-based models – simulate and formulate the production-consumption rate of every chemical species due to every chemical reaction (both equilibrium and kinetic)

***Ad hoc* models** - typically formulate only the rate of the most significant reaction as an empirical function fit to experimental data

Diagonalized Reaction-Based Models

Formal procedure - Gauss-Jordian elimination or QR decomposition - to separate M equations (needed to solve for M unknowns) into three subsets:

Mass Conservation Equations for Components

Mass Action Equations for Equilibrium Reactions

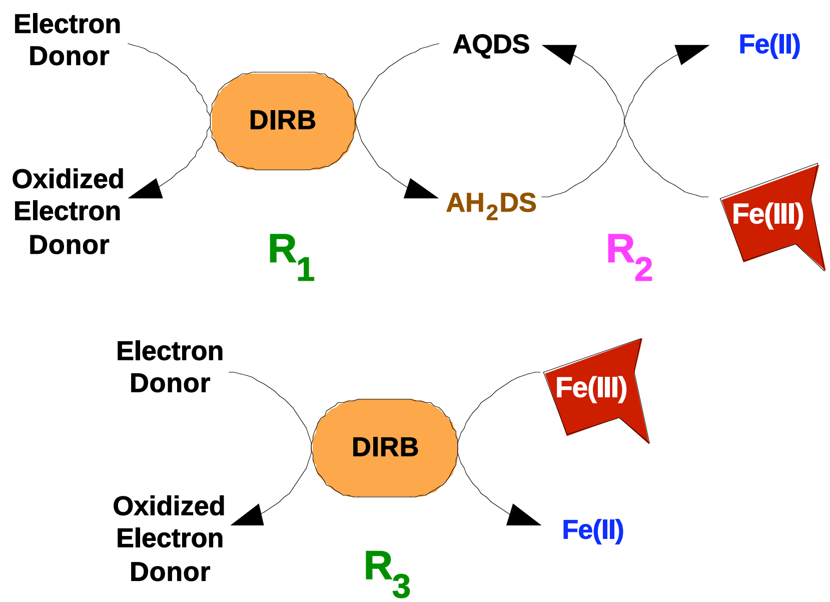
Kinetic-Variable Equations for Kinetic Reactions

Most Important! – in the absence of parallel kinetic reactions, all kinetic reactions are independent of each other for independent evaluation

Fang et al. 2003 *Water Resources Res.* **39**:1083

Previous Demonstration / Validation

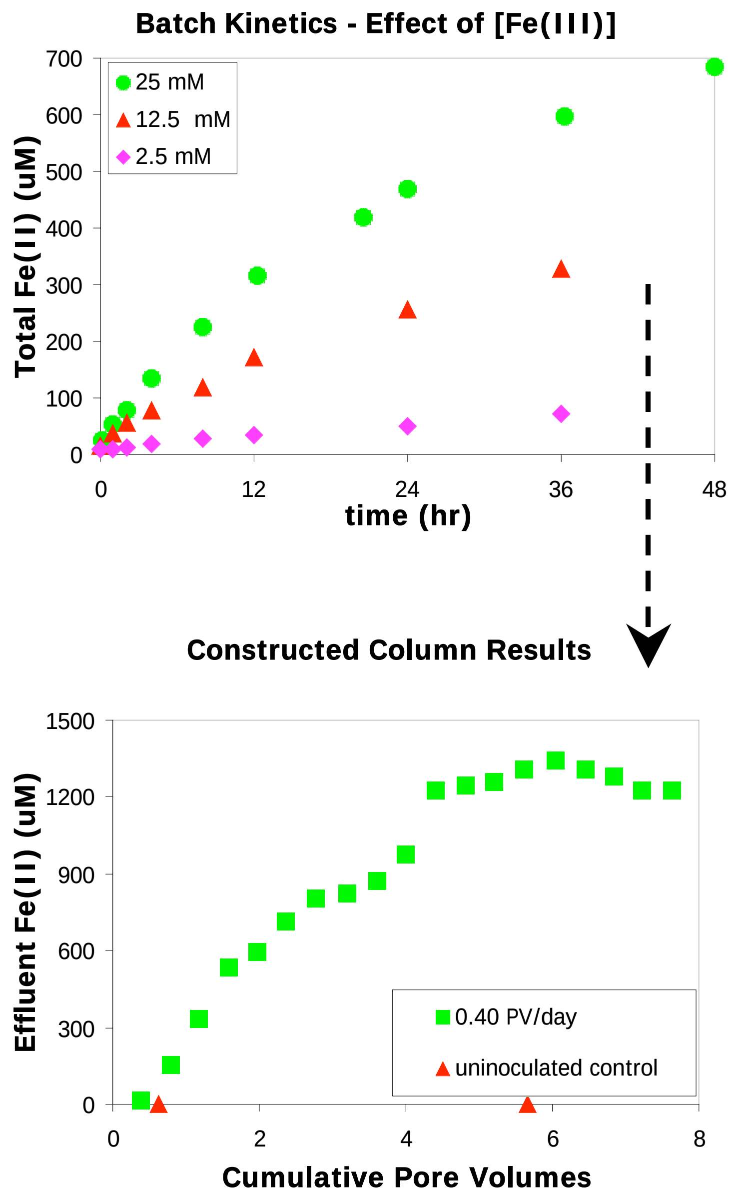
- Obtained rate formulations/parameters for kinetic reactions independently from batch experiments
- With no modifications, these rate equations were able to simulate parallel kinetic reactions during hematite-with-AQDS experiments



Burgos et al. 2003 *Geochim. Cosmochim. Acta* **67**:2735

Current Demonstration/Validation

- Model and measure biological iron(III) reduction in natural sediments
- Obtain rate formulations/ parameters for kinetic reactions independently from batch experiments
- With no modifications, use rate equations to simulate biological iron(III) reduction in constructed column reactors



Proposed Reaction Network for Biological Iron(III) Reduction

$4FeOOH + lactate^{-} + 7H^{+} \rightarrow 4Fe^{2+} + acetate^{-} + HCO_3^{-} + 6H_2O$ R1

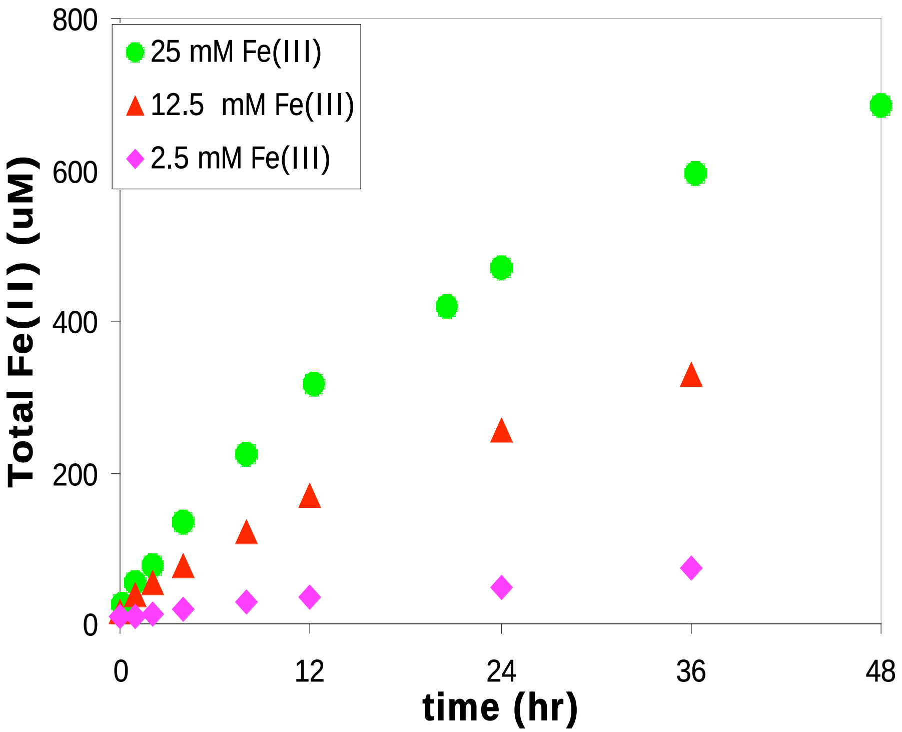
$FeOOH(bulk) \rightarrow {=}FeOOH(surf)$ R2

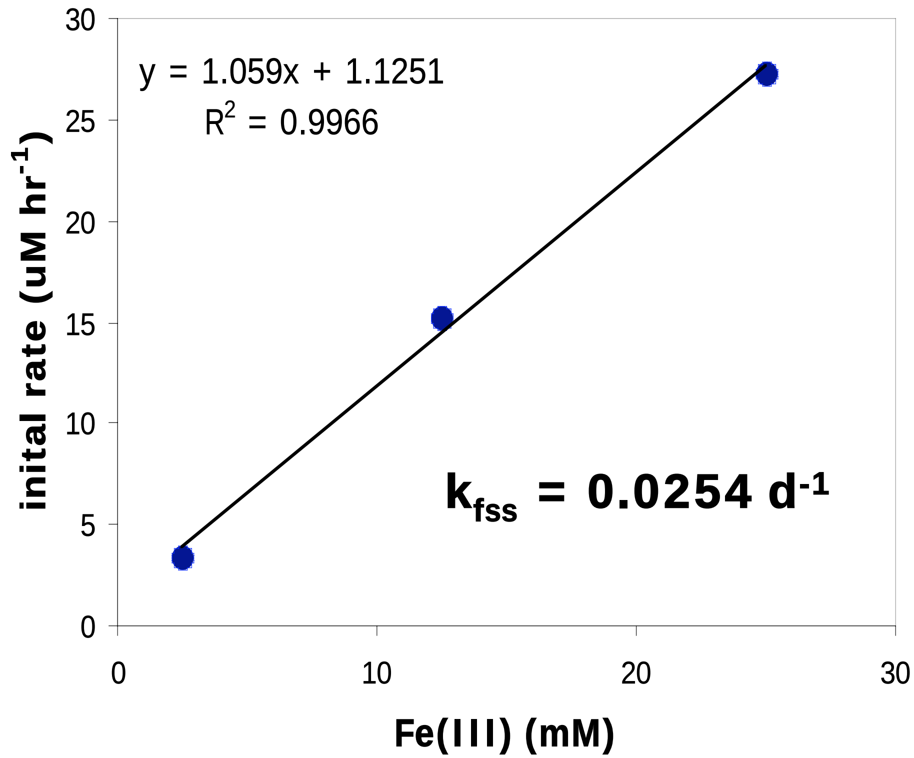
$Fe^{2+} + {=}FeOOH \rightarrow {=}FeOO\text{-}Fe^{(II)+} + H^{+}$ R3

$HPIPES \rightarrow PIPES^{-} + H^{+}$ R4

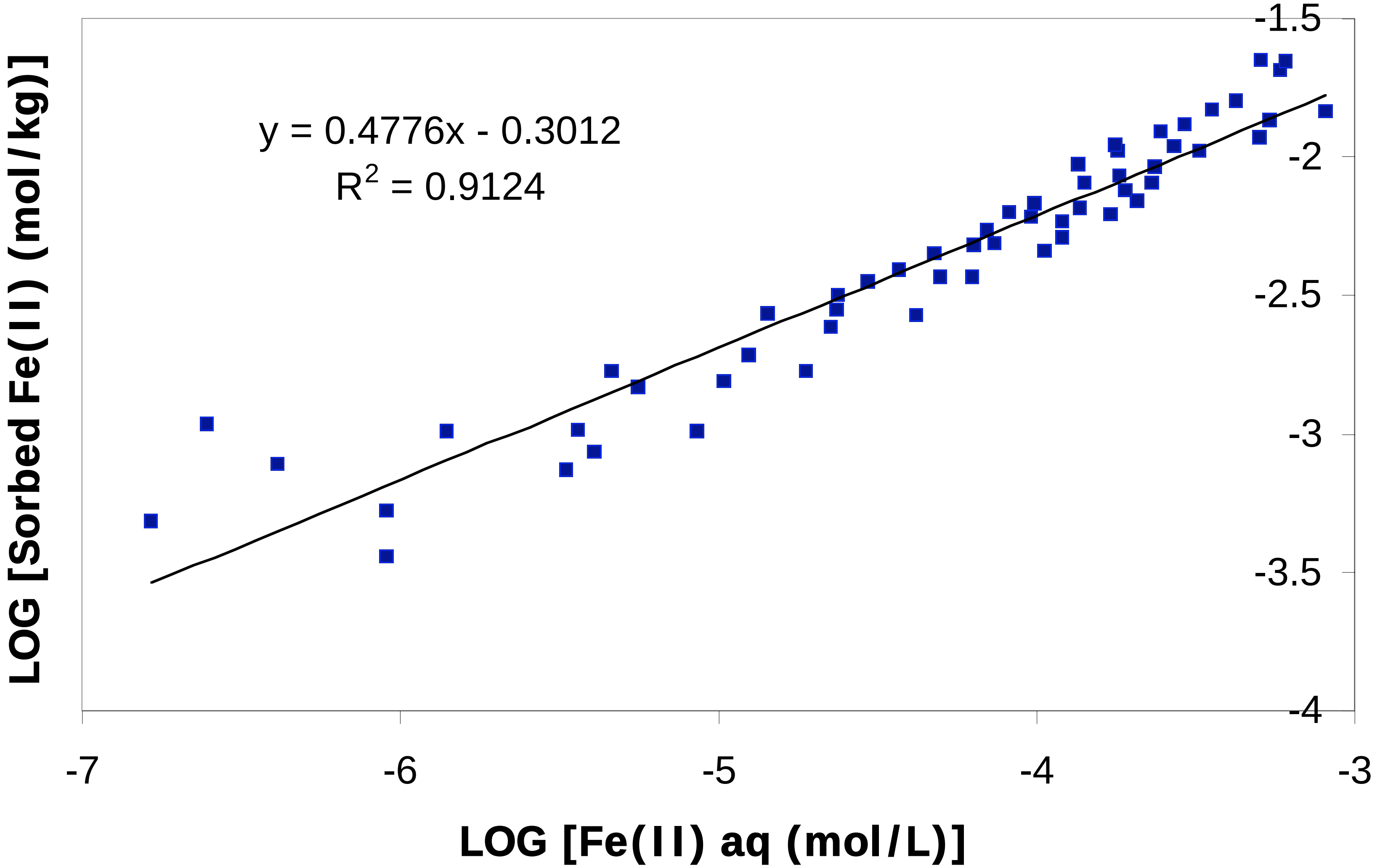
M = 10 species, N = 4 reactions

FeOOH bioreduction modeled as 1st-order with respect to “free surface sites”

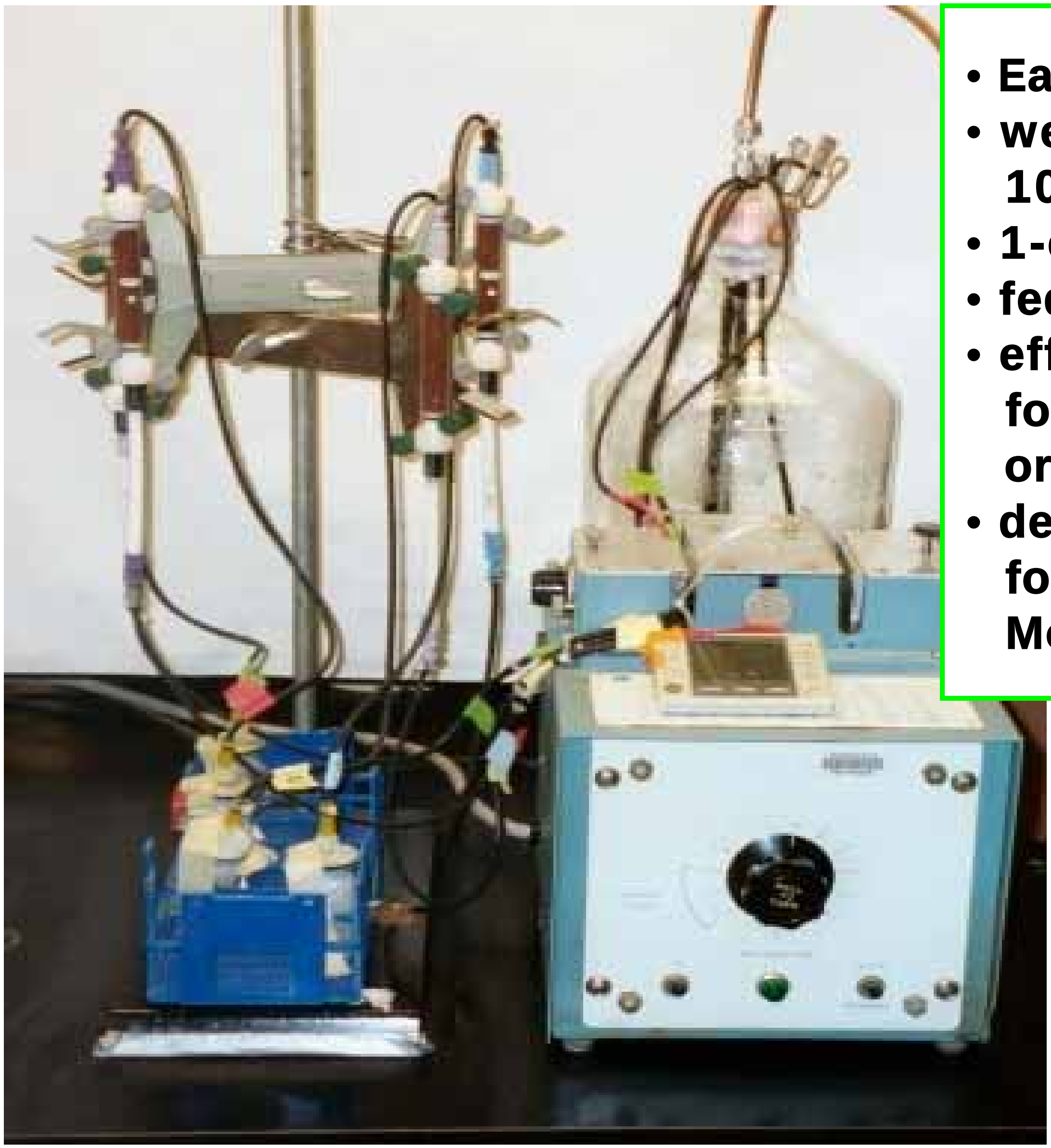




Fe^{2+} sorption modeled as Freundlich isotherm

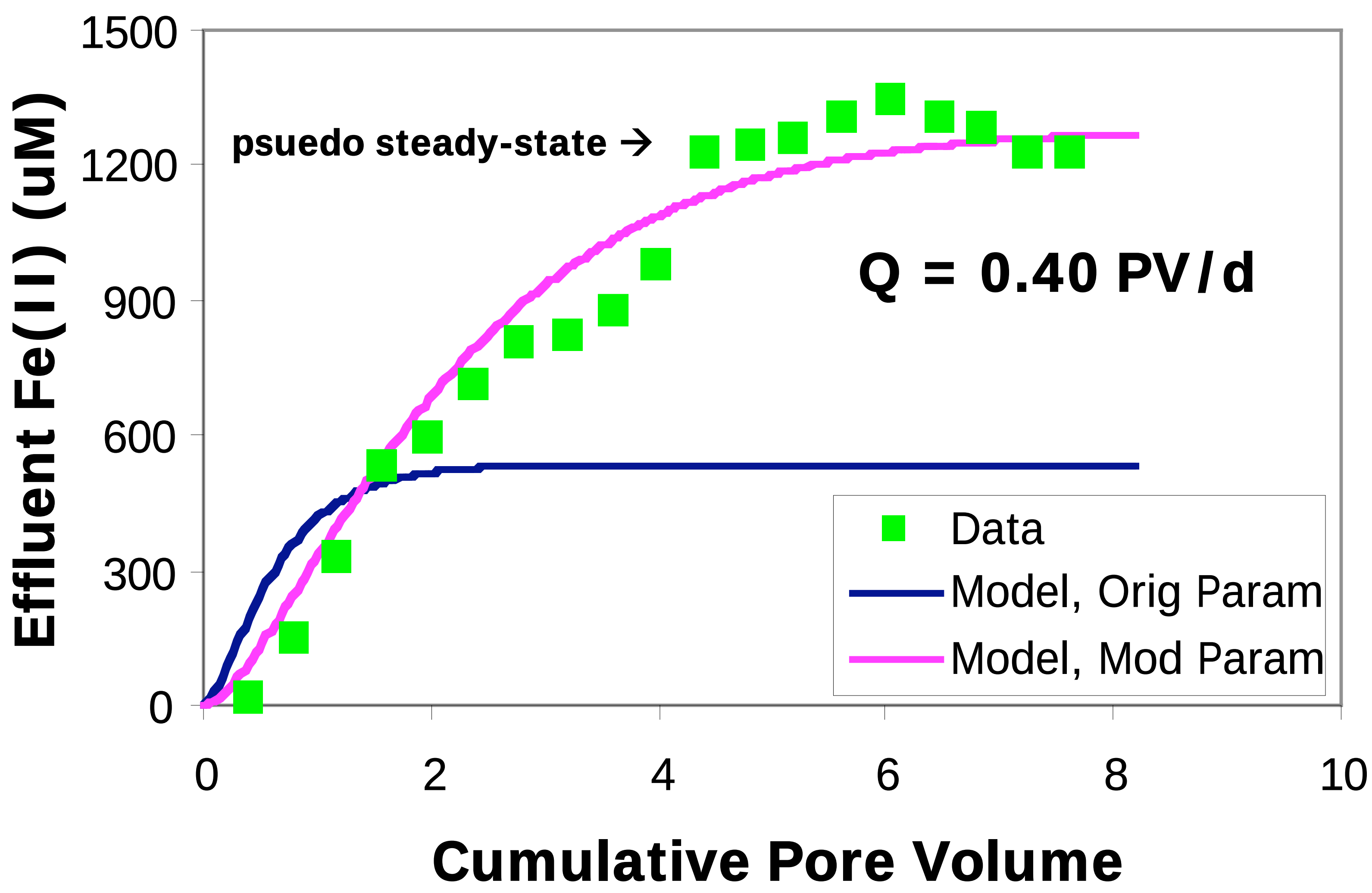


Constructed Column Experiments

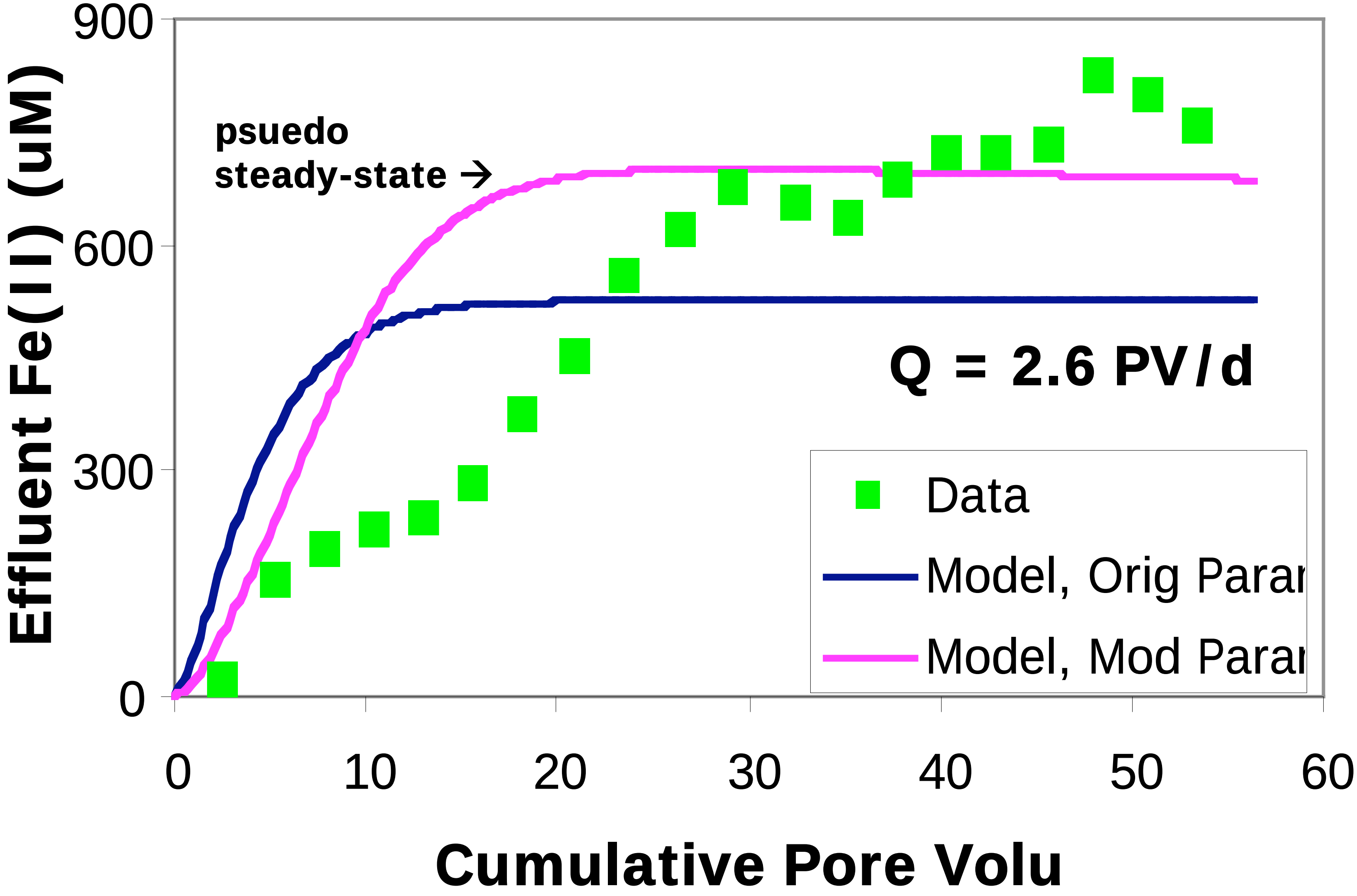


- Eatontown hematite sand
- wet-packed columns with 10^8 cells / mL *S. putrefaciens* CN32
- 1-cm dia, 7.5-cm bed length
- fed 5 mM Na-lactate in AGW
- effluent samples collected daily for 21 d, analyzed for Fe(II) and organic acids
- deconstructed columns analyzed for 0.5 N HCl Fe(II), and by Mossbauer spectroscopy

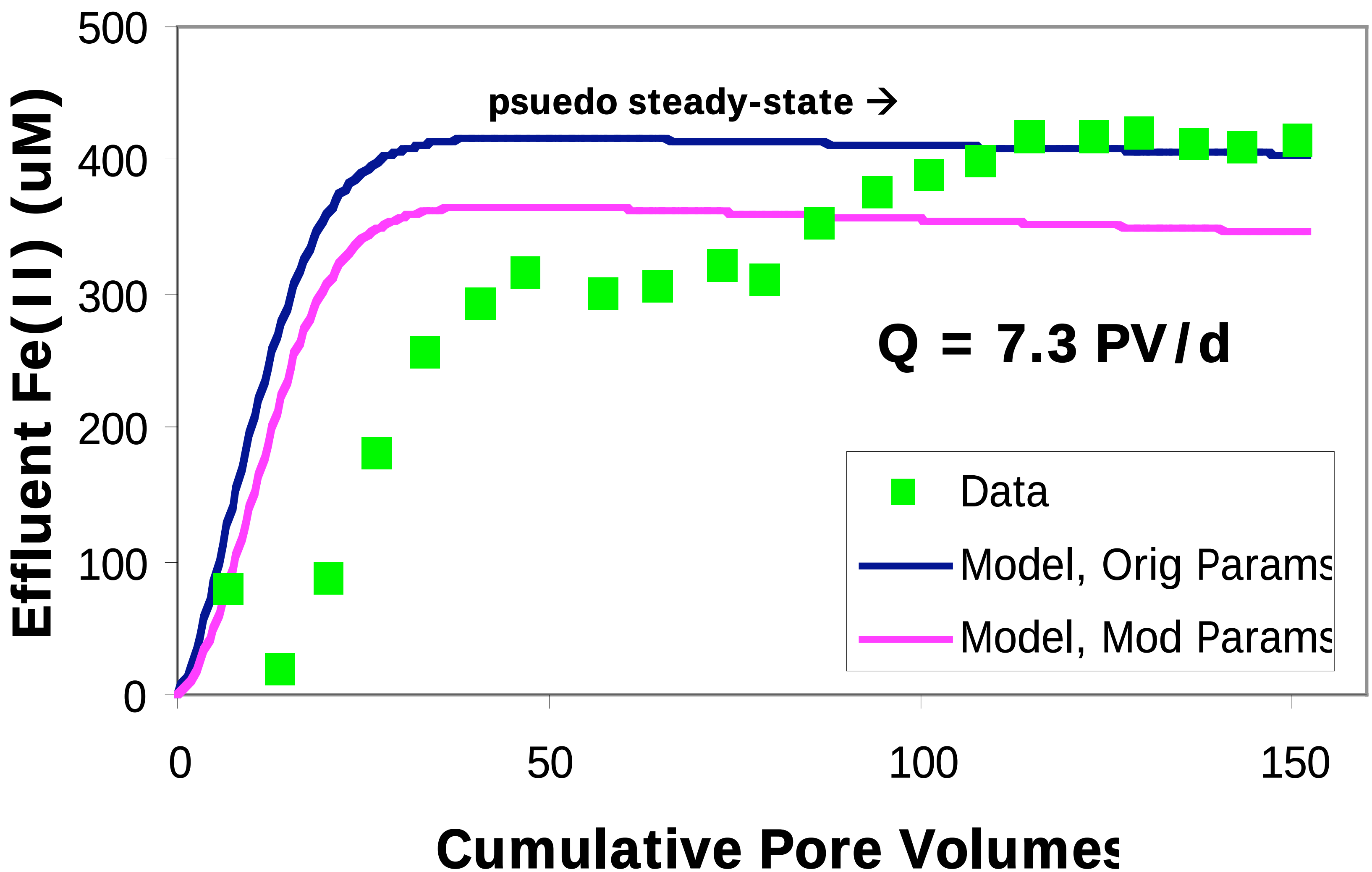
Bioreduction of Iron-Rich Coastal Sand



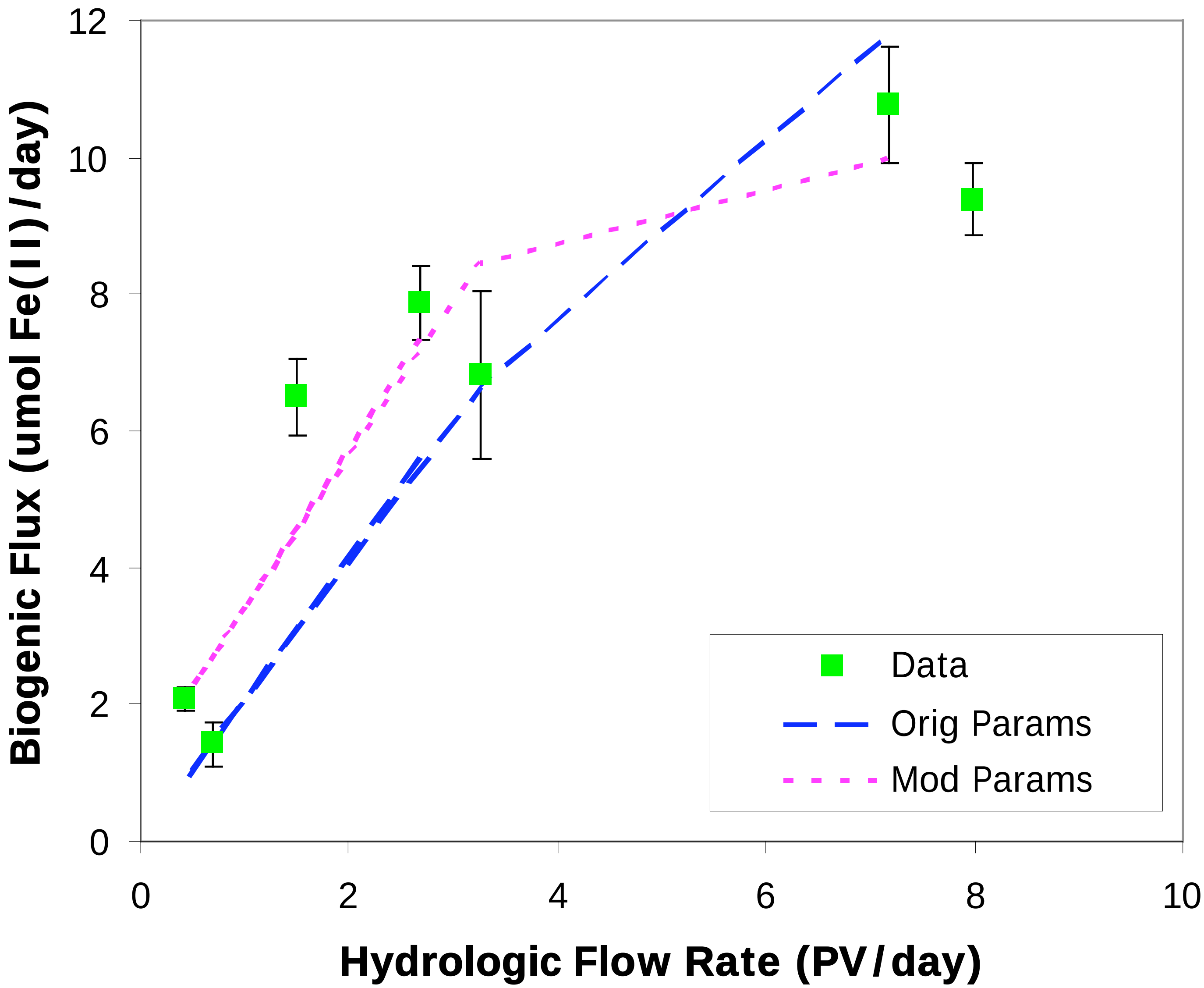
Bioreduction of Iron-Rich Coastal Sand



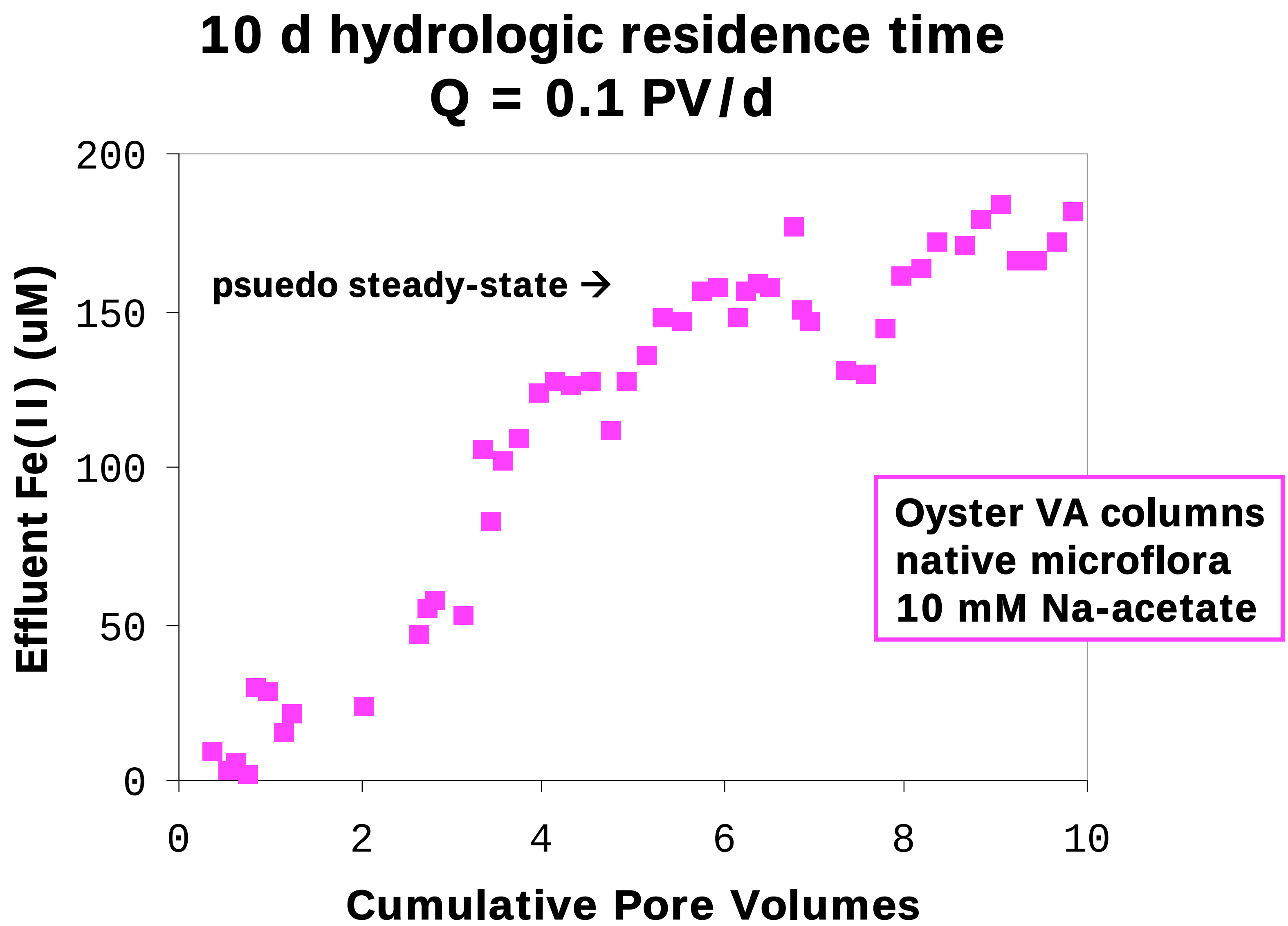
Bioreduction of Iron-Rich Coastal Sand



Hydrologic Effect on Biologic Activity



Iron(III) Reduction at low flow rates

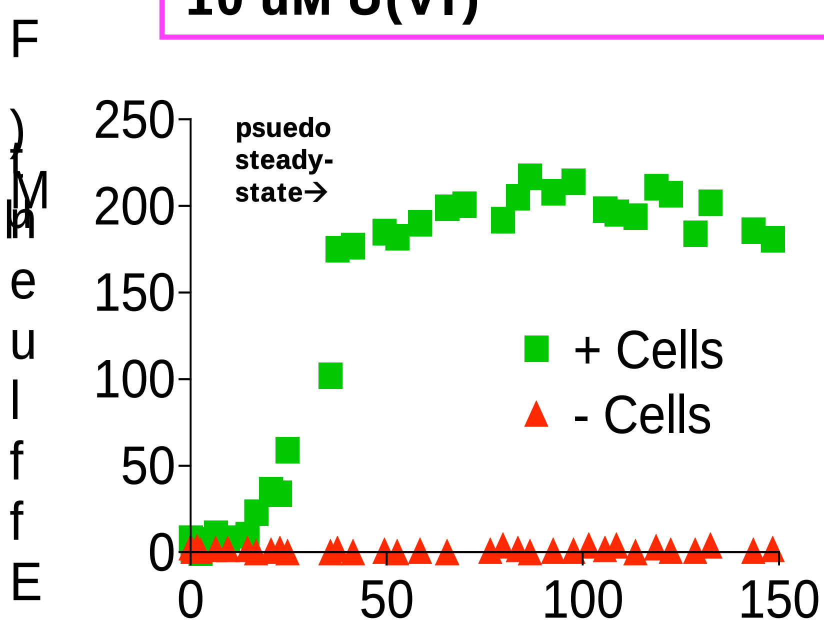


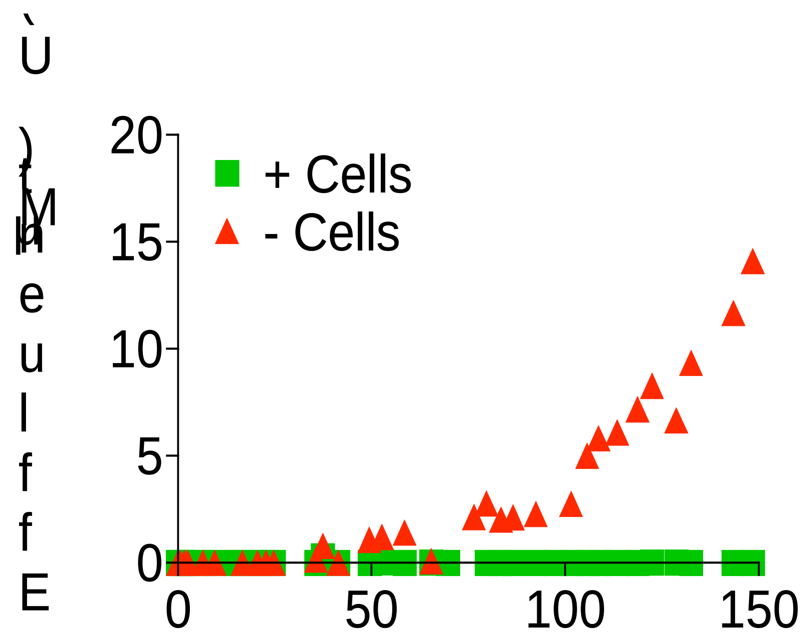
E.E. Roden, unpublished

Coupled Fe(III)/U(VI) Reduction

Oyster VA columns
10^8 cells/mL *G. sulfurreducens*
10 mM Na-acetate
10 uM U(VI)

1 d hydrologic residence time
Q = 1.0 PV/d





Roden et al. 2004 *Environ. Sci. Technol.*, Submitted

Summary

- Biogenic flux increases as hydrologic residence time decreases
- Reaction-based reactive transport modeling can capture this effect
- Solid-phase Fe(III) bioreduction can be sustained at long residence times in natural sediments
- Long-term coupled Fe(III)/U(VI) bioreduction can be sustained in natural sediments

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Future Directions

- Continuous refinement, improvement and expansion of reaction-based models
- Provide evidence for uranium immobilization in long-term, long-residence time, initially low DMRB-biomass FRC sediment columns
- Provide kinetic information on solid-phase reactants and products

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