COLLOID FACILITATED TRANSPORT IN NATURAL POROUS MEDIA

PHENAMENA AND MODELLING

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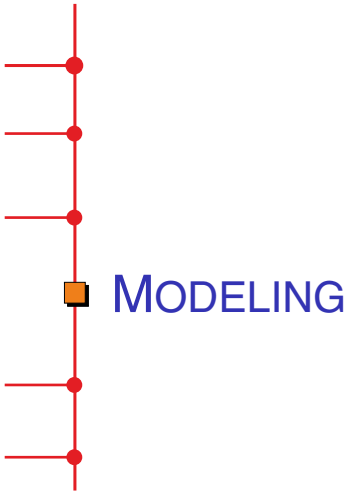
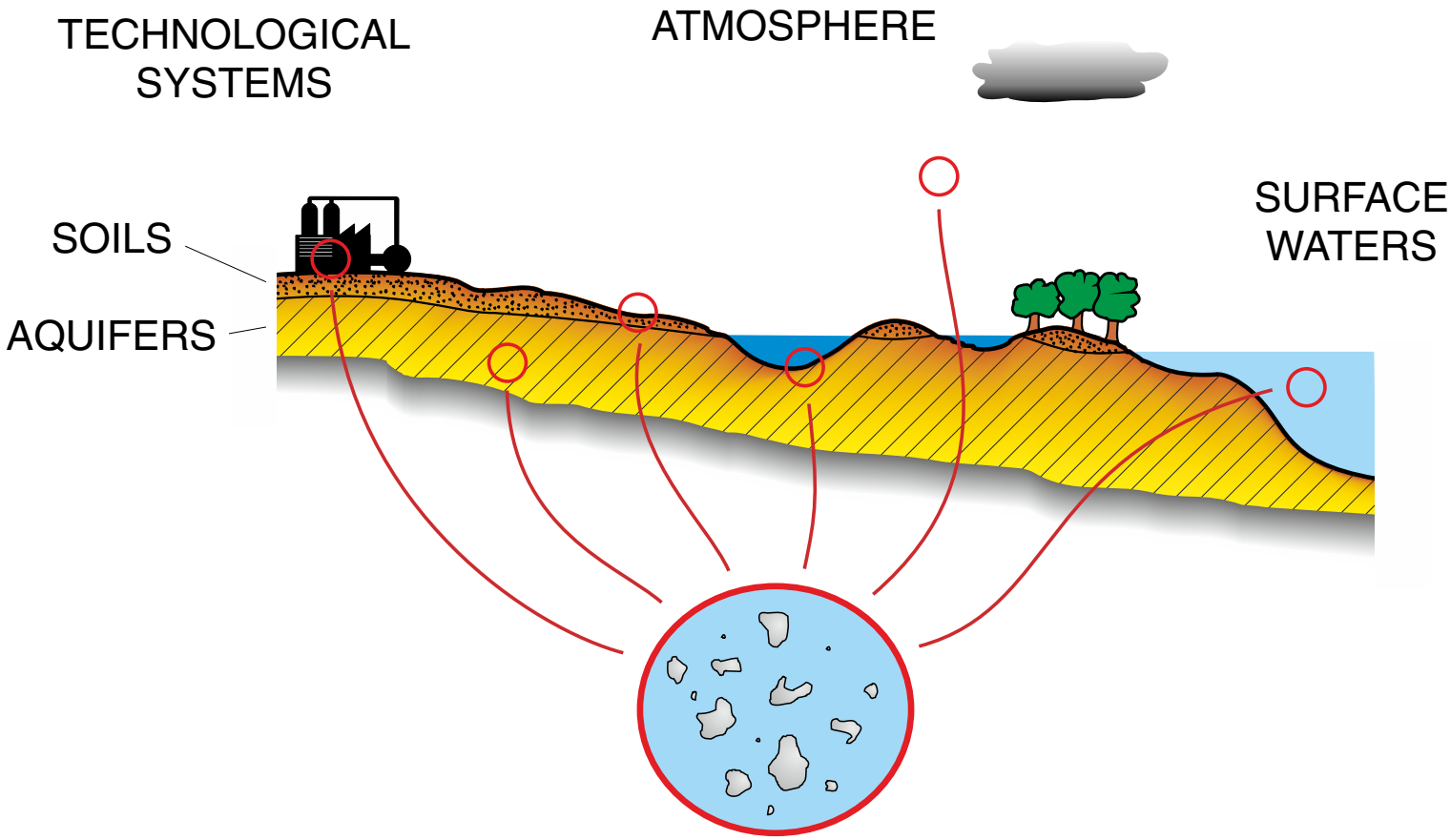
OVERVIEW

- INTRODUCTION
  - COLLOIDAL PARTICLES
  - REACTIVE TRANSPORT IN POROUS MEDIA
- COLLOIDAL TRANSPORT PHENOMENA IN SUBSURFACE SYSTEMS
  - FUNDAMENTAL PHENOMENA
    - RELEASE/MOBILIZATION
    - TRANSPORT
    - PERSISTENCE
  - POLLUTION AND REMEDIATION
    - COLLOID-FACILITATED TRANSPORT
    - "AQUIFER-WASHING"
- CONCLUSIONS



INTRODUCTION

Colloidal Particles in the Environment



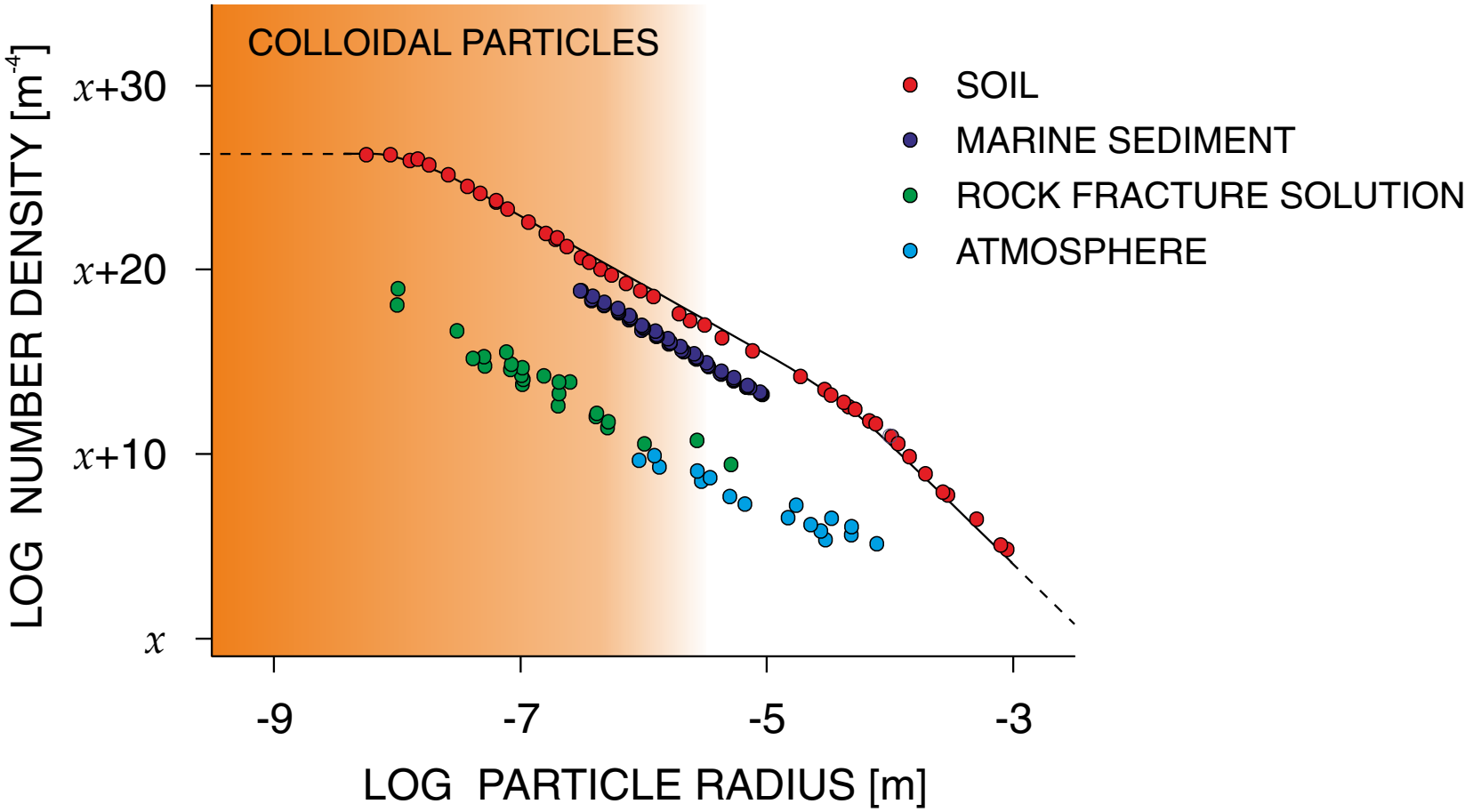
INTRODUCTION

Colloidal Phenomena in Natural/Technical Systems

- TRANSPORT OF BIOCOLLOIDS (VIRUSES AND BACTERIA) IN SOILS AND AQUIFERS (→ BIOREMEDIATION)
- TRACE ELEMENT CYCLING IN SURFACE WATERS
- FILTRATION / CHROMATOGRAPHY
- SOIL FORMATION / CLAY TRANSLOCATION
- WASTE WATER TREATMENT (FLOCCULATION)
- MIGRATION OF FINES IN AQUIFERS AND OIL RESERVOIRS
- BLOOD-CORPUSCLES IN ARTERIES/VEINS
- *COLLOID-FACILITATED TRANSPORT* OF CONTAMINANTS IN THE SUBSURFACE

INTRODUCTION

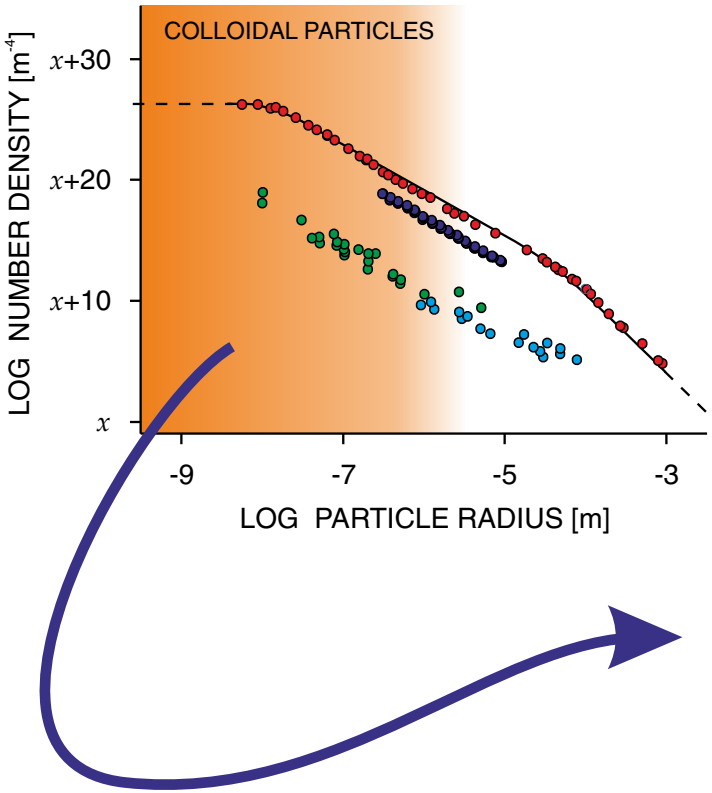
Particle Size Distribution

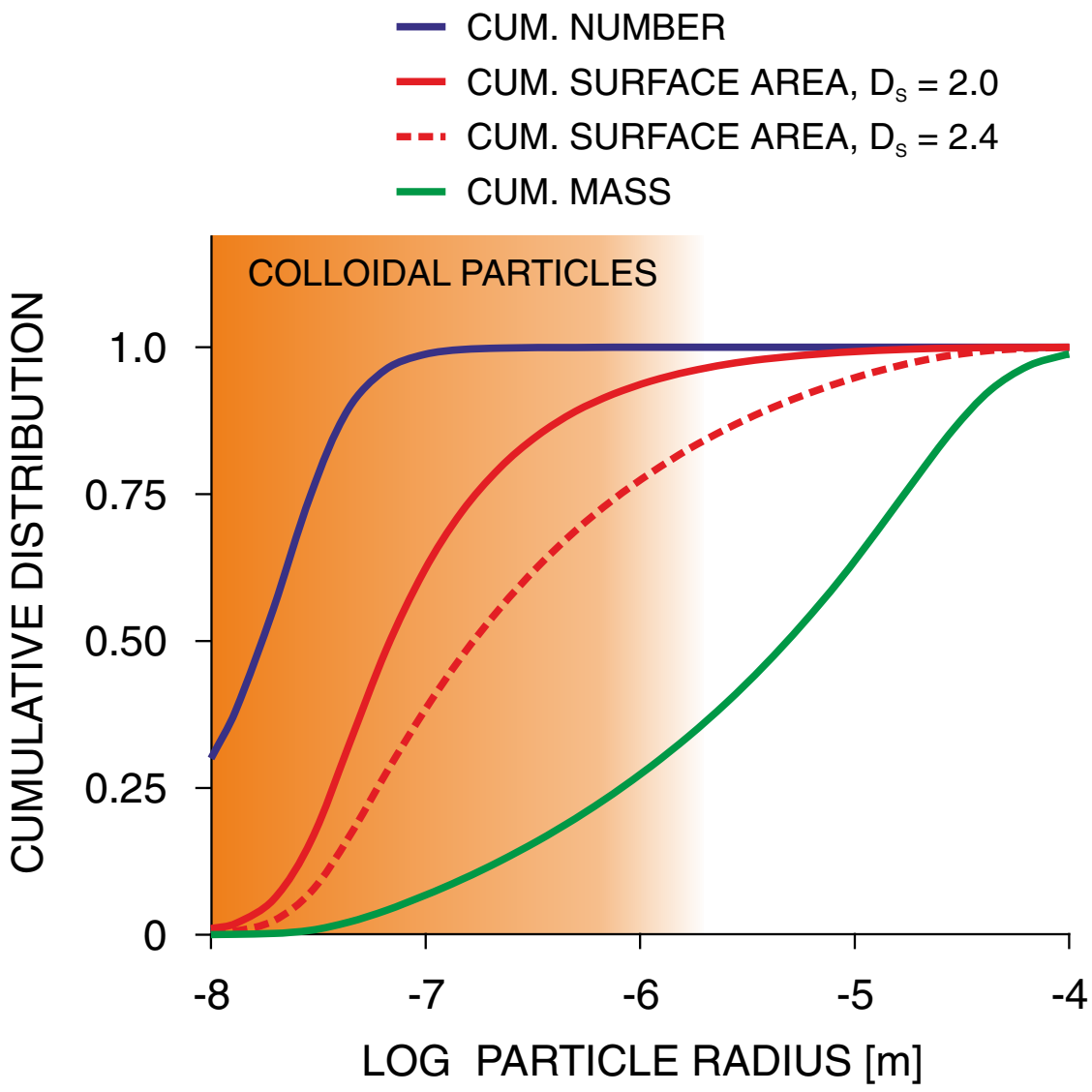


- Borkovec *et al.* (1993)
- Lerman (1978)
- Degueldre *et al.* (1989)
- Schütz & Jaenicke (1974)

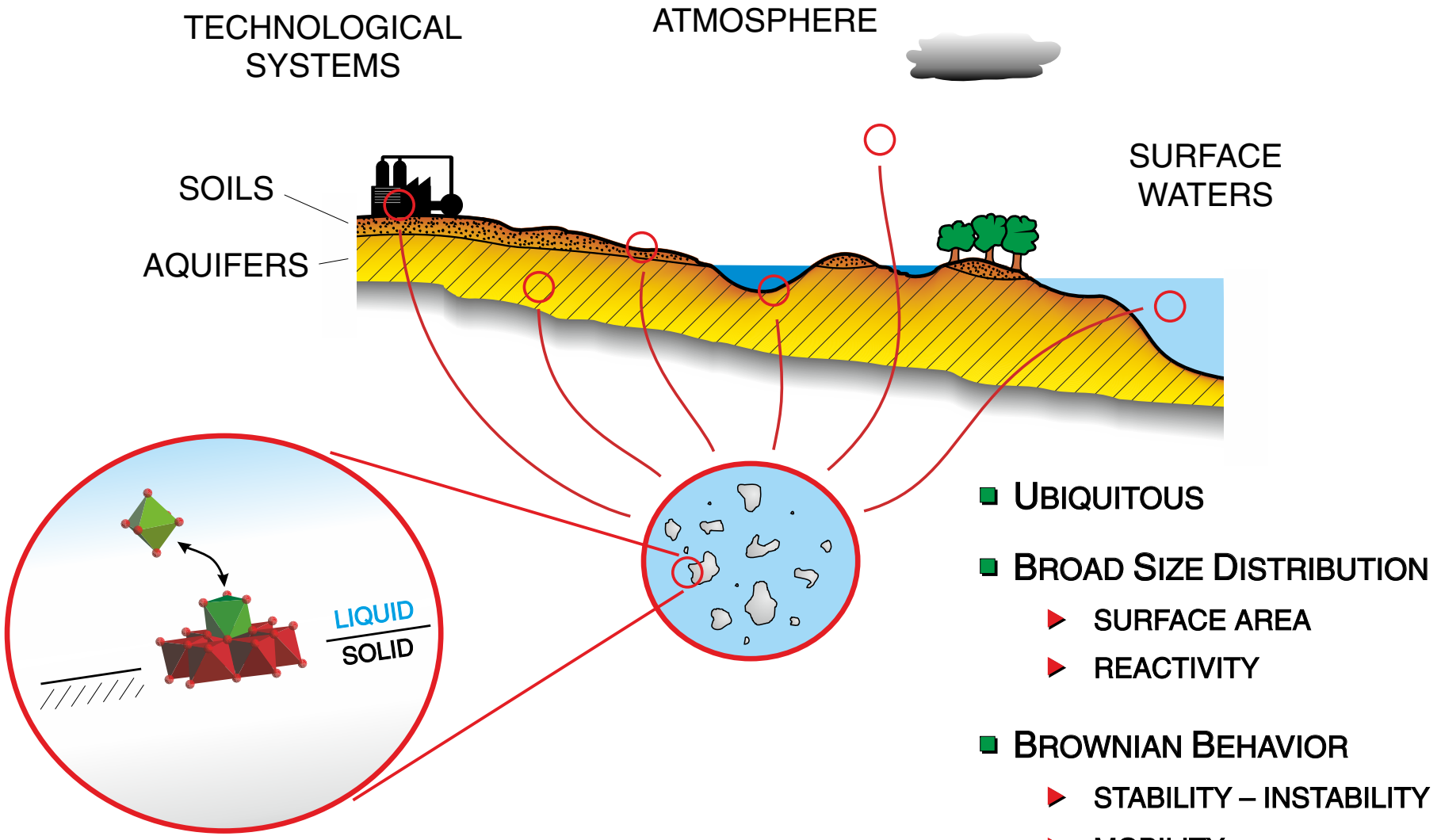
INTRODUCTION

Particle Size Distribution





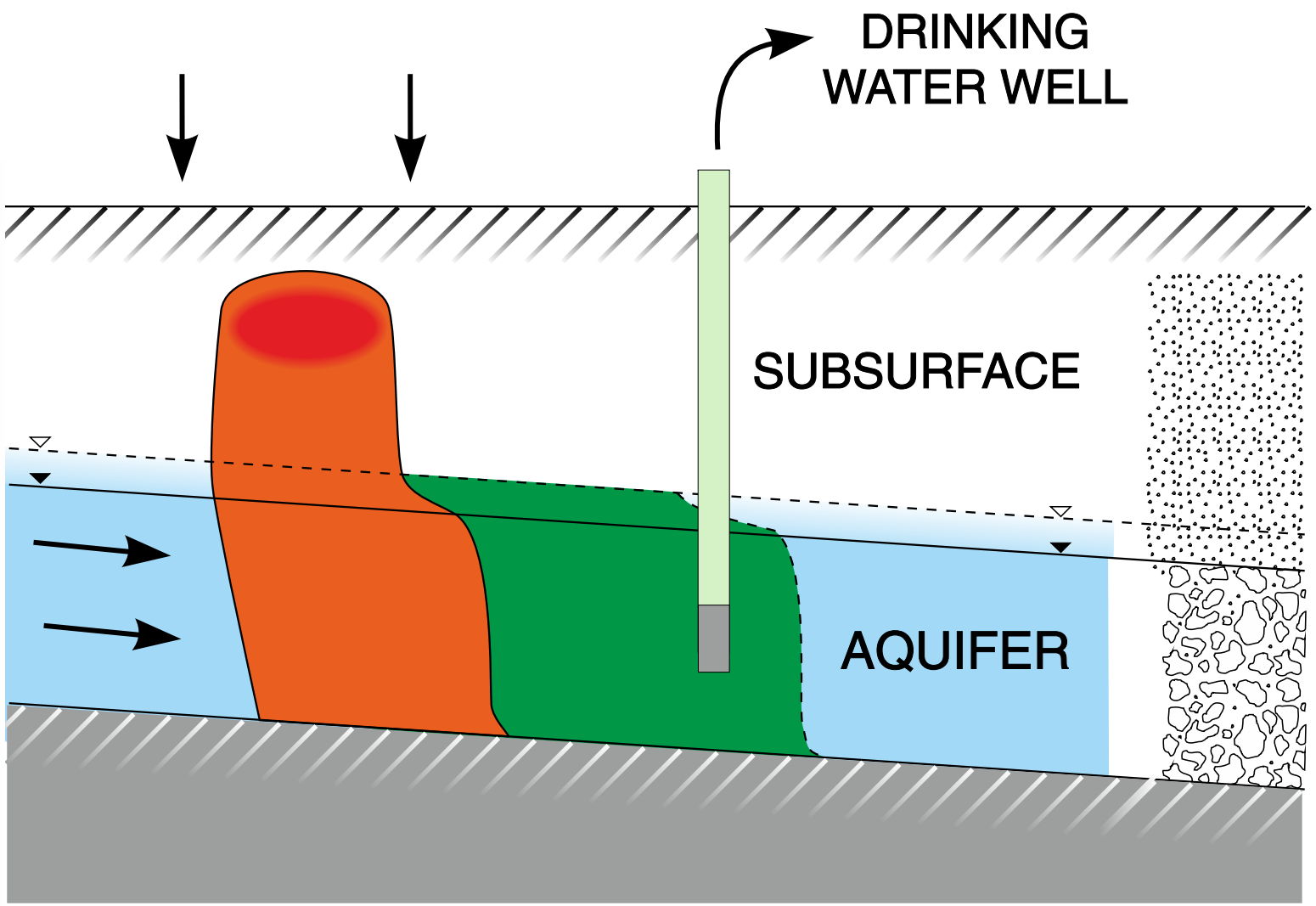
COLLOIDAL PARTICLES IN THE ENVIRONMENT



- UBIQUITOUS
- BROAD SIZE DISTRIBUTION
  - SURFACE AREA
  - REACTIVITY
- BROWNIAN BEHAVIOR
  - STABILITY – INSTABILITY
  - MOBILITY

INTRODUCTION

Pollution - Remediation Scenario



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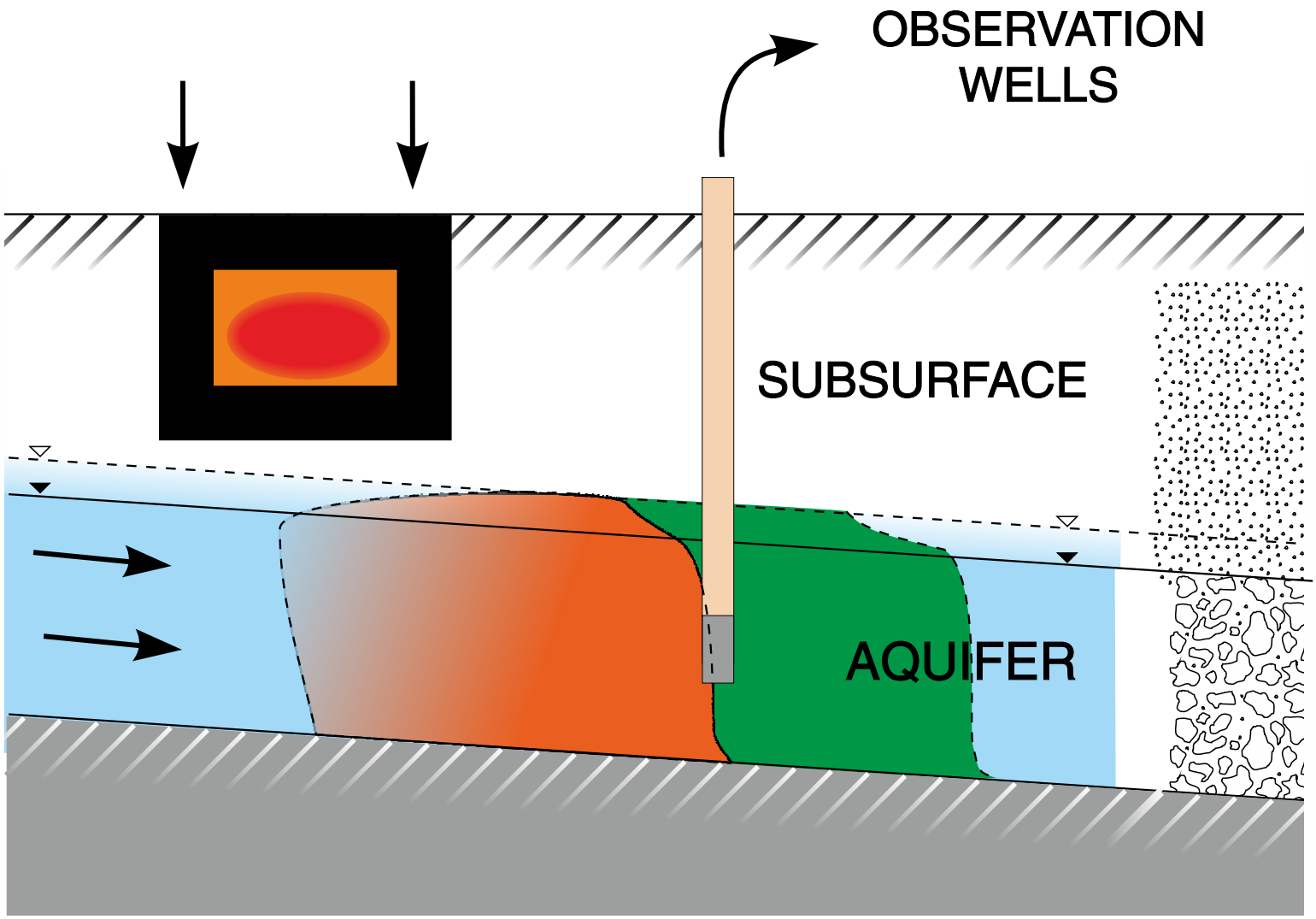
Pollution - Remediation Scenario



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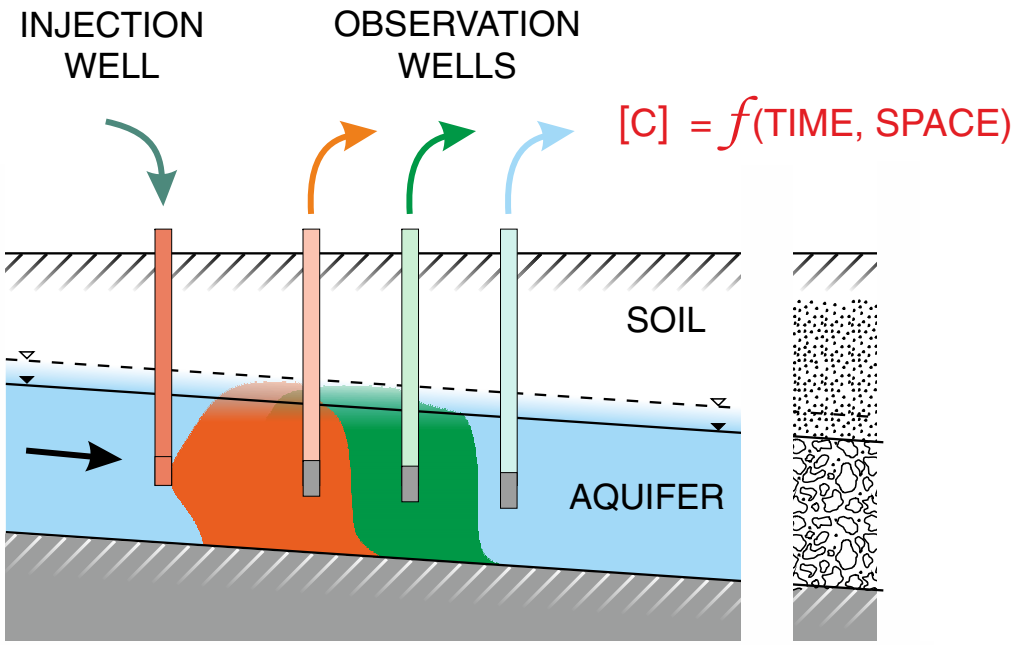
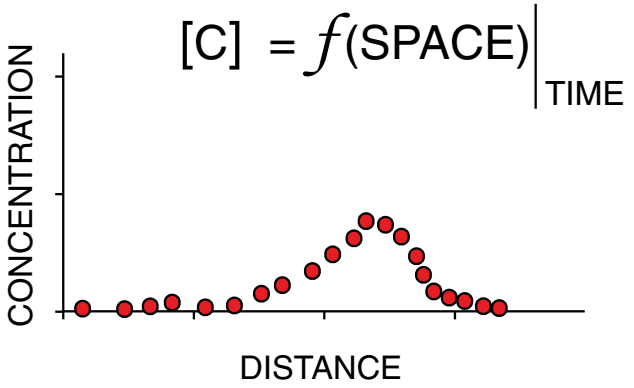
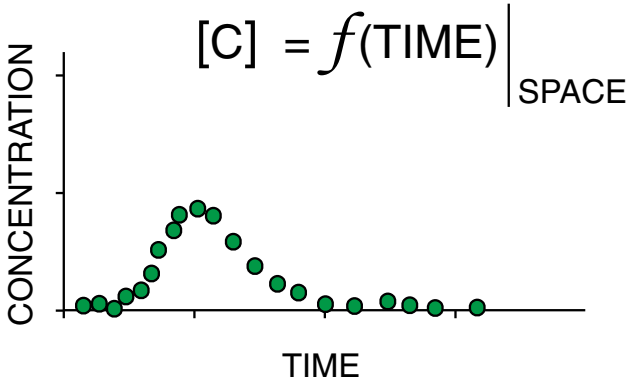
Transport Experiments





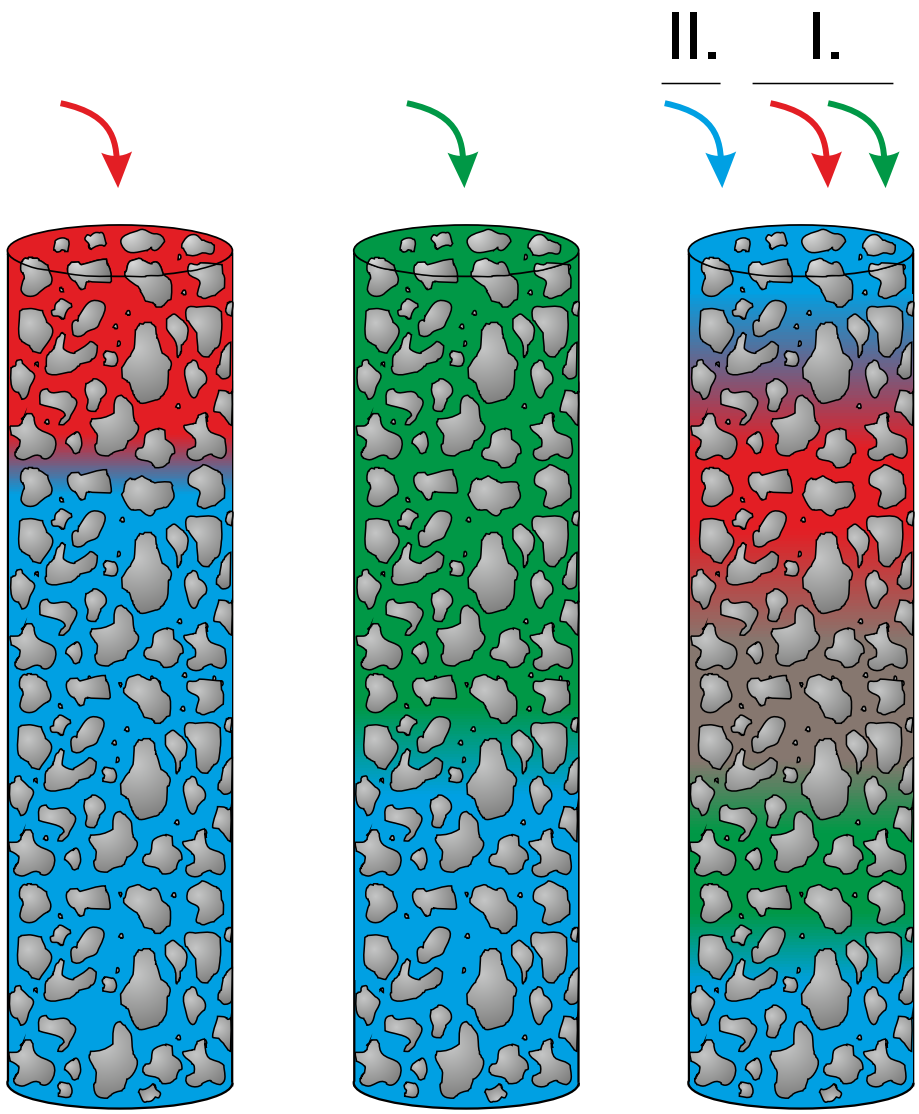
'PROFILE' / 'SPREADING'

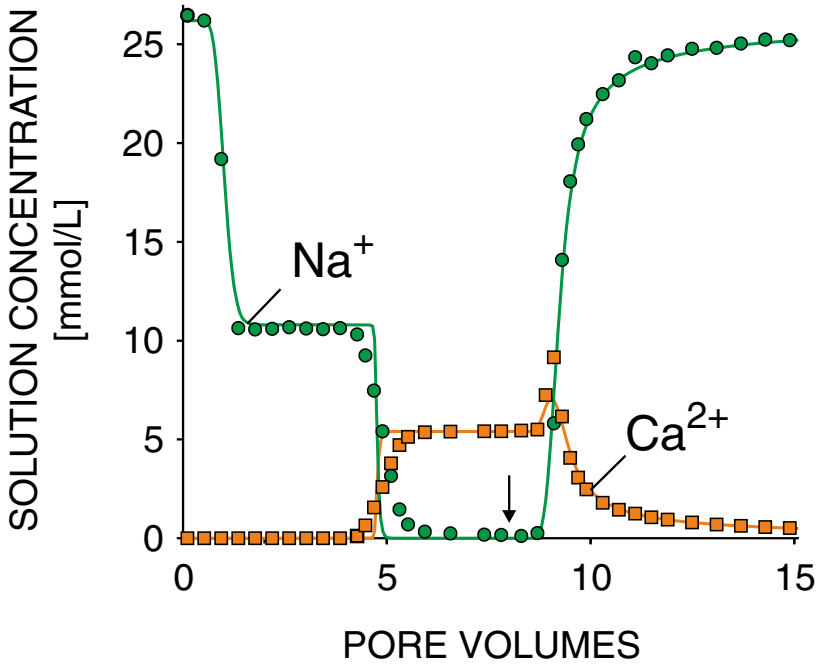


'BREAK-THROUGH CURVE'

INTRODUCTION

Transport Experiments





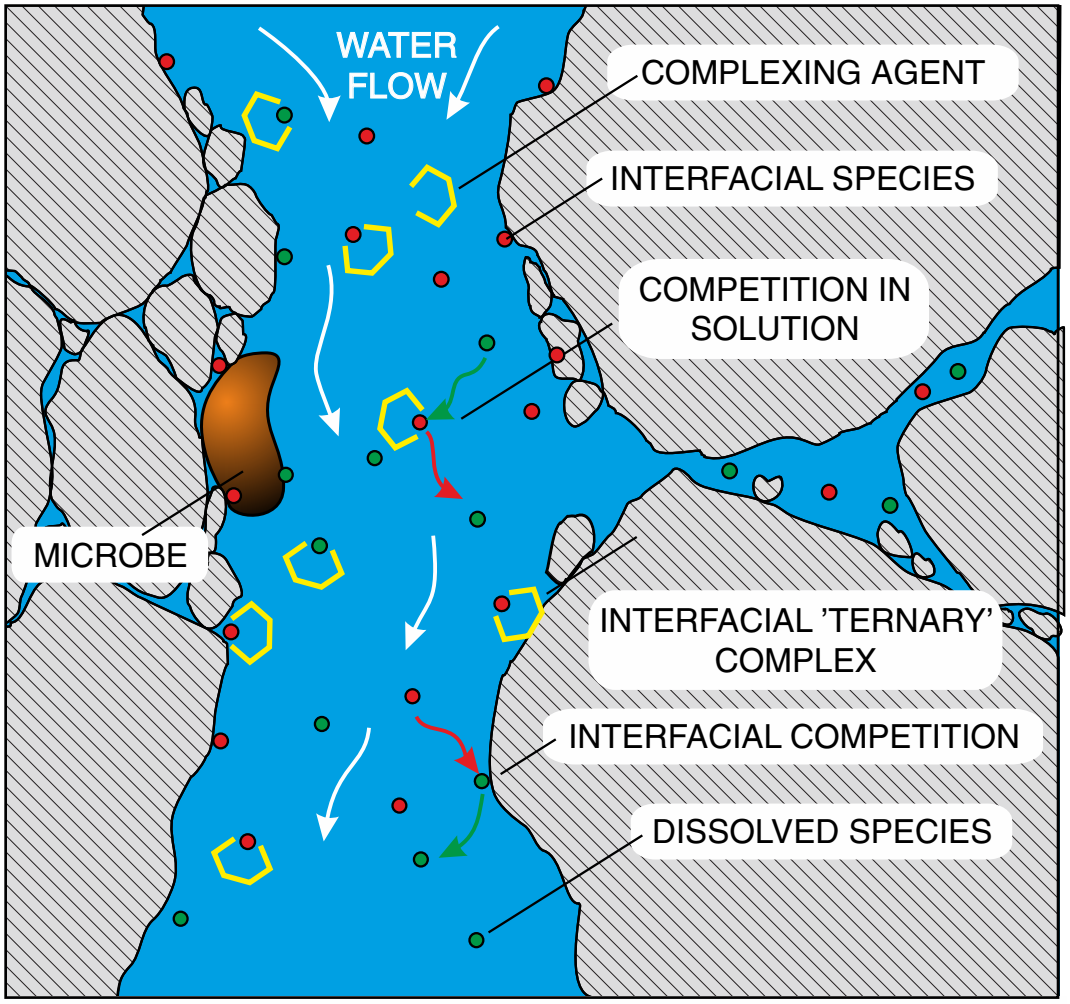
'BREAK-THROUGH CURVE'

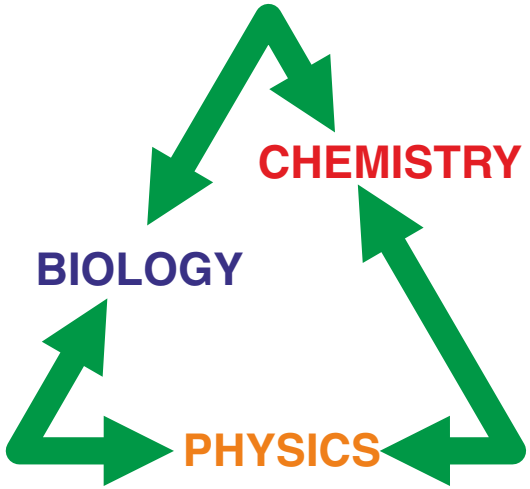
$$[C] = f(\text{TIME})\Big|_{\text{SPACE}}$$

INTRODUCTION

Nature's Complexity

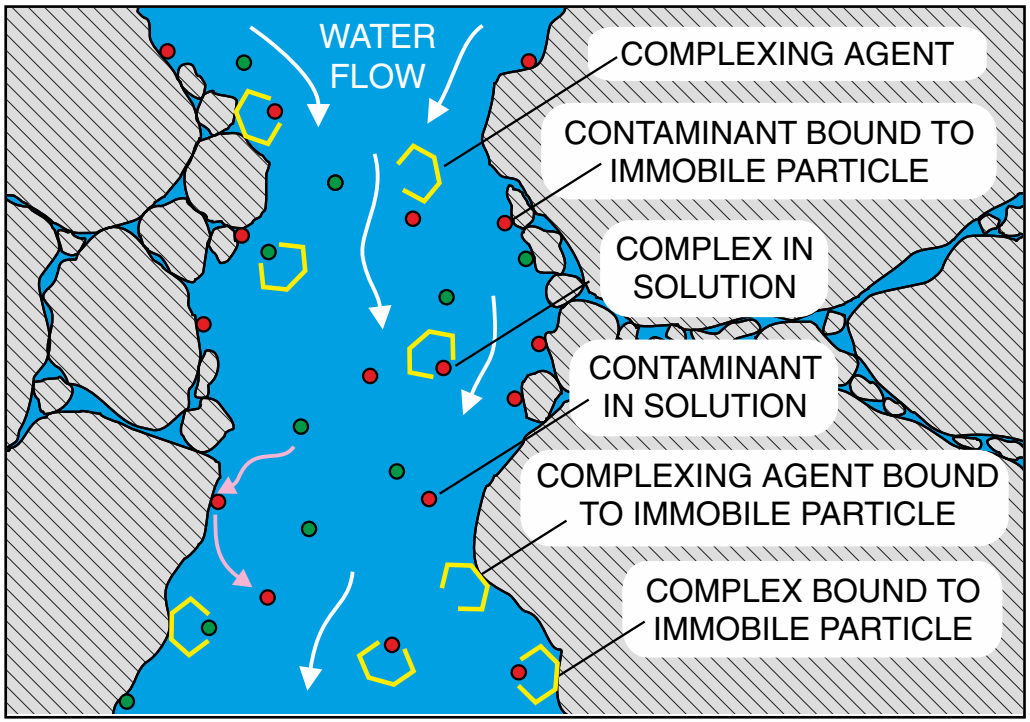
CONVECTIVE — DIFFUSIVE





INTRODUCTION

‘Classical’ Contaminant Transport Modelling



$$\frac{\partial c_{i,tot}}{\partial t} = D\frac{\partial^2 c_{i,tot}}{\partial x^2} - v\frac{\partial c_{i,tot}}{\partial x} - \sum_i \sum_k \frac{\partial q_i}{\partial c_k}\frac{\partial c_k}{\partial t}$$

NON-LINEARITY

HETEROGENEITY

MULTI-COMPONENT EFFECTS

KINETIC

MODELING

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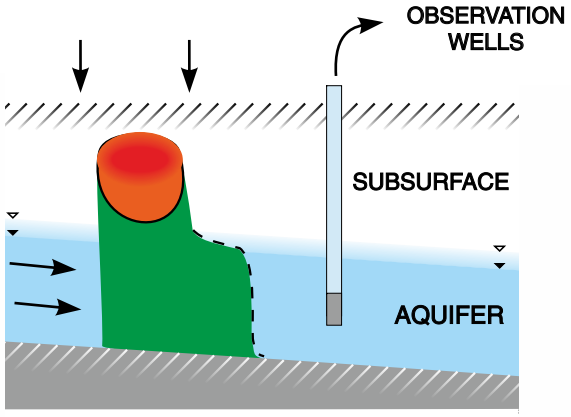

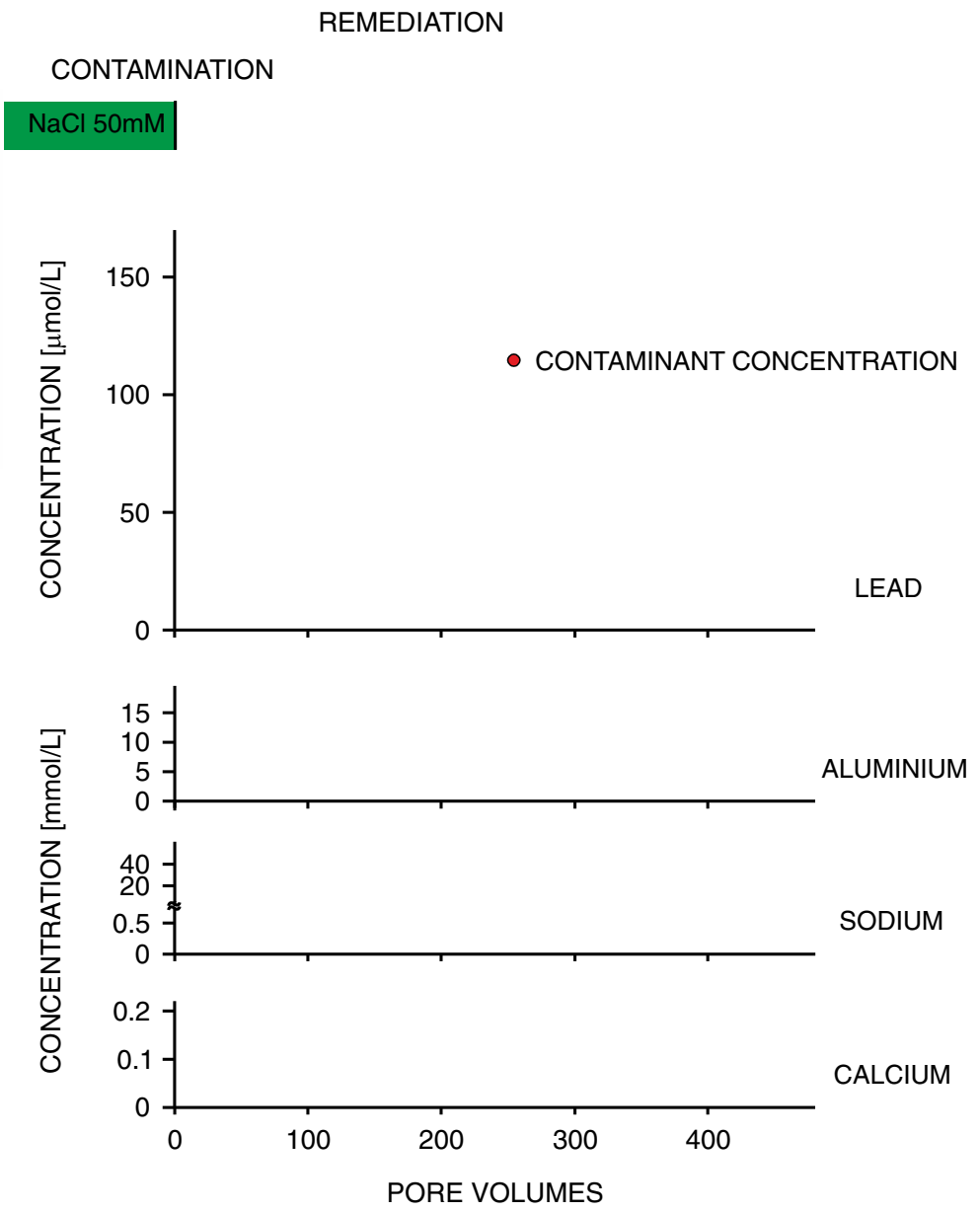

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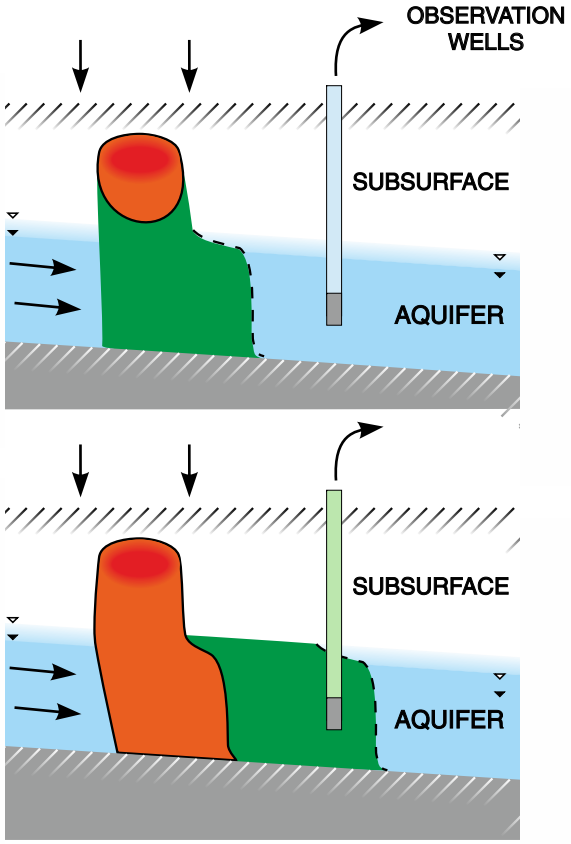
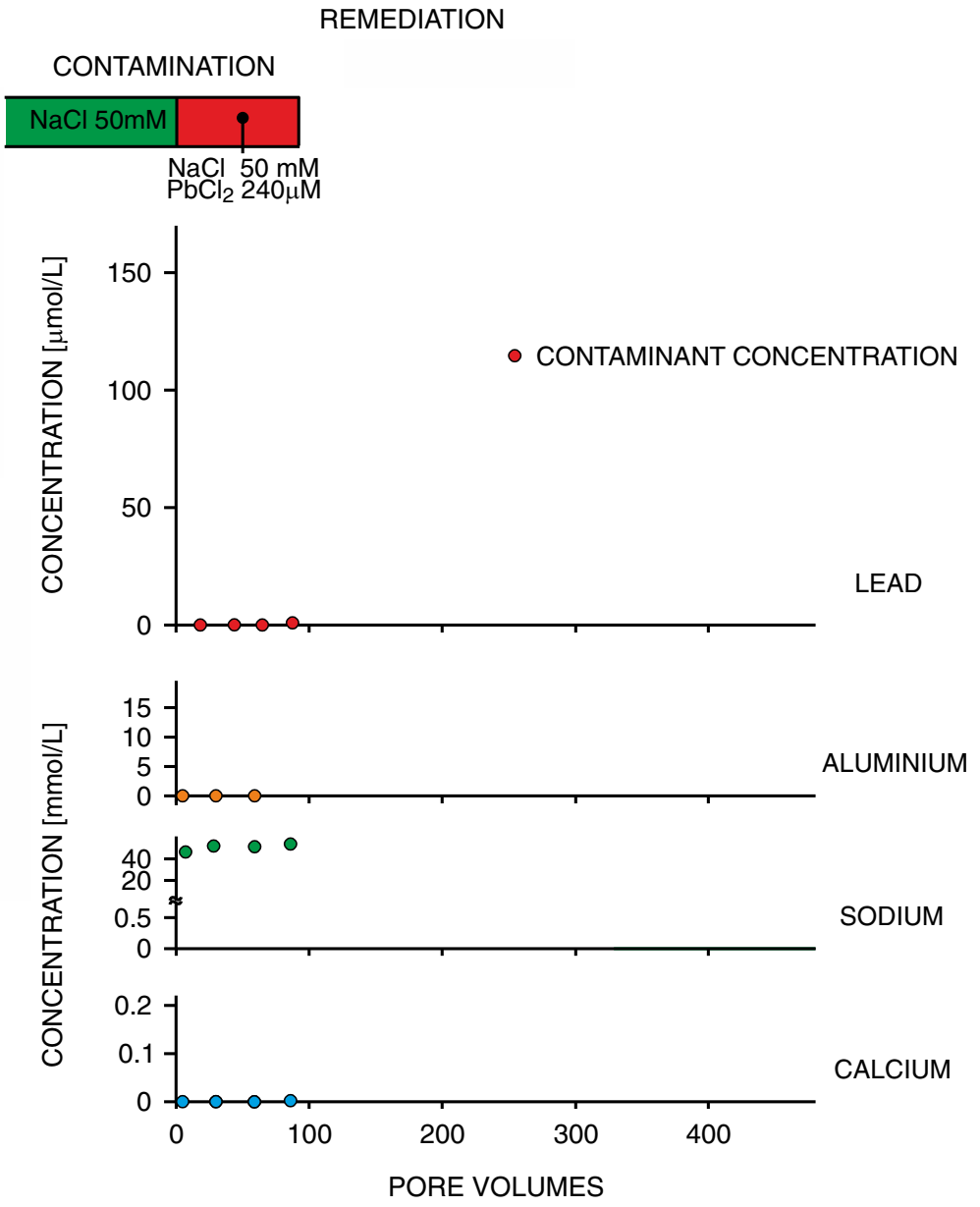
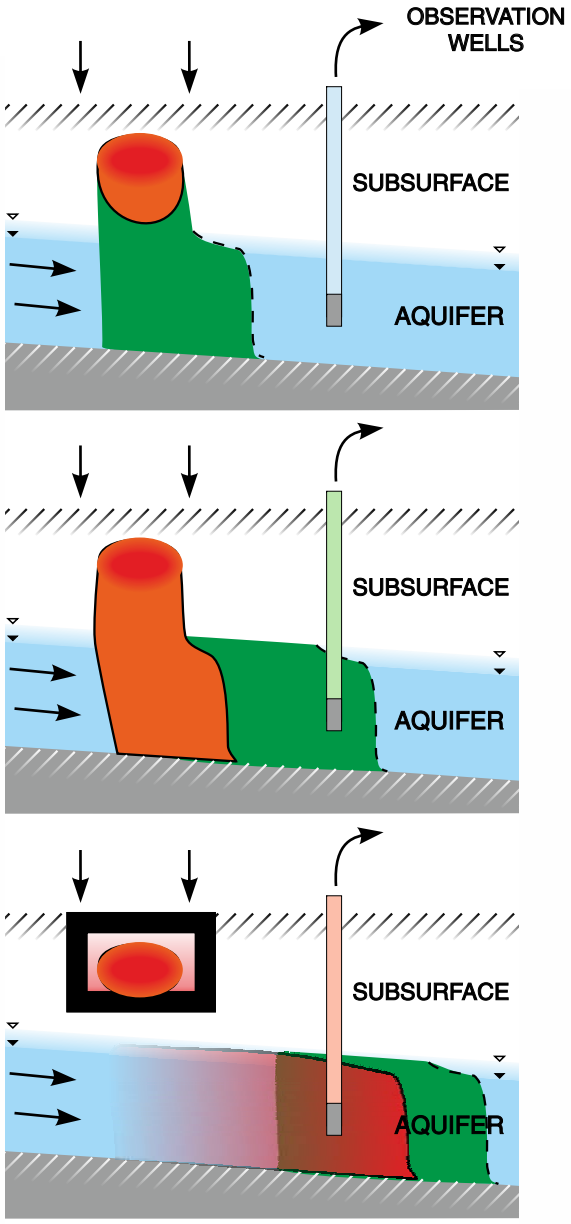
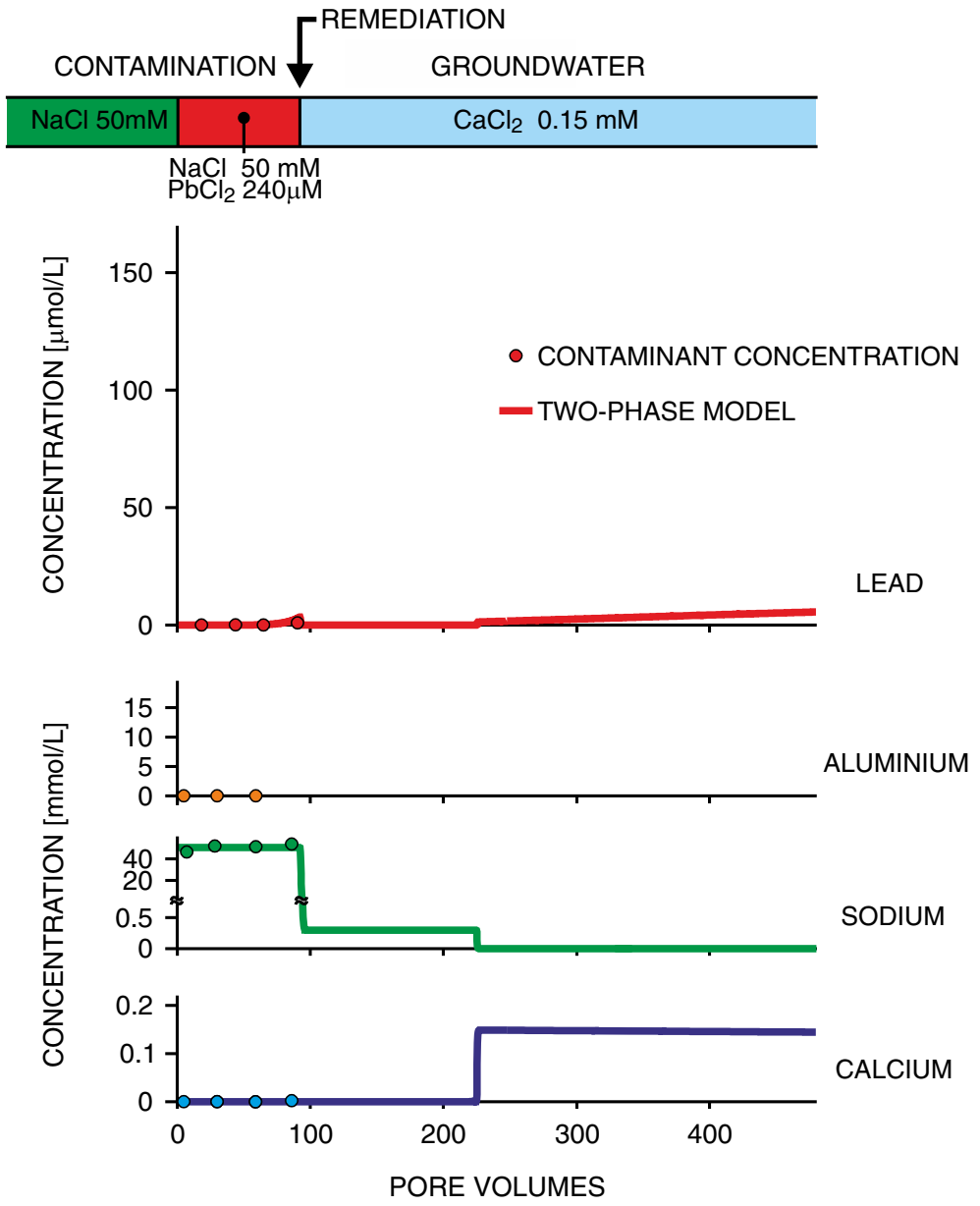




Daniel Grolimund

INTRODUCTION





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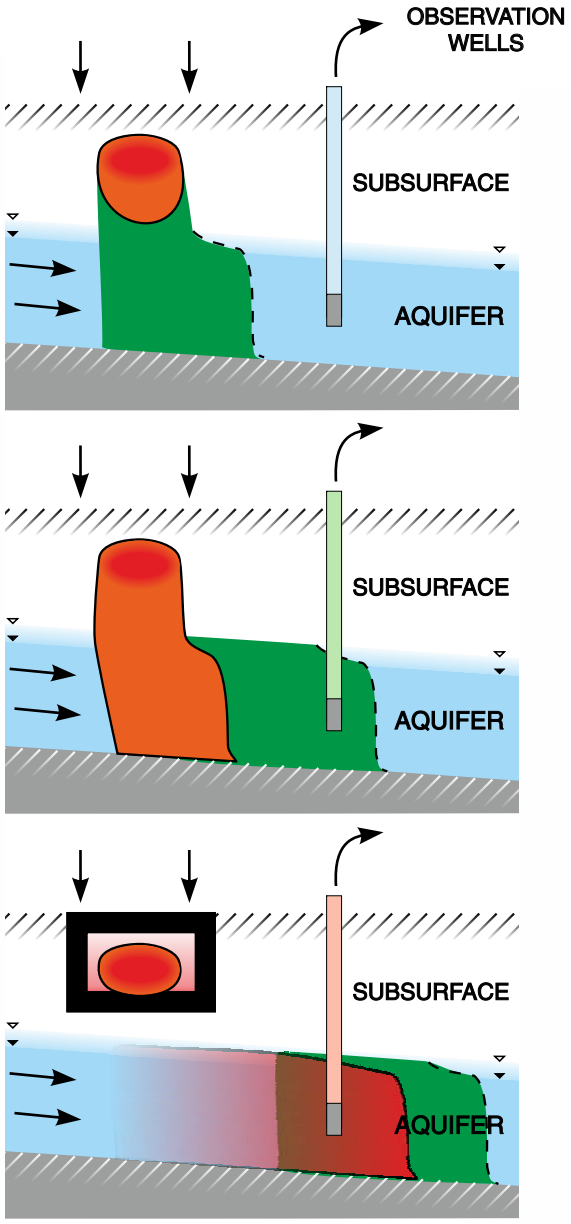

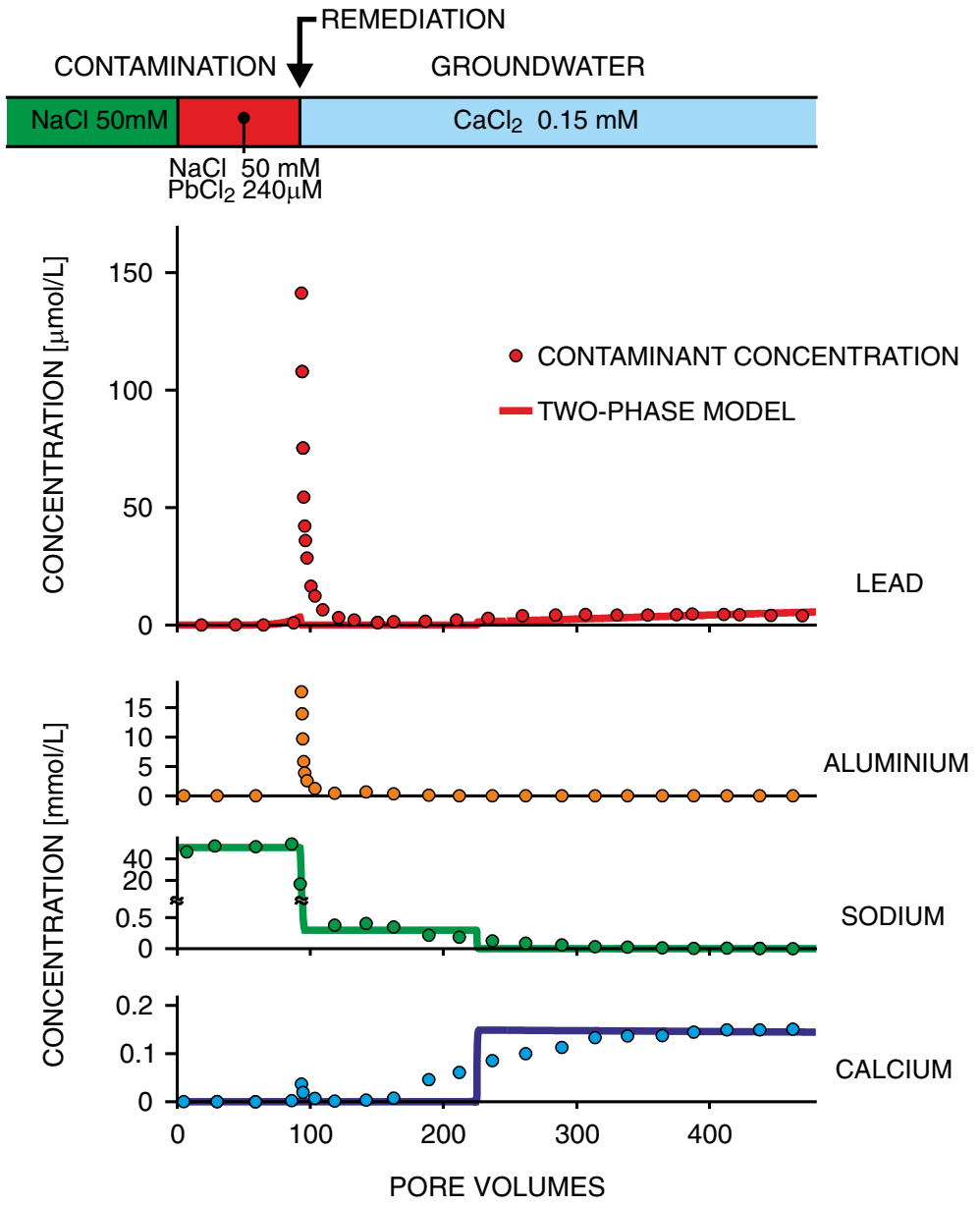

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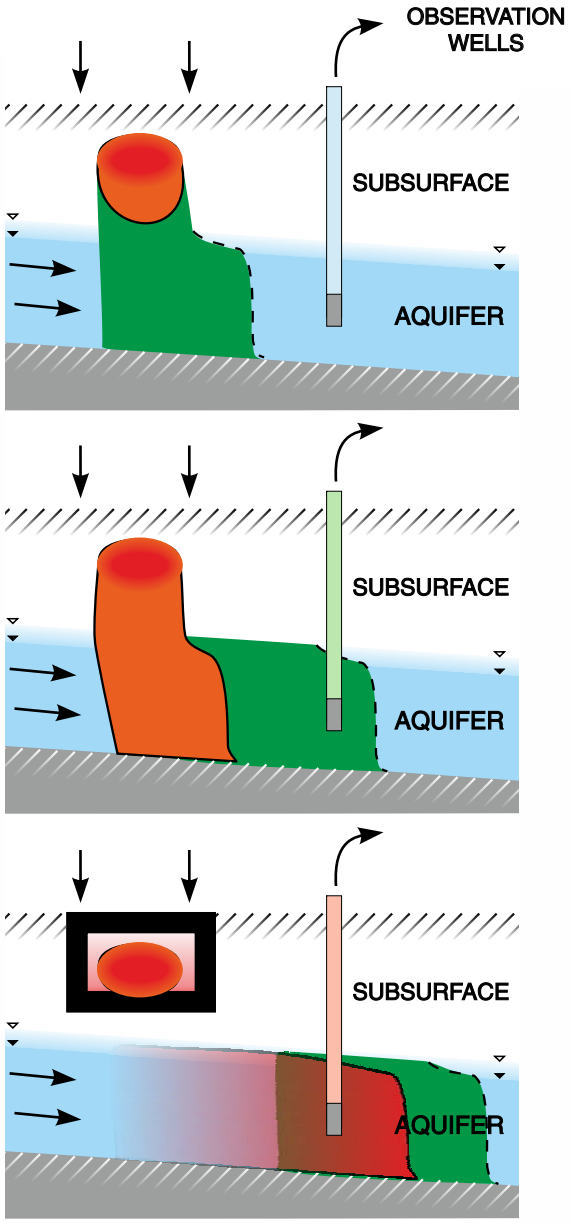
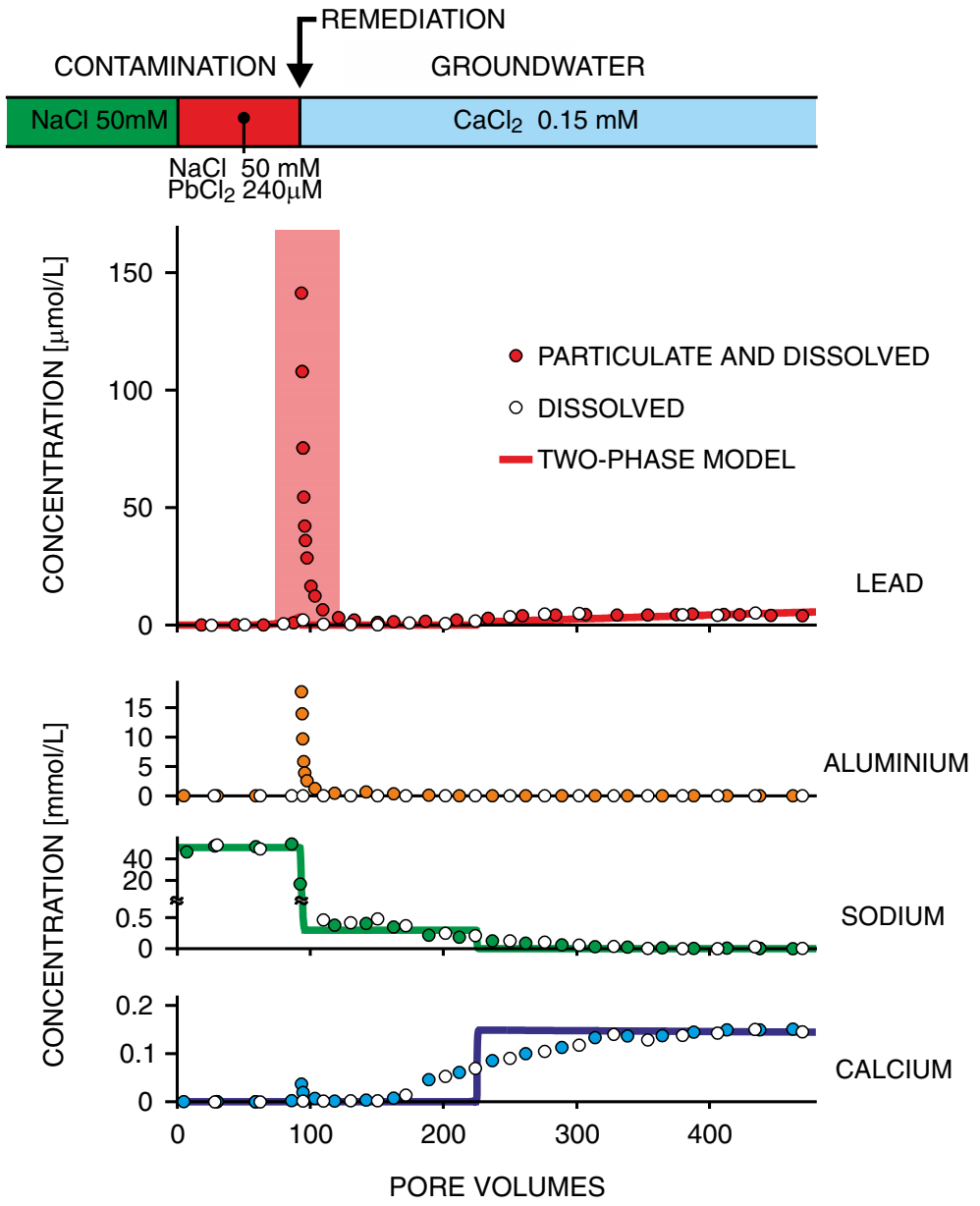
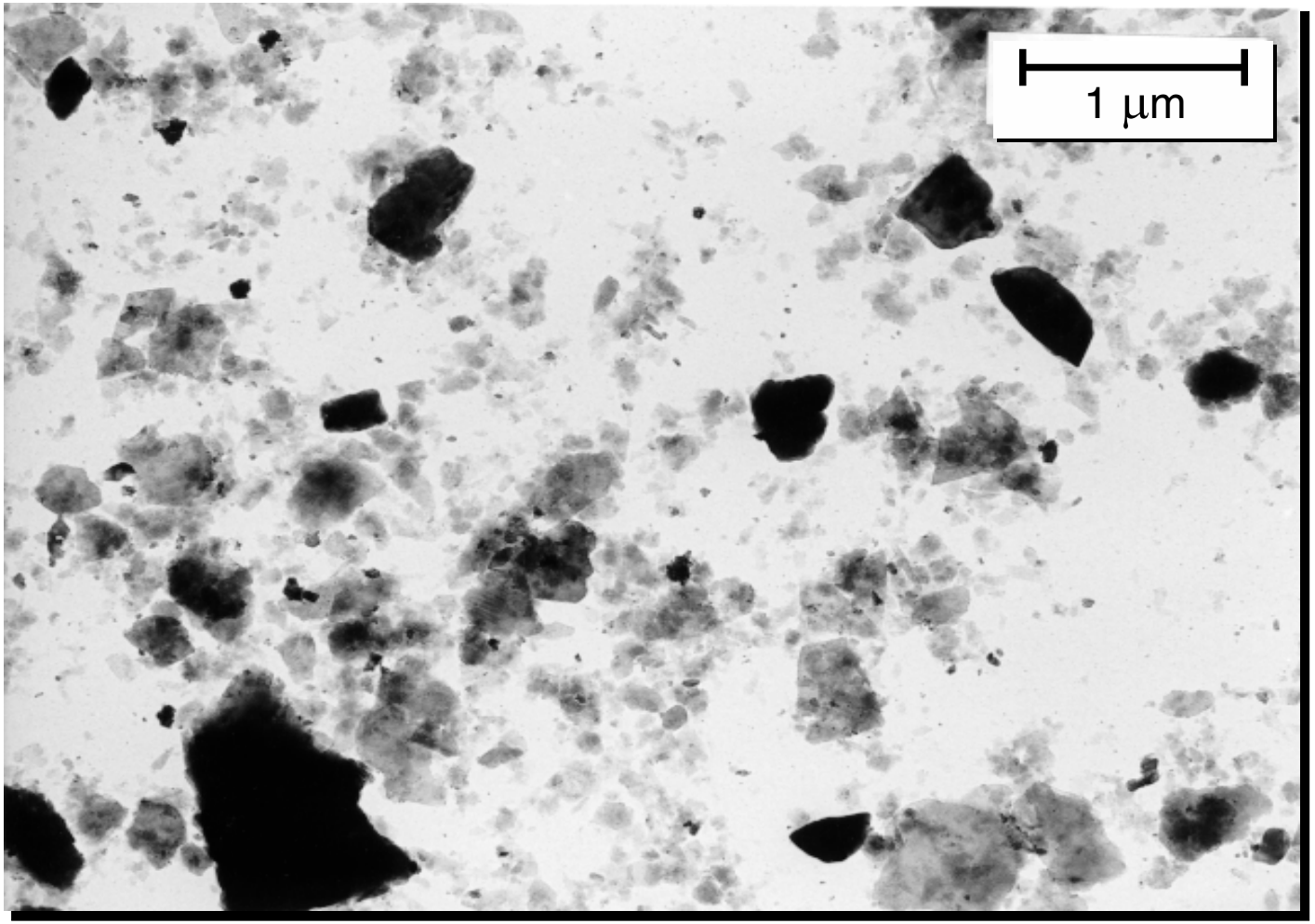




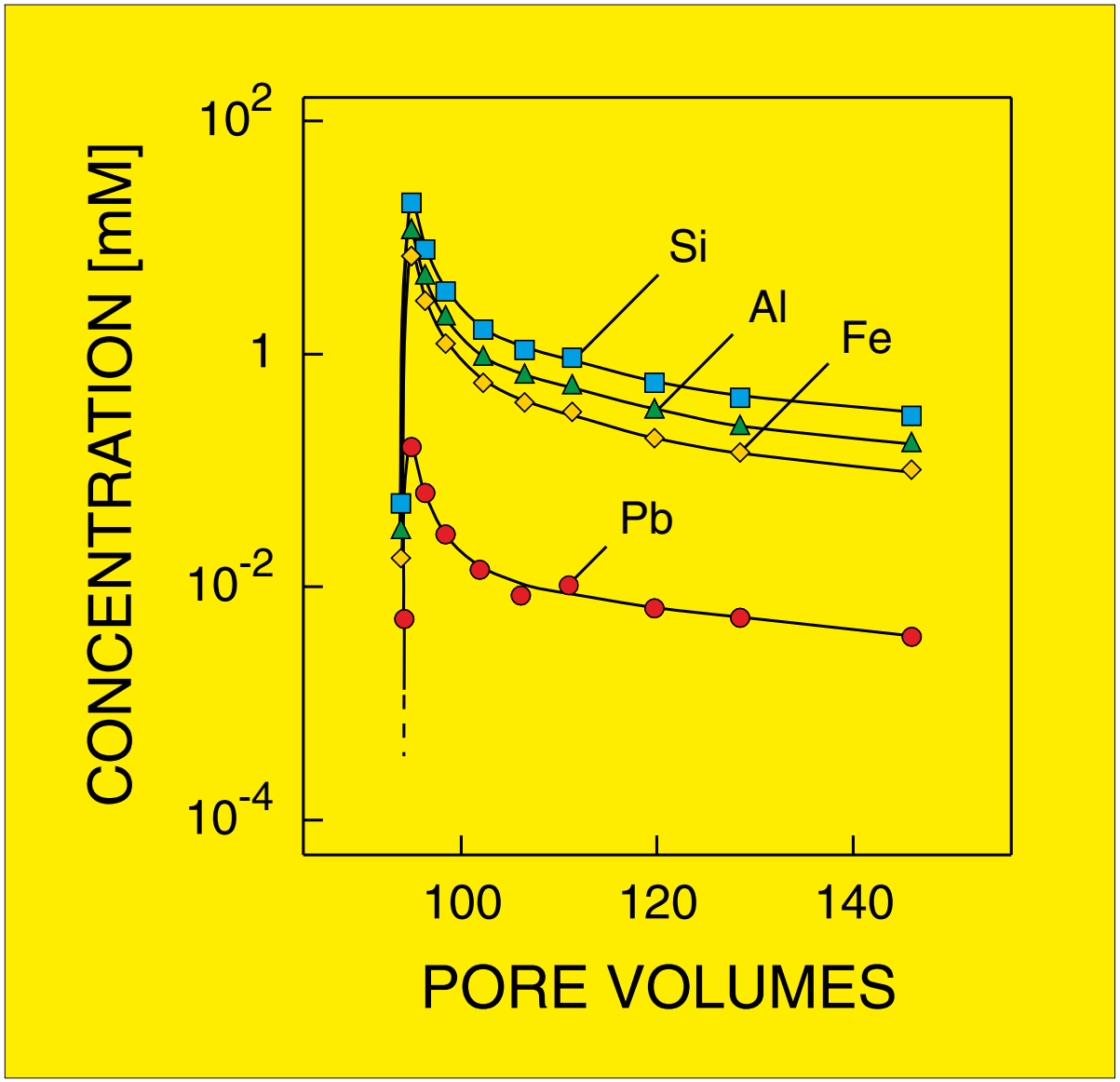
INTRODUCTION

IN-SITU Mobilized Colloidal Particles



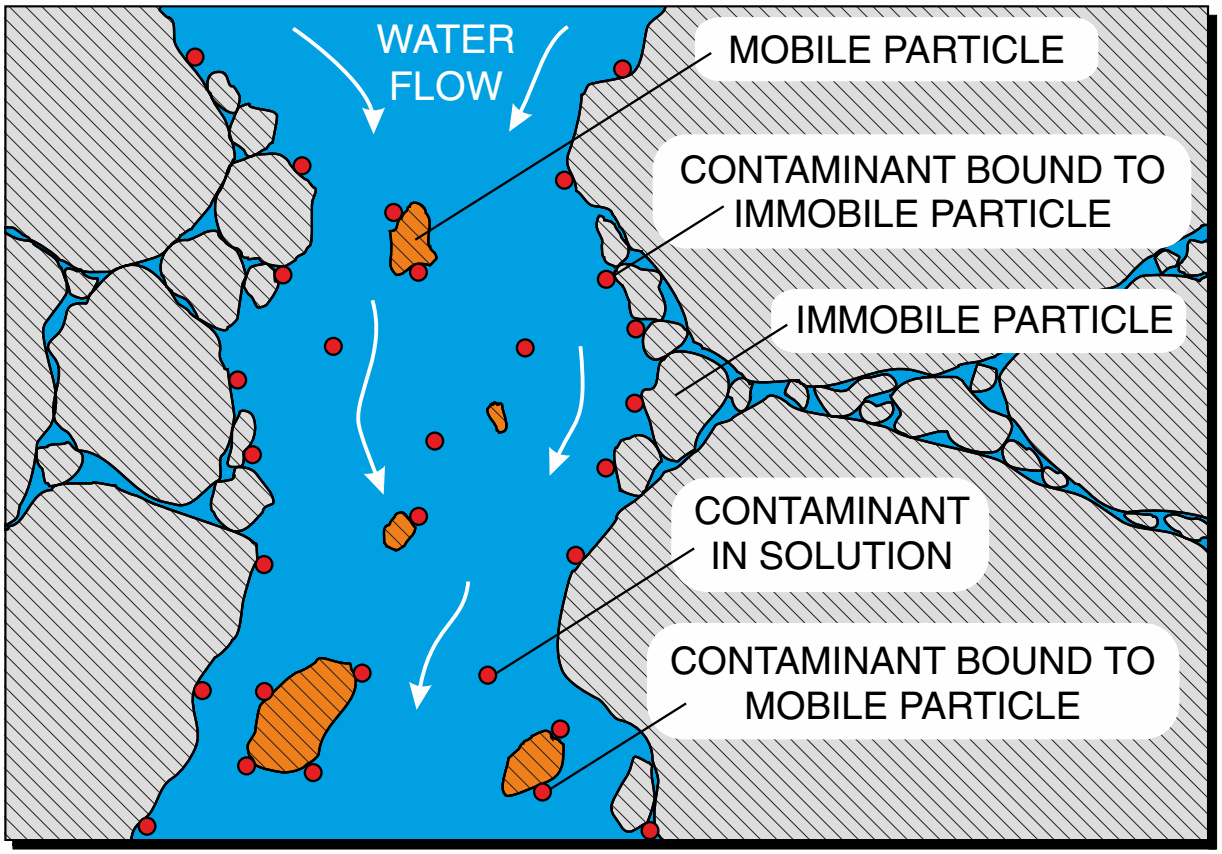
INTRODUCTION

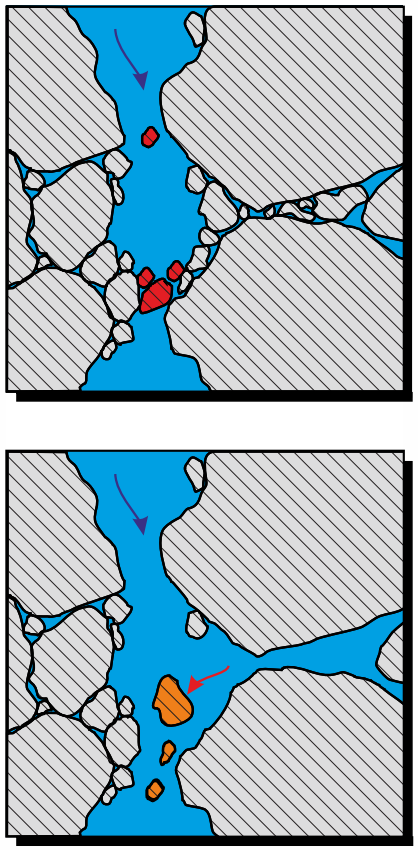
Colloid Facilitated Transport



COLLOID TRANSPORT PHENOMENA

Mobile Colloidal Particles





COLLOID FACILITATED CONTAMINANT TRANSPORT

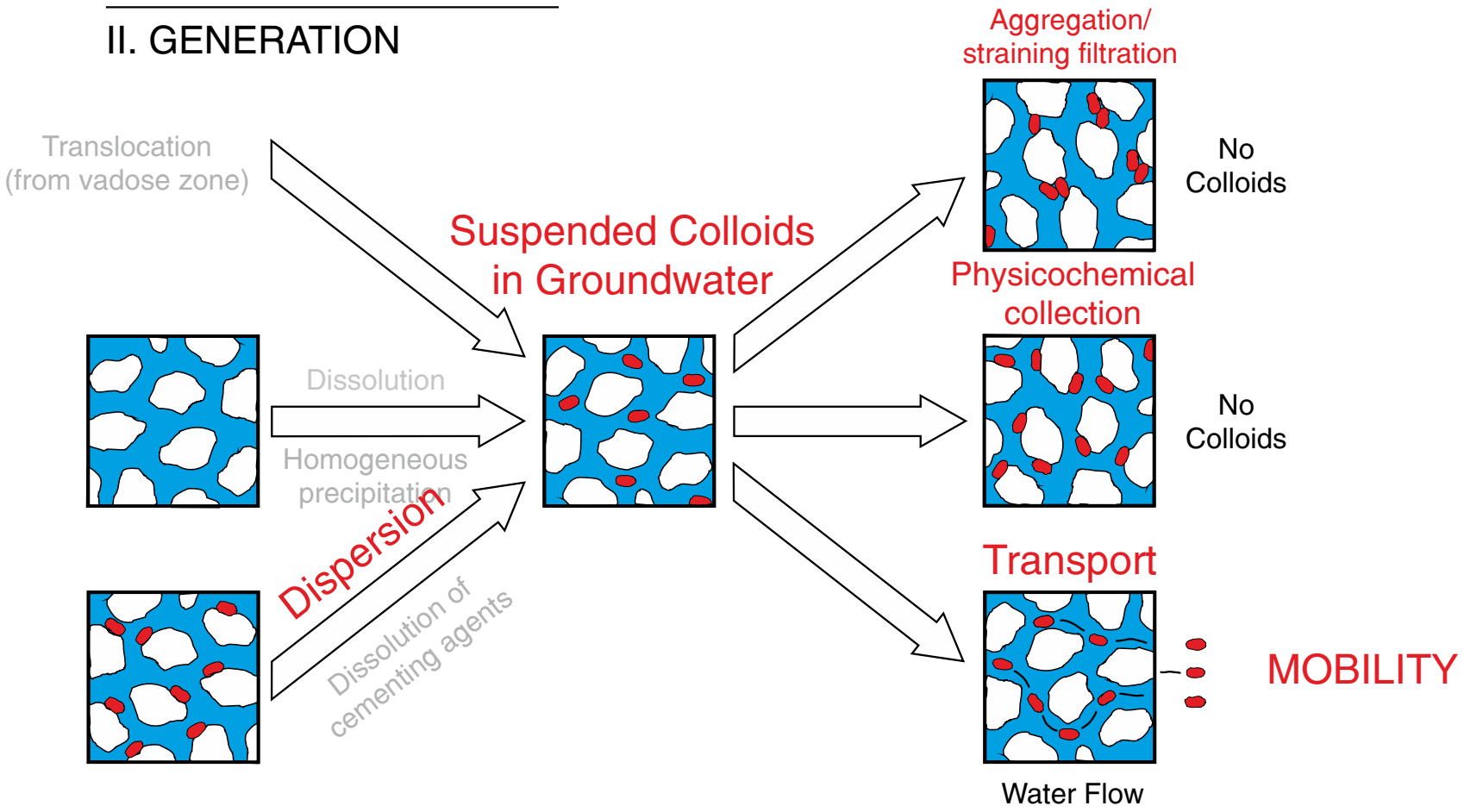
PORE STRUCTURE and REACTIVITY

COLLOID TRANSPORT PHENOMENA

I. CONTAMINANT - PARTICLE INTERACTIONS

III. PERSISTENCE

II. GENERATION



adapted from McCarthy & Zachara, ES&T, 1989

COLLOID TRANSPORT PHENOMENA

http://www.psi.ch/~grolimund/list_of_publications.html

I. GENERATION

- Grolimund, D.; Borkovec, M., Long term release kinetics of colloidal particles from natural porous media, Environmental Science & Technology 1999, 33, 4054-4060.
- Grolimund, D.; Borkovec, M., Release and Transport of Colloidal Particles in Natural Porous Media: 1. Modeling, Water Resources Res., 37, 559, (2001).
- Grolimund, D.; Barmettler, K.; Borkovec, M., Release and transport of colloidal particles in natural porous media 2. Experimental results and effects of ligands, Water Resour. Res. 2001, 37, 571-582.
- Grolimund, D.; Borkovec, M., Release of Colloidal Particles in Natural Porous Media by Monovalent and Divalent Cations, submitted 2005.

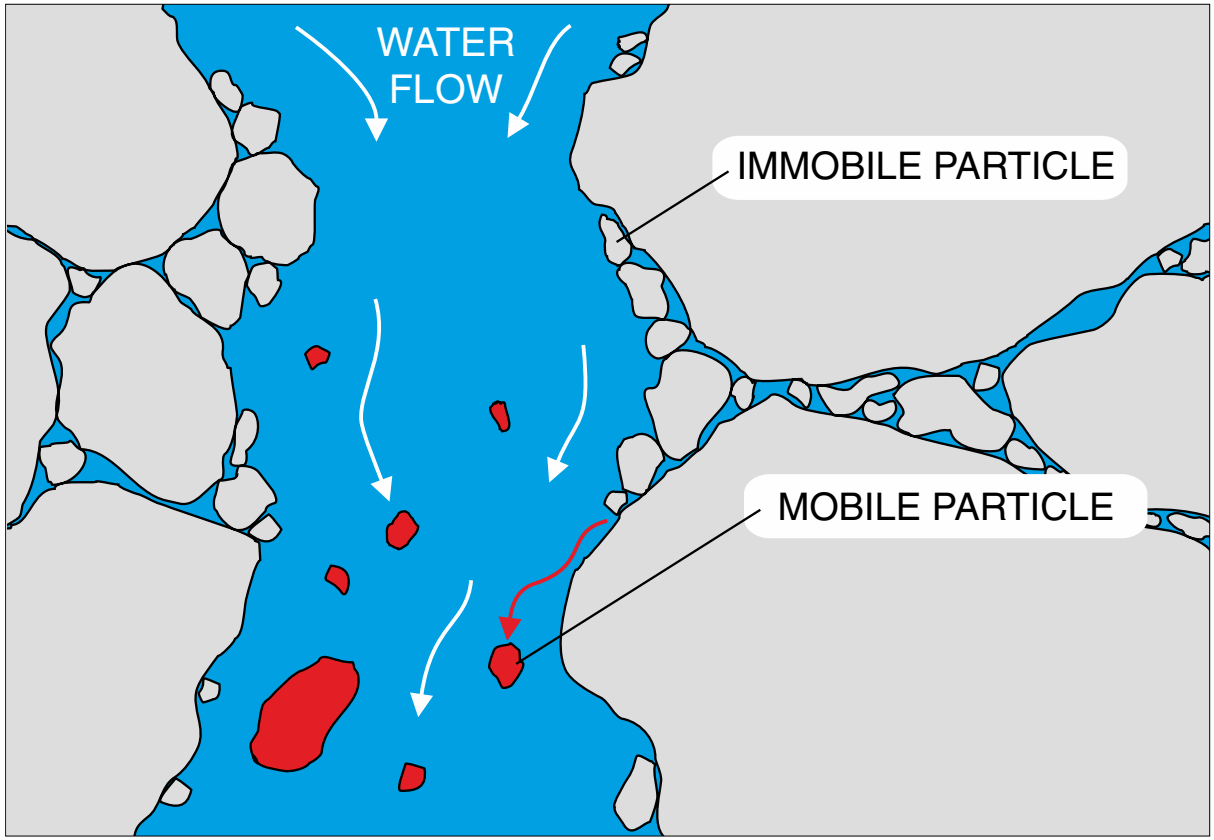
II. PERSISTENCE

- Grolimund, D.; Elimelech, M.; Borkovec, M.; Barmettler, K.; Kretzschmar, R.; Sticher, H., Transport of in situ mobilized colloidal particles in packed soil columns, Environmental Science & Technology 1998, 32, 3562-3569.
- Grolimund, D.; Elimelech, M.; Borkovec, M., Aggregation and deposition kinetics of mobile colloidal particles in natural porous media, Colloid Surf. A-Physicochem. Eng. Asp. 2001, 191, 179-188.

III. COLLOID FACILITATED TRANSPORT

- Grolimund, D.; Borkovec, M.; Barmettler, K.; Sticher, H., Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: A laboratory column study, Environmental Science & Technology 1996, 30, 3118-3123.
- Grolimund, D.; Borkovec, M., Colloid-Facilitated Transport of Strongly Sorbing Contaminants in Natural Porous Media: Mathematical Modeling and Laboratory Column Experiments, Environmental Science & Technology, in press 2005.

RELEASE of COLLOIDAL PARTICLES



$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} + \rho k_{rel} q$$

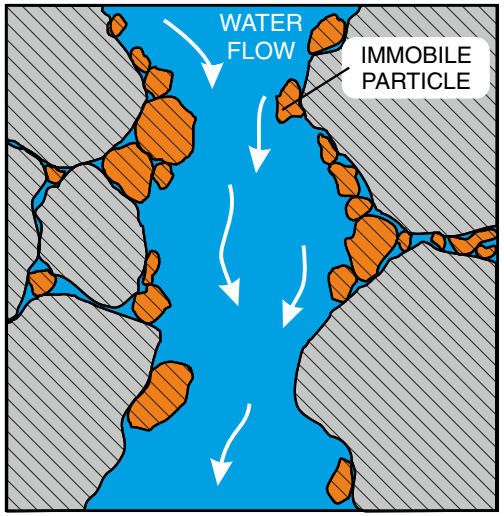
Dispersion Convection **'Source'**

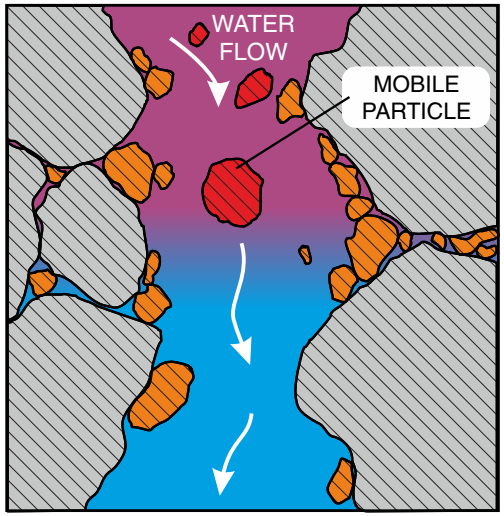
RELEASE of COLLOIDAL PARTICLES

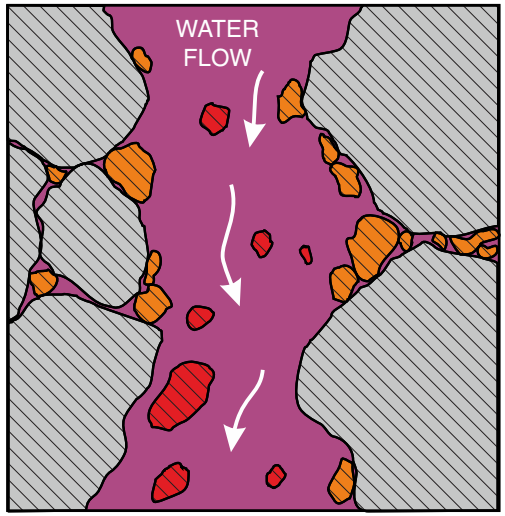
Subsurface Systems: Disturbances

DISTURBANCE

- CHEMICAL (chromatographic fronts)
- PHYSICAL



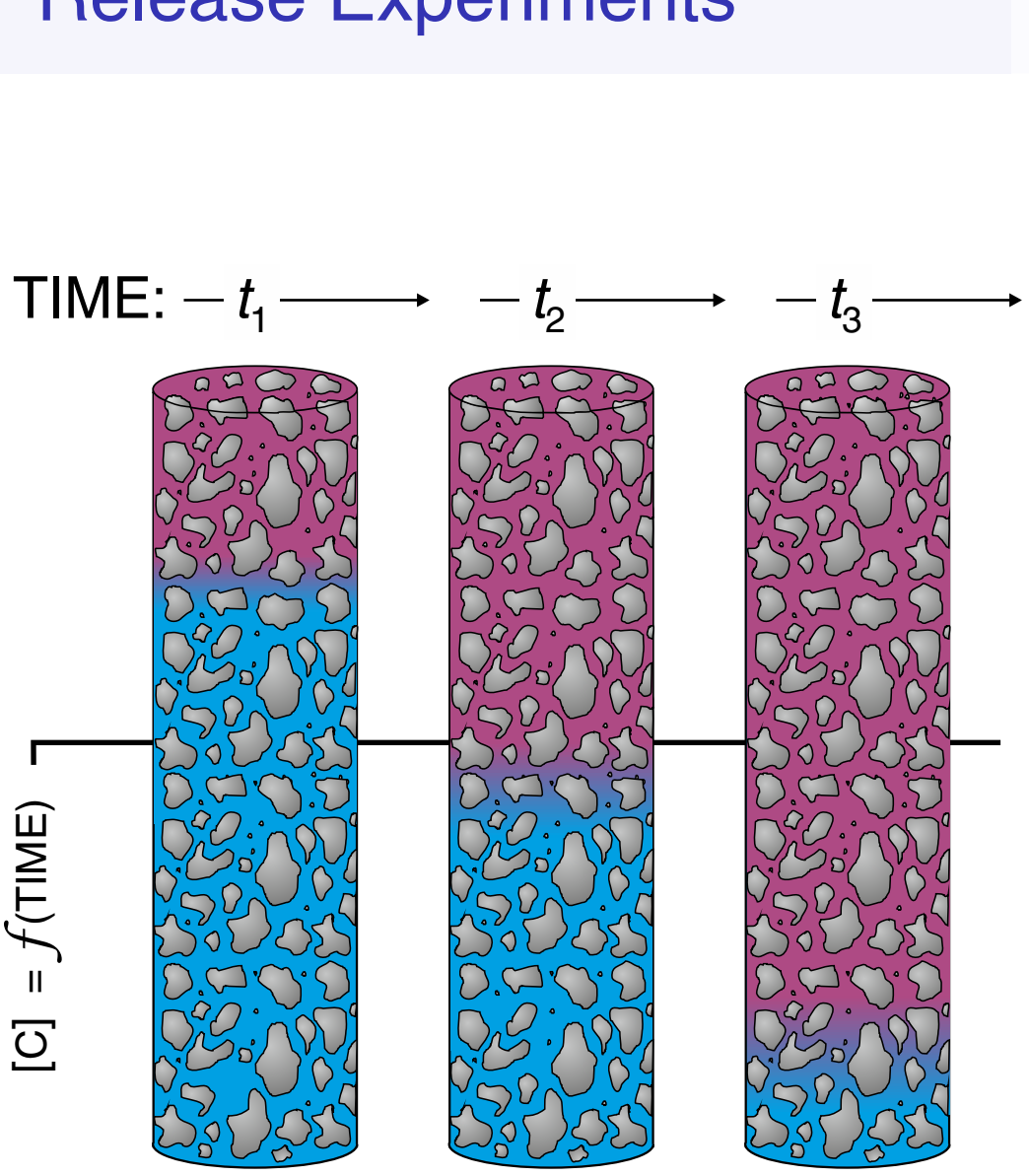


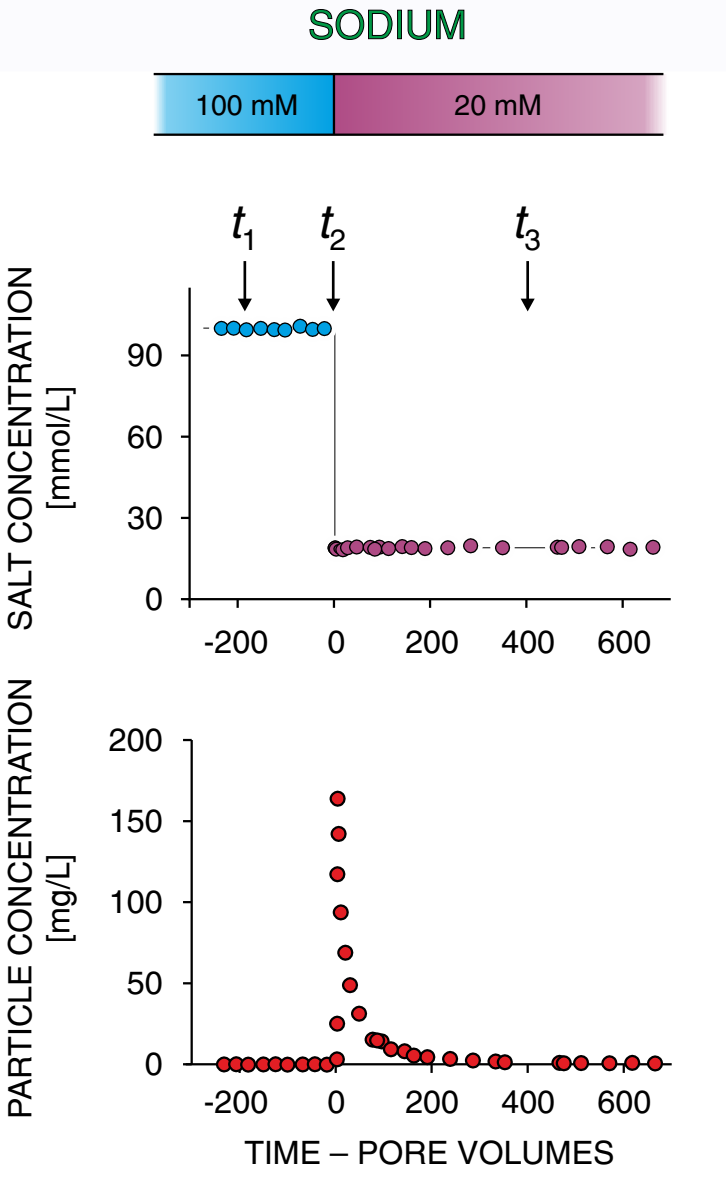


- MOBILIZATION
- RELEASE
- TRANSPORT
- PERSISTENCE

RELEASE of COLLOIDAL PARTICLES

Release Experiments

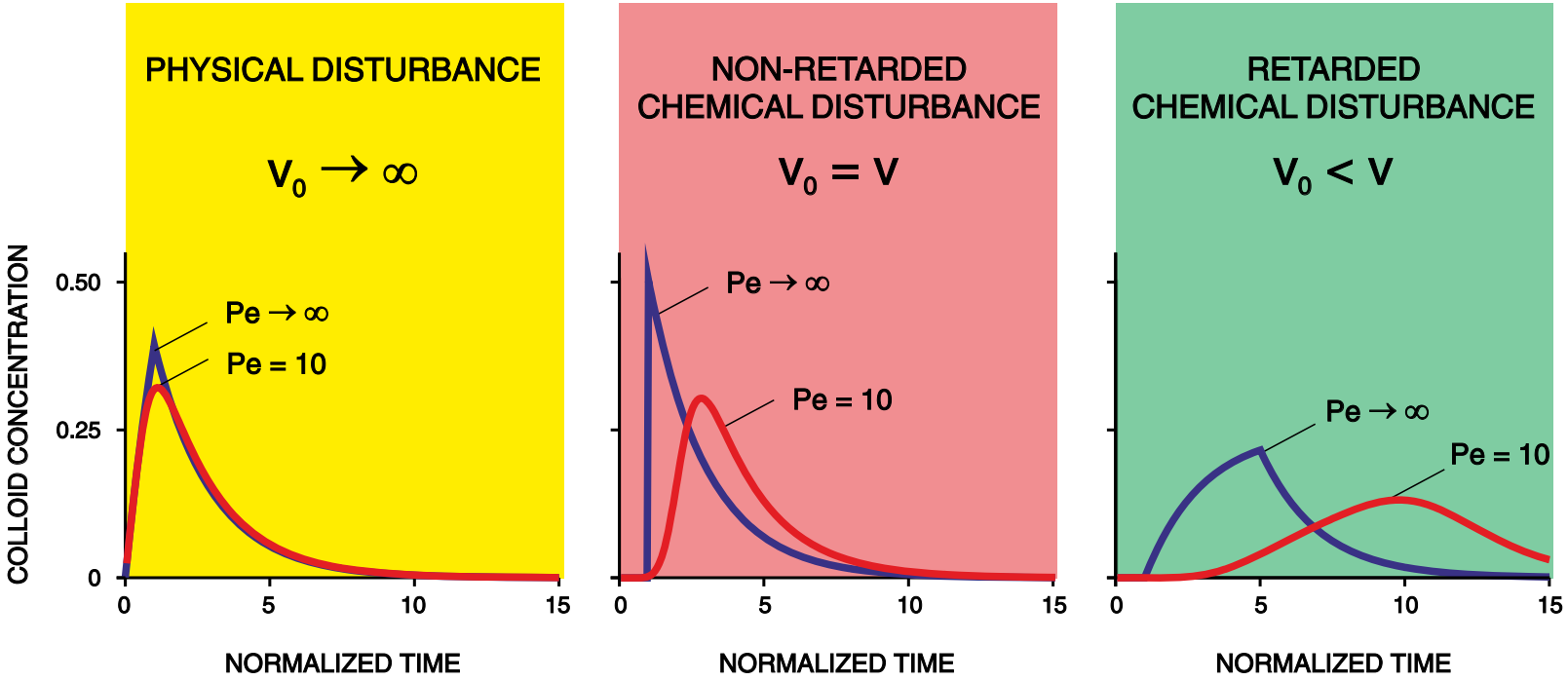




'BREAK-THROUGH CURVE'

RELEASE of COLLOIDAL PARTICLES

Mobilization of Colloidal Particles

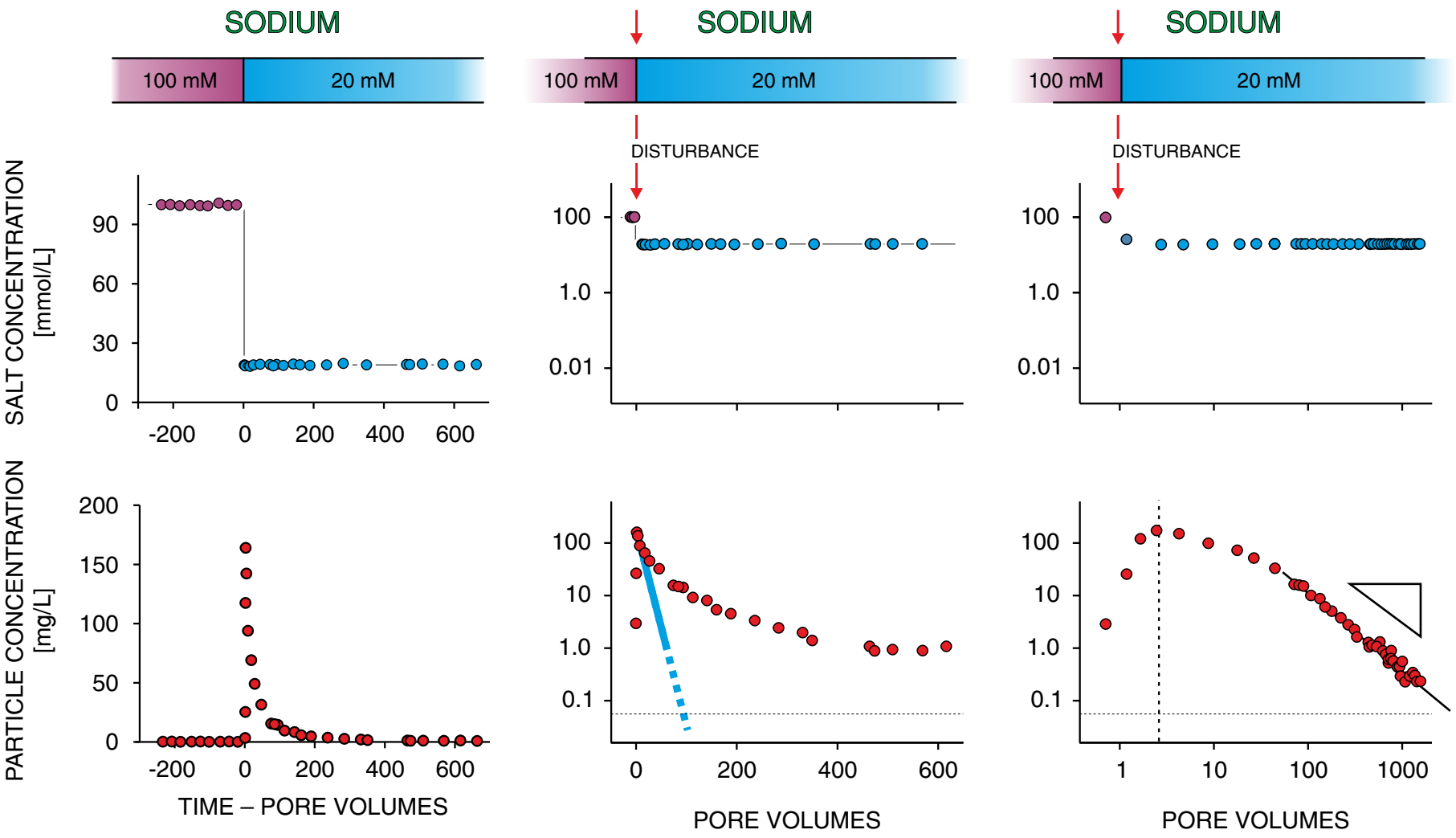


$$R_0 \frac{\partial c_0}{\partial t} = D_0 \frac{\partial^2 c_0}{\partial x^2} - v_0 \frac{\partial c_0}{\partial x}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} + \rho\, j^{(rel)}(x,t)$$

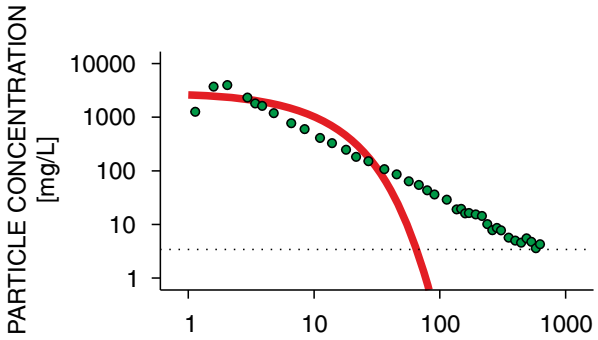
RELEASE of COLLOIDAL PARTICLES

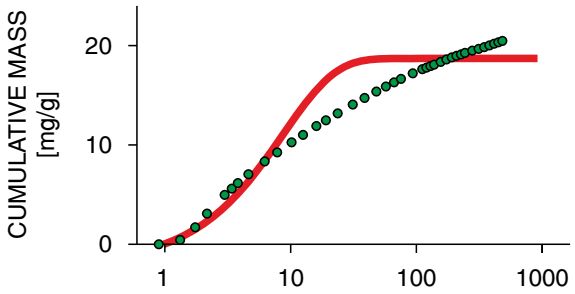
‘Basics’

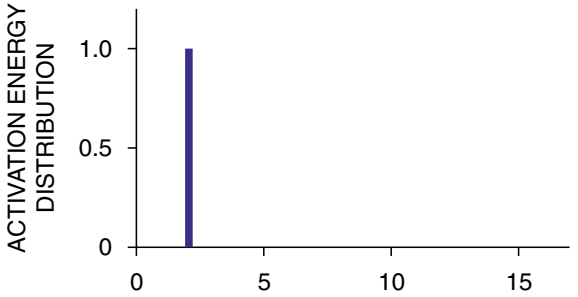


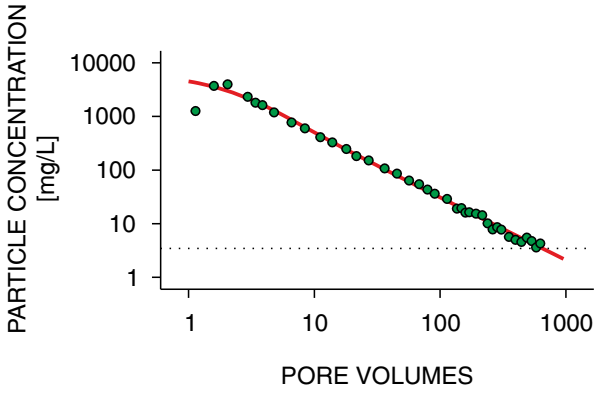
RELEASE of COLLOIDAL PARTICLES

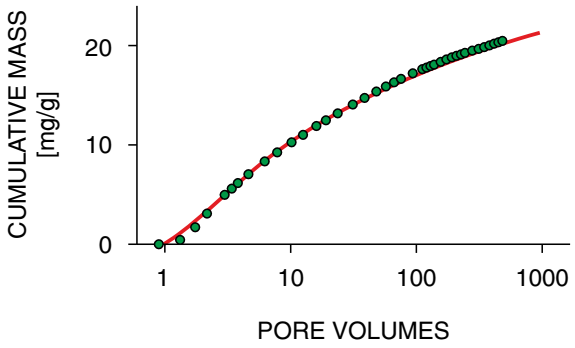
Distribution of Populations

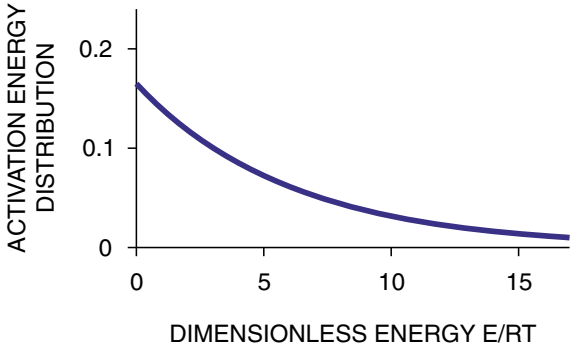






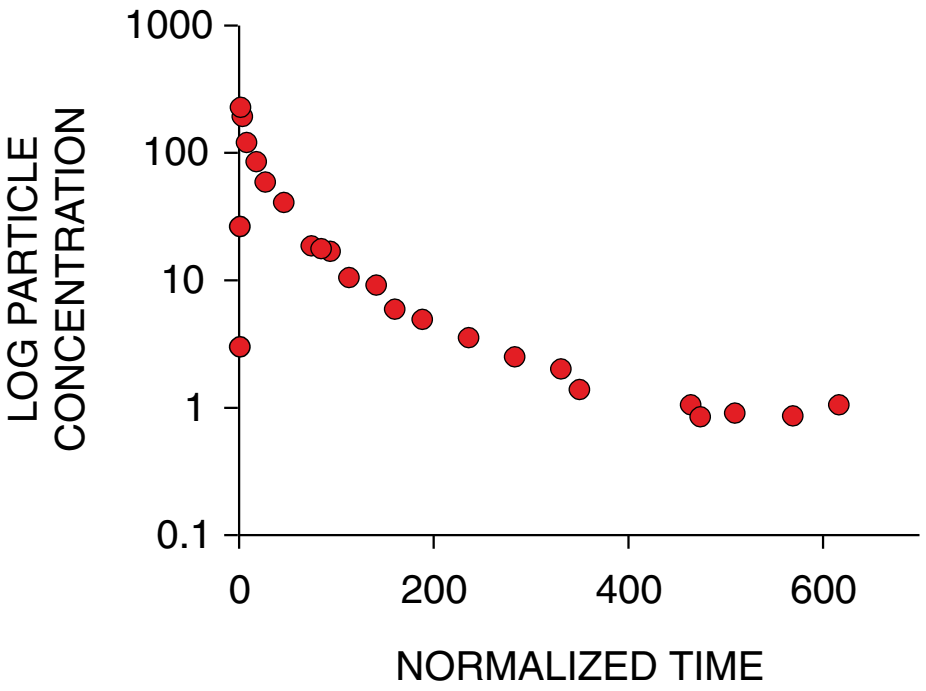


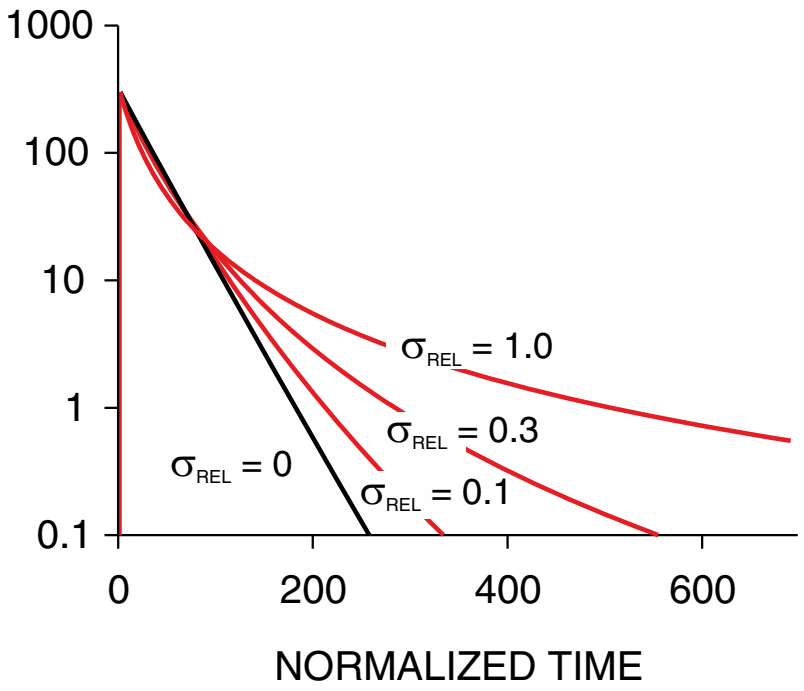




RELEASE of COLLOIDAL PARTICLES

Distribution of Populations



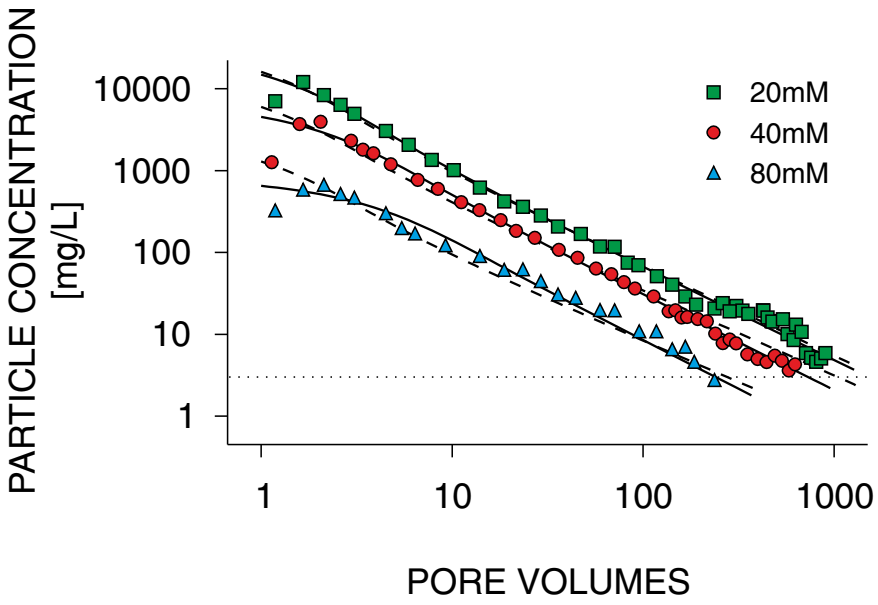


$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} + \sum_i k_i^{(rel)} Q_i \qquad with \quad \frac{\partial Q_i}{\partial t} = -k_i^{(rel)} Q_i$$

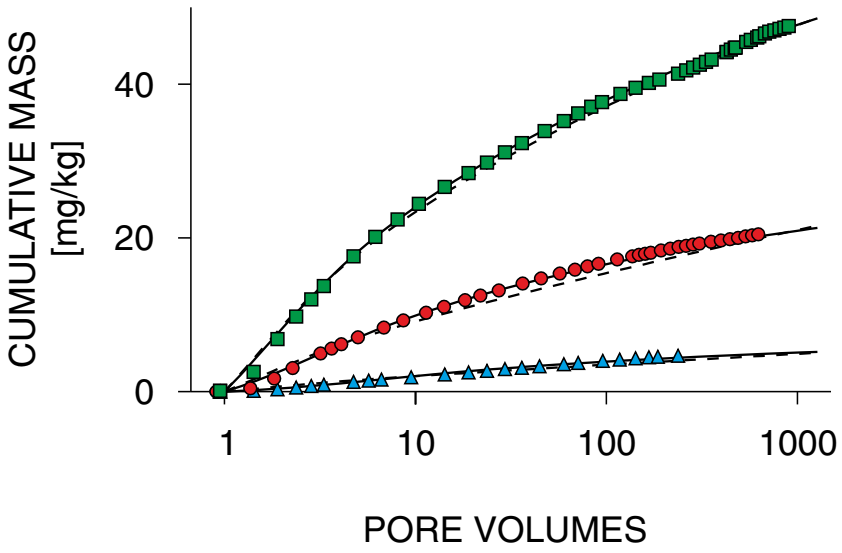
RELEASE of COLLOIDAL PARTICLES

Ionic Strength Dependence

PARTICLE CONCENTRATION



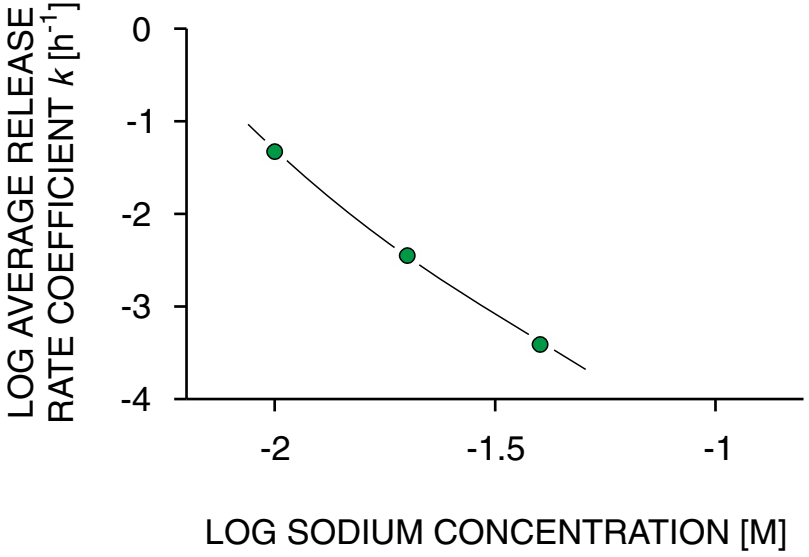
CUMULATIVE MASS



RELEASE of COLLOIDAL PARTICLES

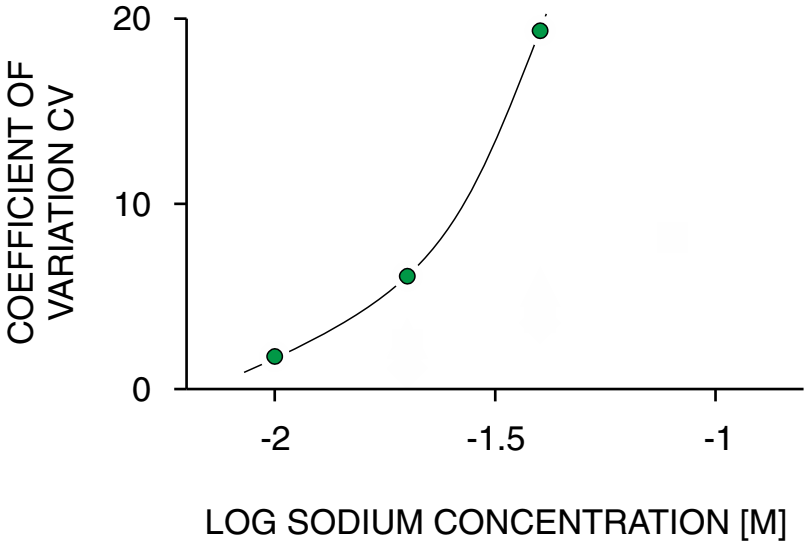
Ionic Strength Dependence

AVERAGE
RELASE RATE COEFFICIENT



$\bar{k}^{(rel)} \propto (IS)^{x}$

COEFFICIENT OF
VARIATION



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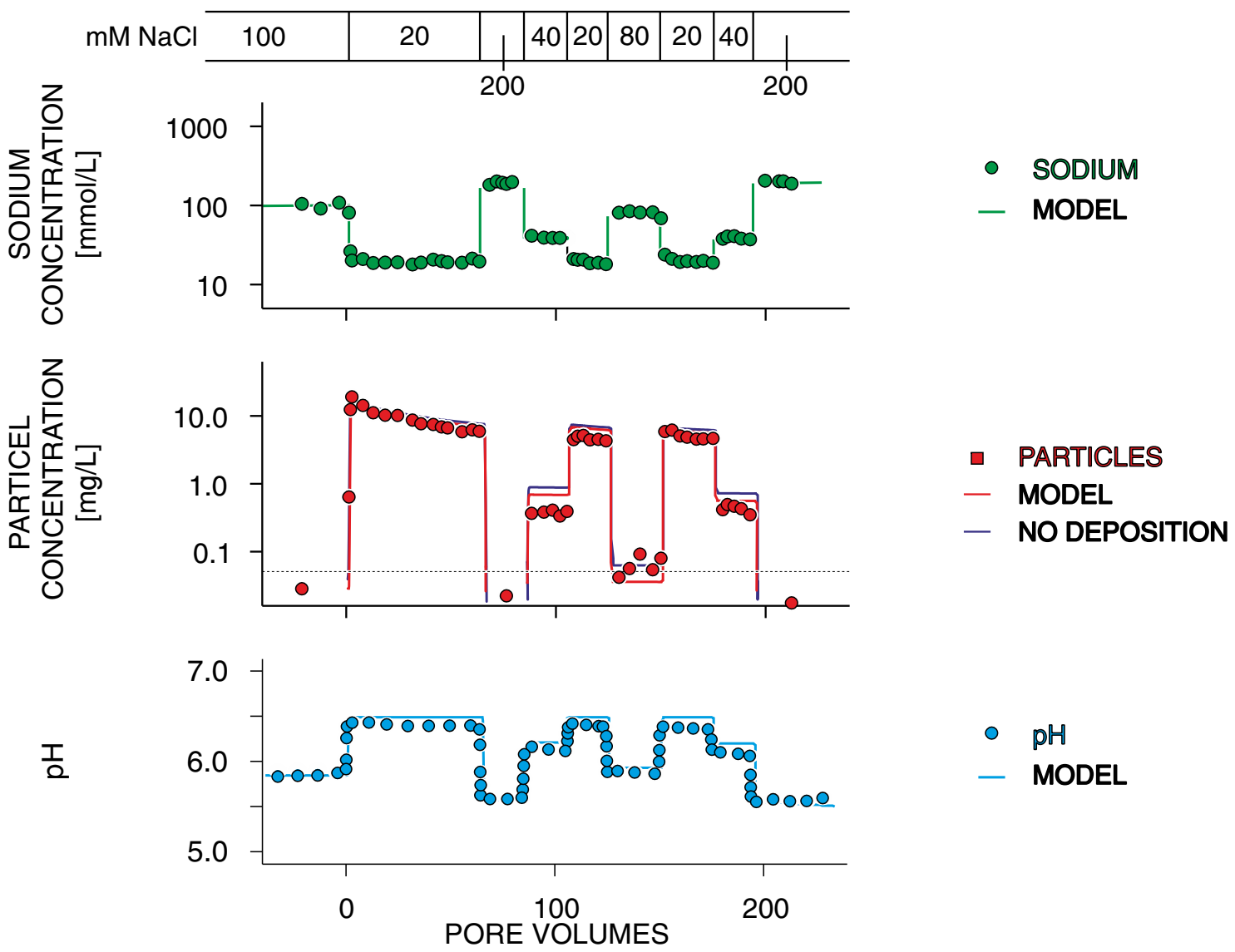
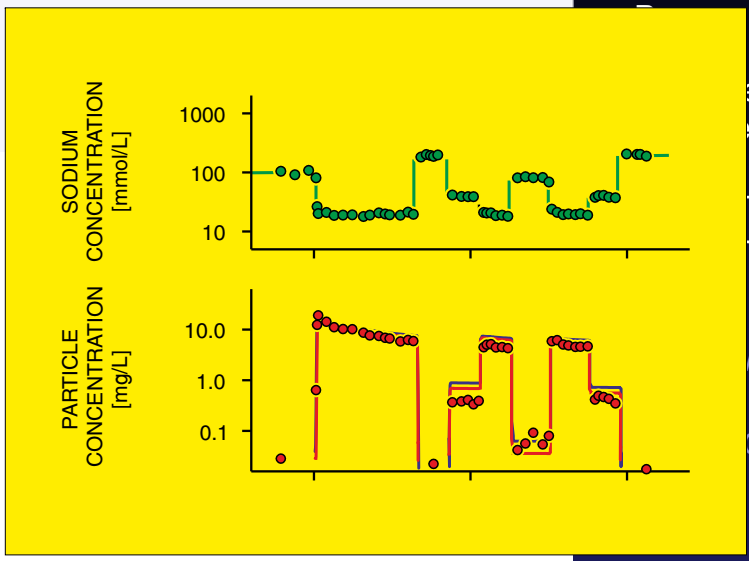
RELEASE of COLLOIDAL PARTICLES

Ionic Strength Dependence



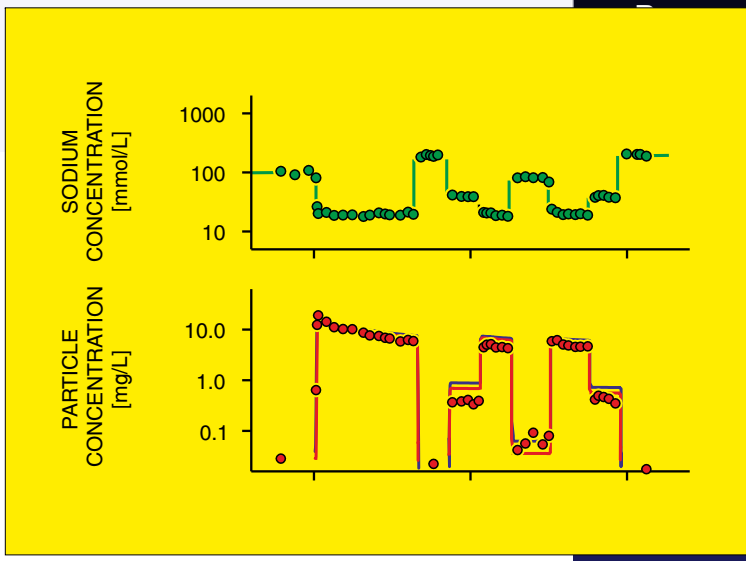
RELEASE of COLLOIDAL PARTICLES

Ionic Strength Dependence

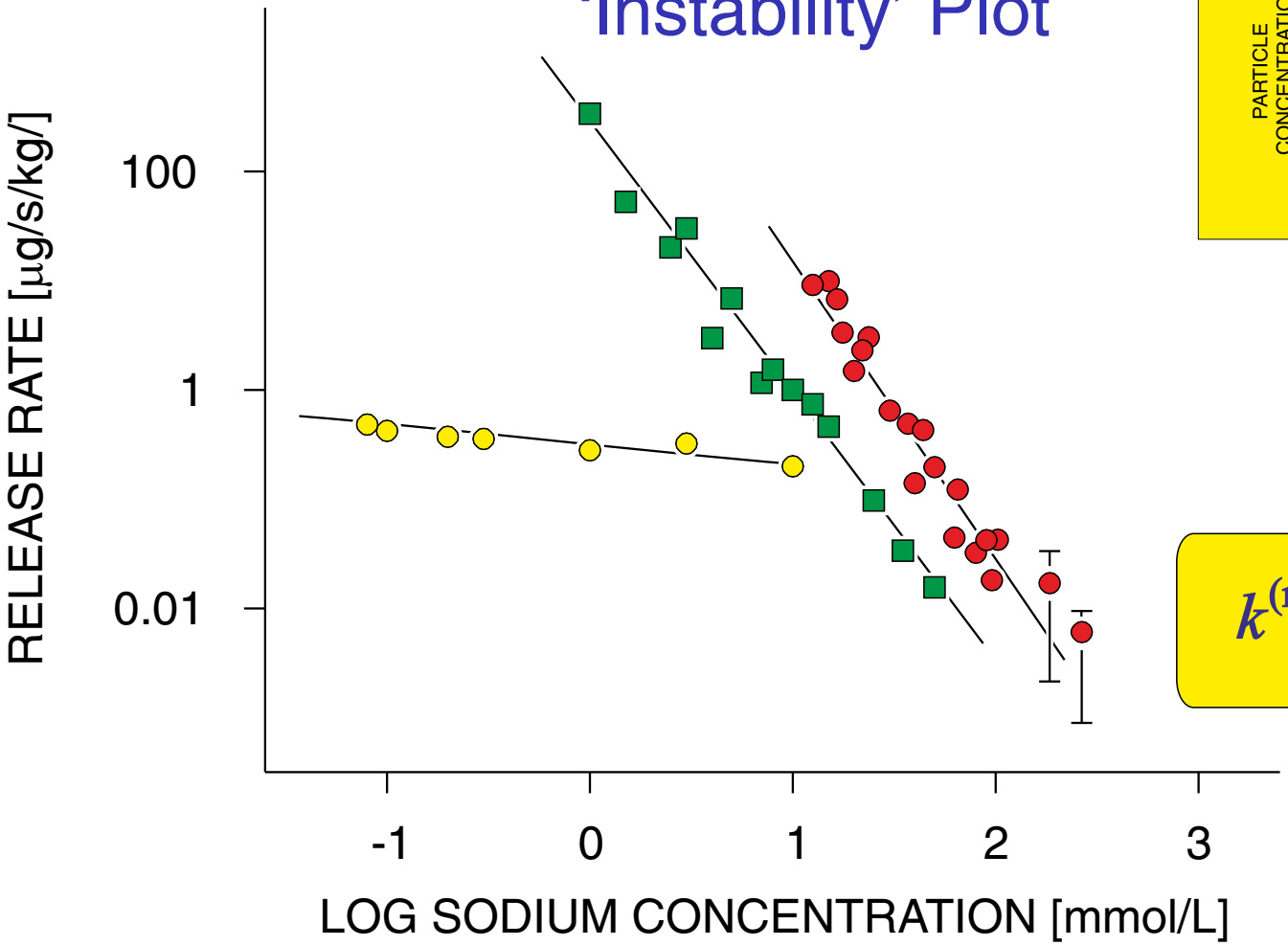


RELEASE of COLLOIDAL PARTICLES

Ionic Strength Dependence



'Instability' Plot

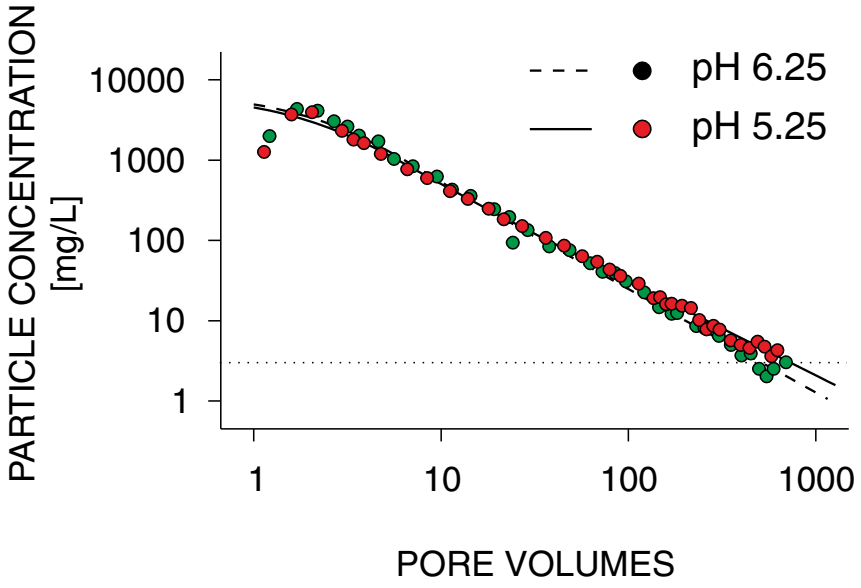


$$k^{(rel)} \propto (IS)^{x}$$

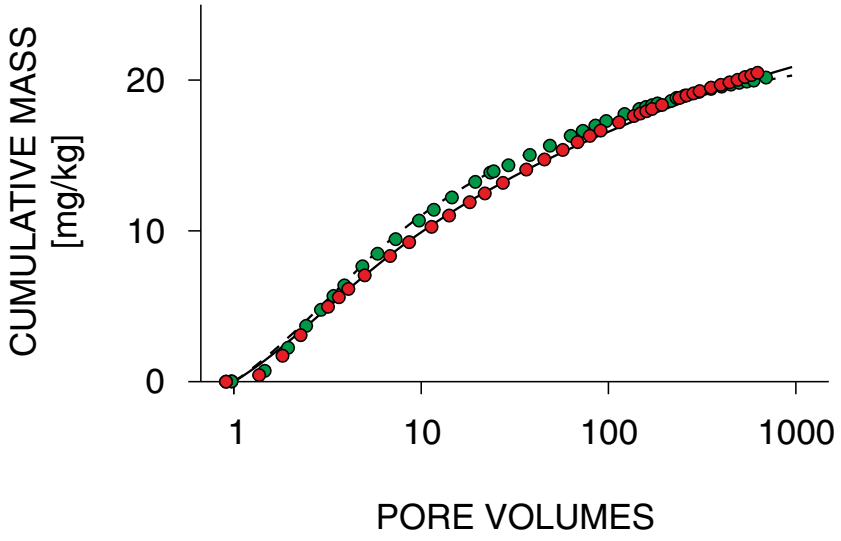
RELEASE of COLLOIDAL PARTICLES

pH Dependence

PARTICLE CONCENTRATION

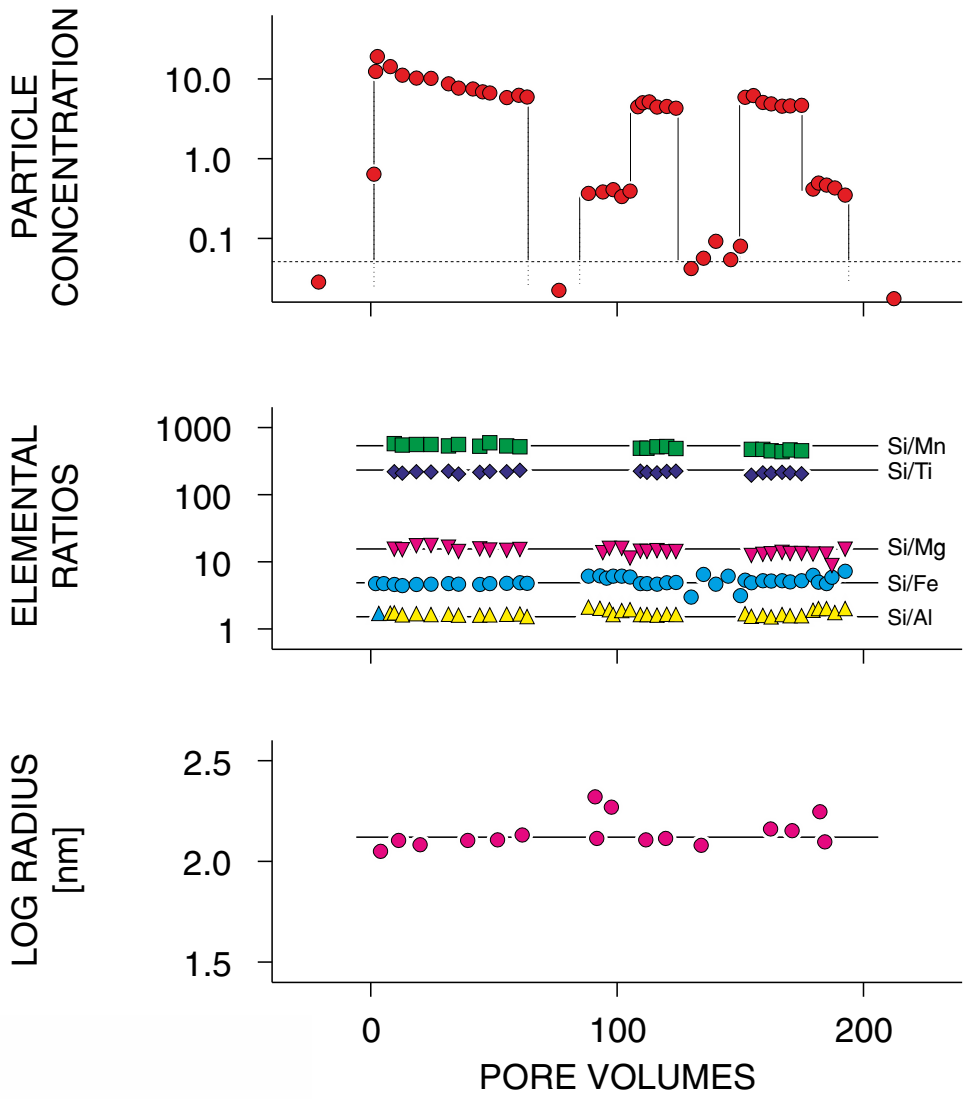


CUMULATIVE MASS



RELEASE of COLLOIDAL PARTICLES

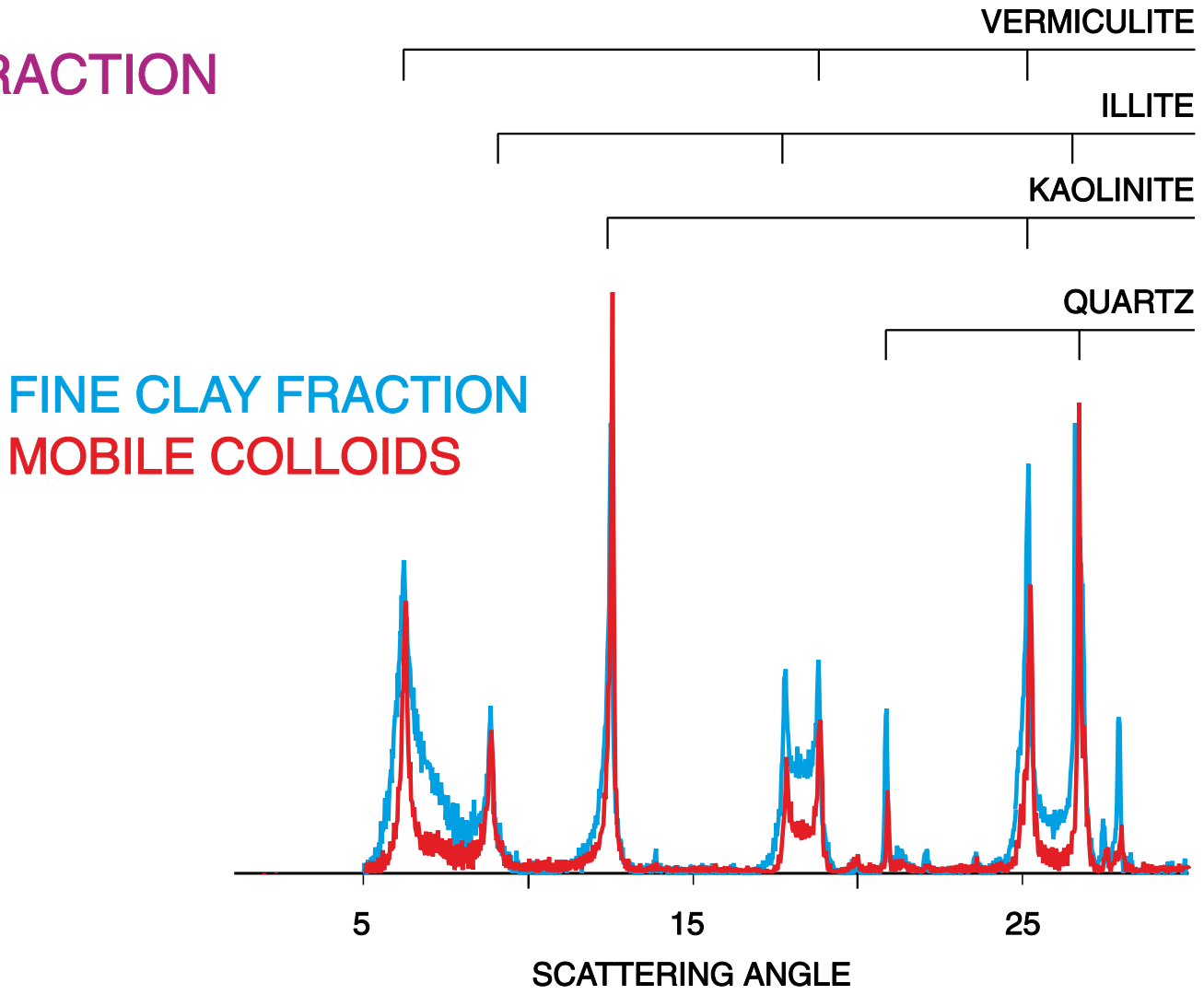
Particle Characterization



RELEASE of COLLOIDAL PARTICLES

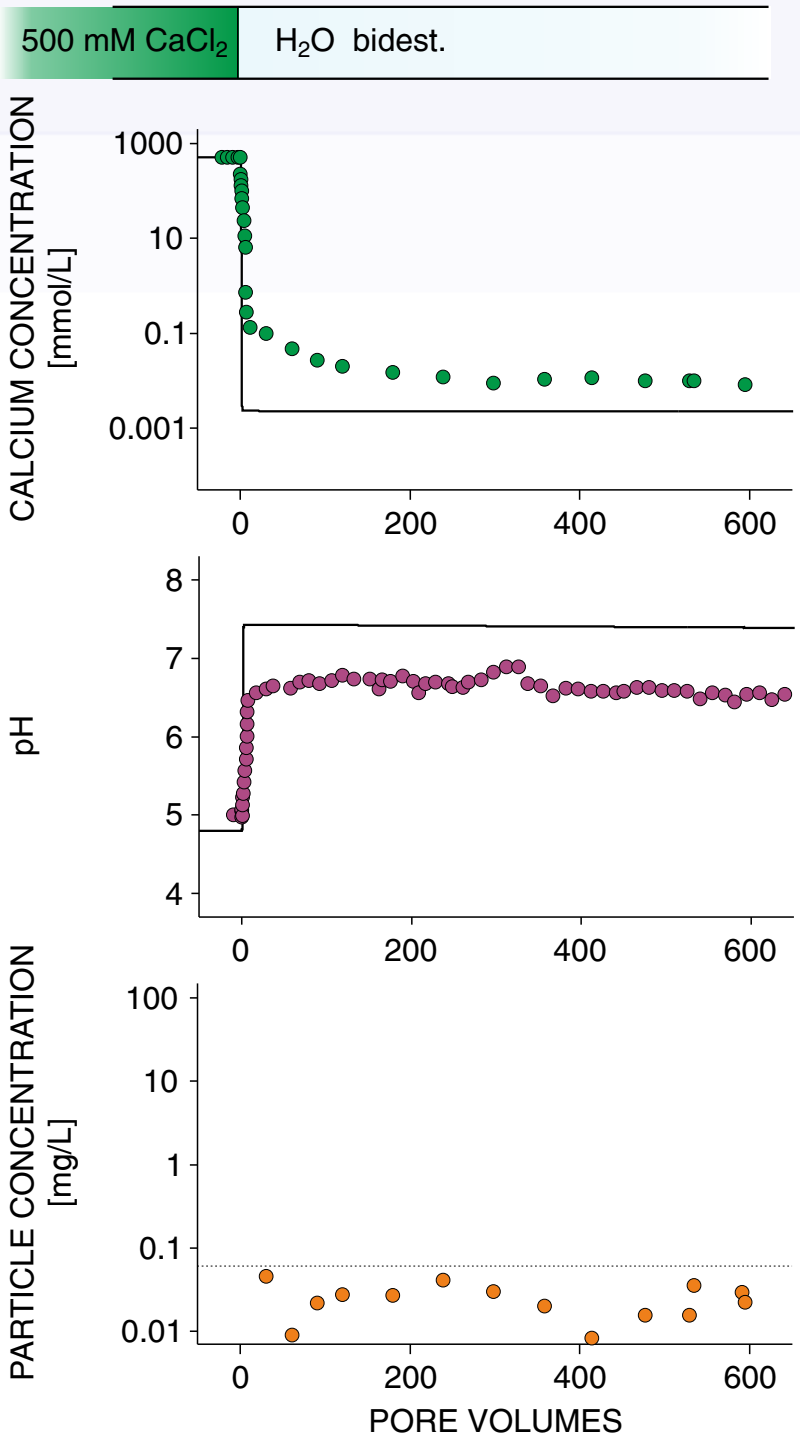
Particle Characterization

X - RAY DIFFRACTION
Cu K_α



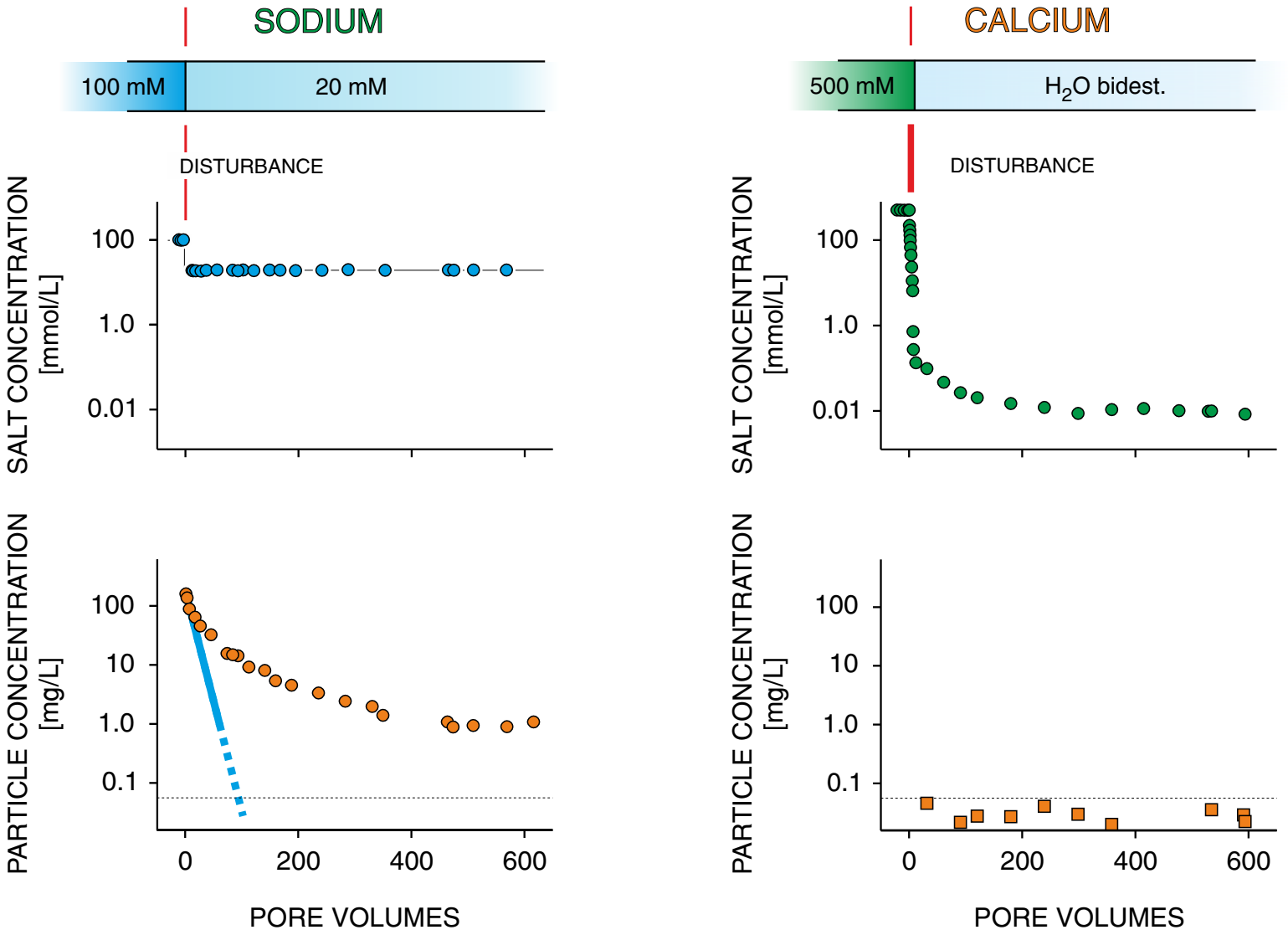
RELEASE

Ca dominated System



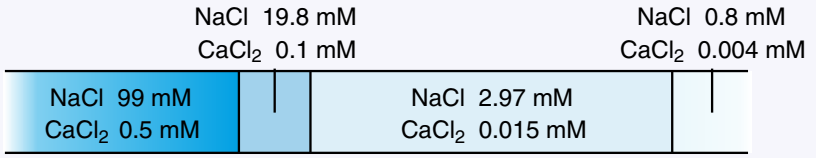
RELEASE of COLLOIDAL PARTICLES

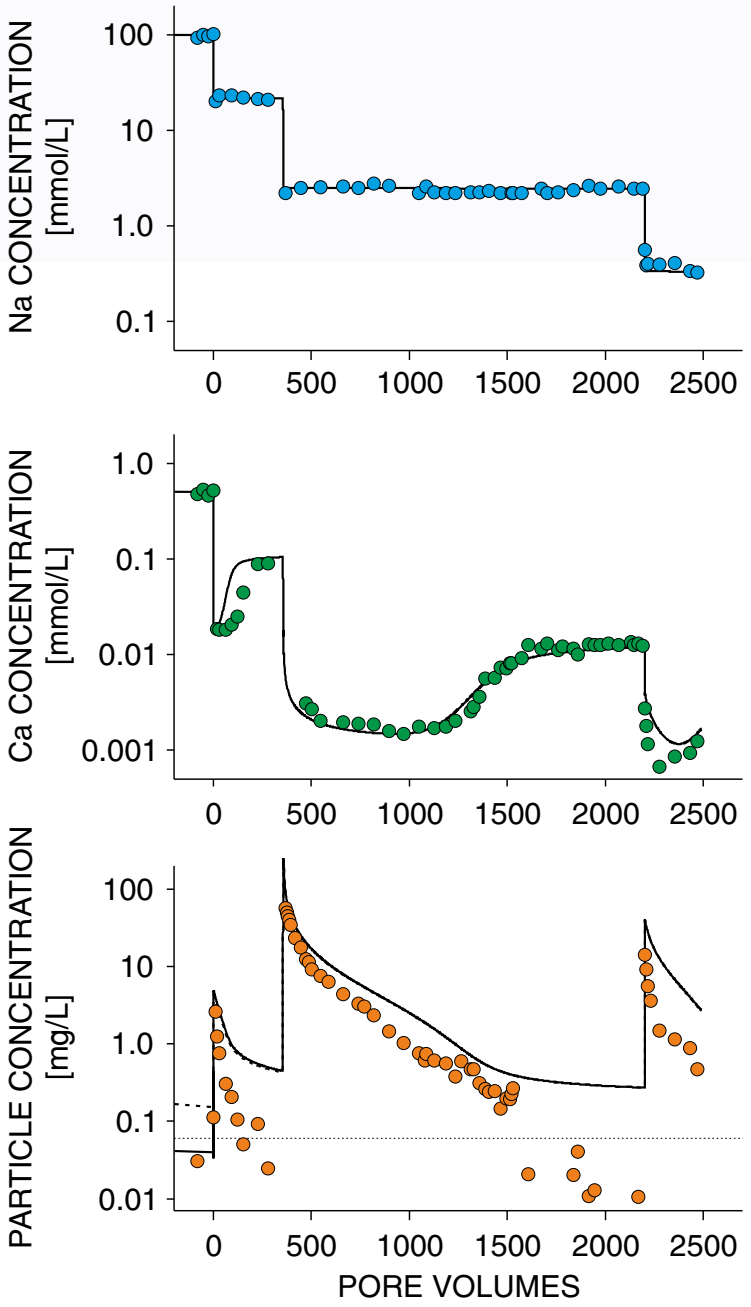
Na versus Ca dominated System



RELEASE

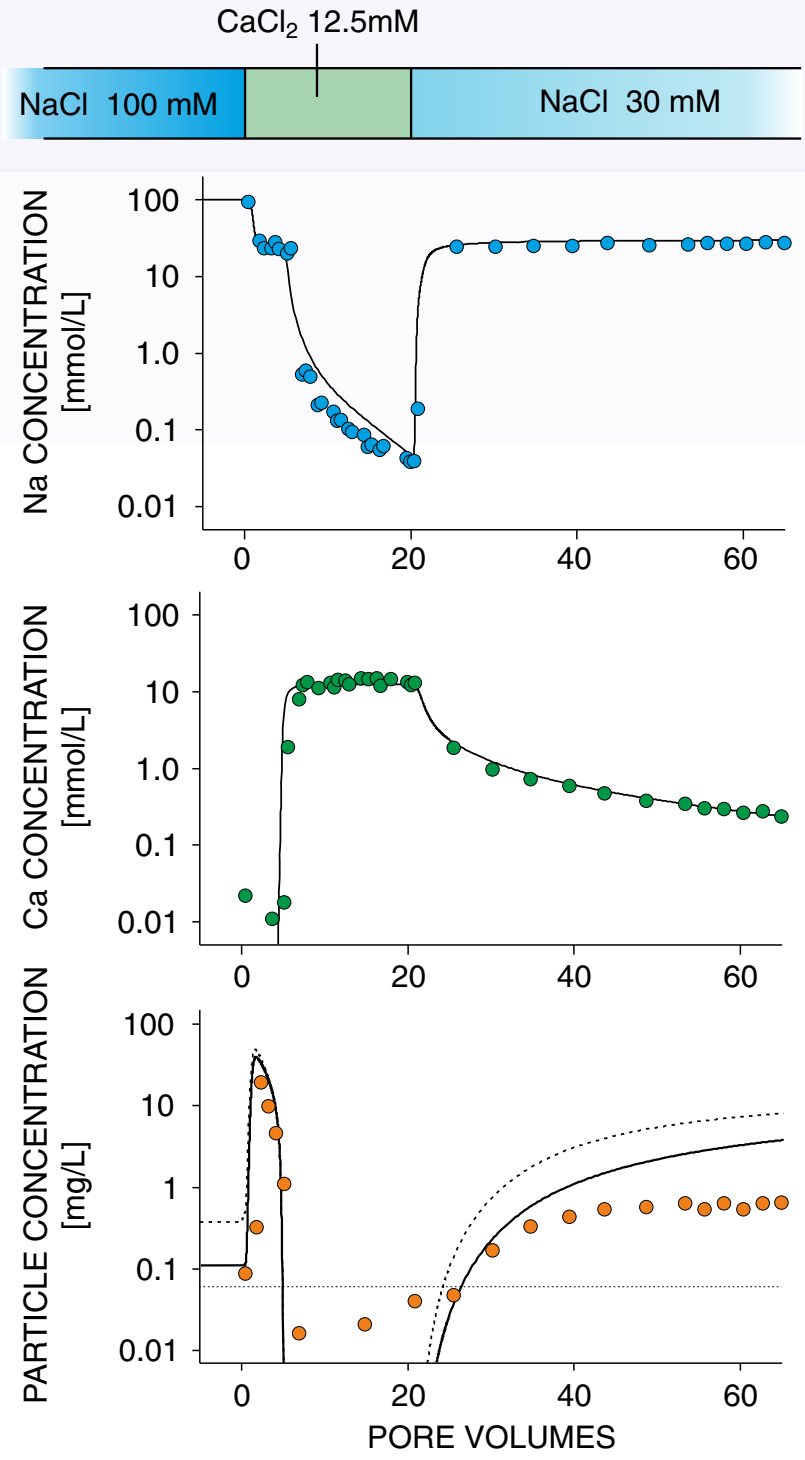
Multi-Component System: Na ■ Ca





RELEASE

Multi-Component System: Na ■ Ca



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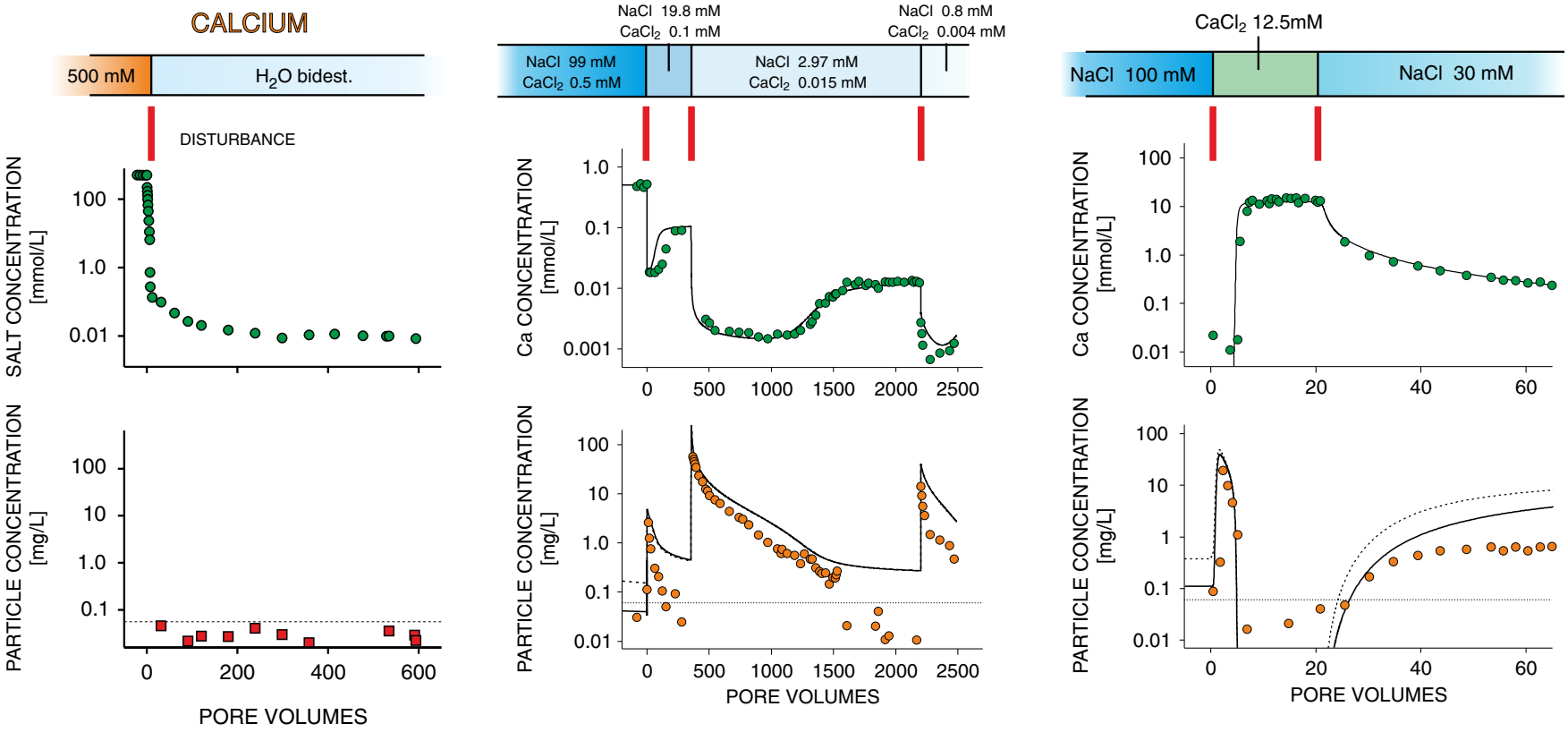
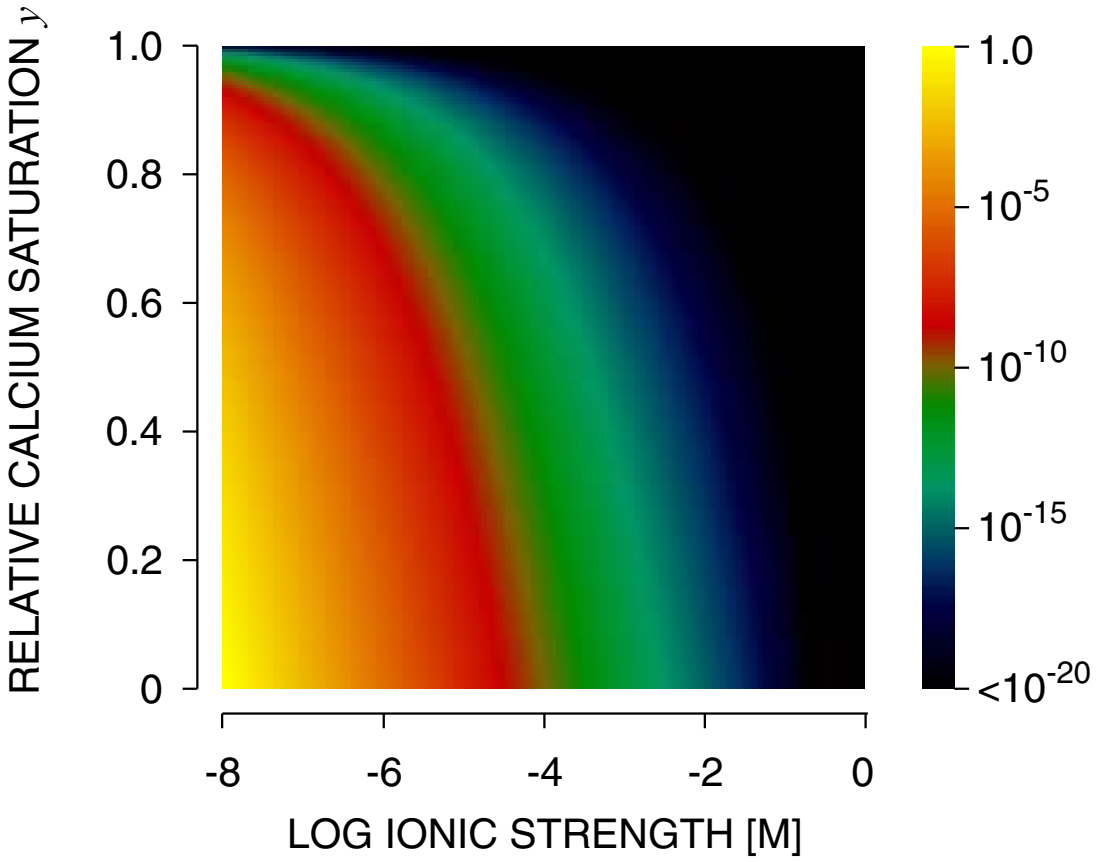
RELEASE of COLLOIDAL PARTICLES

Importance of Interfacial Speciation

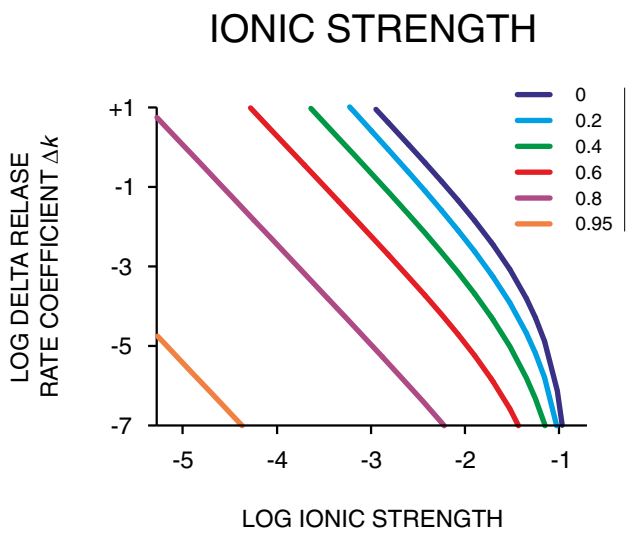


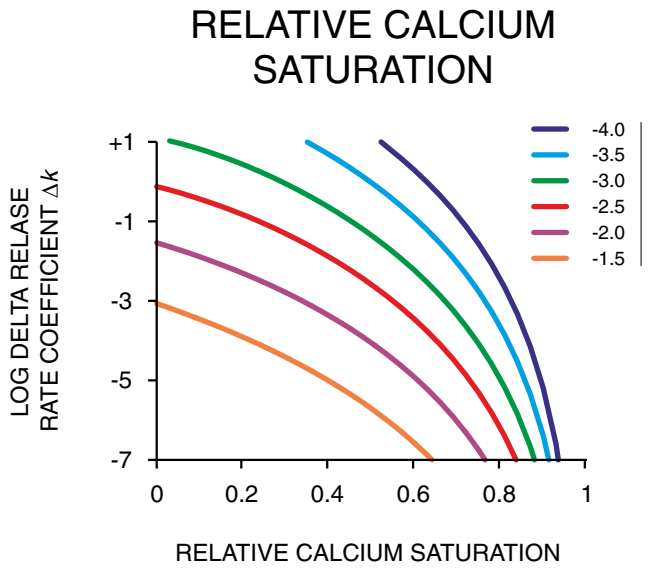
RELEASE of COLLOIDAL PARTICLES

Multi-Component System: Na ■ Ca



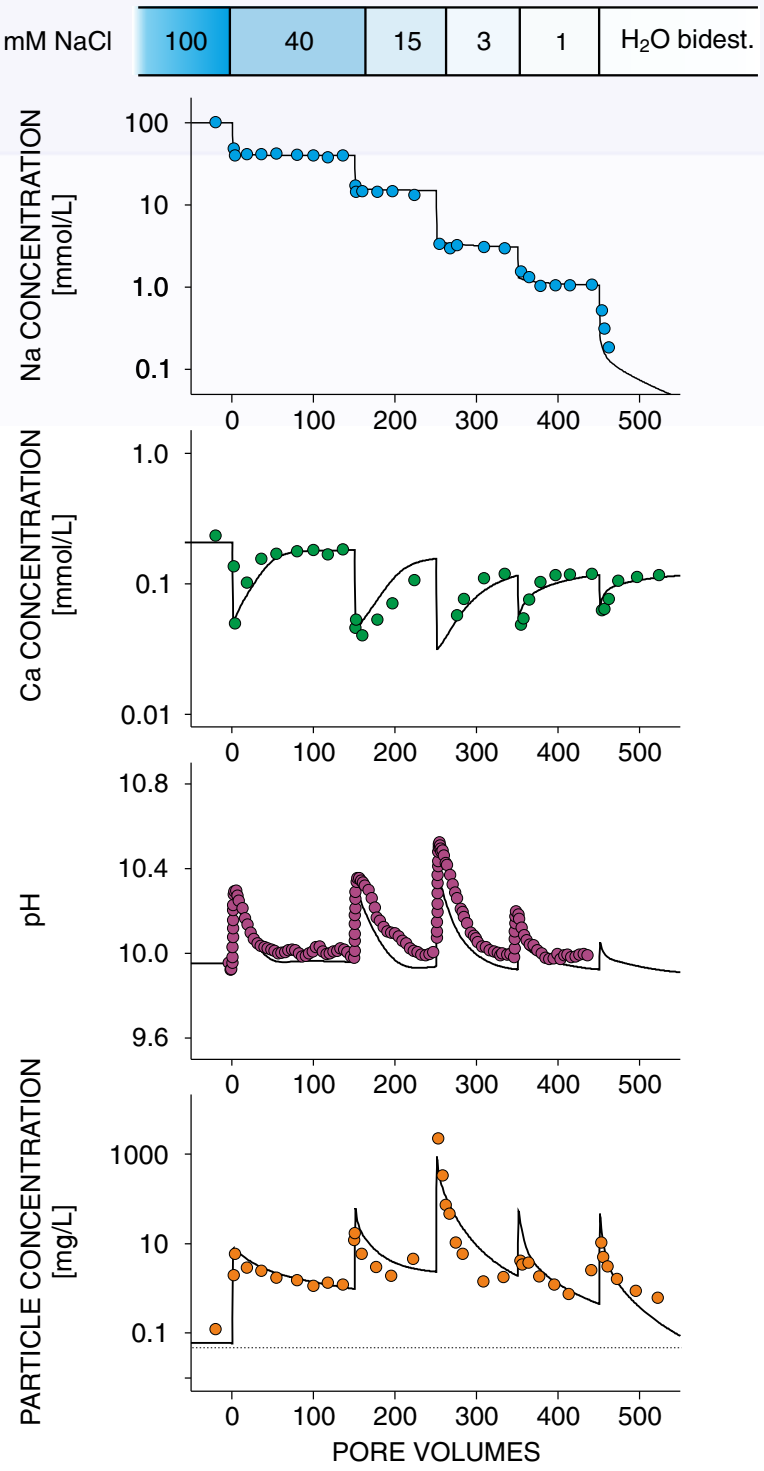
$$k^{(rel)} \propto (1-y)^{x}$$





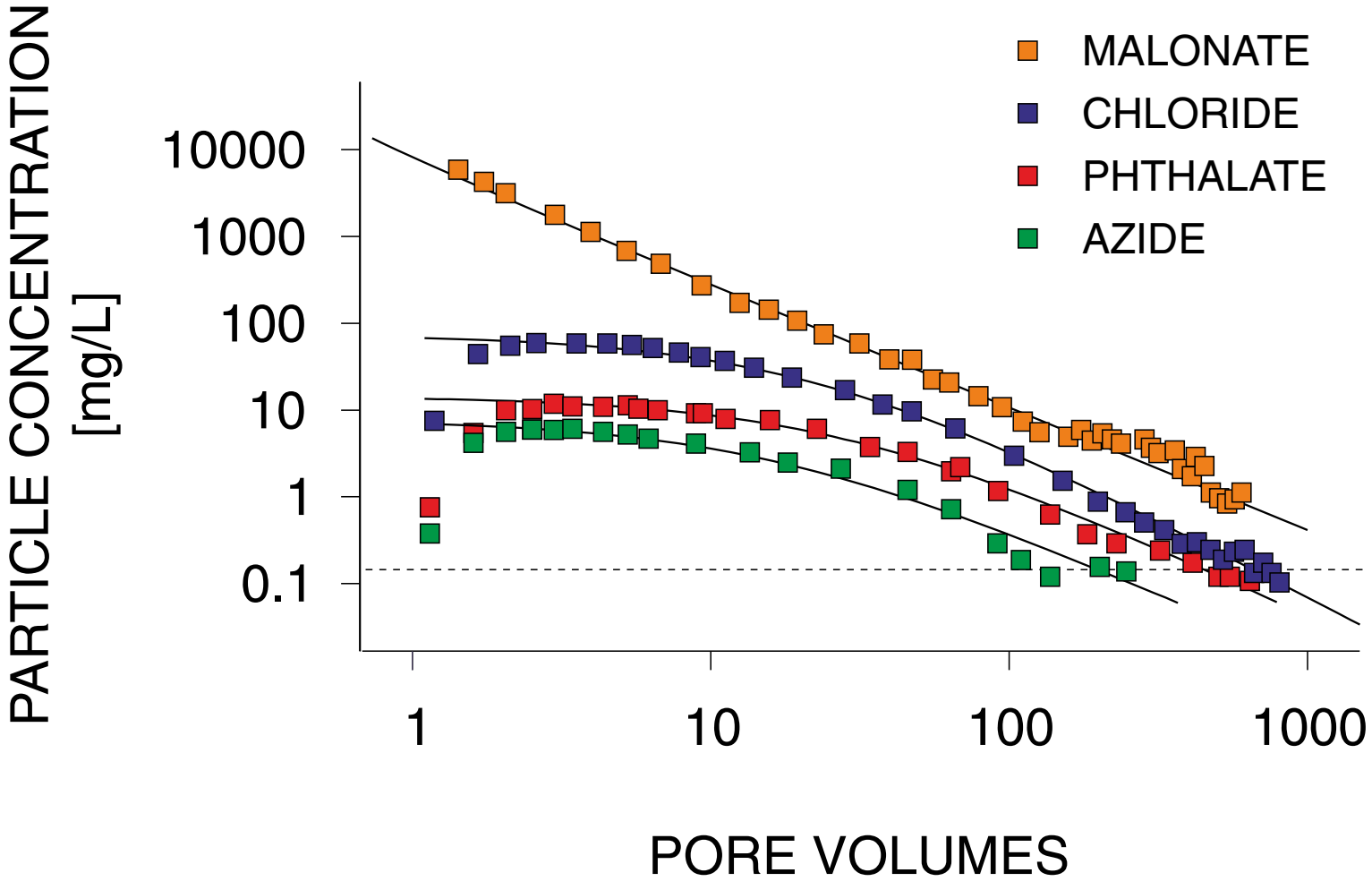
RELEASE

Multi-Component System: Na ■ Ca ■ $CaCO_3$



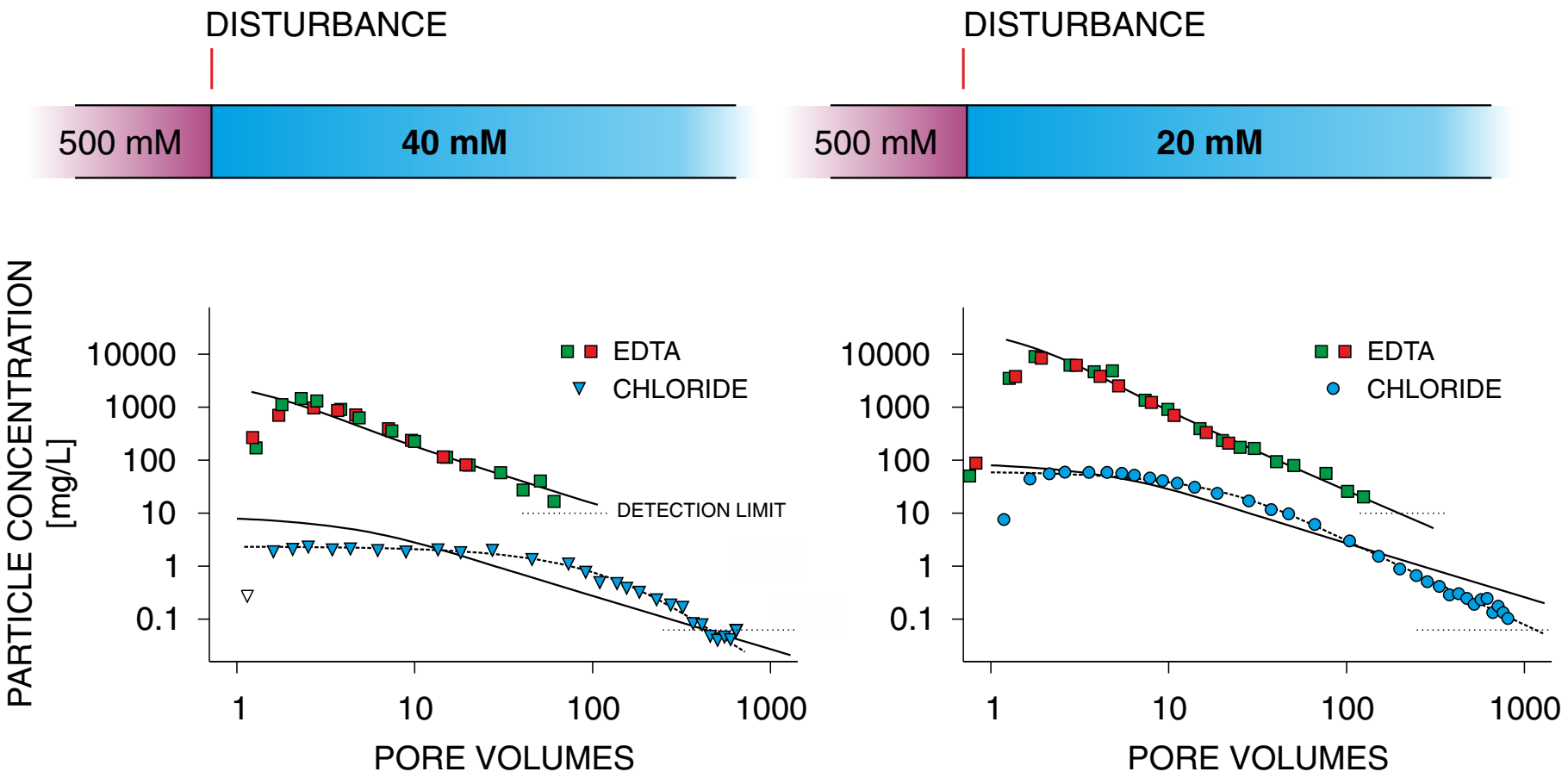
RELEASE of COLLOIDAL PARTICLES

Co-Ion Effect



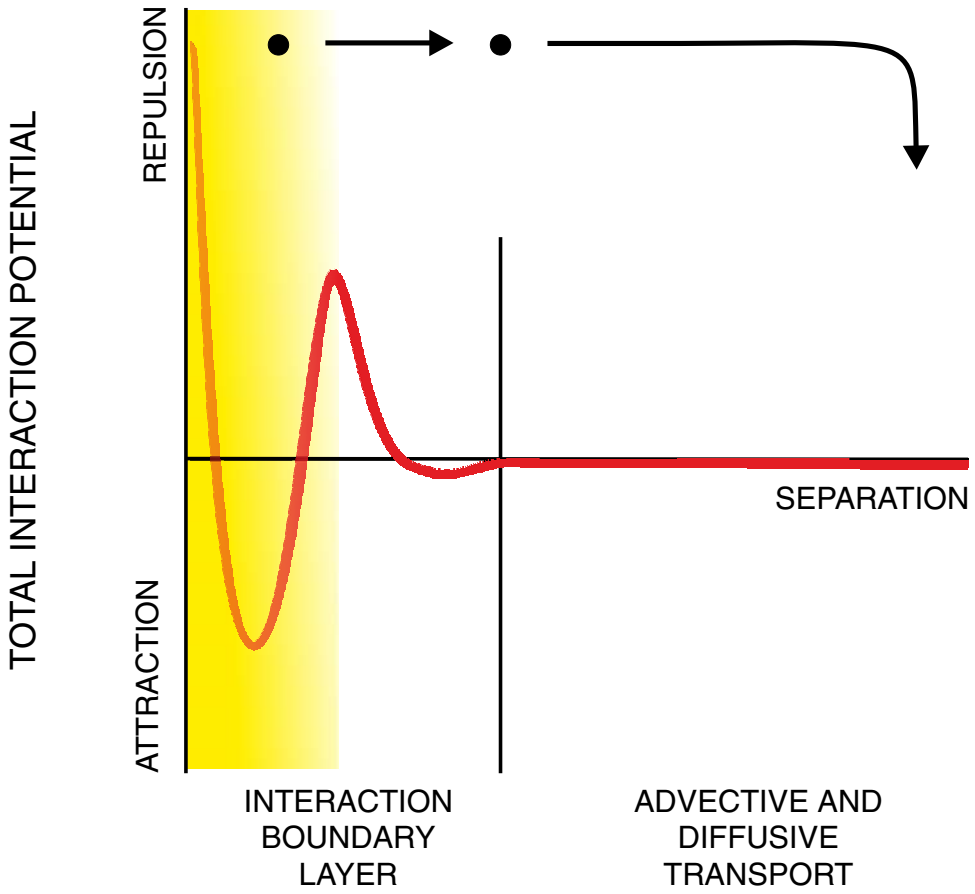
RELEASE of COLLOIDAL PARTICLES

Complexing Agents (EDTA)



RELEASE of COLLOIDAL PARTICLES

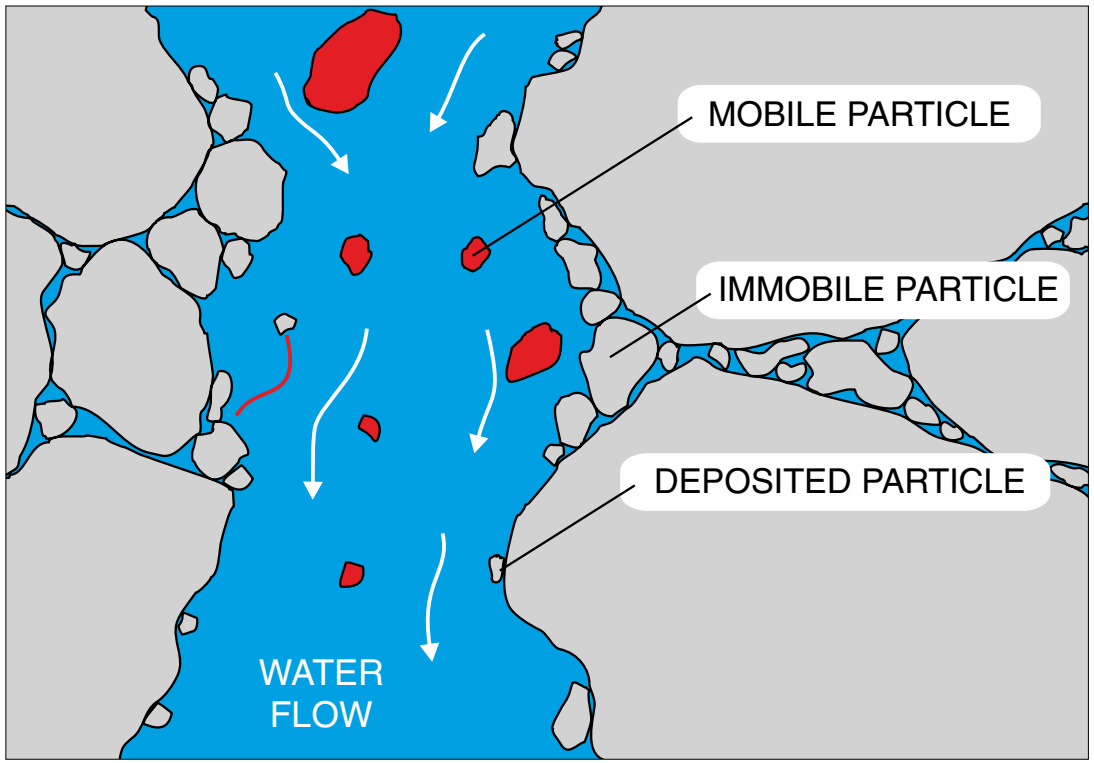
Reaction Limited Release



UNCERTAINTIES:

- CHEMICAL HETEROGENEITY
- MORPHOLOGICAL HETEROGENEITY
- NON - DLVO CHEMICAL INTERACTIONS
- SHORT-RANGE FORCES

TRANSPORT of COLLOIDAL PARTICLES

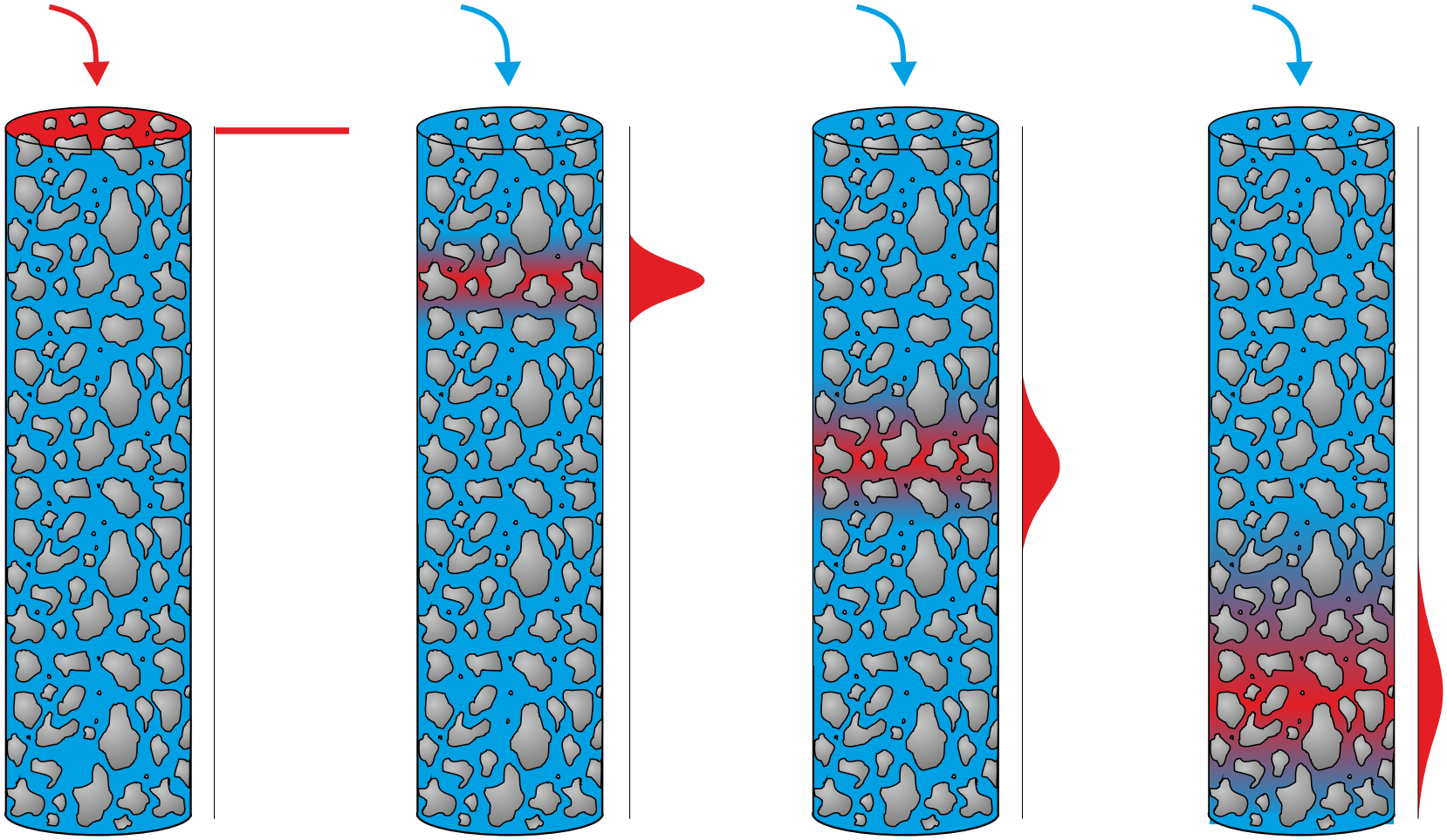


$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - k(c_0)\,c$$

Dispersion Convection **Deposition**

TRANSPORT of COLLOIDAL PARTICLES

Particle Transport Experiments



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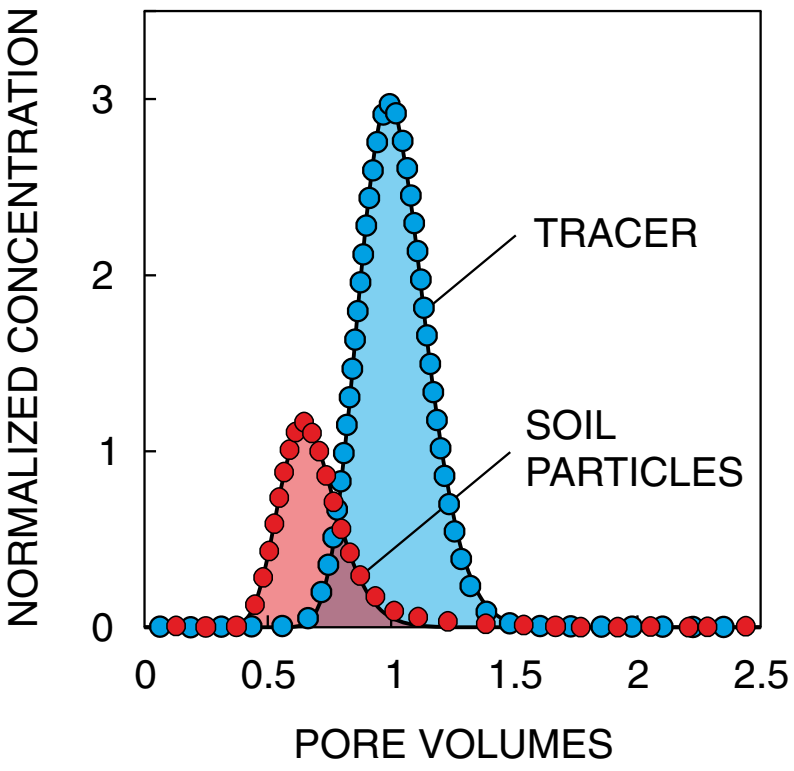
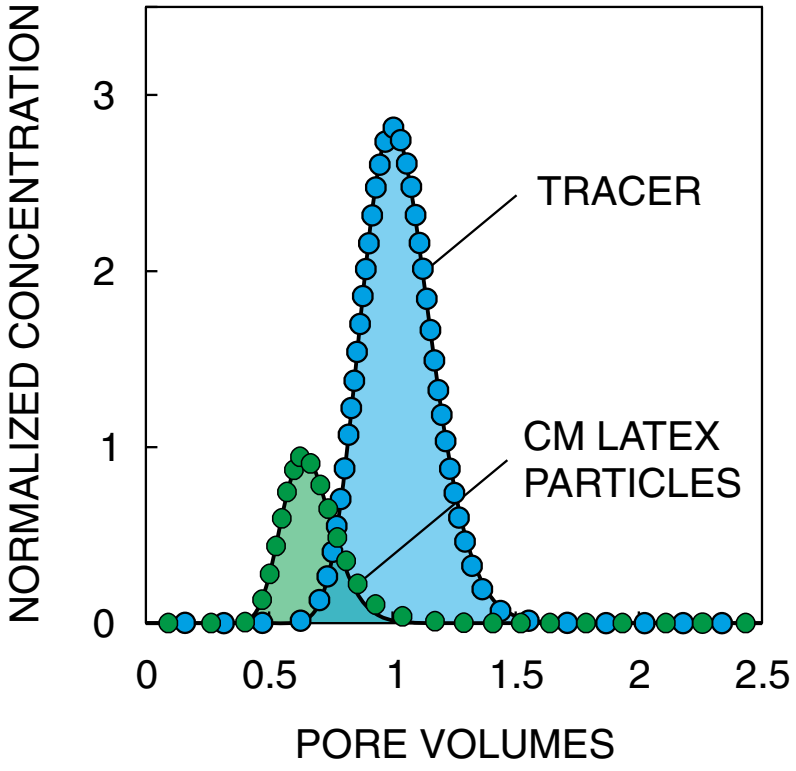
TRANSPORT of COLLOIDAL PARTICLES

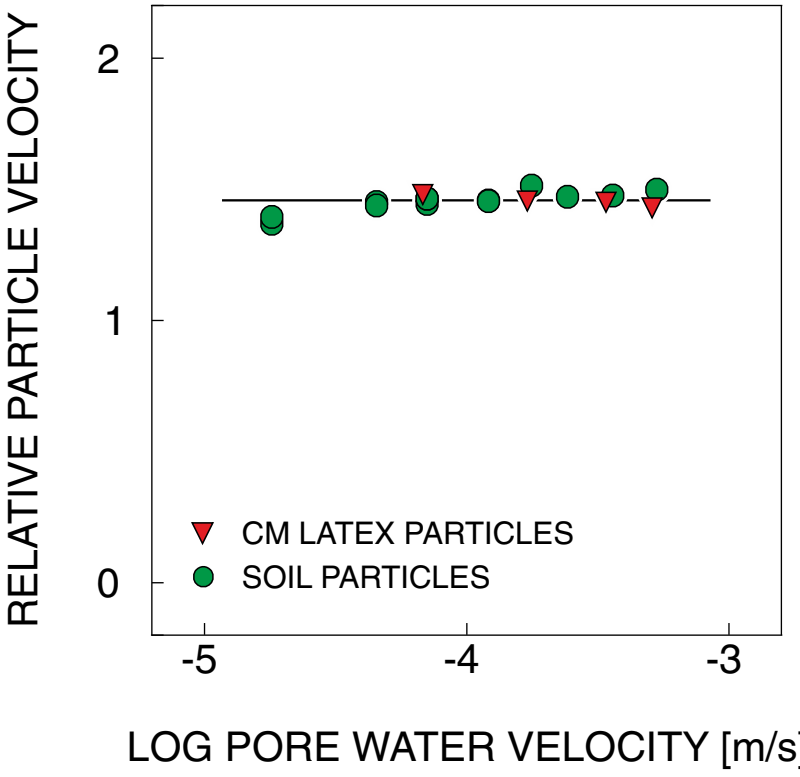
Particle versus Chemical Tracer

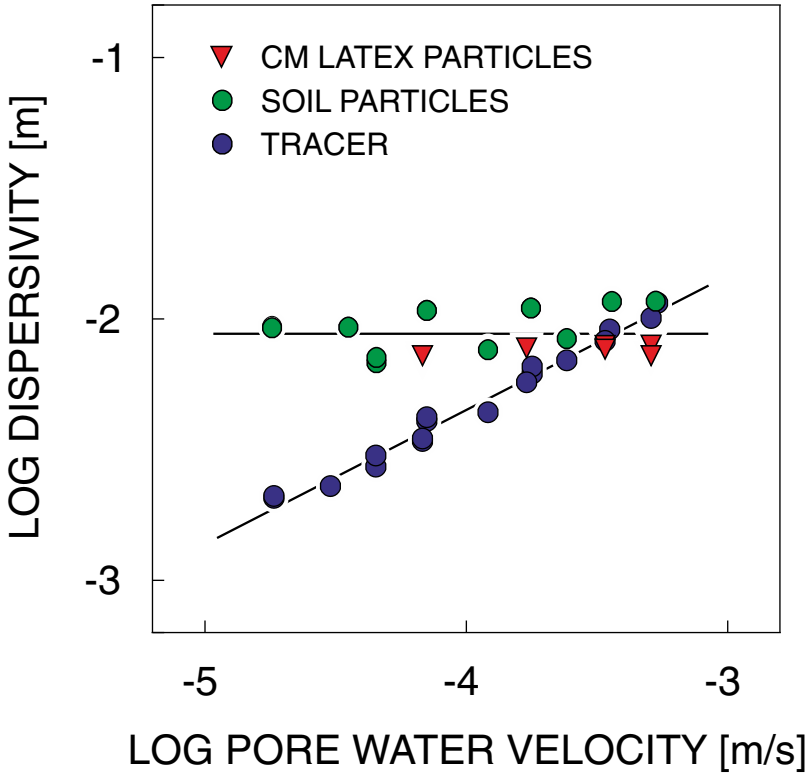




TRANSPORT of COLLOIDAL PARTICLES

Pore Water Velocity Dependence

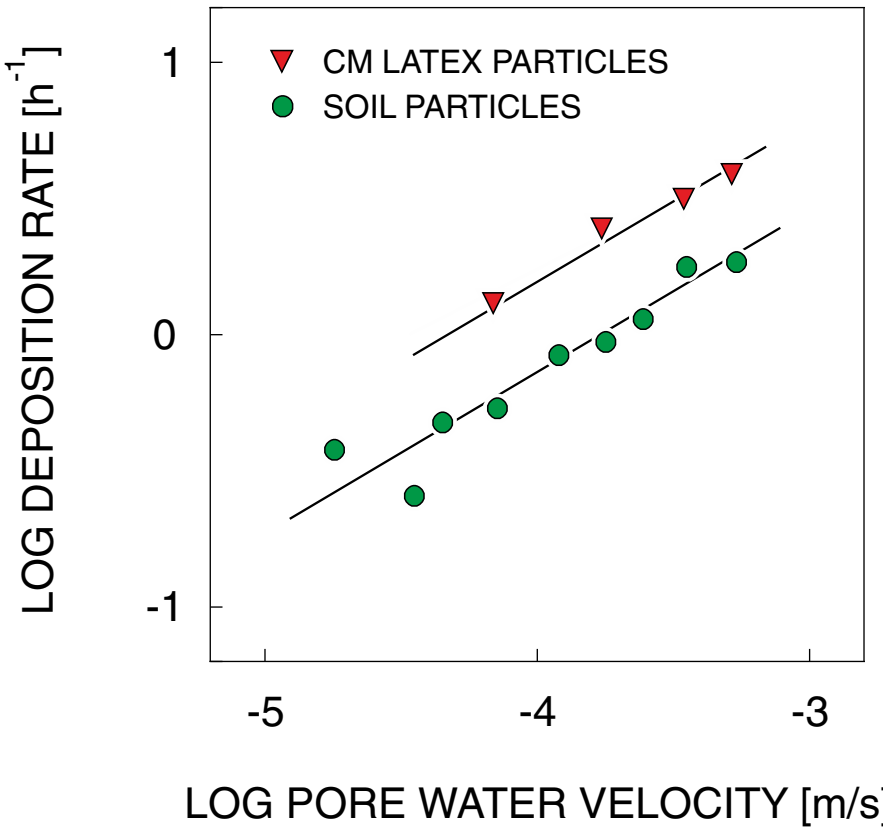




$$\frac{\partial c}{\partial t} = \tilde{D}\frac{\partial^2 c}{\partial x^2} - \tilde{v}\frac{\partial c}{\partial x} - k^{(dep)}c$$

TRANSPORT of COLLOIDAL PARTICLES

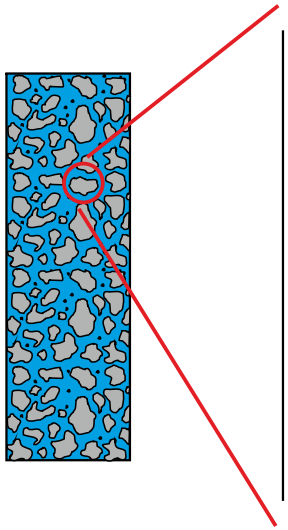
Pore Water Velocity Dependence

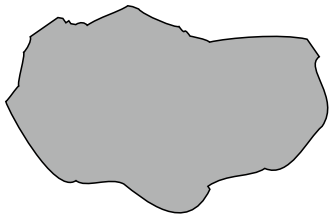


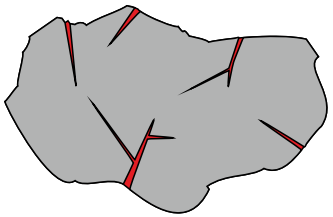
$$\frac{\partial c}{\partial t} = \tilde{D}\frac{\partial^2 c}{\partial x^2} - \tilde{v}\frac{\partial c}{\partial x} - k^{(dep)}(v,\ldots)\,c$$

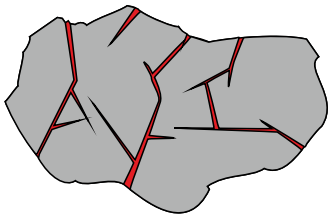
TRANSPORT of COLLOIDAL PARTICLES

Double Porous Media









’solid’

dead-end regions

permeable regions

MECHANICAL DISPERSION

’HOLDUP DISPERSION’

Dispersivity $\propto (v_0)^0$

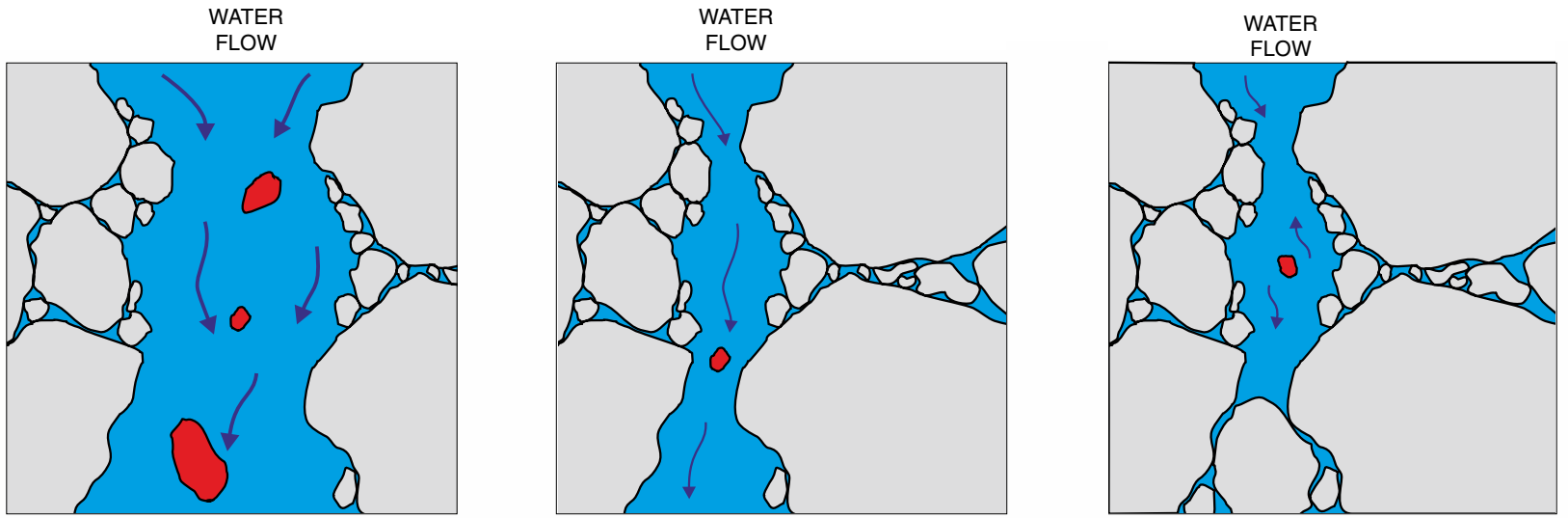
Dispersivity $\propto (v_0)^1$

Deposition Rate $\propto (v_0)^{1/3}$

Deposition Rate $\propto (v_0)^1$

TRANSPORT of COLLOIDAL PARTICLES

Double Porous Media

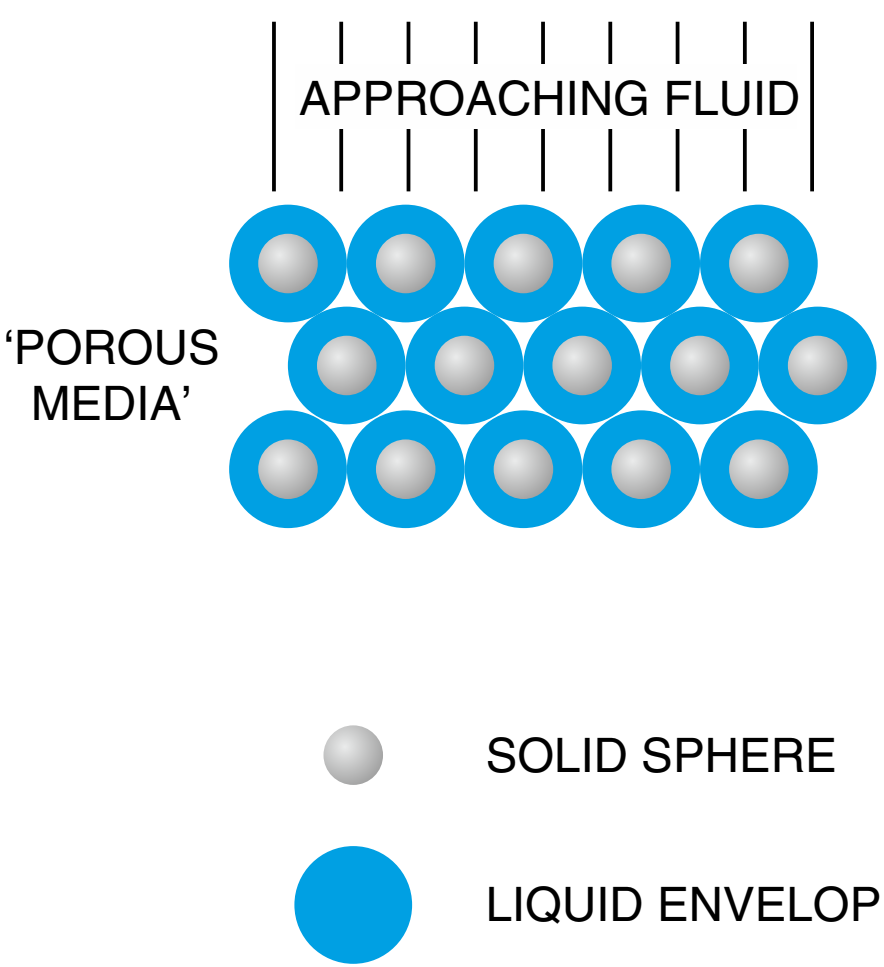


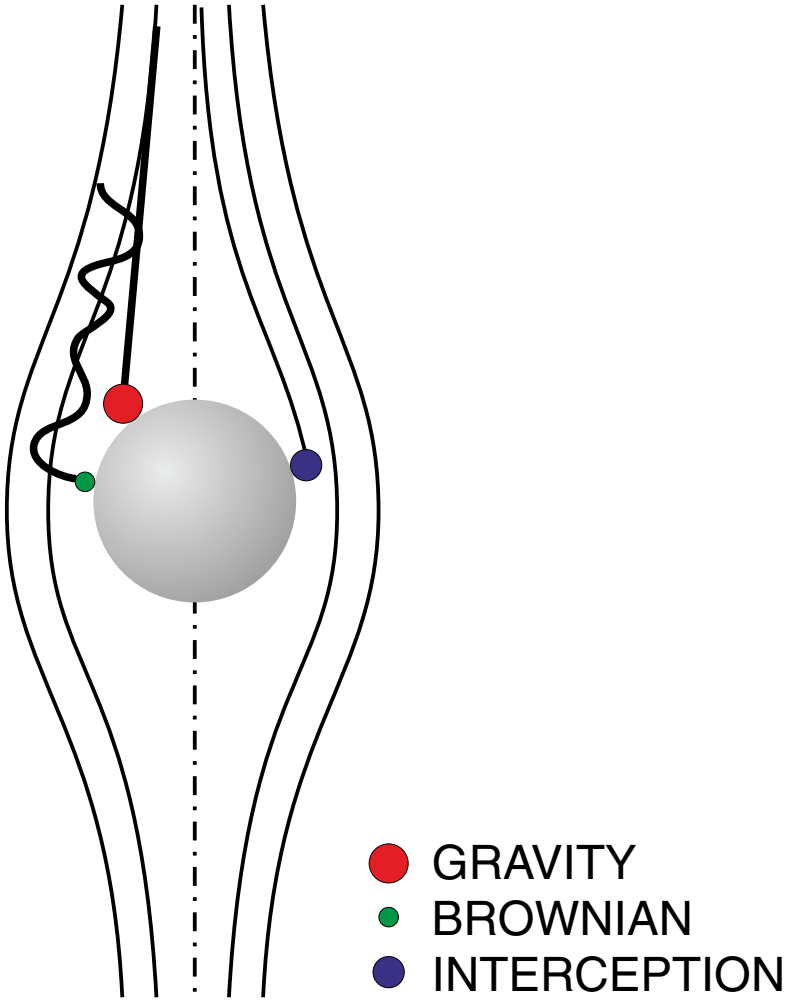
MOBILE COLLOIDAL PARTICLES

DISSOLVED CHEMICAL SPECIES

TRANSPORT of COLLOIDAL PARTICLES

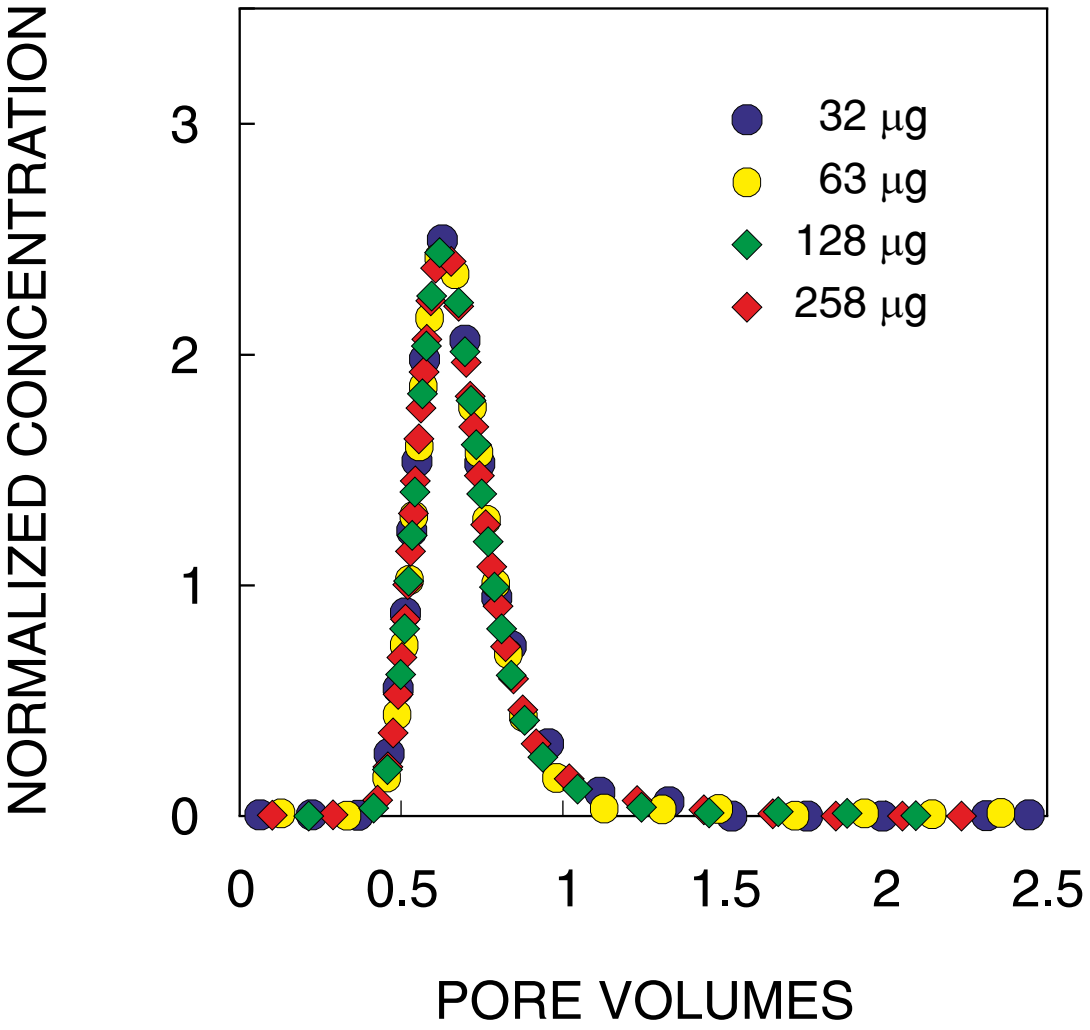
‘Filtration Theory’





TRANSPORT of COLLOIDAL PARTICLES

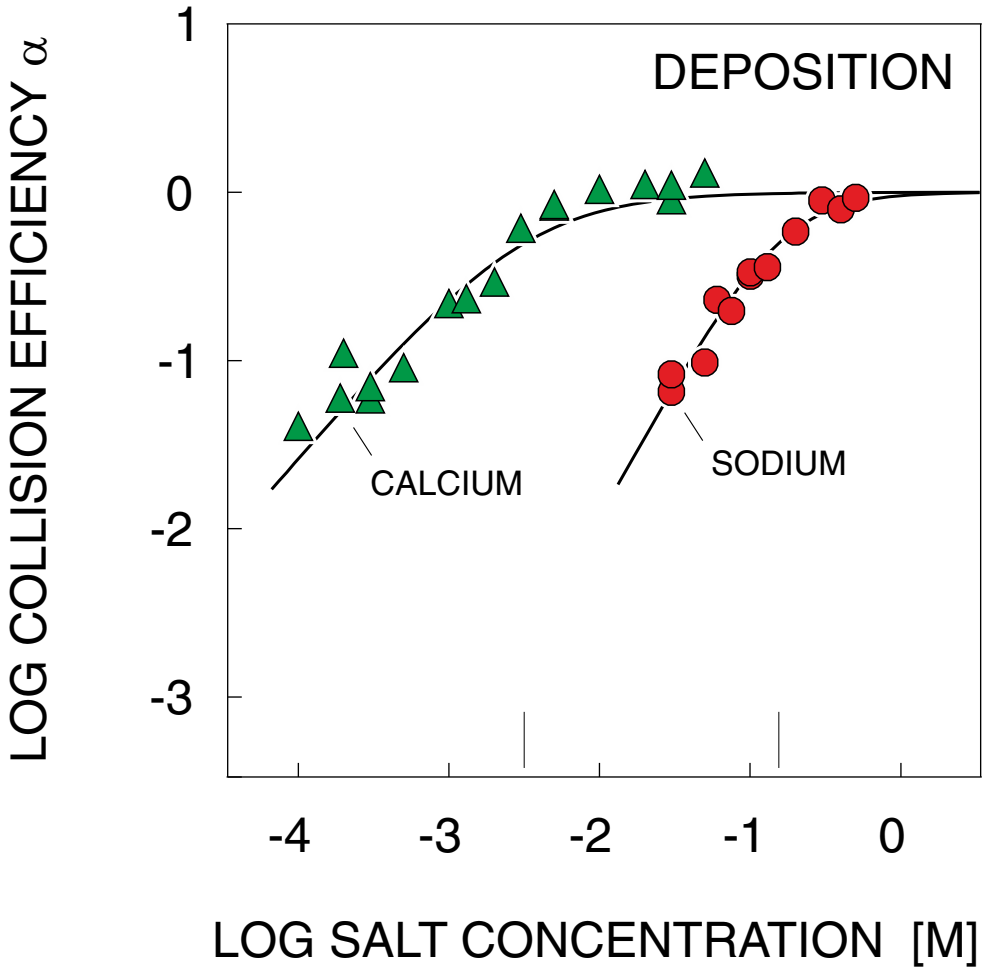
Concentration Dependence



$$\frac{\partial c}{\partial t} = \tilde{D}\frac{\partial^2 c}{\partial x^2} - \tilde{v}\frac{\partial c}{\partial x} - k^{(dep)}(v,\ldots)\,c$$

TRANSPORT of COLLOIDAL PARTICLES

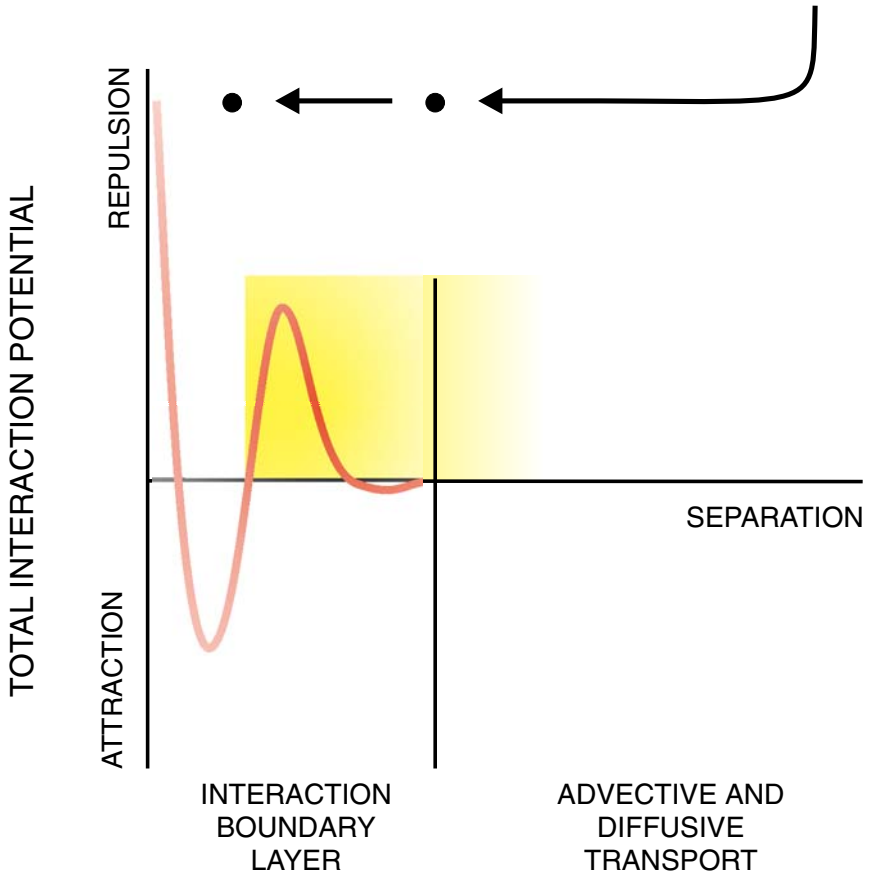
Chemical Dependence



$$k^{(dep)} = f\left([Na^{+}], [Ca^{2+}], \ldots\right)$$

TRANSPORT of COLLOIDAL PARTICLES

Reaction Limited Deposition



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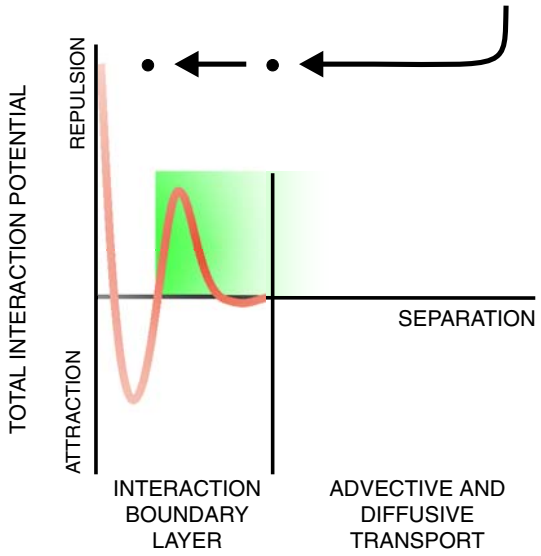
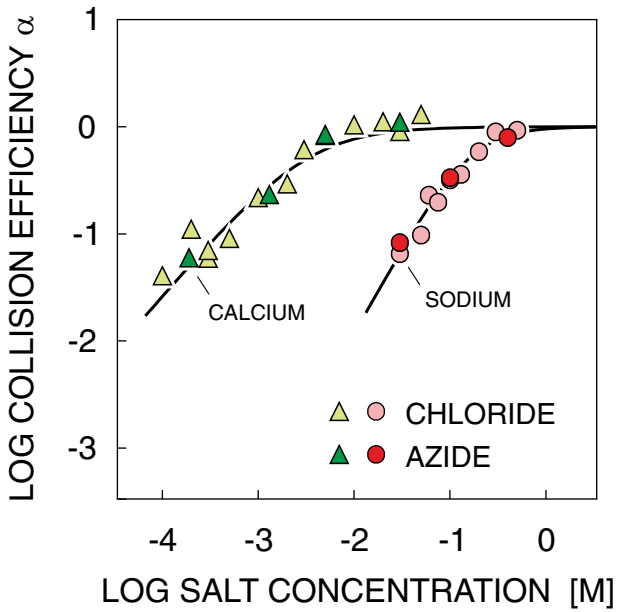
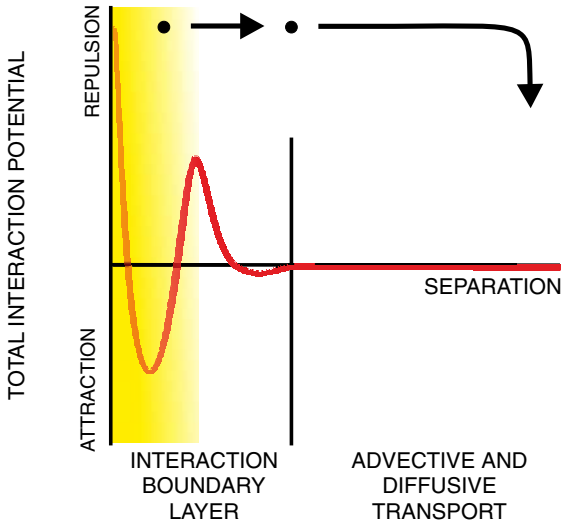
TRANSPORT of COLLOIDAL PARTICLES

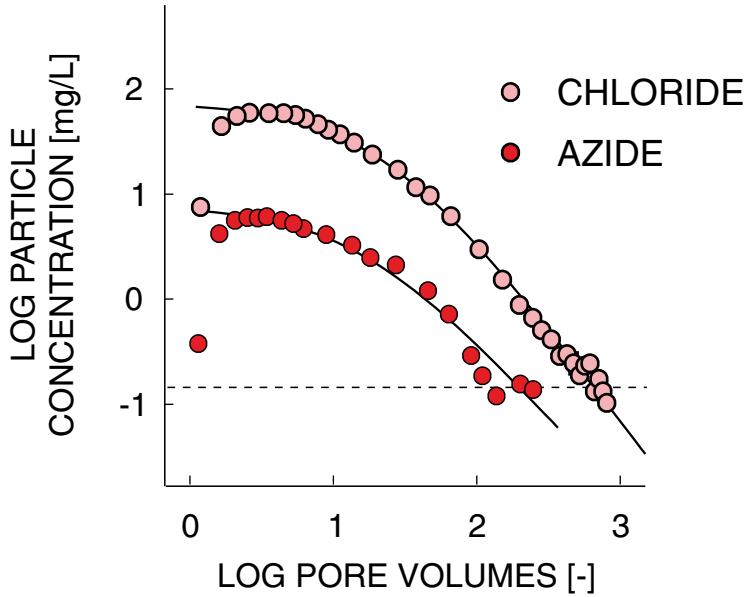


DEPOSITION

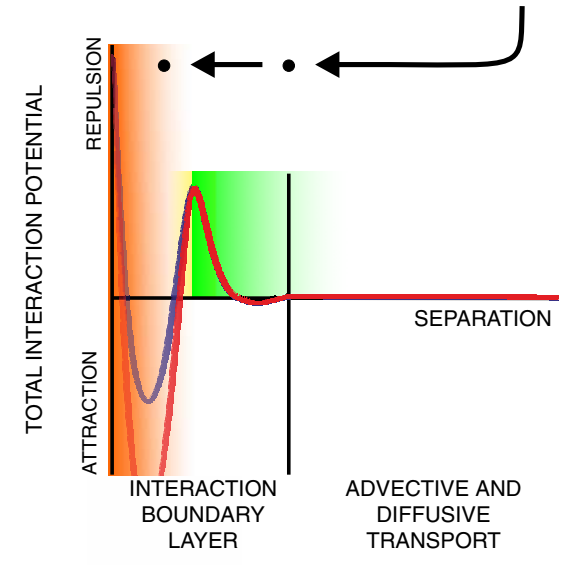




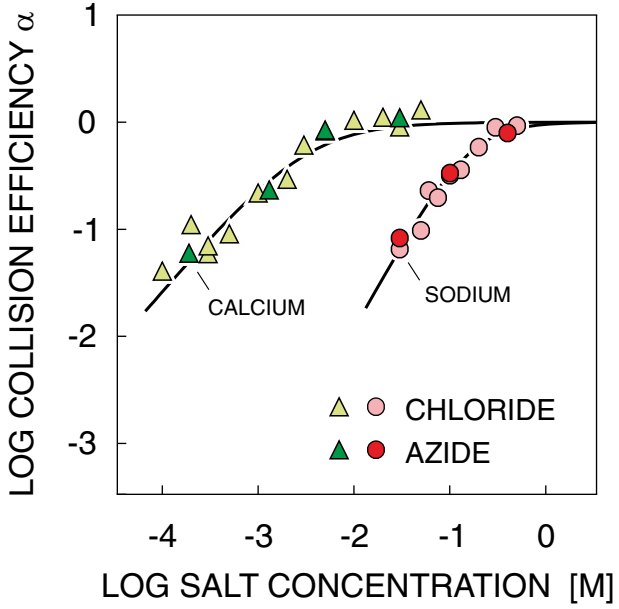
RELEASE

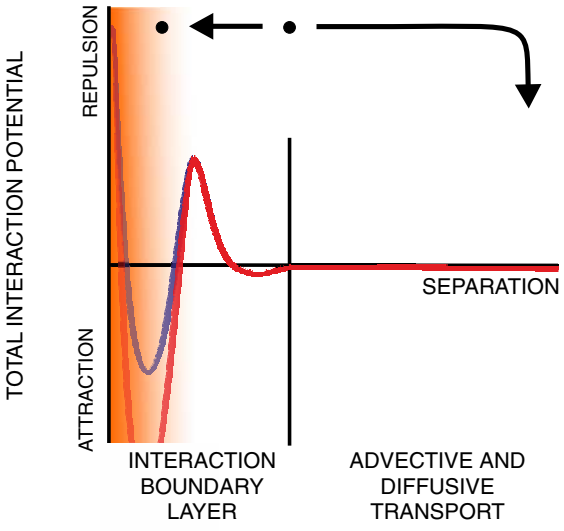


TRANSPORT of COLLOIDAL PARTICLES

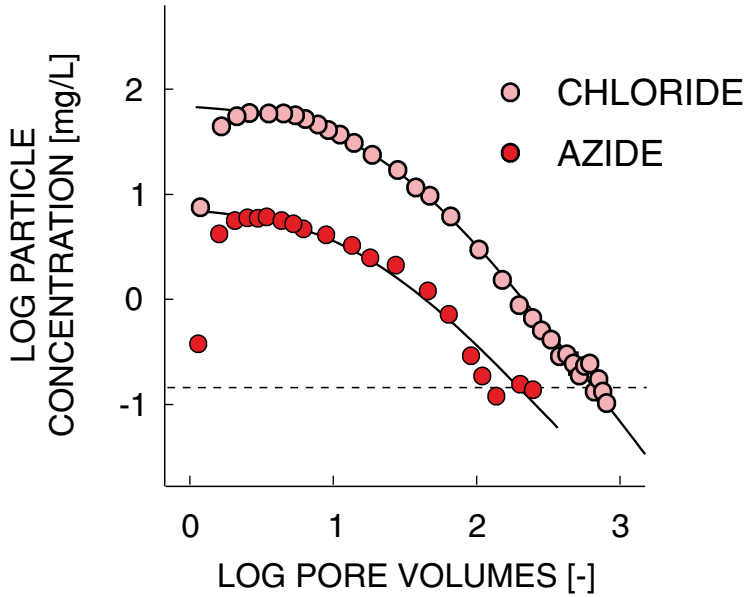


DEPOSITION

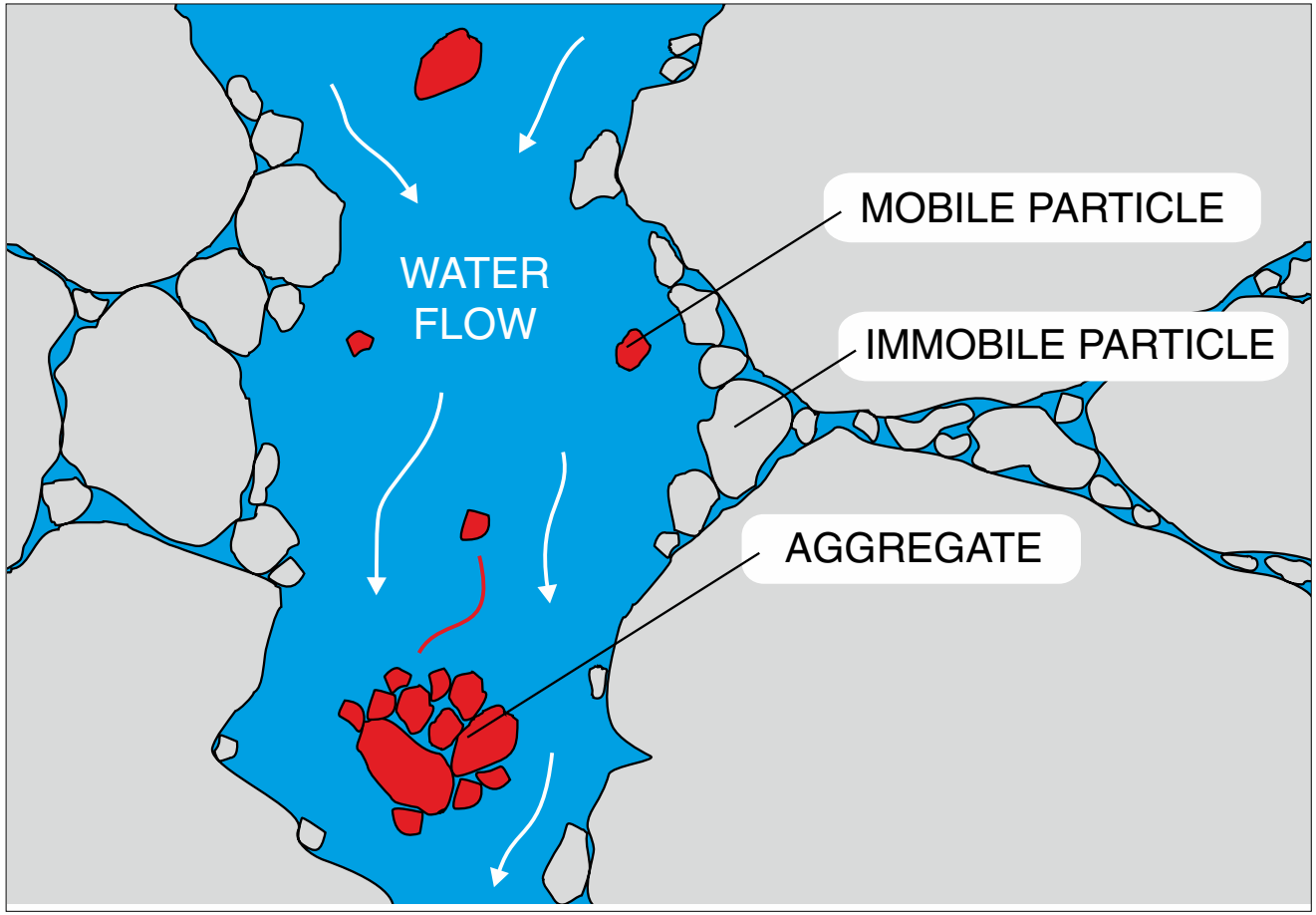




RELEASE

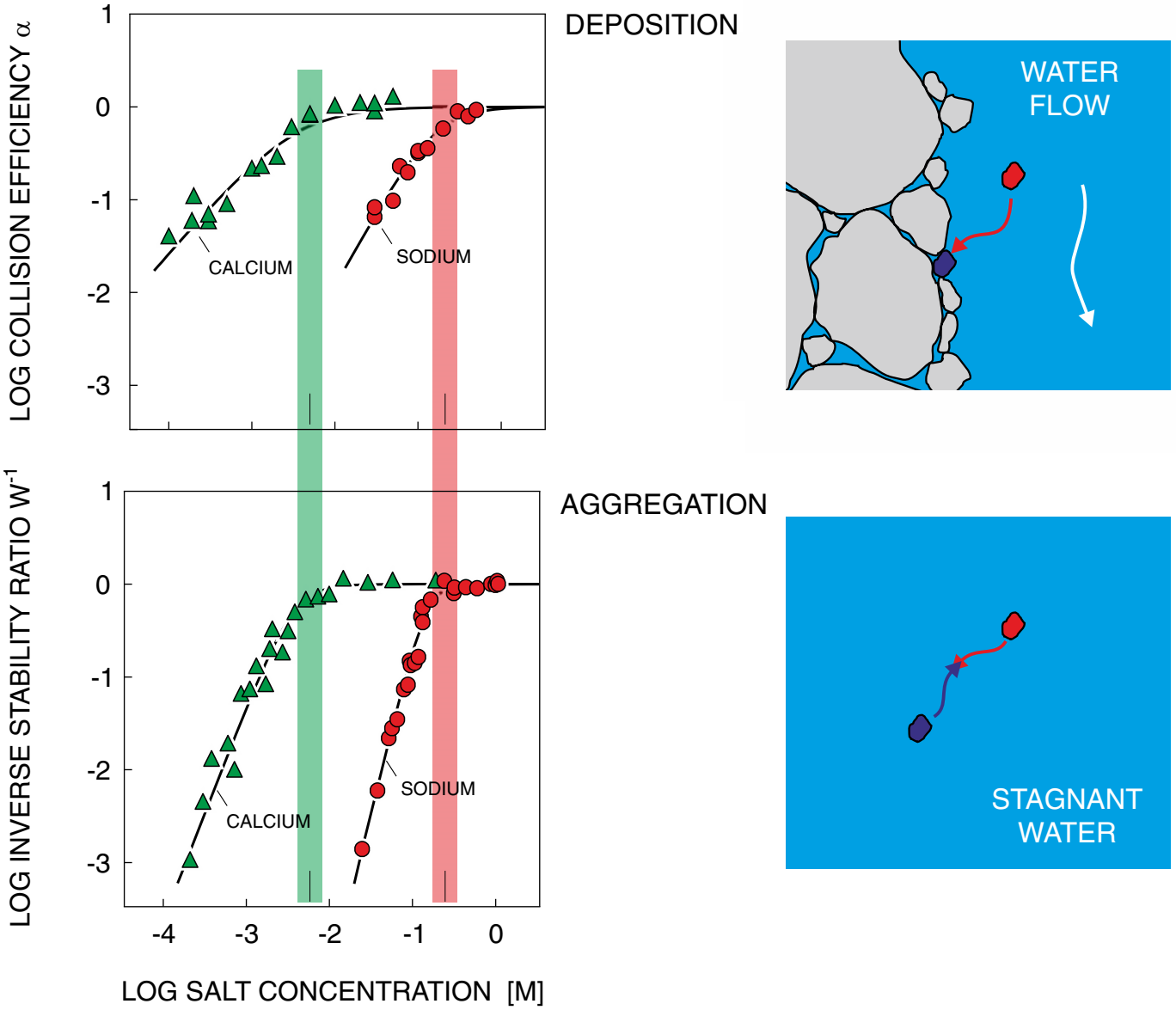


AGGREGATION of COLLOIDAL PARTICLES



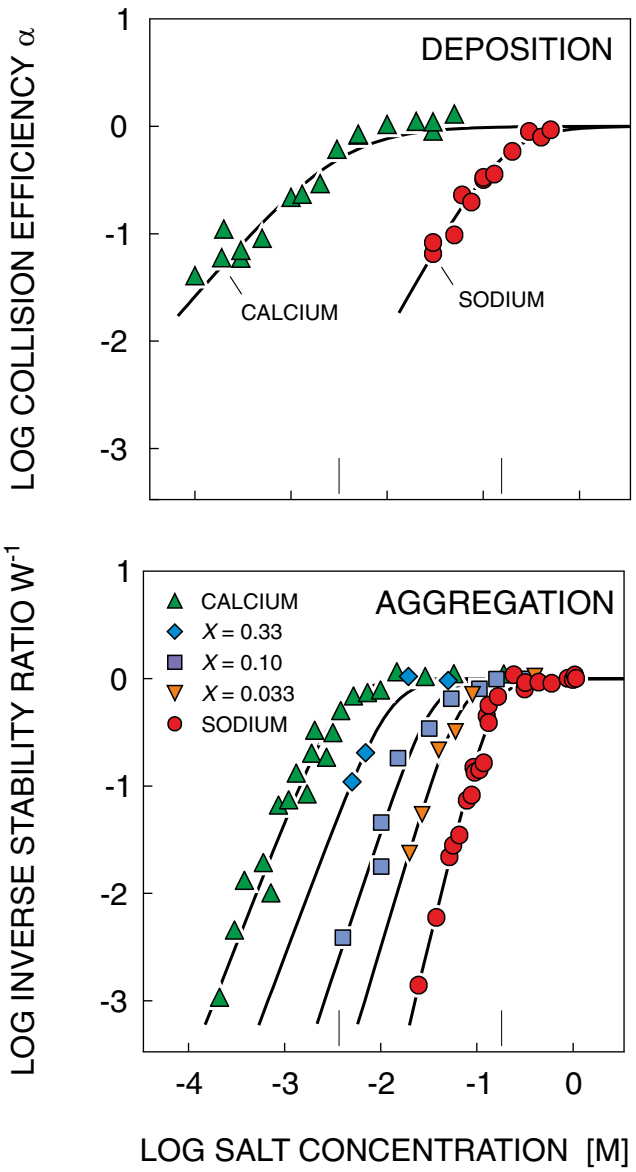
AGGREGATION of COLLOIDAL PARTICLES

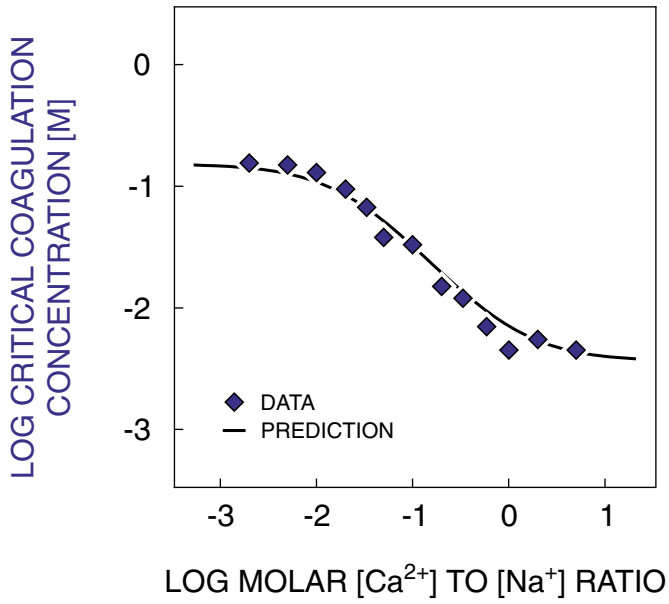
Analogy Aggregation - Deposition



AGGREGATION of COLLOIDAL PARTICLES

Analogy Aggregation - Deposition





$$k^{(dep)} = f([Na^+], [Ca^{2+}], \ldots)$$

MODELLING

1. Reactive Solute Transport (incl. contaminant - particle interactions)

- NON-REACTIVE SPECIES

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x}$$

c_i = concentration of species i
D_i = dispersion coefficient
v = pore-water velocity

- REACTIVE SPECIES

$$\frac{\partial c_i}{\partial t} + \frac{\partial q_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x}$$

q_i = sorbed concentration of species i

$$\frac{\partial q_i}{\partial t} = \sum_j^N \sum_i \frac{\partial q_{i,j}}{\partial c_i} \frac{\partial c_i}{\partial t}$$

competitive sorption

I. CONTAMINANT - PARTICLE INTERACTIONS

MODELLING

2. Particle Transport

$\tilde{c}$ = mobile particle concentration

$$\frac{\partial \tilde{c}}{\partial t} = D\frac{\partial^2 \tilde{c}}{\partial x^2} - v\frac{\partial \tilde{c}}{\partial x} + j_p^{(rel)}(x,t) - j_p^{(dep)}(x,t)$$

III. PERSISTENCE

II. GENERATION

$$\frac{\partial \tilde{c}}{\partial t} = D\frac{\partial^2 \tilde{c}}{\partial x^2} - v\frac{\partial \tilde{c}}{\partial x} + \sum_i^N k^{(rel)} Q_i - k^{(dep)} \tilde{c}$$

Q = immobile particle concentration

$$\frac{\partial Q}{\partial t} = -\sum_i^N \underbrace{k^{(rel)}} Q_i + \underbrace{k^{(dep)}} \tilde{c}$$

$$k^{(rel)},\ k^{(dep)} \neq const. = f(c_i, q_i, \ldots)$$

MODELLING

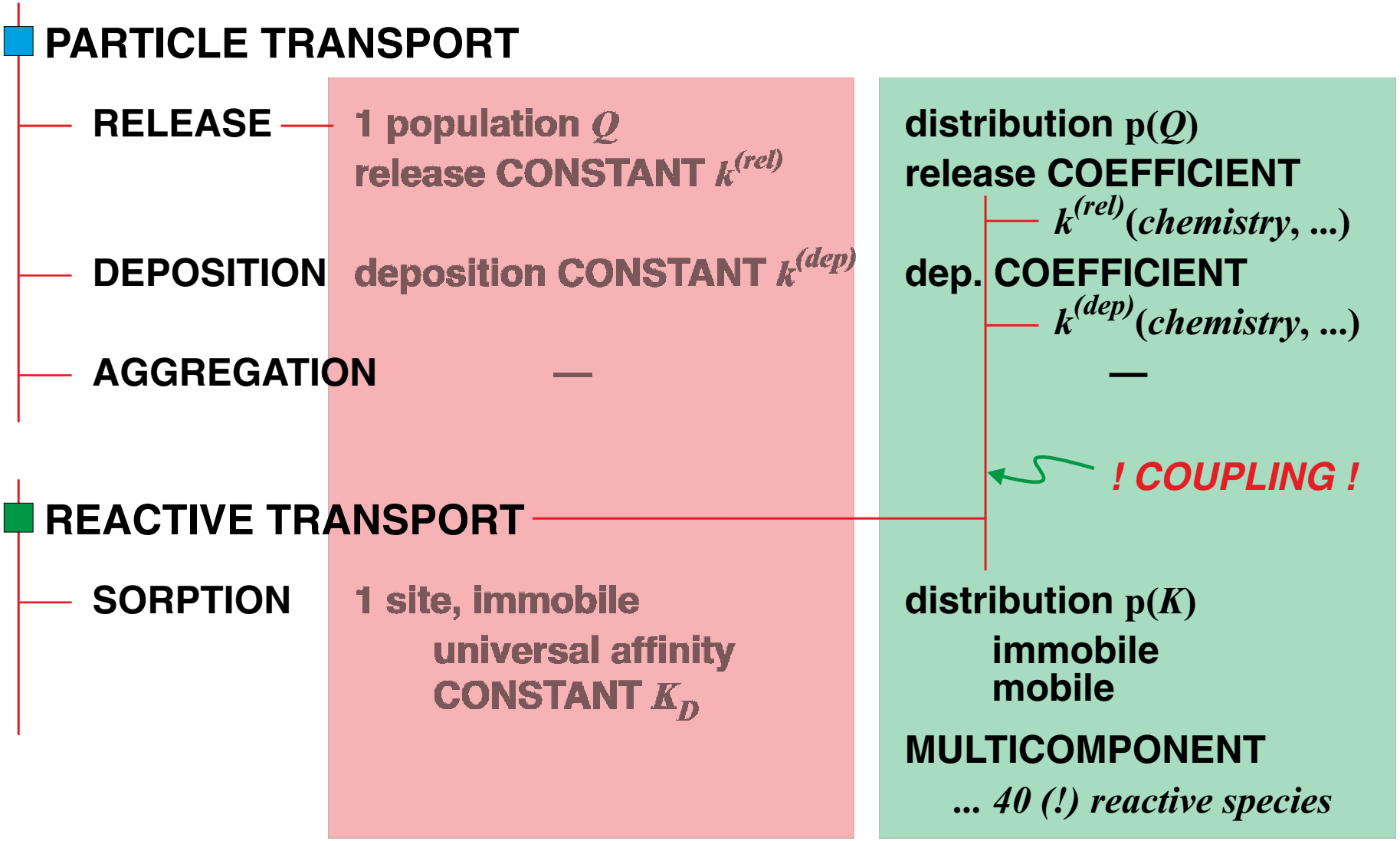
PARTICLE TRANSPORT

- **RELEASE** — 1 population Q, release CONSTANT $k^{(rel)}$
- **DEPOSITION** — deposition CONSTANT $k^{(dep)}$
- **AGGREGATION** — —

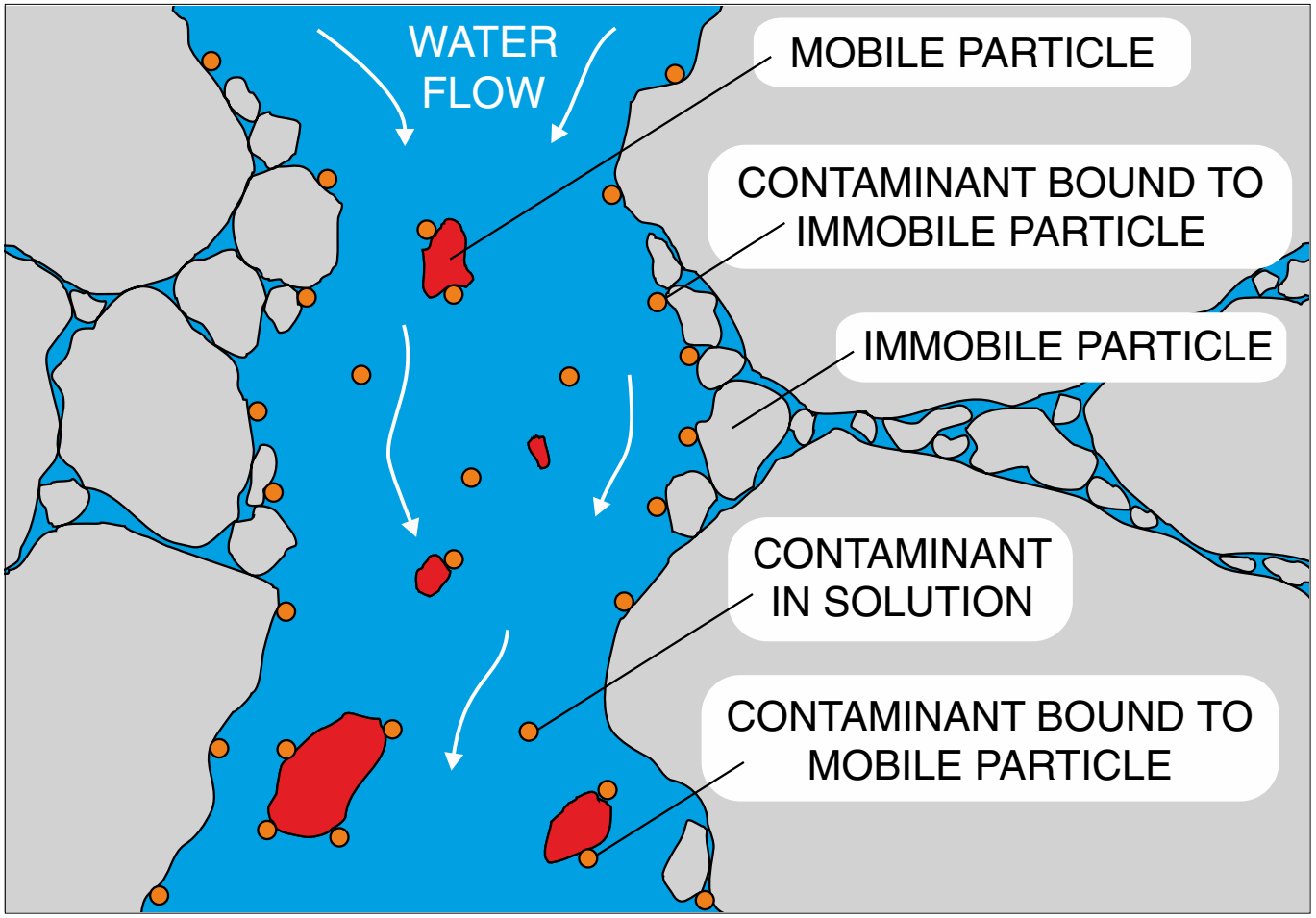
REACTIVE TRANSPORT

- **SORPTION** — 1 site, immobile, universal affinity CONSTANT K_D

MODELLING

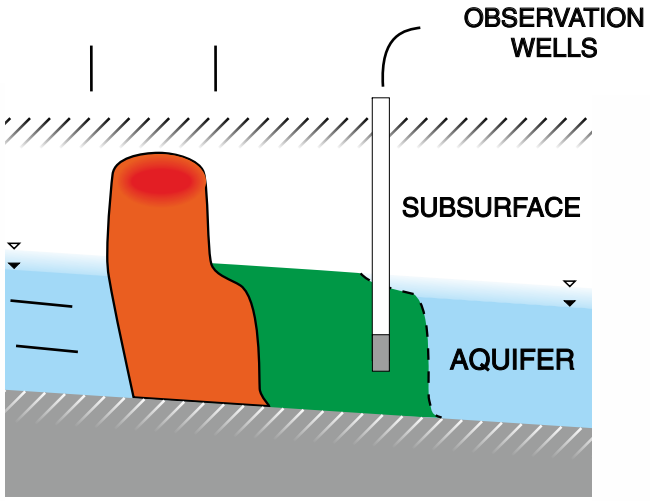

PARTICLE TRANSPORT
RELEASE
1 population Q
release CONSTANT k(rel)
DEPOSITION
deposition CONSTANT k(dep)
AGGREGATION
—
REACTIVE TRANSPORT
SORPTION
1 site, immobile
universal affinity
CONSTANT KD
distribution p(Q)
release COEFFICIENT
k(rel)(chemistry, ...)
dep. COEFFICIENT
k(dep)(chemistry, ...)
—
! COUPLING !
distribution p(K)
immobile
mobile
MULTICOMPONENT
... 40 (!) reactive species

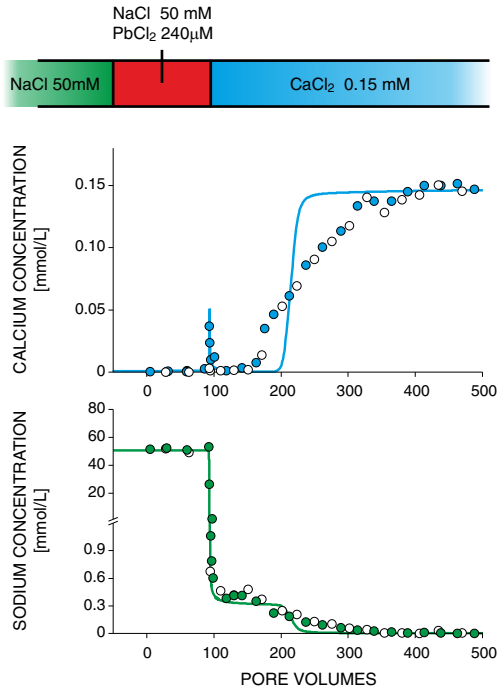
COLLOID FACILITATED TRANSPORT

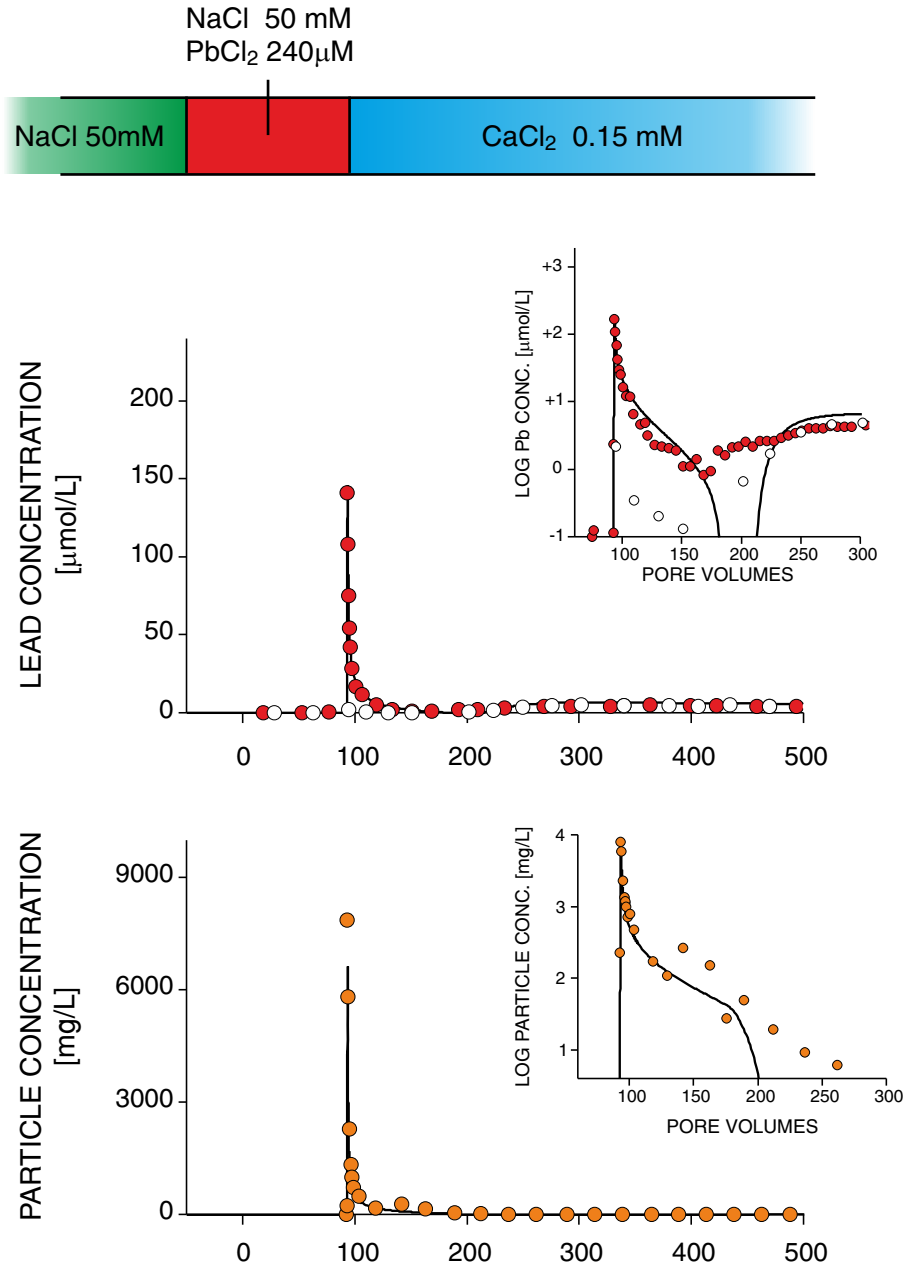


D. Grolimund, K. Barmettler, M. Borkovec, H. Sticher, *Environ. Sci. Technol.,1996*, 30/10, 3118-3123

COLLOID FACILITATED TRANSPORT

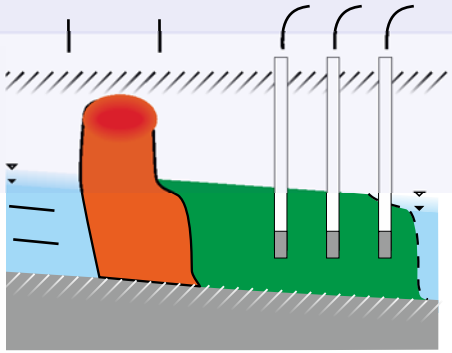


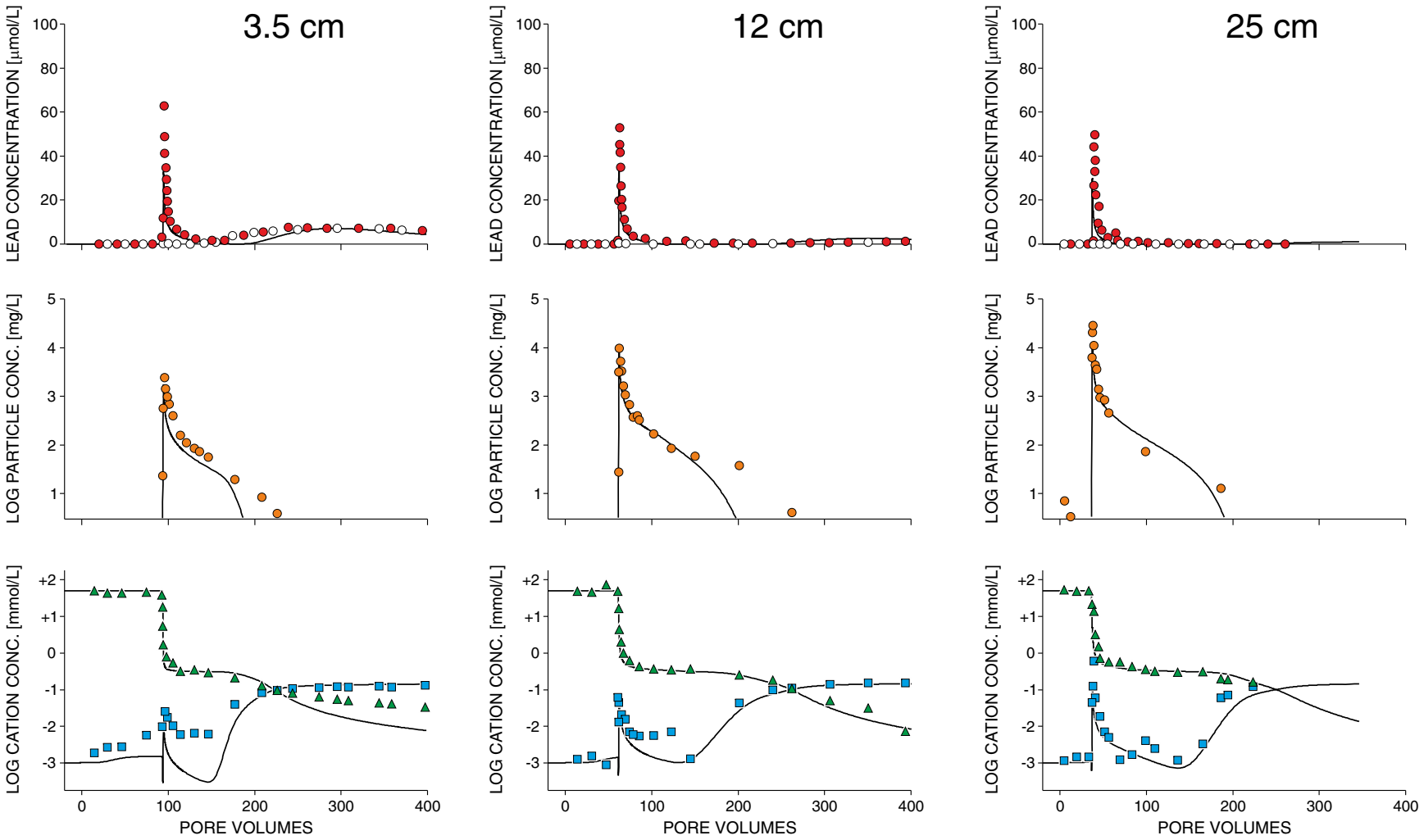




COLLOID FACILITATED TRANSPORT

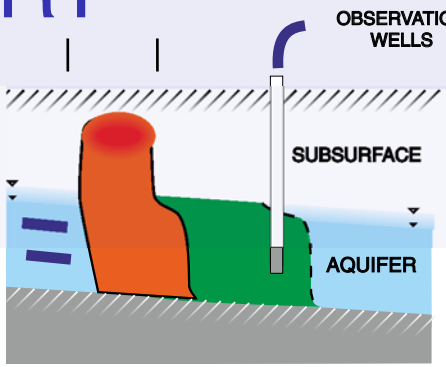
Length uncontaminated zone

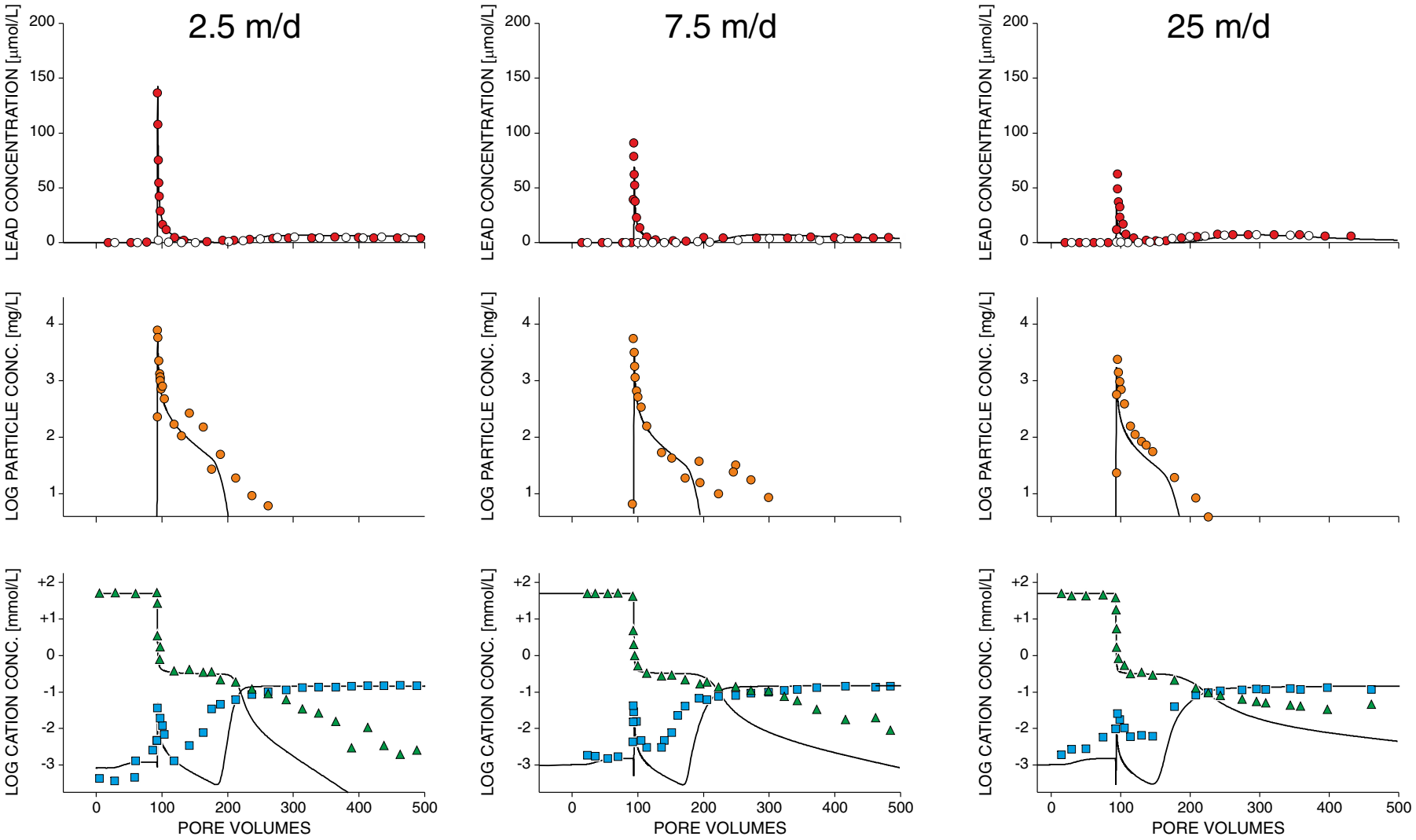




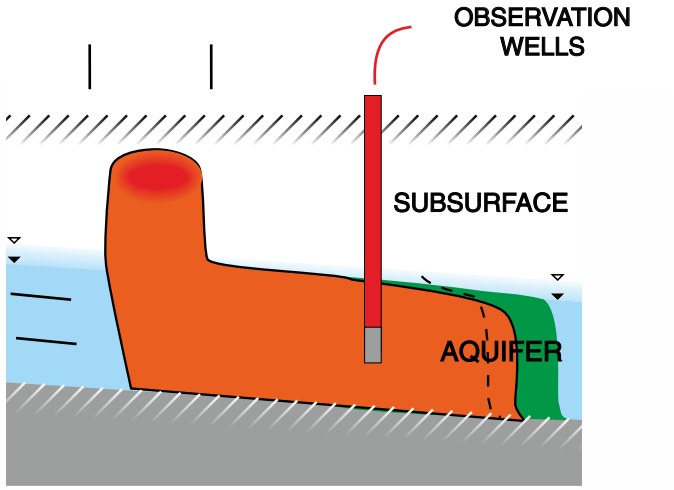
COLLOID FACILITATED TRANSPORT

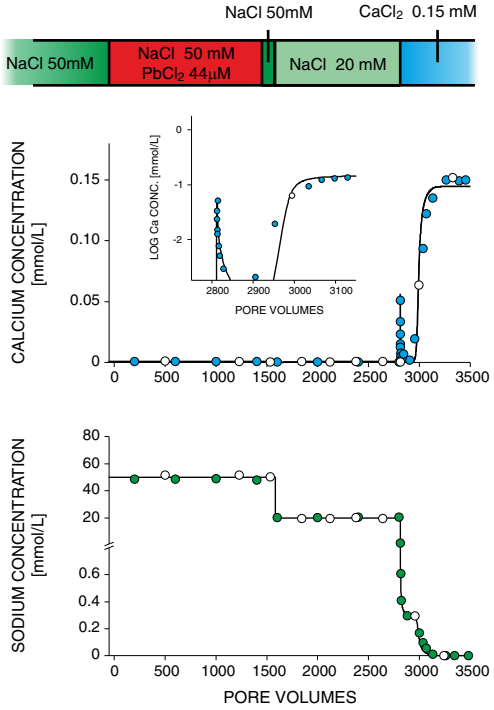
Flow Velocity Dependence

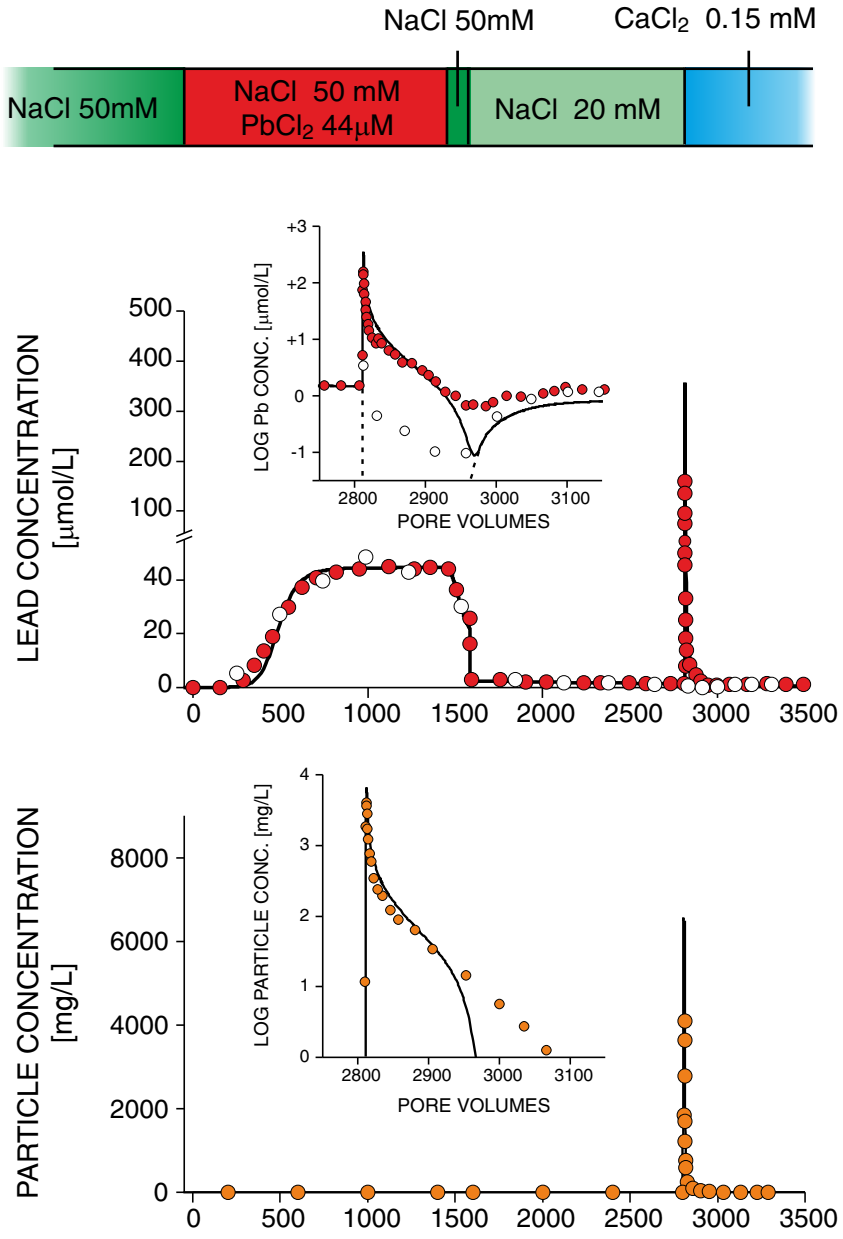




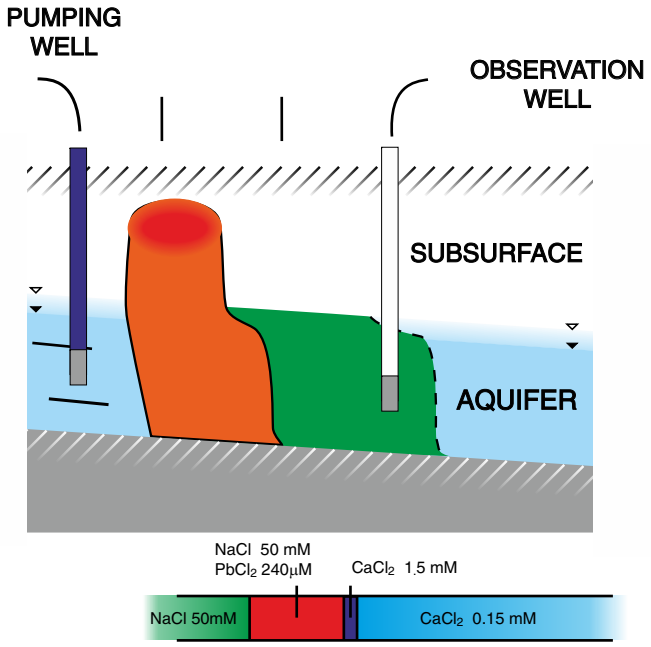
COLLOID FACILITATED TRANSPORT

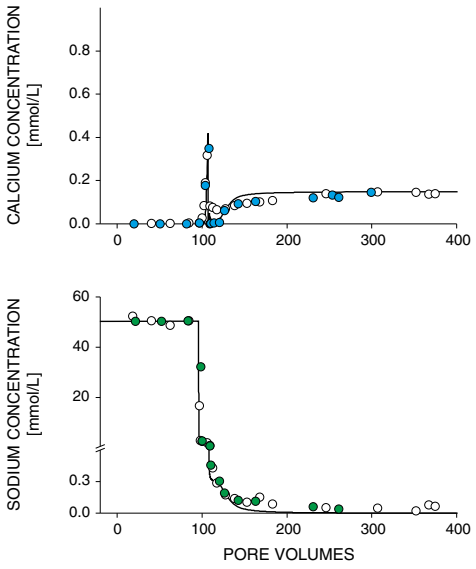


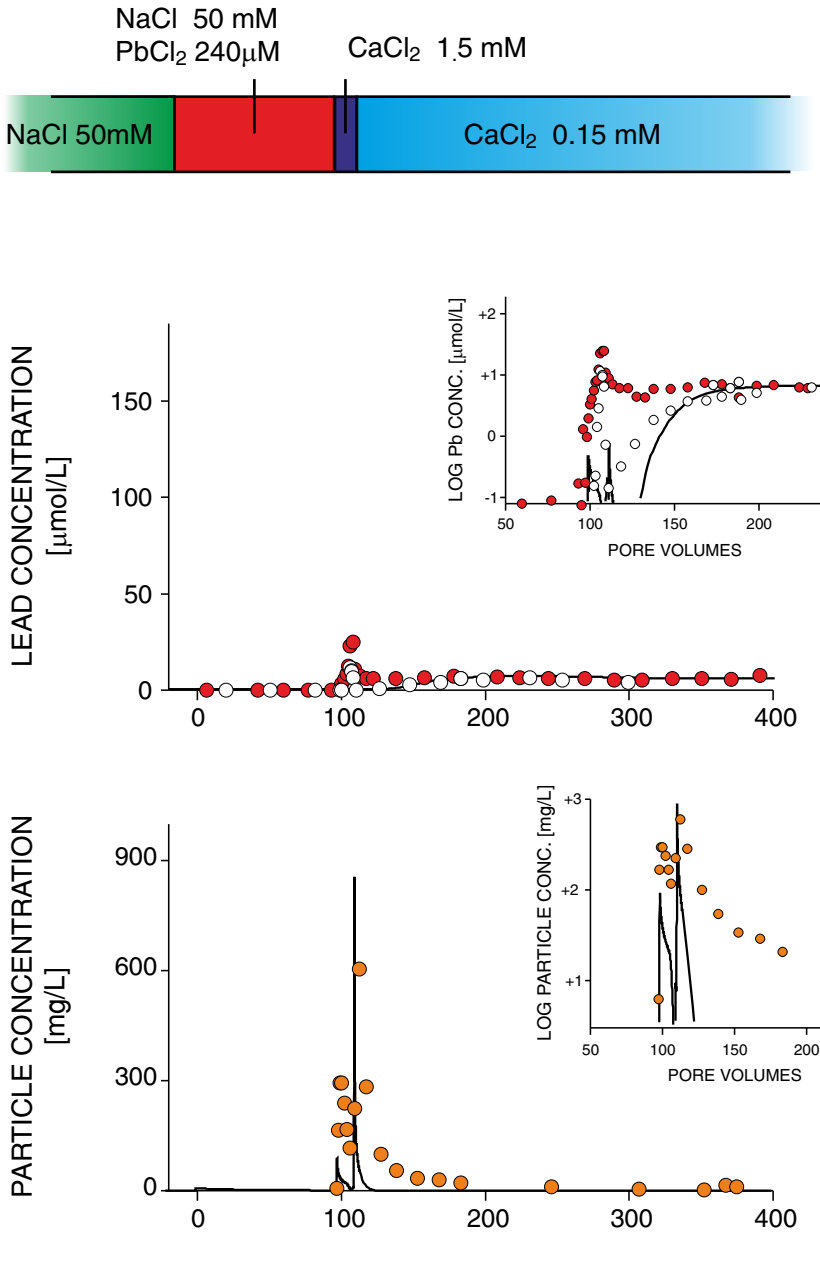




COLLOID FACILITATED TRANSPORT

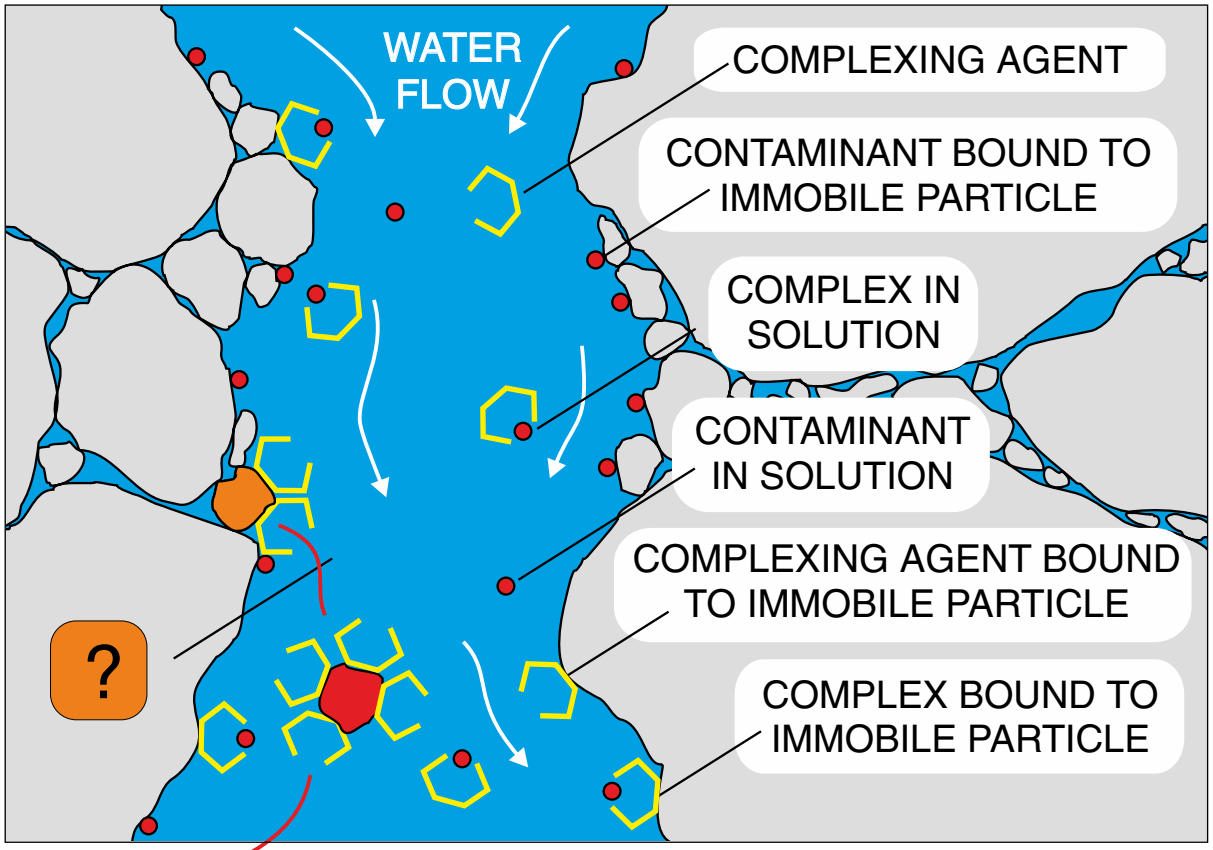






COLLOID FACILITATED TRANSPORT

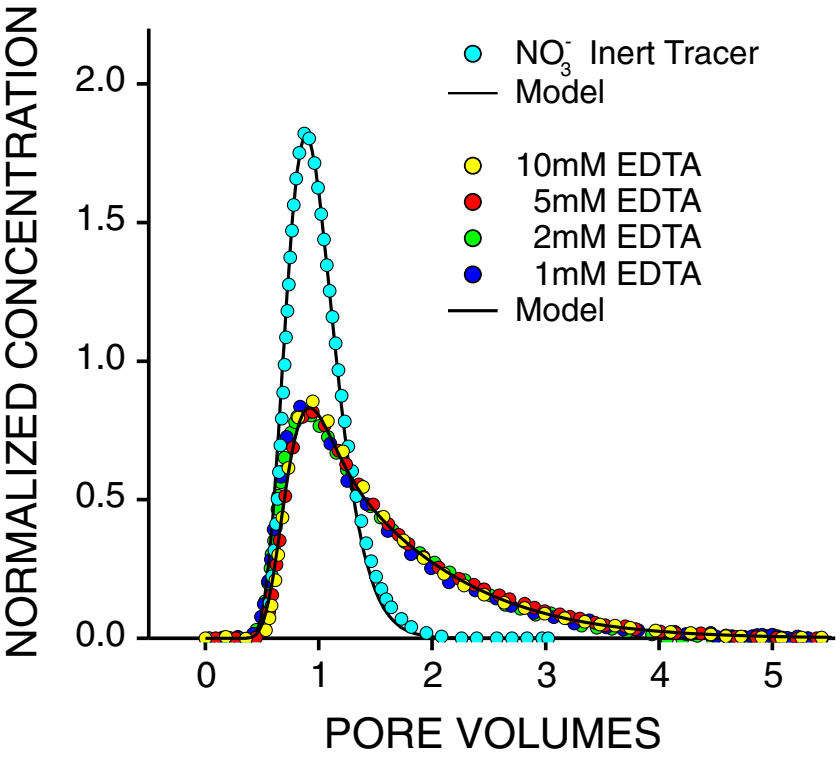
Complexing Agents - “Aquifer Clean-up”

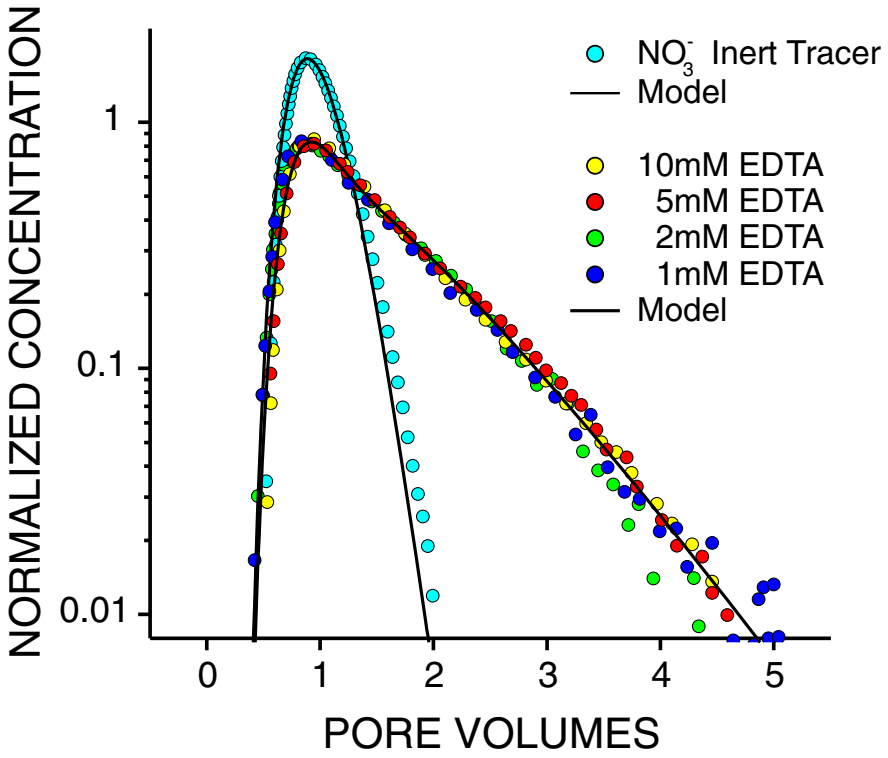


- COLLOID FACILITATED TRANSPORT
- AFFECTED HYDRAULIC PROPERTIES
- REDUCED CHEMICAL REACTIVITY

COLLOID FACILITATED TRANSPORT

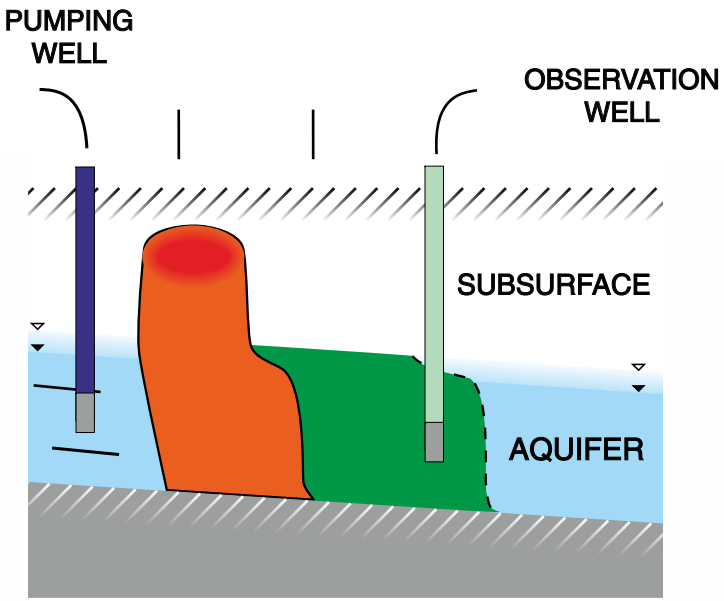
EDTA - Reactive Transport

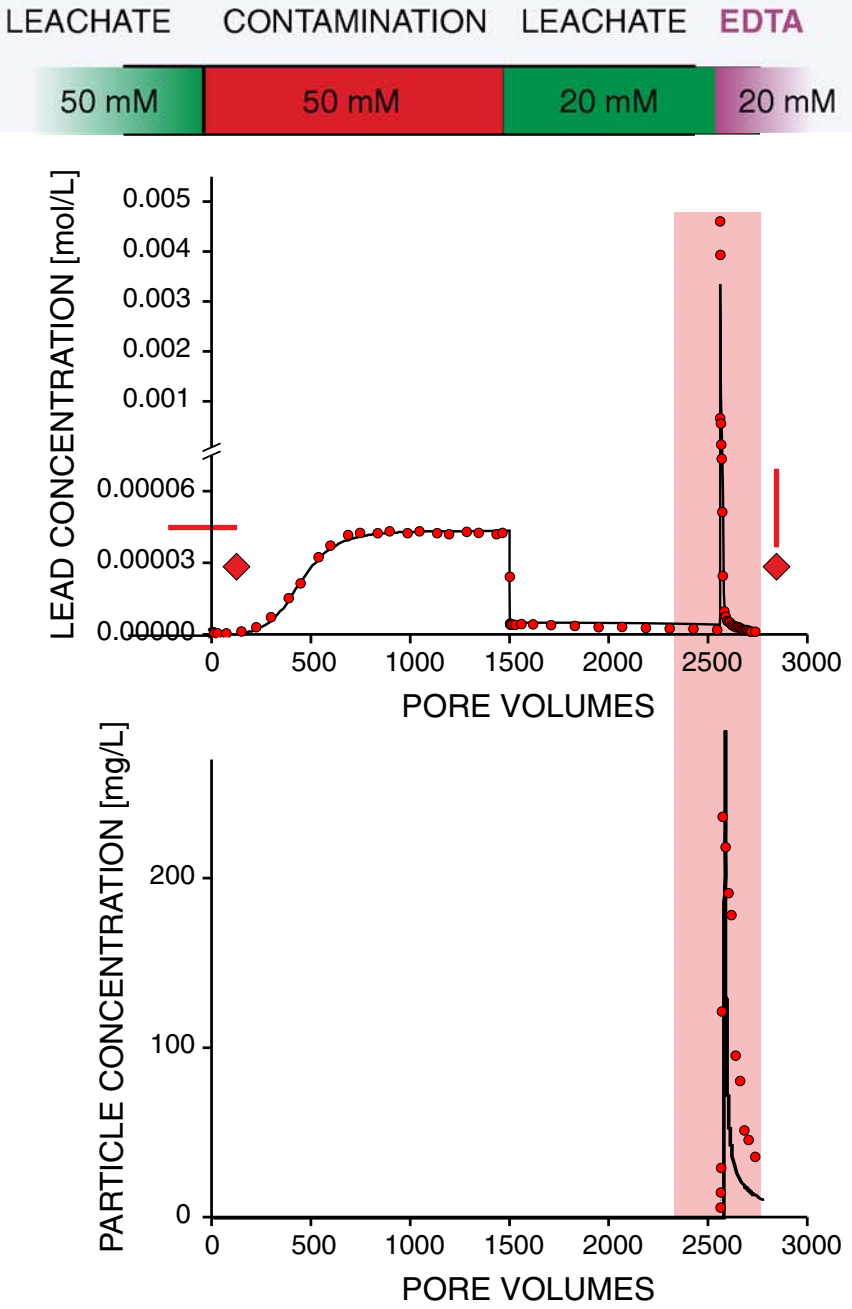




COLLOID FACILITATED TRANSPORT

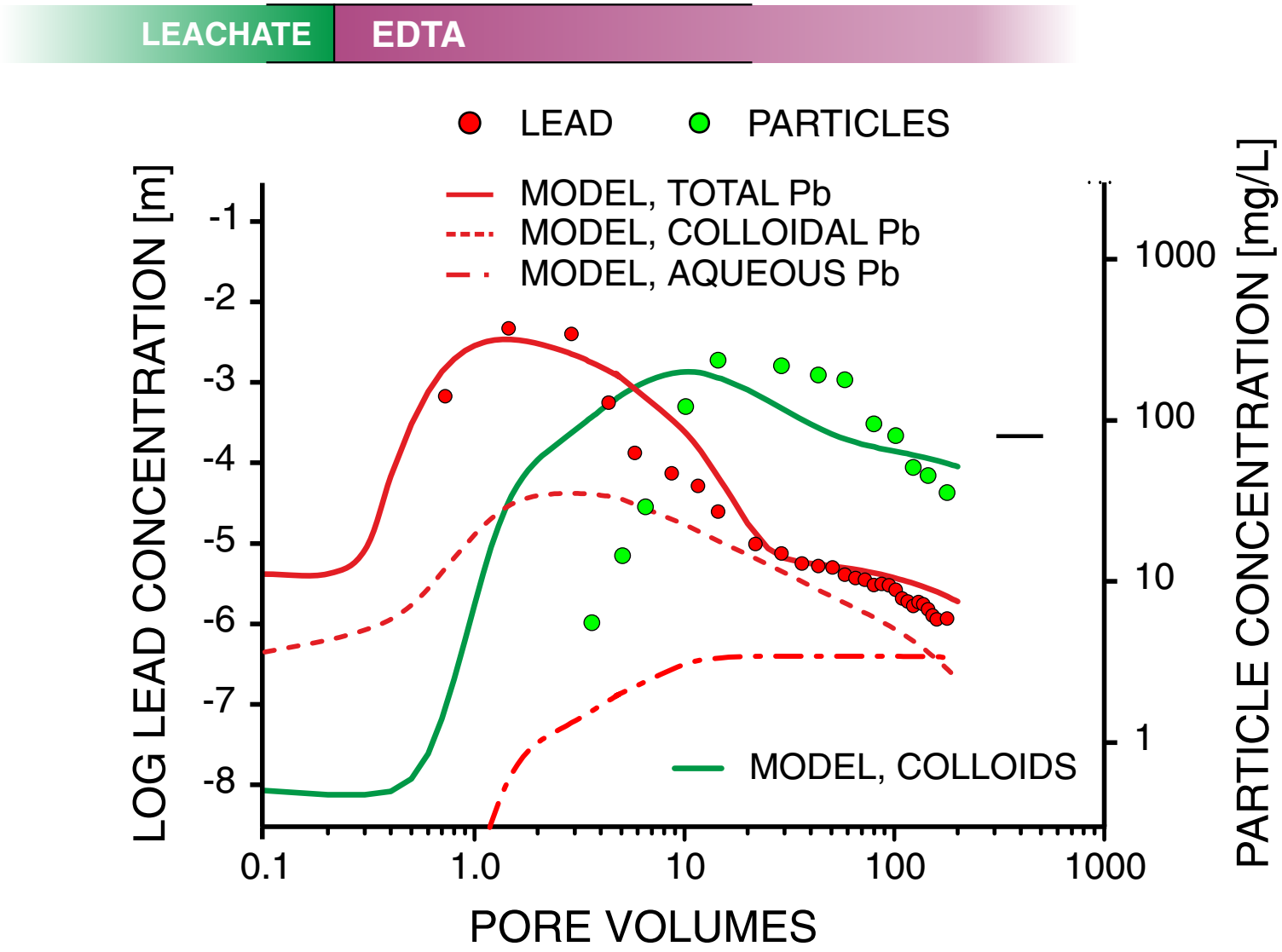
"Aquifer Clean-up"





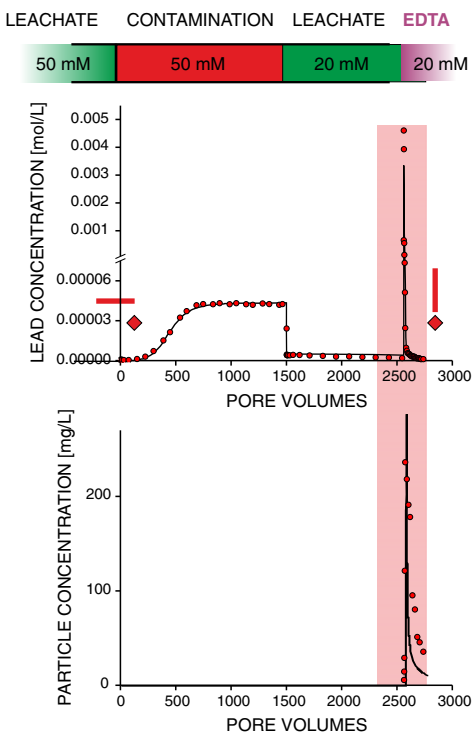
COLLOID FACILITATED TRANSPORT

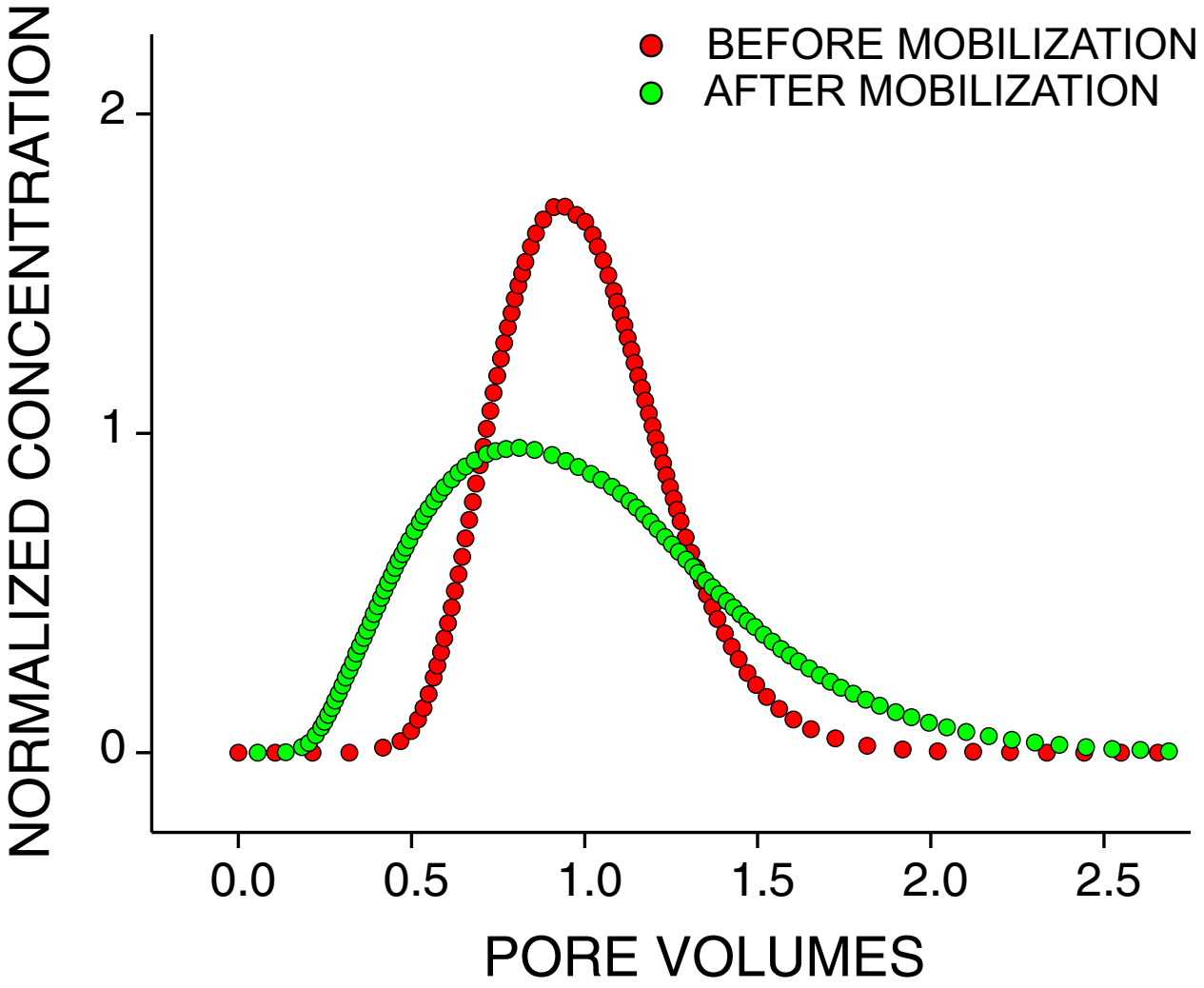
“Aquifer Clean-up”



COLLOID MOBILIZATION

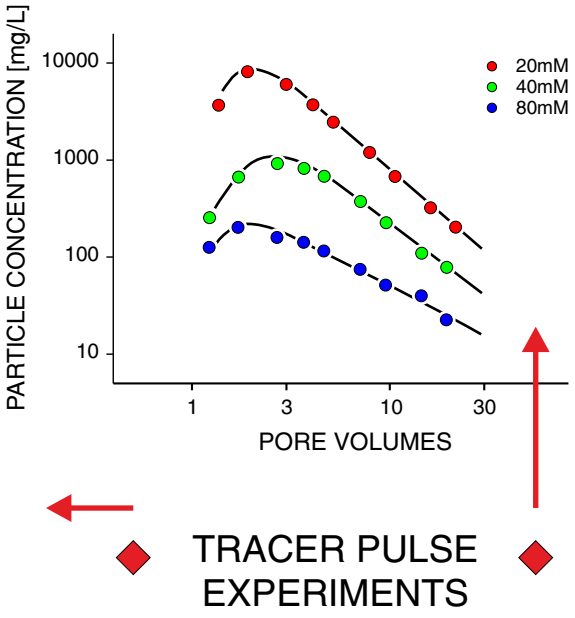
Structural Damage during “Aquifer Clean-up”

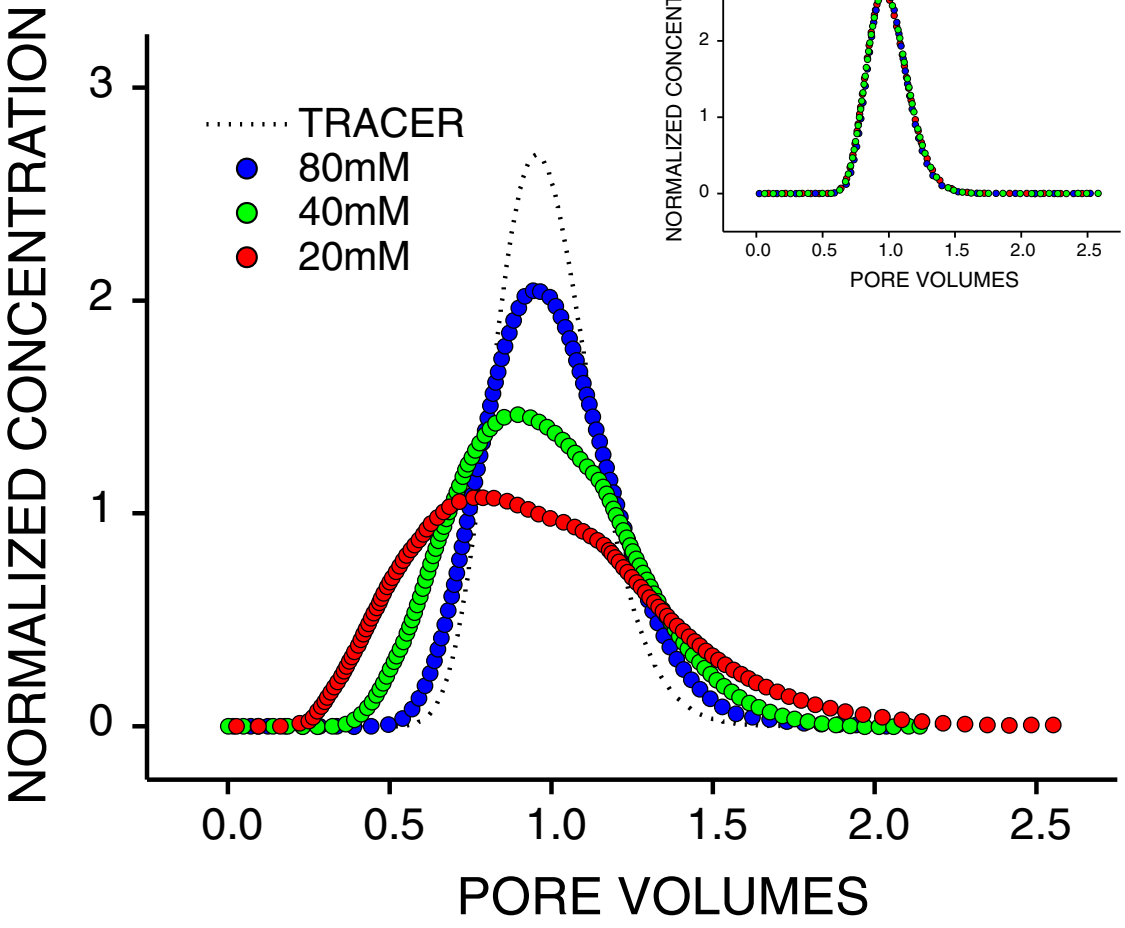




COLLOID MOBILIZATION

Structural Damage





CONCLUSIONS and OUTLOOK

- COLLOIDAL PARTICLES ARE *'UBIQUITOUS'* AND REPRESENT THE *'REACTIVE PHASE'* IN MOST NATURAL AND TECHNICAL SYSTEMS
- GENERATION AND PERSISTENCE OF MOBILE COLLOIDAL PARTICLES IS STRONGLY COUPLED TO SOLUTION AND SURFACE CHEMISTRY (-> REACTIVE TRANSPORT PHENOMENA)
- KINETICS ▪ NON-LINEARITIES ▪ HETEROGENEITIES
- ENHANCED CONTAMINANT MOBILITY BY *IN-SITU* MOBILIZED COLLOIDAL PARTICLES
- PARTICLE RELEASE RESULTS IN 'STRUCTURAL DAMAGE'
- EMPIRICAL DESCRIPTION OF THE CENTRAL PHENOMENA
  - PROCESS-ORIENTED, MECHANISTIC CONCEPTS
- INTERFACIAL PHENOMENA ARE CRITICAL
  - MOLECULAR LEVEL UNDERSTANDING