TETRA TECH

Effects of Heterogeneity and Back-Diffusion on Cleanup Timeframe

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Tetra Tech

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Non-Fickian (“Anomalous”) Plumes are the Norm

- Large dilute plumes with asymmetric spatial distribution and nonuniform spreading rates not proportional with time (non-Fickian)

- Long COC concentration vs time tails in wells and/or rebound, resulting in long cleanup times!

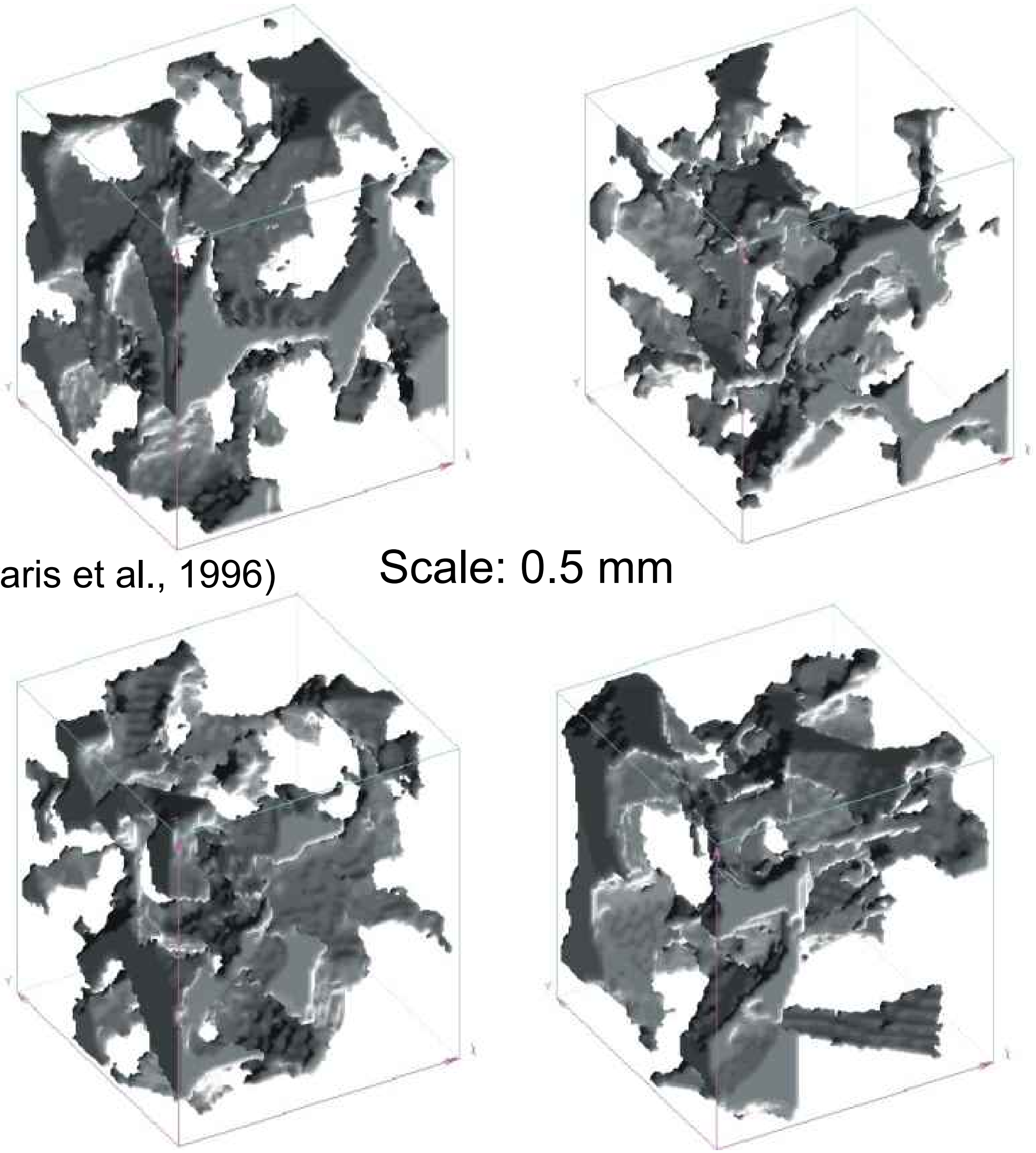
- Causes: 1) multi-scale (pore to field) heterogeneity (ln K variance >>1) causes broad velocity spectrum and preferential transport); 2) multiple rates of back-diffusion from heterogeneous immobile zones; 3) nonlinear sorption-desorption rates

- Current models based on standard ADE can underestimate the cleanup timeframe

Question: *Are better modeling tools available that upscale sub-grid heterogeneity and back-diffusion to better estimate the cleanup time?*

I. Multi-Scale Heterogeneity: Pore to Field Scale

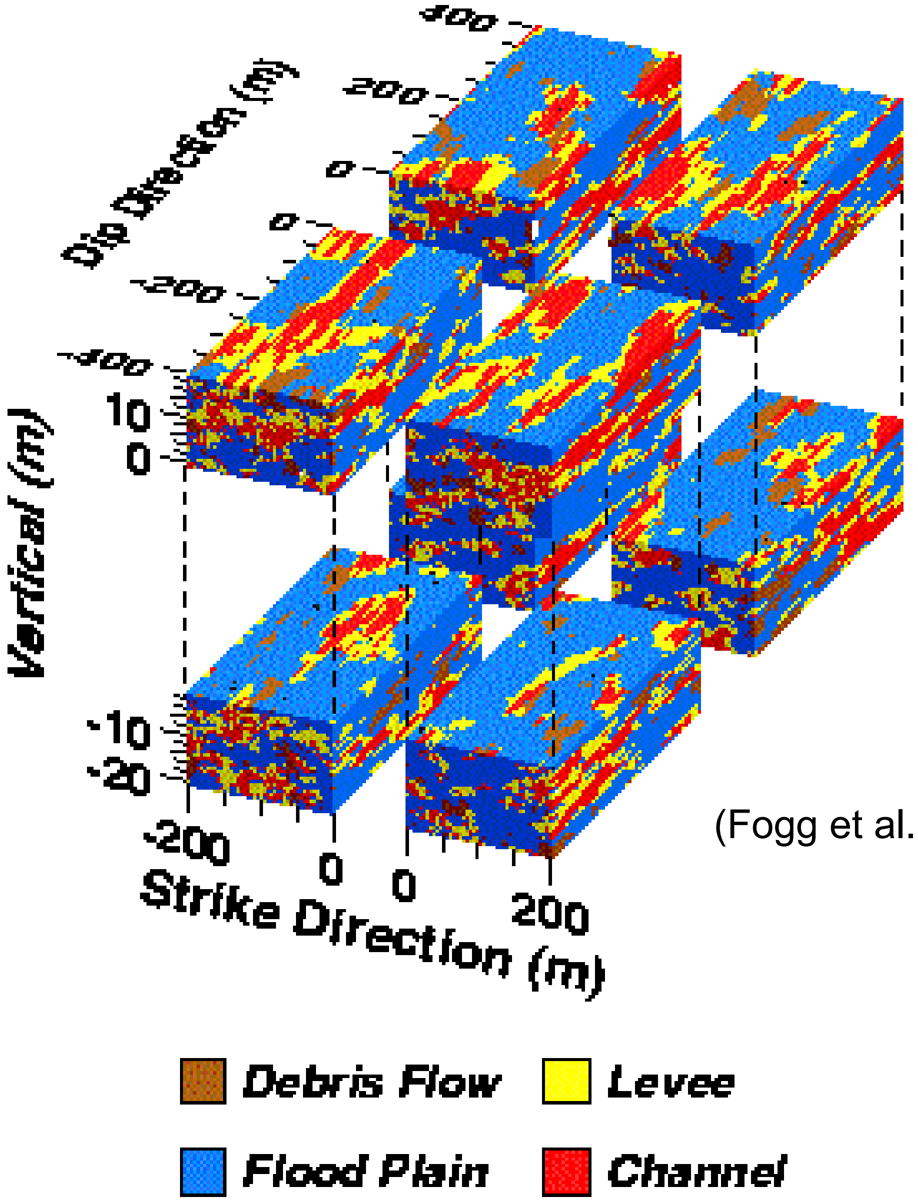
X-ray images of pore space in sandstone



(Auzeraris et al., 1996)

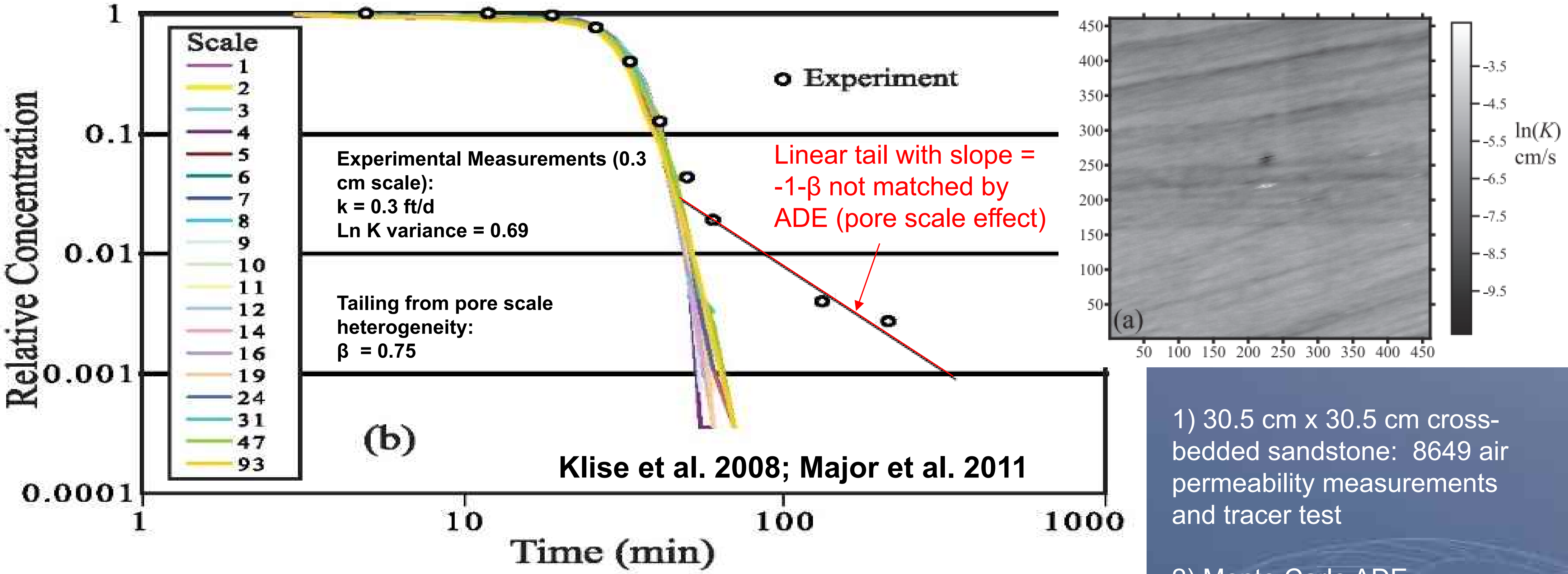
Scale: 0.5 mm

Fluvial depositional environment



(Fogg et al.,1998)

Sandstone K Sampling and Tracer Lab Test with “Tailing” from Pore-Scale Heterogeneity



Experimental Measurements (0.3 cm scale):
k = 0.3 ft/d
Ln K variance = 0.69

Tailing from pore scale heterogeneity:
β = 0.75

Linear tail with slope = -1-β not matched by ADE (pore scale effect)

Klise et al. 2008; Major et al. 2011

1) 30.5 cm x 30.5 cm cross-bedded sandstone: 8649 air permeability measurements and tracer test

2) Monte Carlo ADE simulations based on ln K statistics for different grids

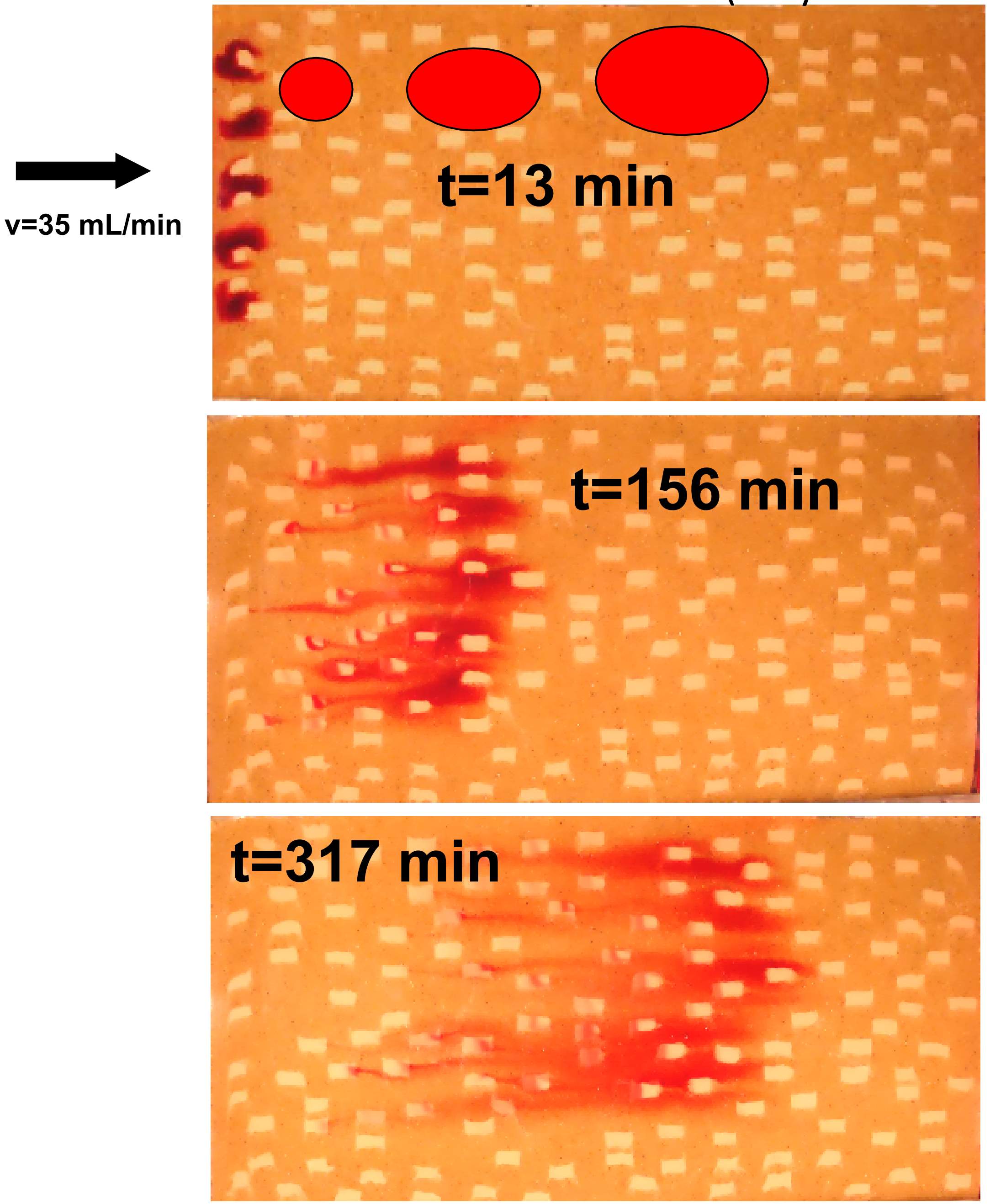
Key points:

(1) Tailing not matched by ADE with high resolution data (cm scale grid)

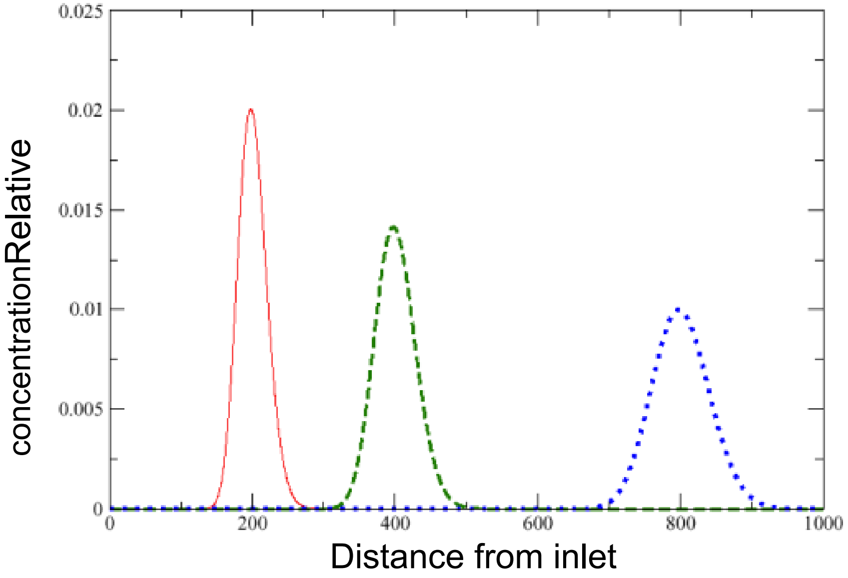
(2) Long tail from pore scale heterogeneity

a) Heterogeneous Advection: Meter Scale Uniform Sand with Random Silt Lenses

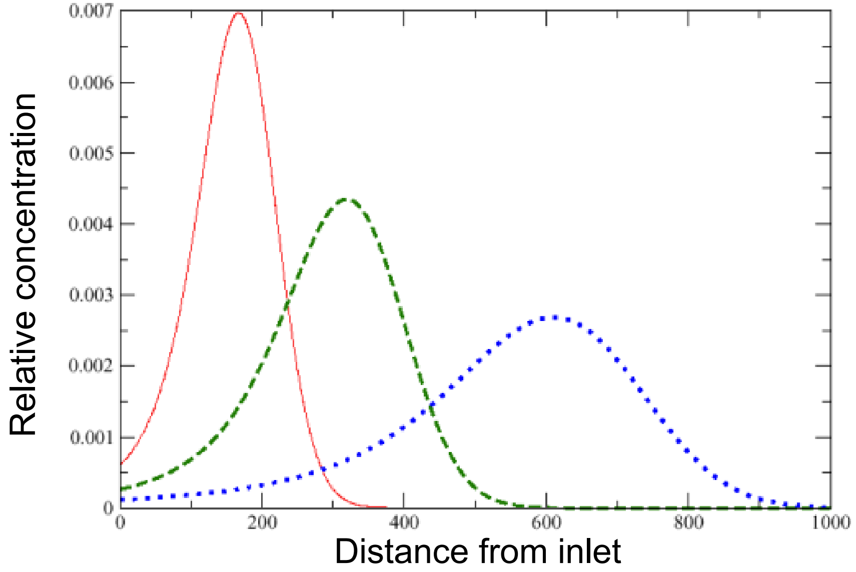
(Levy and Berkowitz, 2003)



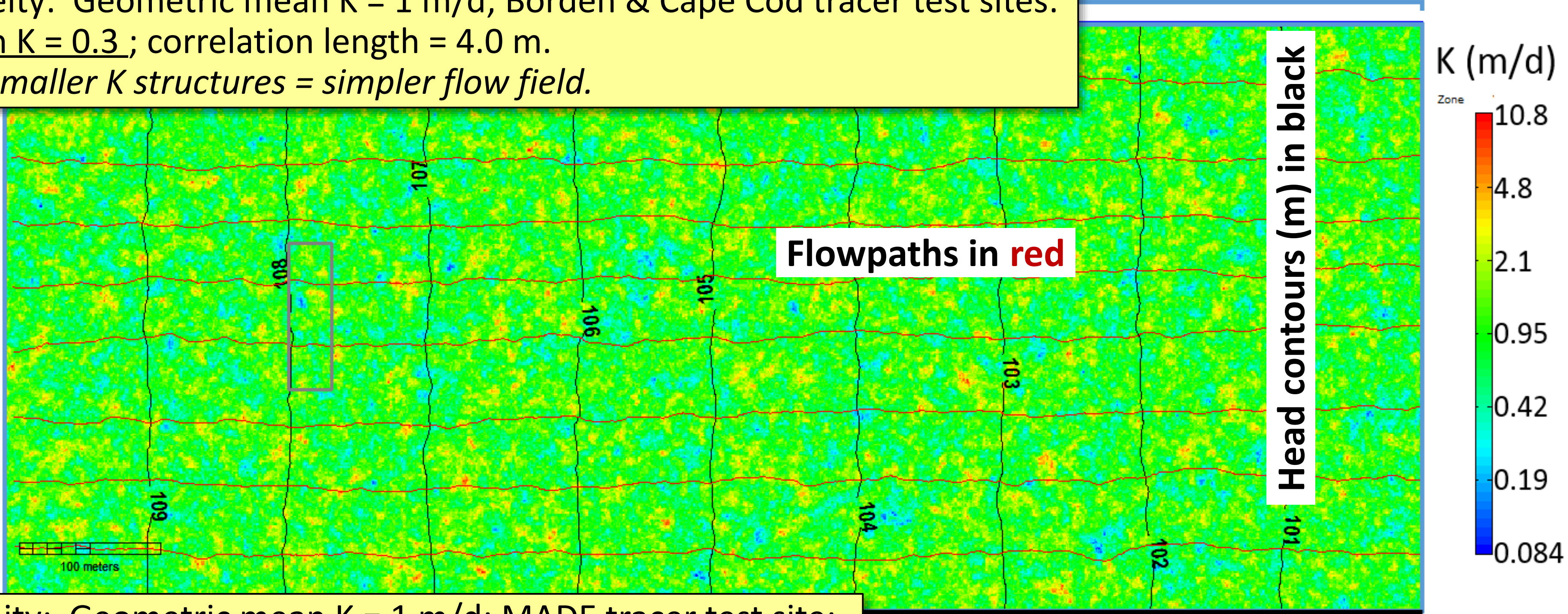
“Expected using ADE”



“Tear Drop Shape” Detected

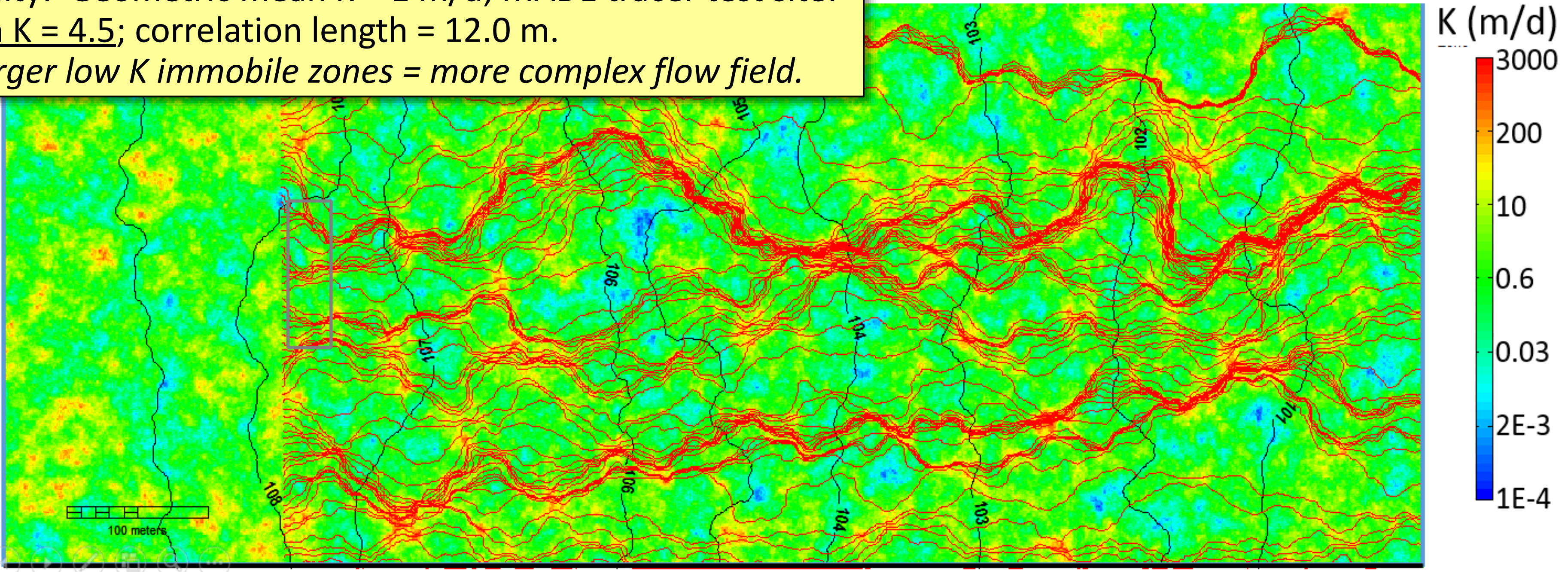


K field heterogeneity: Geometric mean K = 1 m/d; Borden & Cape Cod tracer test sites:
Variance (σ^2) of ln K = 0.3 ; correlation length = 4.0 m.
Smaller K range, smaller K structures = simpler flow field.

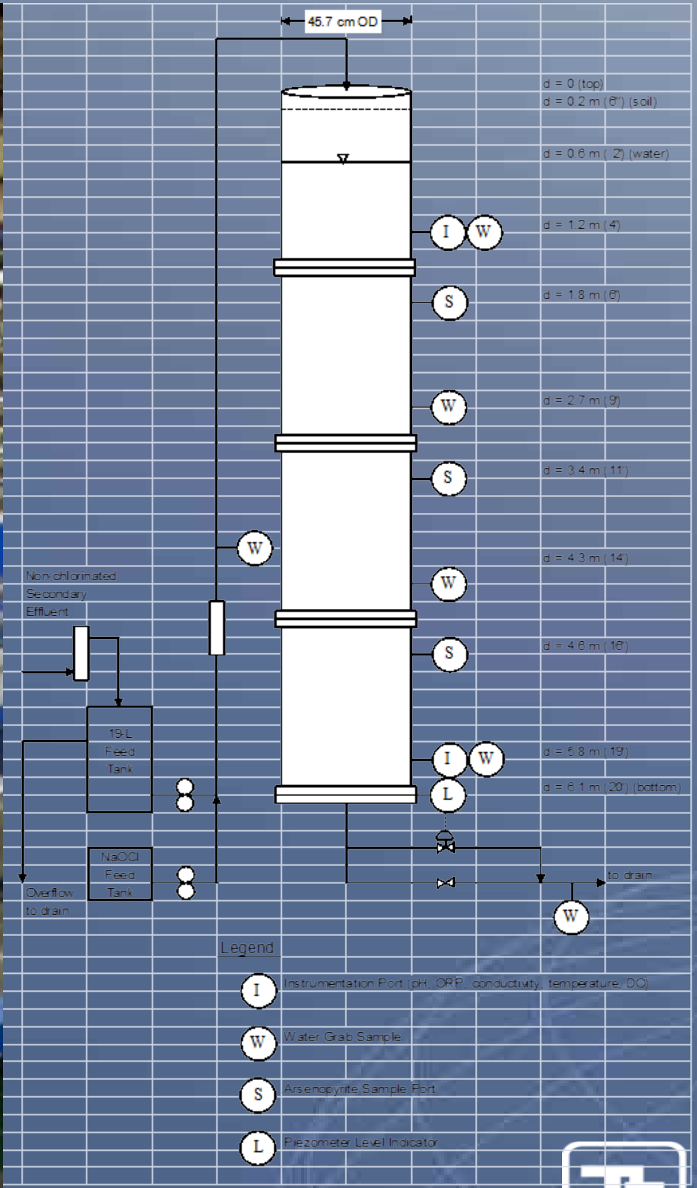

Flowpaths in red

Head contours (m) in black

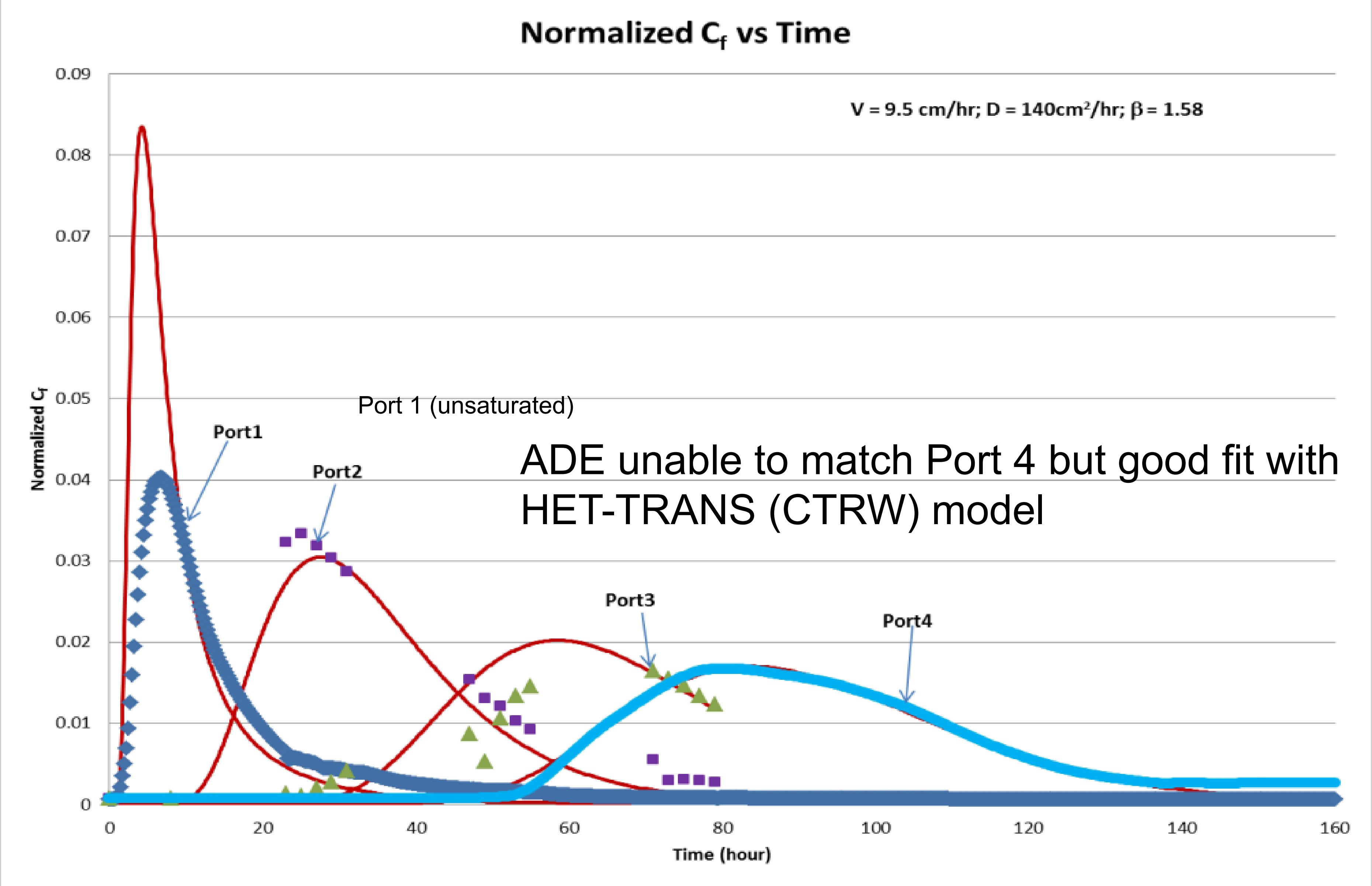
K field heterogeneity: Geometric mean K = 1 m/d; MADE tracer test site:
Variance (σ^2) of ln K = 4.5; correlation length = 12.0 m.
Larger K range, larger low K immobile zones = more complex flow field.



USEPA 20 ft Column Tracer Tests Using Heterogeneous Sediments



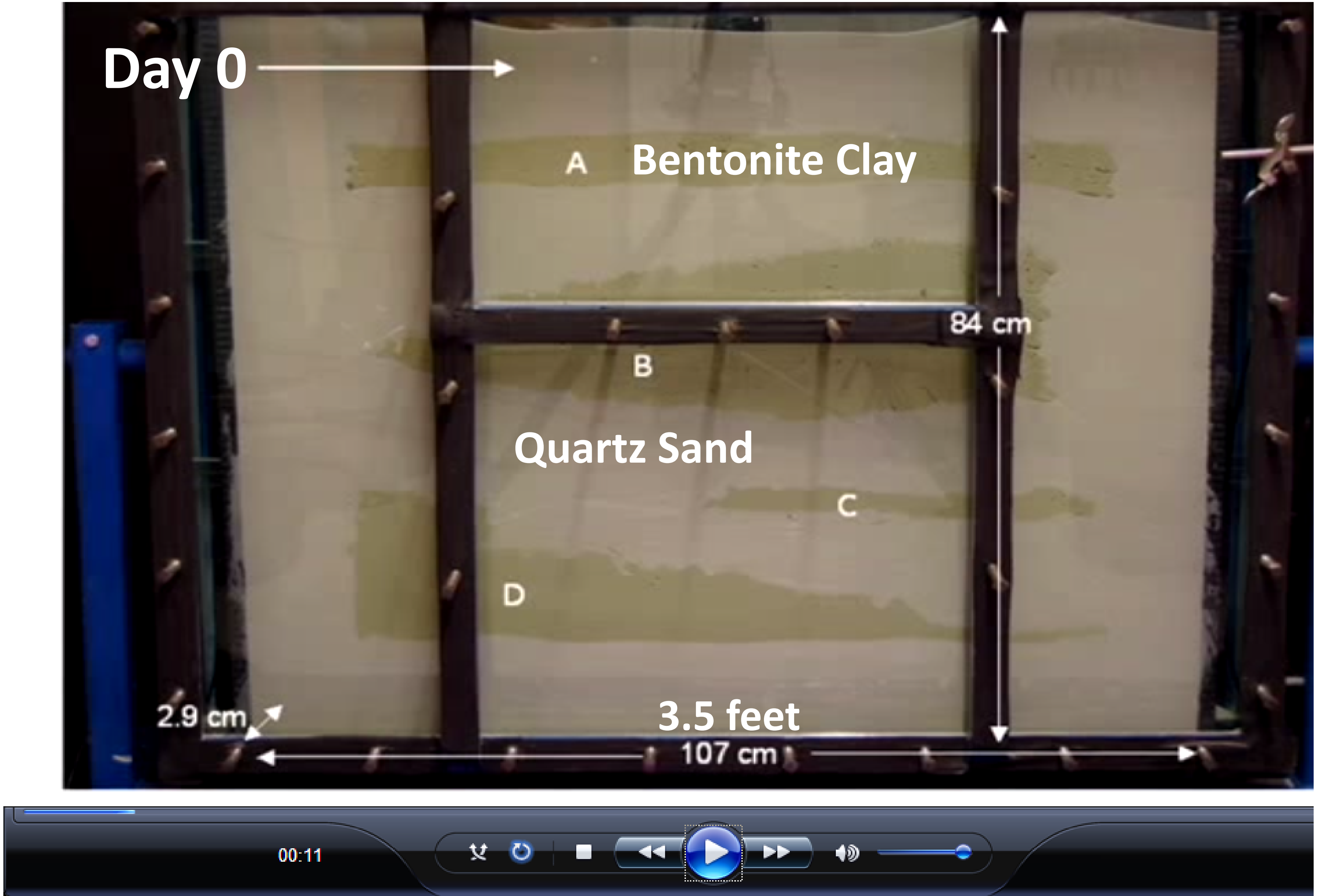
HET-TRANS (CTRW) Model Fit Using K variance = 6.5 at Port 4 in 20 ft column



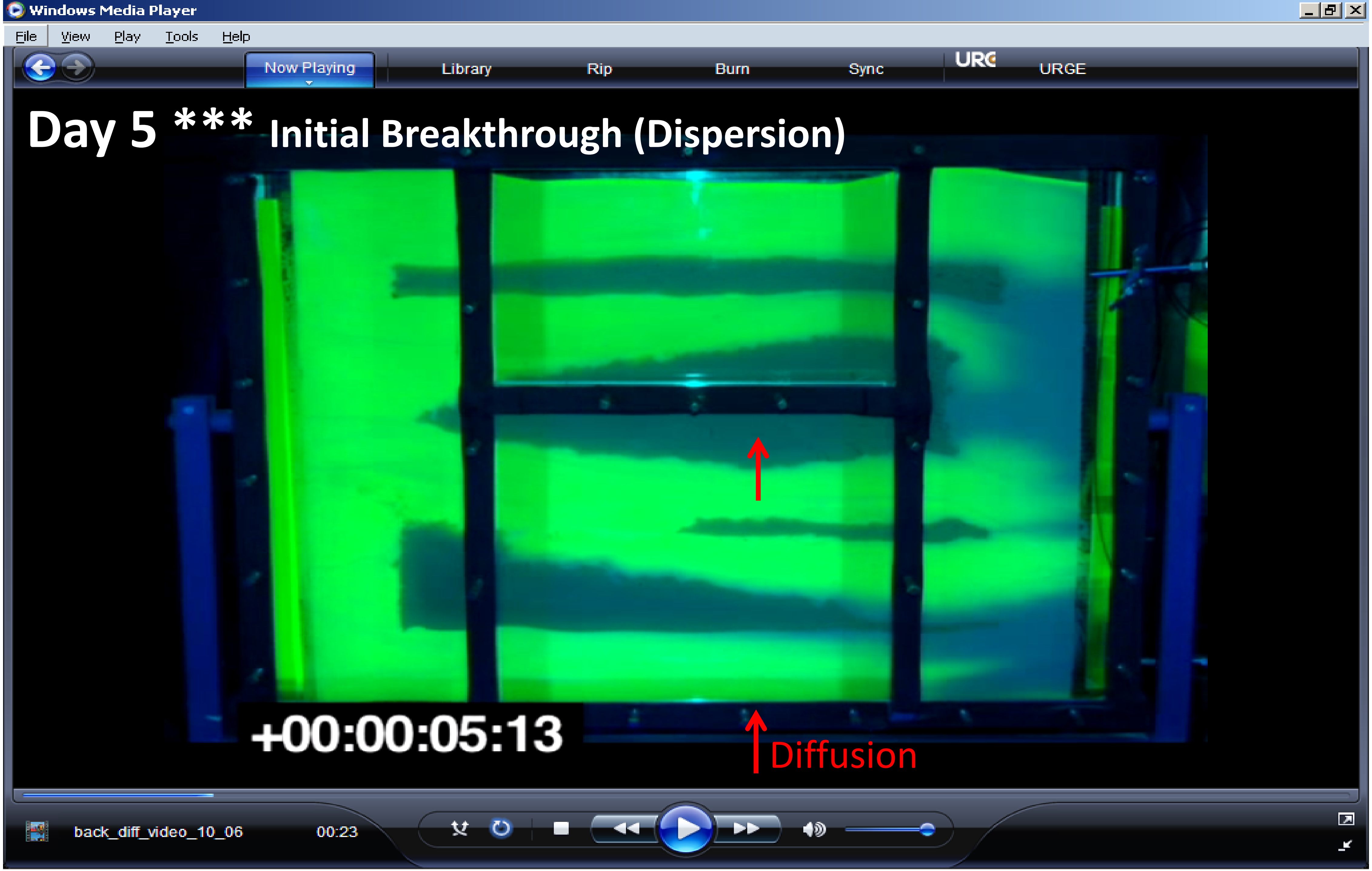
Port 1 (unsaturated)

ADE unable to match Port 4 but good fit with HET-TRANS (CTRW) model

b) Diffusive Mass Transfer and Back Diffusion (Doner and Sale, 2008)

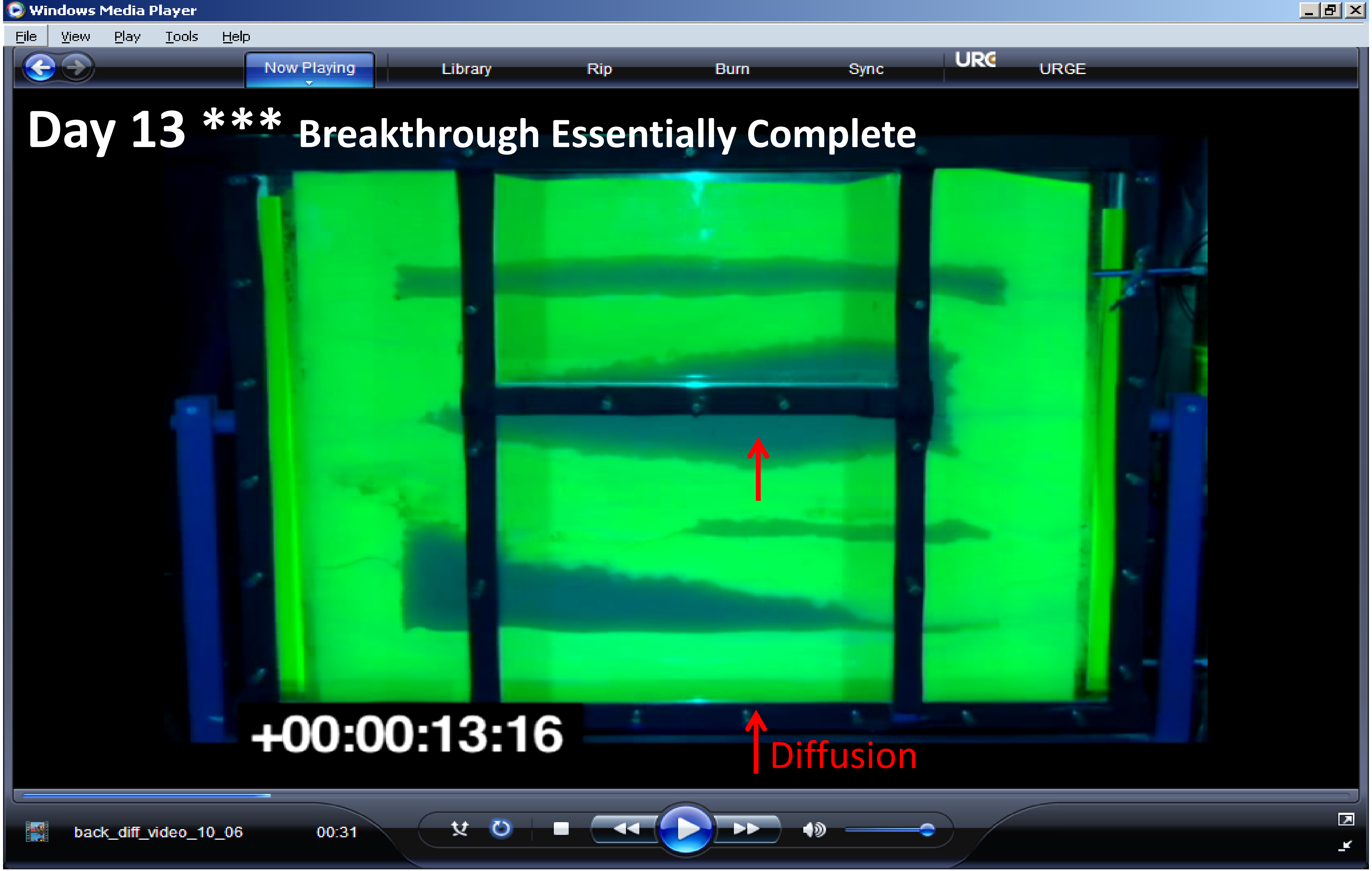


Day 5 *** Initial Breakthrough (Dispersion)



Diffusion

Day 13 *** Breakthrough Essentially Complete



Diffusion

Day 24 *** Flushing After 1 Day (Sweeping High K Zones)

Day 26 *** Flushing Day 3 (Sweeping High K Zones)

Diffusion and Back-Diffusion

Day 43 *** Tailing

Diffusion and Back-Diffusion

Challenges for Standard Advection-Dispersion Equation (ADE)

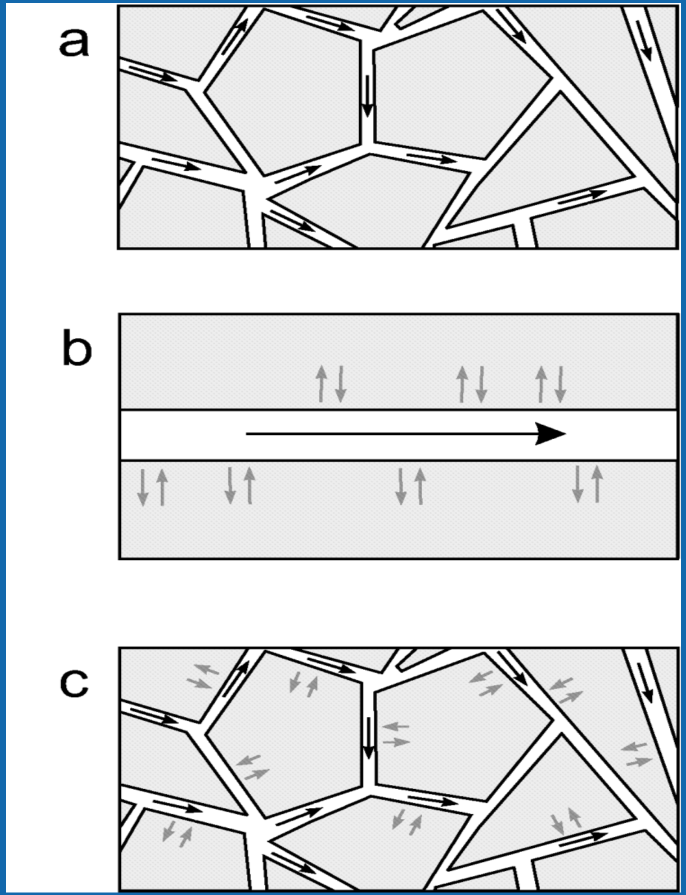
- Overestimates upgradient dispersion
- Difficulty matching tracer test data with one set of consistent parameters (dispersivity increases with scale)
- Uses an average over a representative elementary volume (REV) and thus loses ability to simulate pore scale heterogeneity
- ADE may not match observed tailing from heterogeneous advection and back-diffusion processes and can underestimate cleanup timeframe
- Alternate model and governing equations needed (Konikow, 2011)

Extended ADE Model for Highly Heterogeneous Aquifers

$$\frac{\partial C(x,t)}{\partial t} = \int_0^t M(t-t')e^{-k(t-t')}\left(-v\frac{\partial C(x,t')}{\partial x} + D\frac{\partial^2 C(x,t')}{\partial x^2}\right)dt' - kC(x,t)$$

Notes:

1. M(t) is a memory function that includes mobile and immobile heterogeneity using probability density functions
2. Can include different degradation rates in mobile and immobile zones
3. Reduces to standard ADE for homogenous media



Berkowitz et al., (2008)

Heterogenous advection: mobile zone power law travel time pdf: $\psi(t)$

$\psi(t) \sim 1/t^{1+\beta}$ $0<\beta<2$ (wide velocity spectrum):

$$\beta = 2.07(\sigma^2_{\ln K})^{-0.143}$$

(Burnell et al. 2018)

Matrix diffusion: immobile zone back-diffusion time pdf : $p_{im}(t)$

$p_f(t) \sim 1/t^{1+\delta}$ $0<\delta<2$ (broad distribution of mass transfer rates

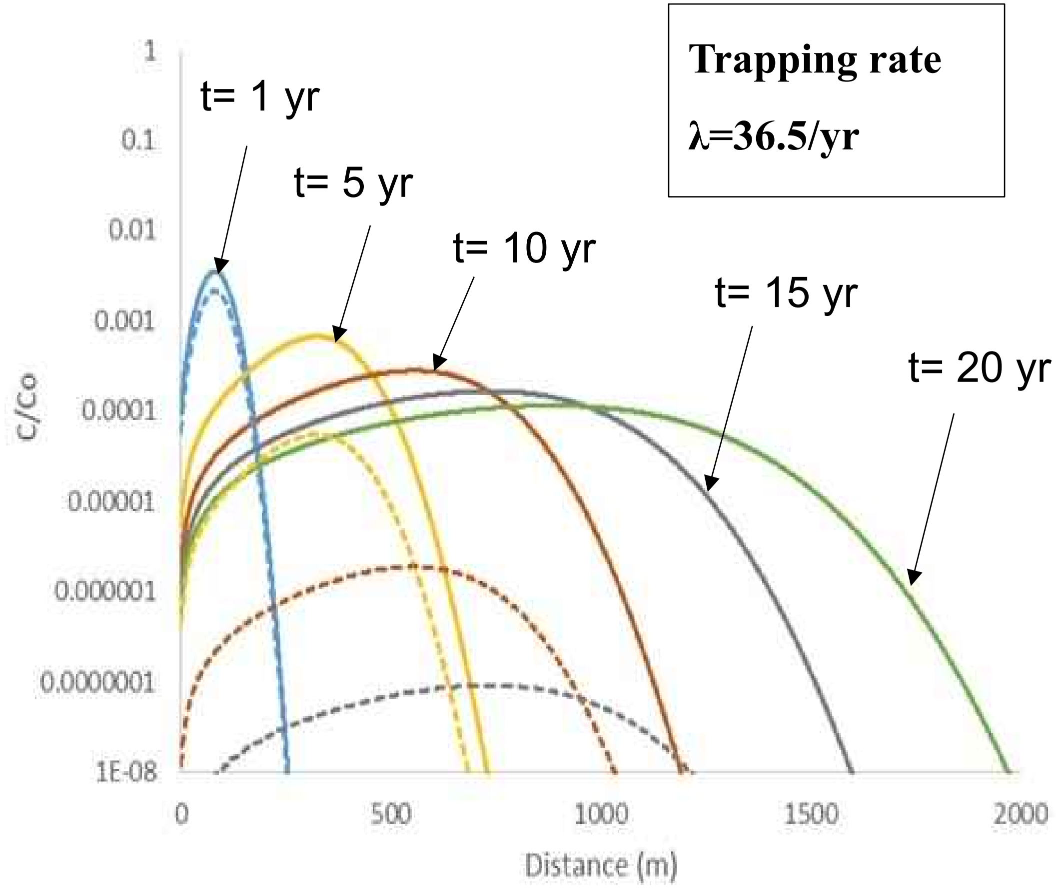
$$\delta = 0.5 \text{ (diffusive scaling)}$$

Heterogeneous advection and matrix diffusion

Compound Poisson: (Margolin et al., 2003; Benson and Meerschaert, 2009)

Semi-analytical HET-TRANS Model for Pulse Source: Heterogeneous Advection (β = 1.5 or ln K variance =9), Matrix Diffusion (δ=0.5), and First-Order Reaction

Plume spatial profile



Trapping rate

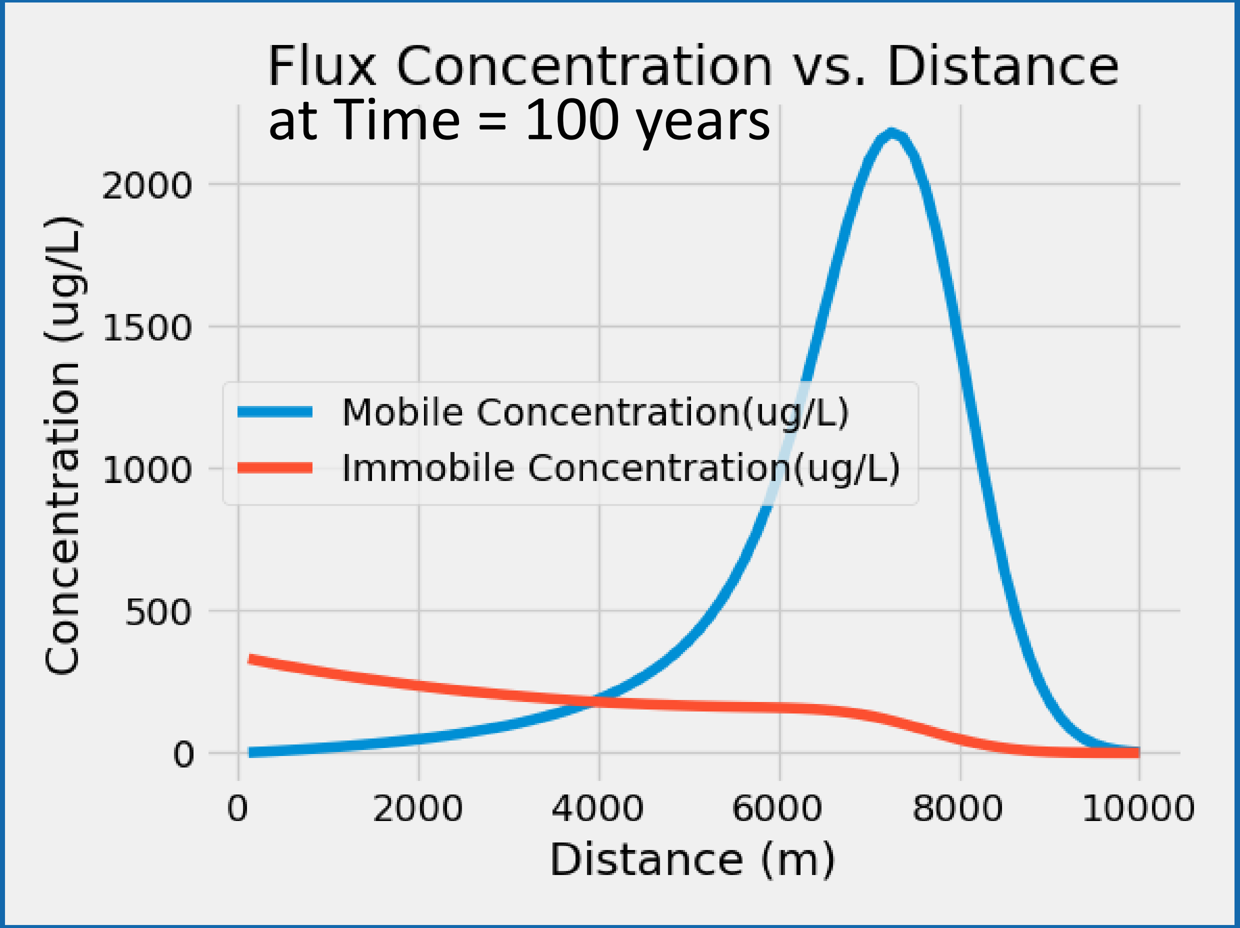
λ=36.5/yr

"Tear drop" shape and slowing down from low back-diffusion rates

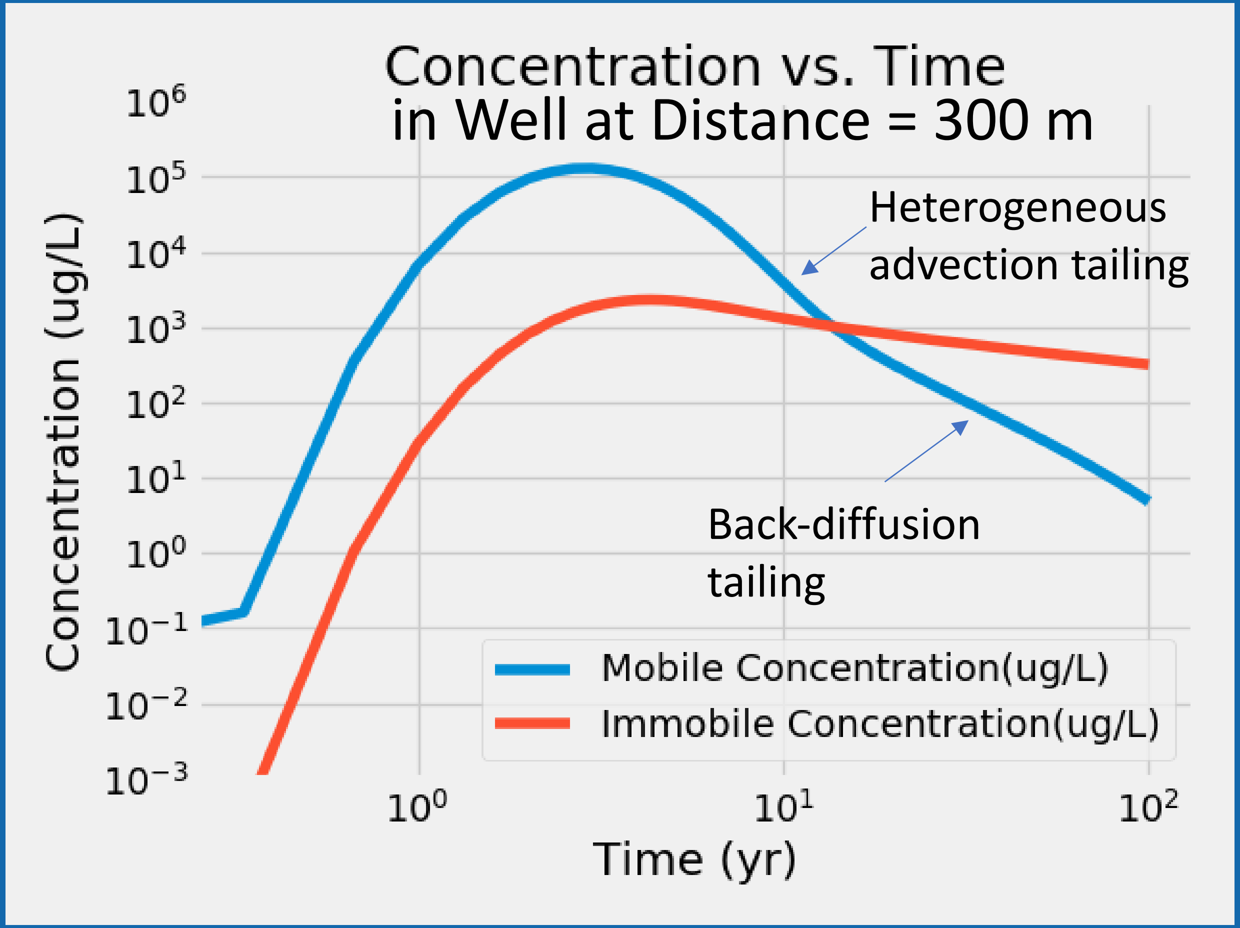
Dashed line indicates reaction

Burnell et al. (2017)

Where and When Will Back-Diffusion Occur? Use of HET-TRANS Model

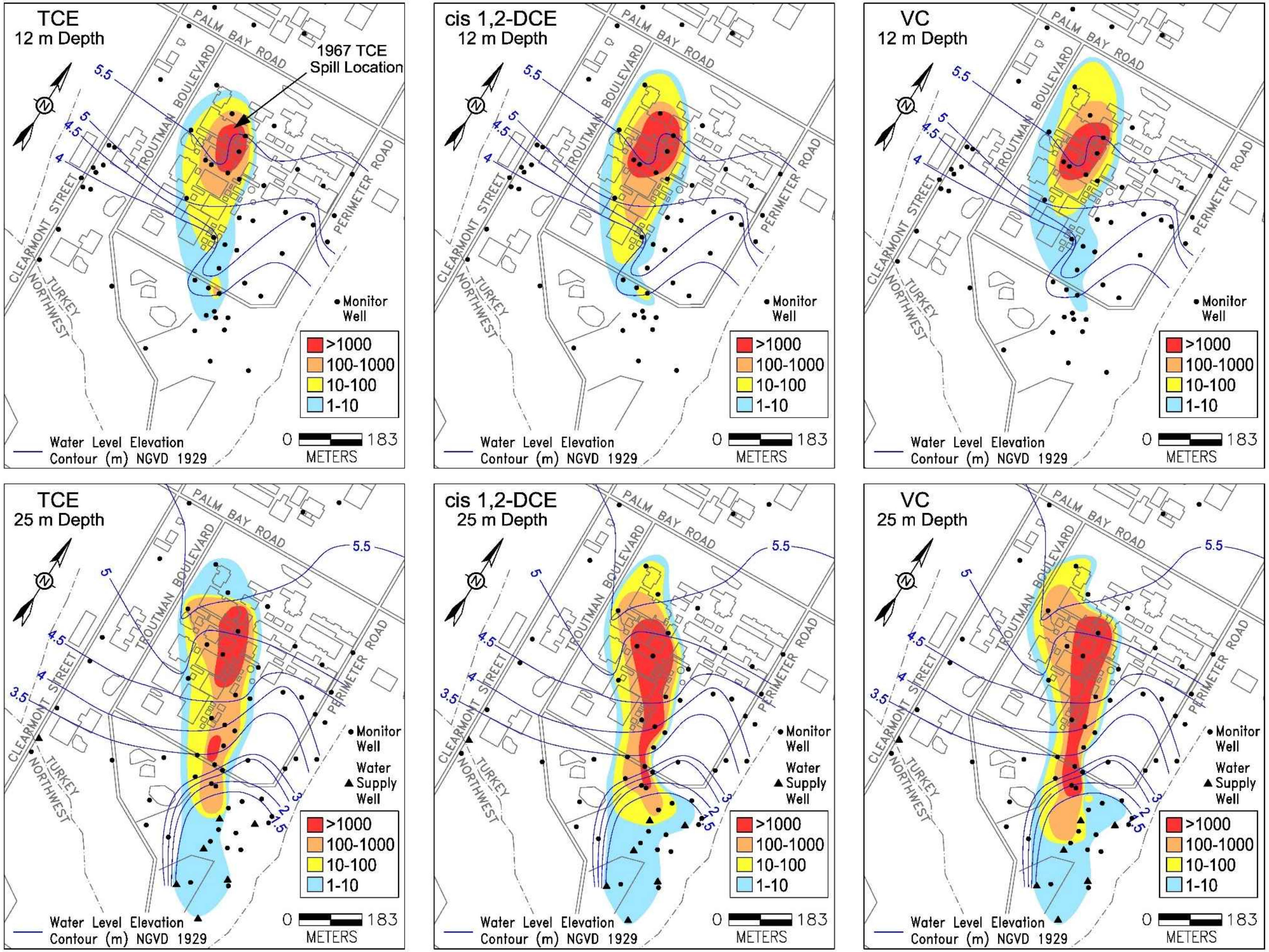


Back-diffusion dominates within distance of 4000 m from source. Plume "charging" in immobile zones at distance > 4000 m from source.

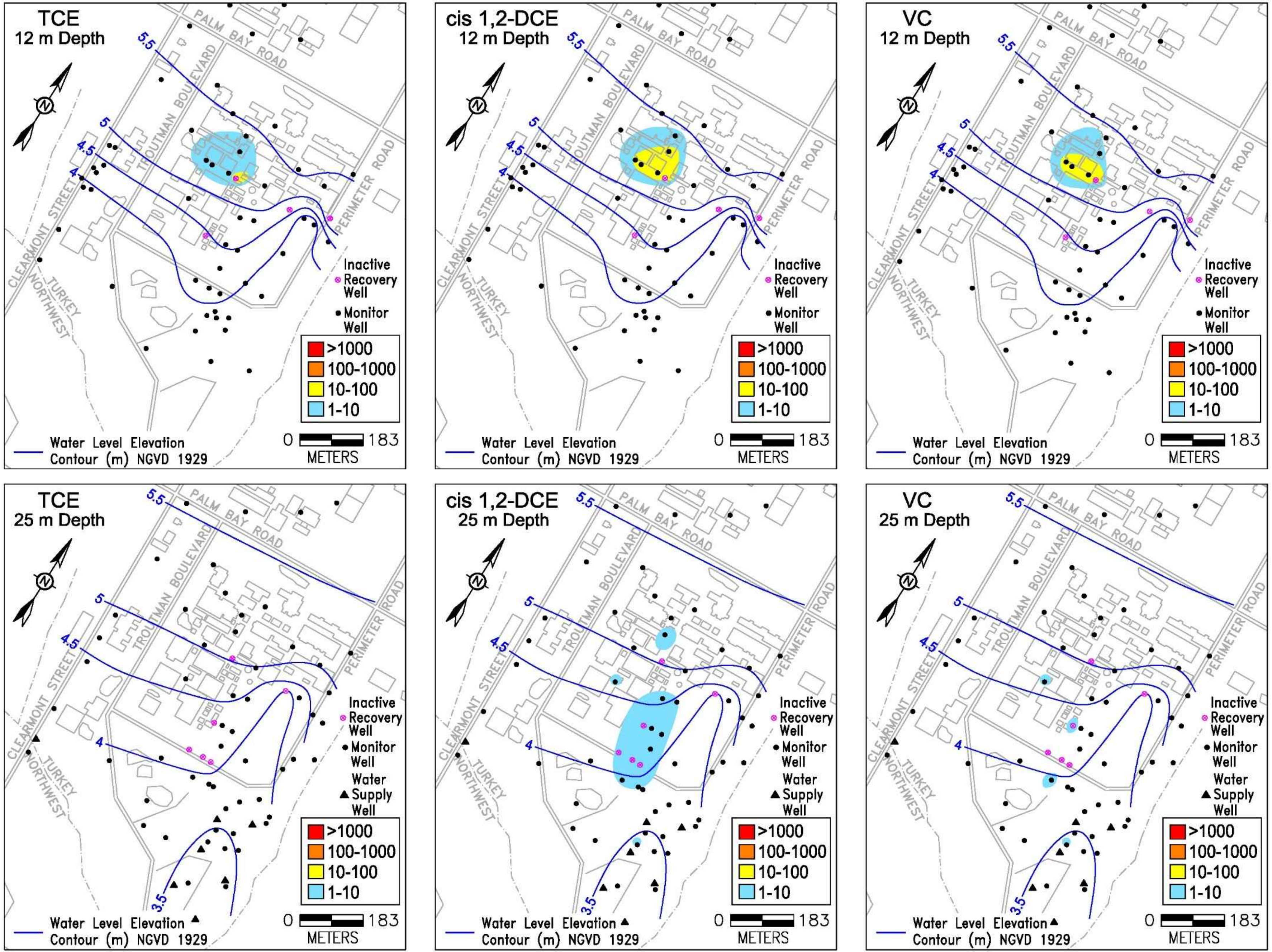


Back-diffusion dominates after 15 years. Peak time, periods of heterogeneous advection, back-diffusion, and subsequent exponential decline from reaction seen in mobile zone plot.

Case Study2: TCE, DCE, and VC Plumes in 1984 at CERCLA Site, FL



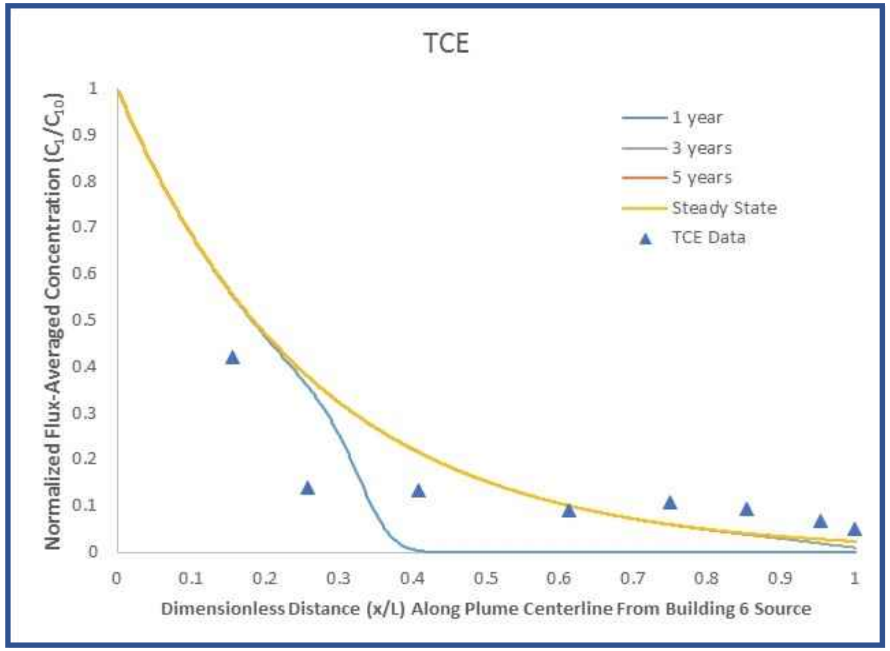
TCE, DCE, and VC Plumes in 2022 at CERCLA Site, FL

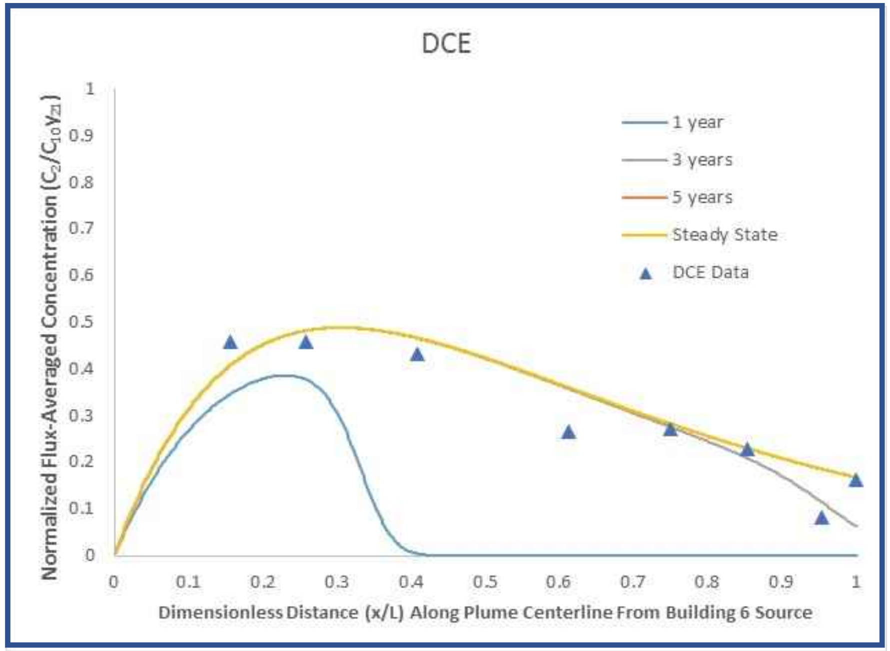


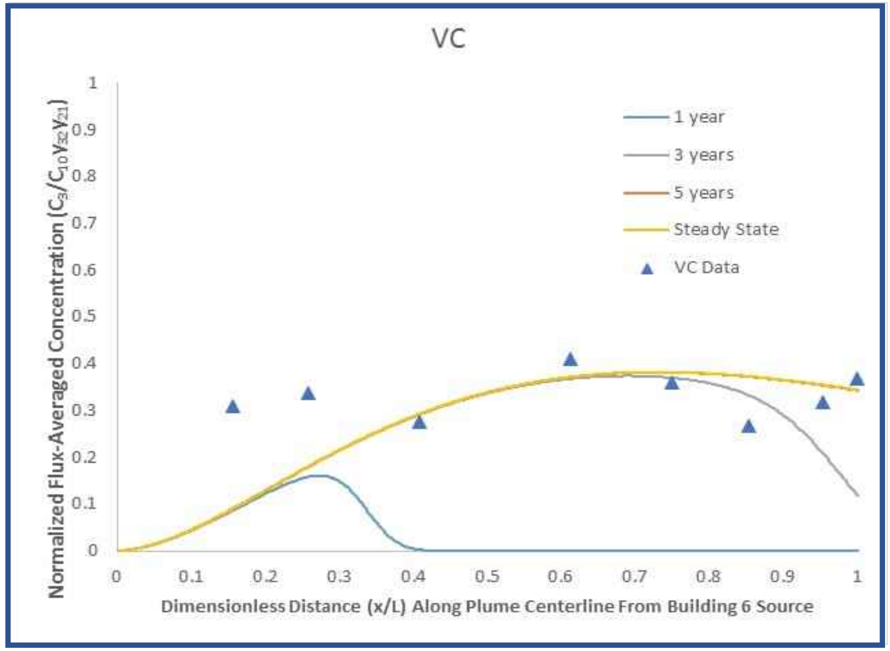
HET-TRANS Model Parameters, CERCLA Site, FL

Model Parameter	Value
Source Concentration (C_{10})	10,000 μg/L (TCE)
Source Duration (t_d)	18 yr
Average Linear Groundwater Velocity (v)	180 m/yr
Longitudinal Dispersivity ($a_L = \ell(\sigma^2_{lnK})^{1.36}$): related to K variance $\sigma^2_{\ln K}$ (Hansen et al. 2018) using estimated K correlation length ℓ	26 m
Heterogeneous Advection Time pdf: $\psi(t) \cong \frac{\tau^{\beta}}{t^{1+\beta}}$ Characteristic advection time $\tau = \frac{\ell}{v}$ over K correlation length $\ell = 0.05\ m$ Hydraulic conductivity data: Geometric mean $= 4.6\frac{m}{day}$ and $\sigma^2_{\ln K} = 3.4$	**Heterogeneity Parameters** $\ell = 0.05$ m $\boldsymbol{\sigma^2_{\ln K} = 3.4}$
Power Law Exponent (β) for degree of heterogeneity using advection travel pdf: $\psi(t) \cong \frac{\tau^{\beta}}{t^{1+\beta}}$ (Edery et al. 2014; Burnell et al. 2018)	$\beta = 2.07(\sigma^2_{\ln K})^{-0.143}$ $=1.74$
Back-diffusion Time pdf: $p_{im}(t) \cong \frac{\tau_{im}^{\delta}}{t^{1+\delta}}$ Diffusive Trapping rate $\lambda = \frac{N}{\tau}$ where N=average # of immobile zones over K correlation length ℓ	**Immobile zone volume fraction = 1.5 %** $\lambda = 0.08\ yr^{-1}$
Power Law Exponent (δ) for degree of immobile zone heterogeneity	$\delta = 0.5$
Characteristic diffusion time ($\tau_{im} \approx b^2/D^*$) where b is clay interbed half-thickness and D* is the molecular diffusion coefficient	Immobile bed average thickness: b = 0.4 m
Retardation Factors (R_1,R_2, and R_3)	1.0
Parent Rate Constant (k_1) $k \sim \frac{N'}{\tau}$ (N' is # of microcolonies over ℓ)	$1.2\ yr^{-1}$
Daughter Rate Constant (k_2)	$0.90\ yr^{-1}$
Granddaughter Rate Constant (k_3)	$0.60\ yr^{-1}$

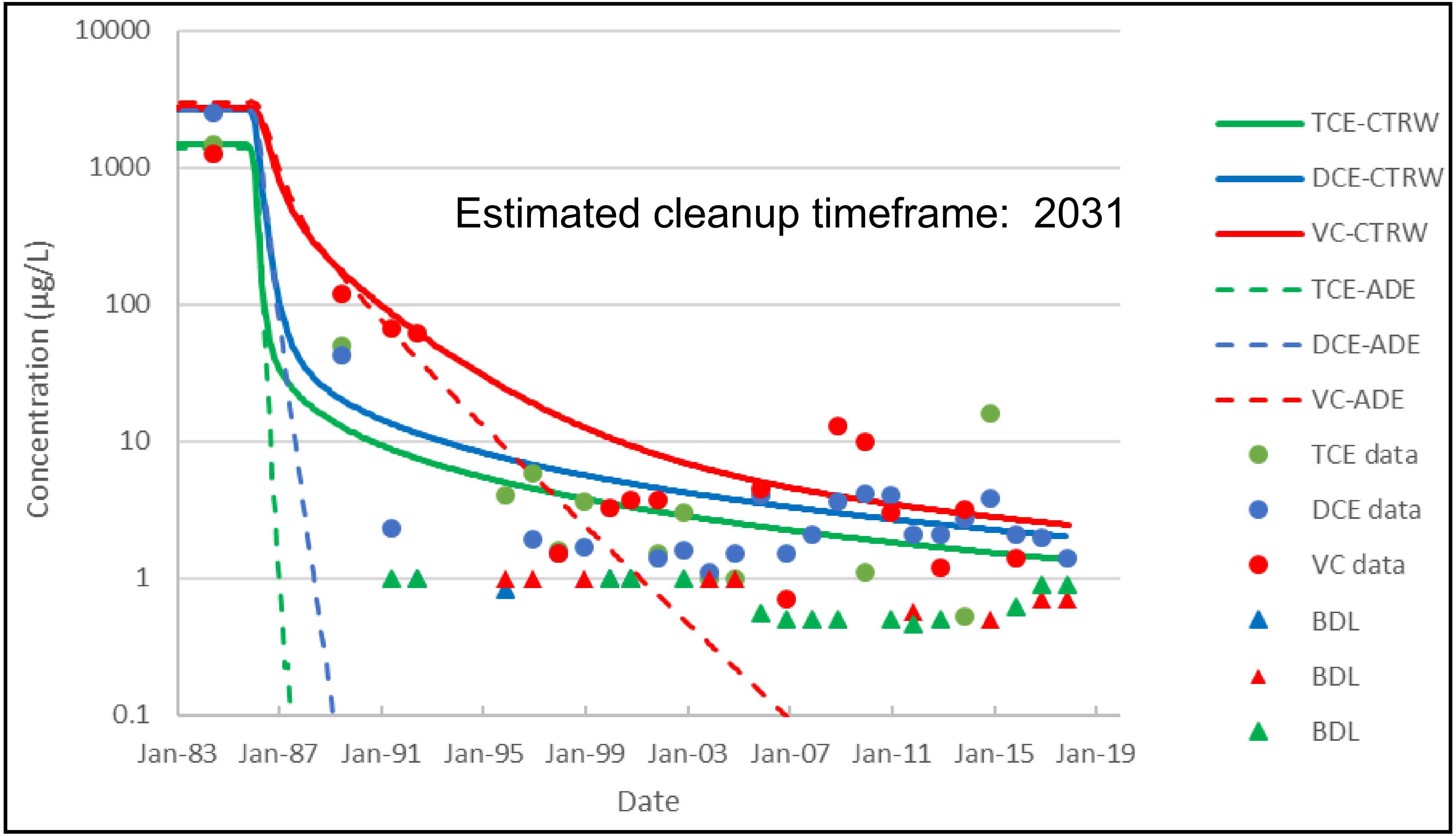
1984 Steady-State Multi-Species Plume Calibration







Match of Transient Model to TCE, cis-1,2-DCE, and VC Data at GS-35D (300 ft Downgradient From Source)



Estimated cleanup timeframe: 2031

IV. Summary and Conclusions

- Subsurface is highly heterogeneous (Log K variance > 1) from pore to field scale. Pore-scale processes strongly affect plumes but not well represented in field-scale models

- Strong heterogeneity and back-diffusion cause tailing in monitor wells with non-Fickian spreading rates not well captured by ADE resulting in underestimated cleanup times

- **Need to integrate data from HRSC tools**: Refine heterogeneity input parameters (K variance and back-diffusion power law exponent): 1) high resolution K and tracer test breakthrough curve data; 2) x-ray data on pore-scale heterogeneity; 3) diffusion studies; and 4) estimate of degradation rates in mobile and immobile zones

- Better models are available! Extended-ADE (HET-TRANS) model: 1) heterogeneous advection and back-diffusion; 2) parsimonious with success in experiments; 3) natural extension of ADE upscaling pore-scale; 4) analytical solutions (Burnell et al. 2017; 2018) for MNA; 5) rapid computational time vs. Monte Carlo approach

Acknowledgements

- Brian Berkowitz, Weizmann Institute of Science
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- Scott Hansen, Ben Gurion University
- Jeffrey Yang, USEPA

Related Work

1) Burnell, D. K., 2023. Documentation for HET-TRANS: Extended ADE model for advection and back-diffusion in highly heterogeneous media.

2) Burnell, Xu, Cooper and Benegar, 2022. Application of quantum computing for flow and transport modeling, MODFLOW 2022 Conference.

3) Burnell, Xu, Hansen, Sims, and Faust, 2018. Practical Modeling Framework for Non-Fickian Transport and Multi-Species Sequential First-Order Reaction, *Groundwater*, 56,102-119.

4) Burnell, D.K., J. Xu, and S. Hansen et al, 2017, Transient Modeling of Non-Fickian Transport and First-Order Reaction, *Adv. Wat. Res.*, 327-345.

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