TETRA TECH

Effects on Cleanup Timeframe from Heterogeneity, Back-Diffusion, and Abiotic\Biotic Degradation

Daniel K. Burnell, Ph.D.
Tetra Tech

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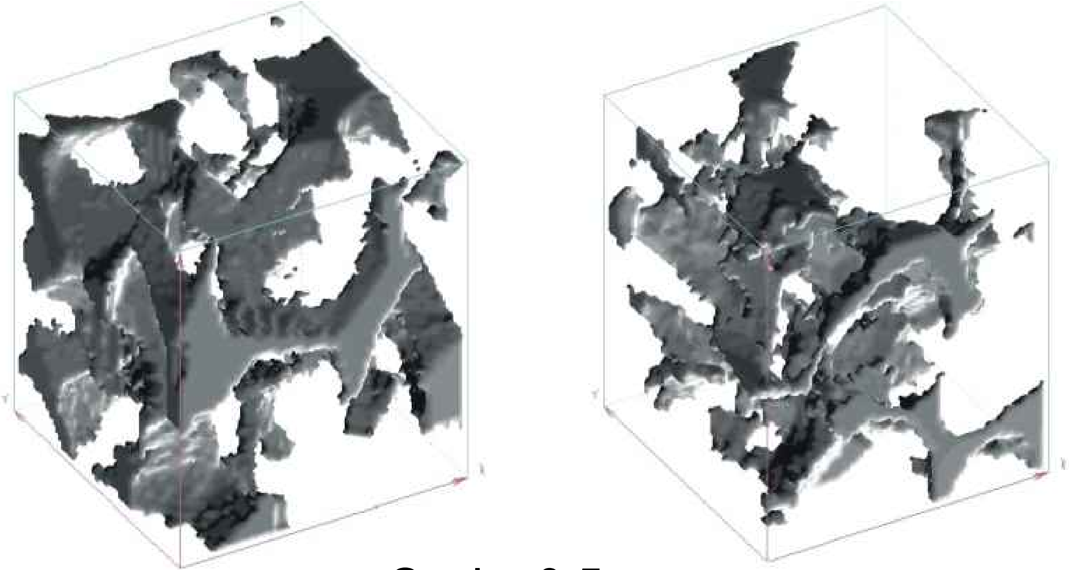
Non-Fickian ("Anomalous") Plumes are the Norm

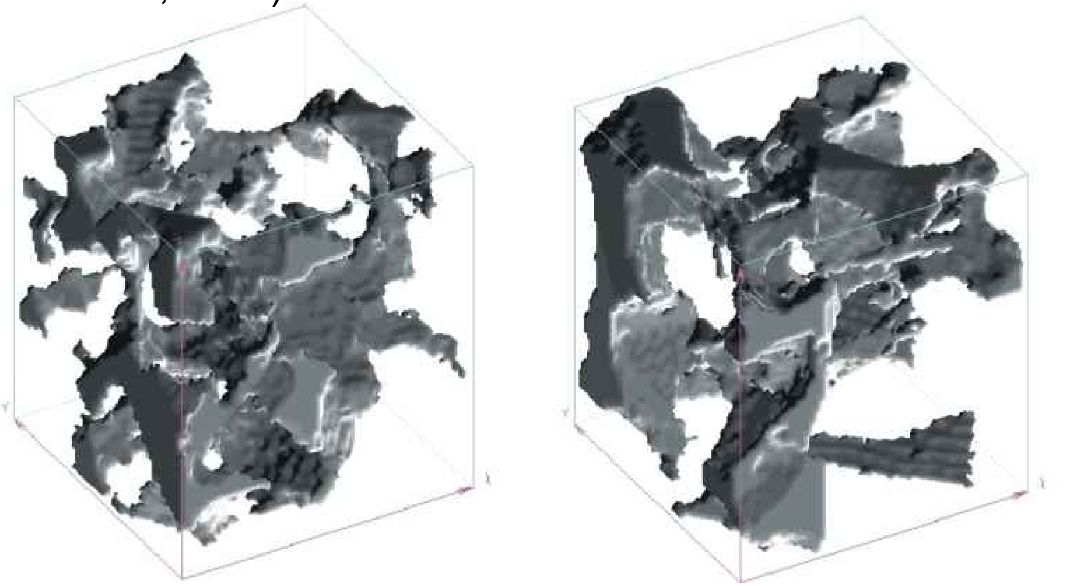
- Large dilute plumes with asymmetric spatial distribution and nonuniform spreading rates not proportional with time (non-Fickian)
- Long COC concentration vs time tails in wells and/or rebound, resulting in long cleanup times!
- Causes: 1) multi-scale (pore to field) heterogeneity (ln K variance >>1) 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
- Extended ADE (HET-TRANS) 3-D 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
- Apply HET-TRANS model to examine how heterogeneity and degradation affect cleanup timeframe

I. Multi-Scale Heterogeneity: Pore to Field Scale

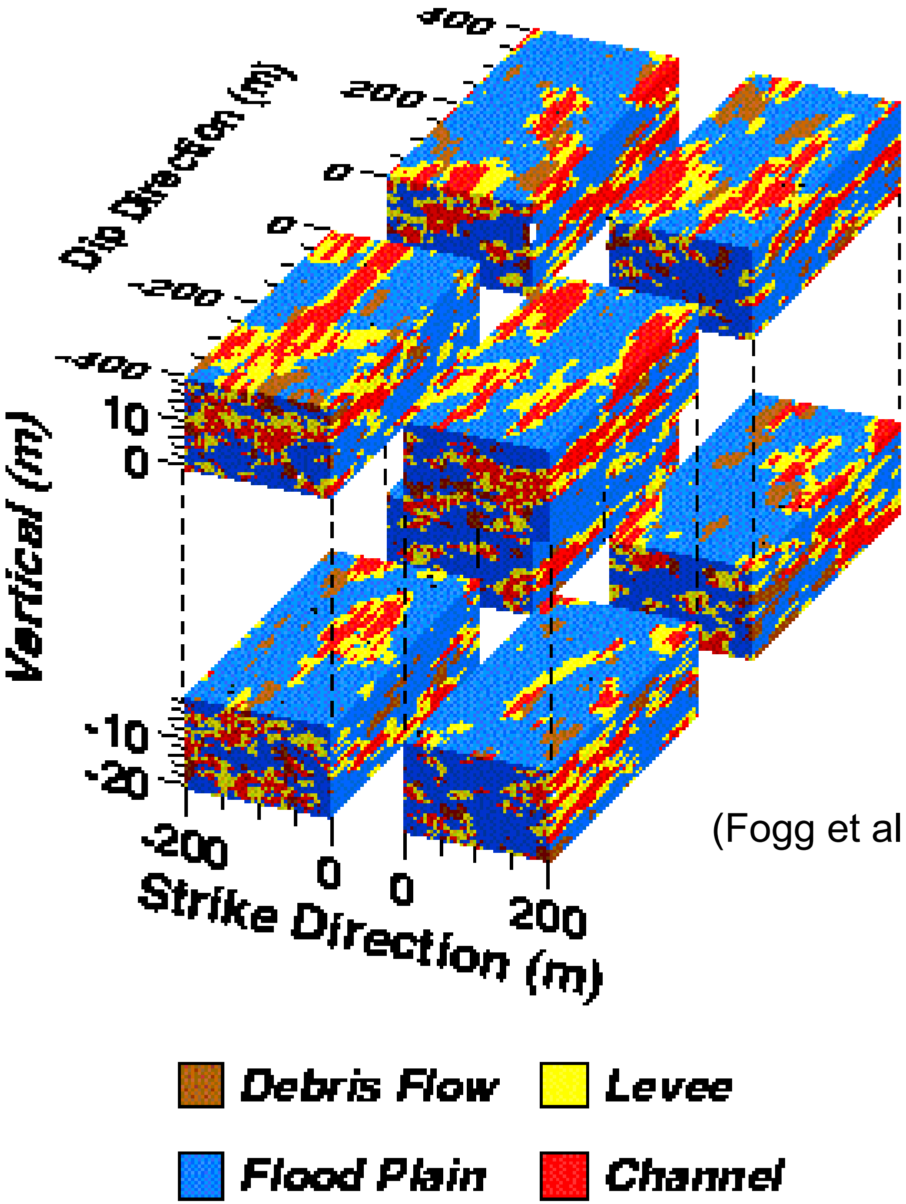
X-ray images of pore space in sandstone



(Auzeraris et al., 1996) Scale: 0.5 mm

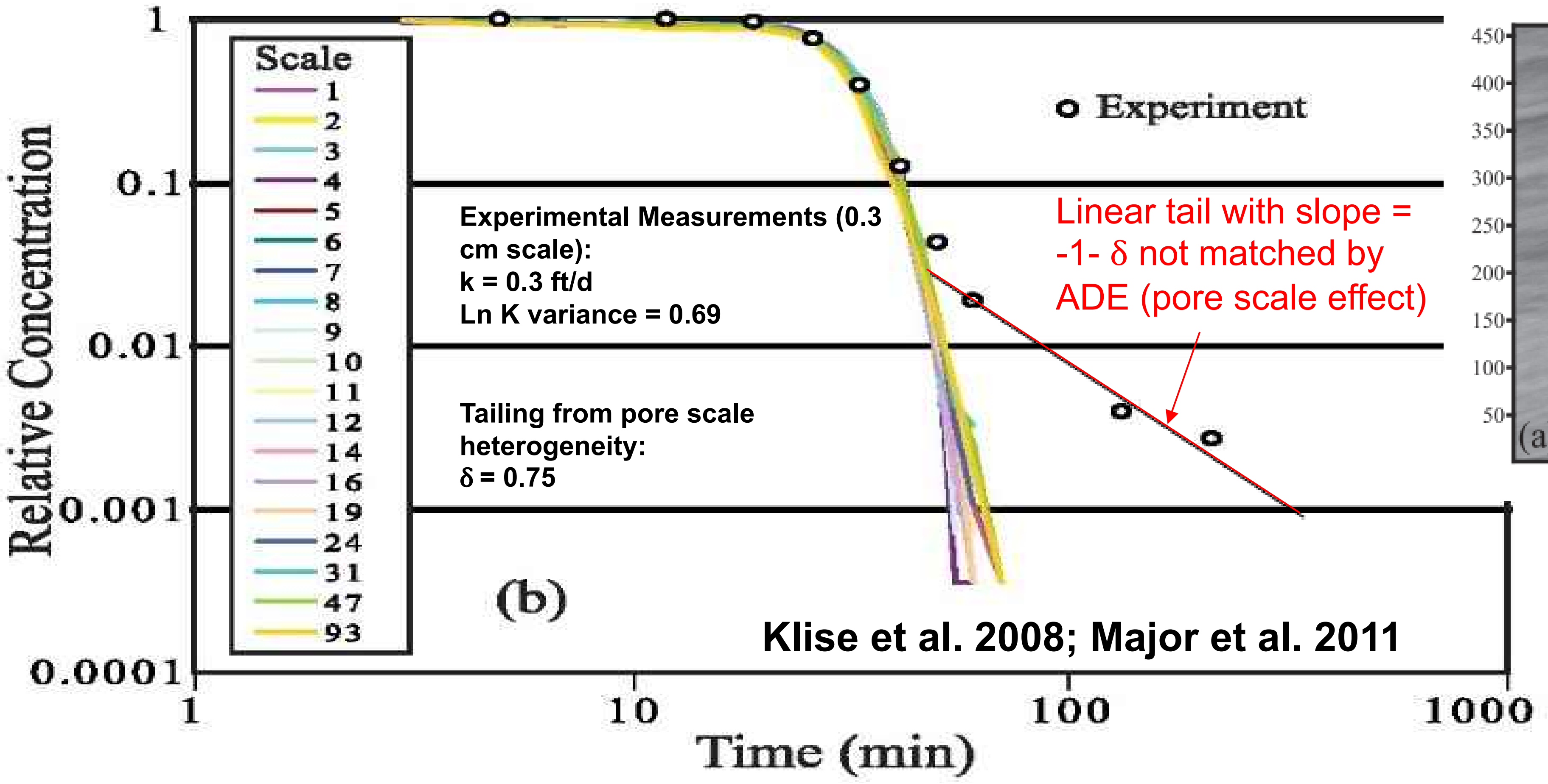


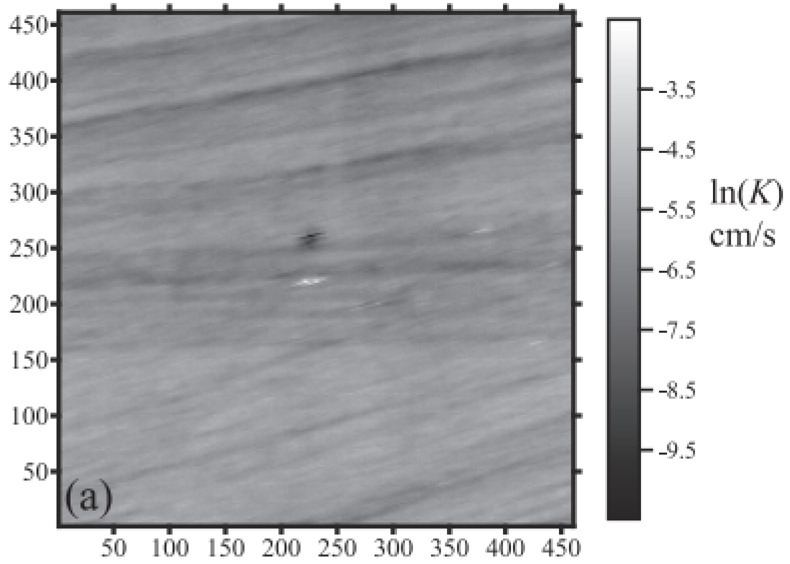
Fluvial depositional environment



(Fogg et al.,1998)

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





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

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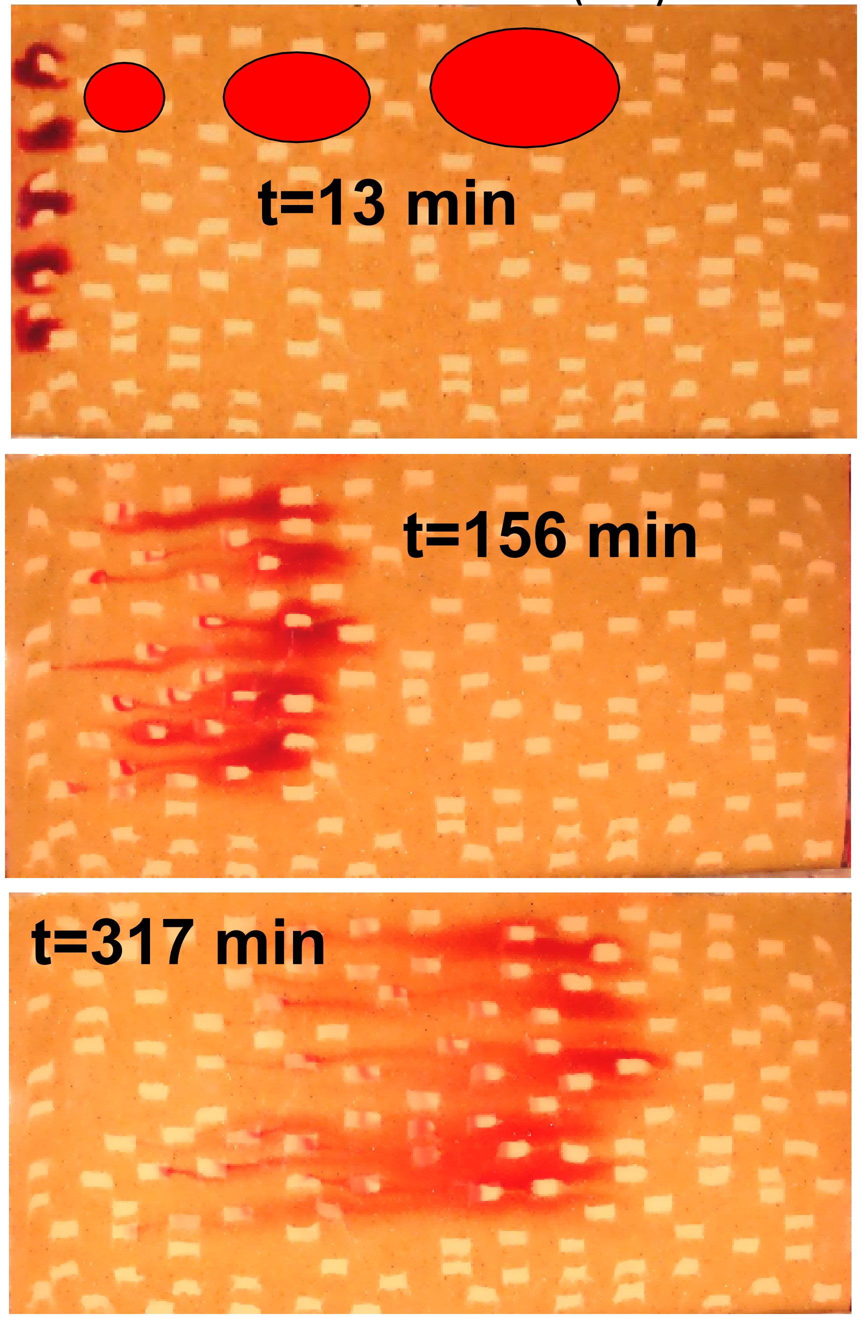
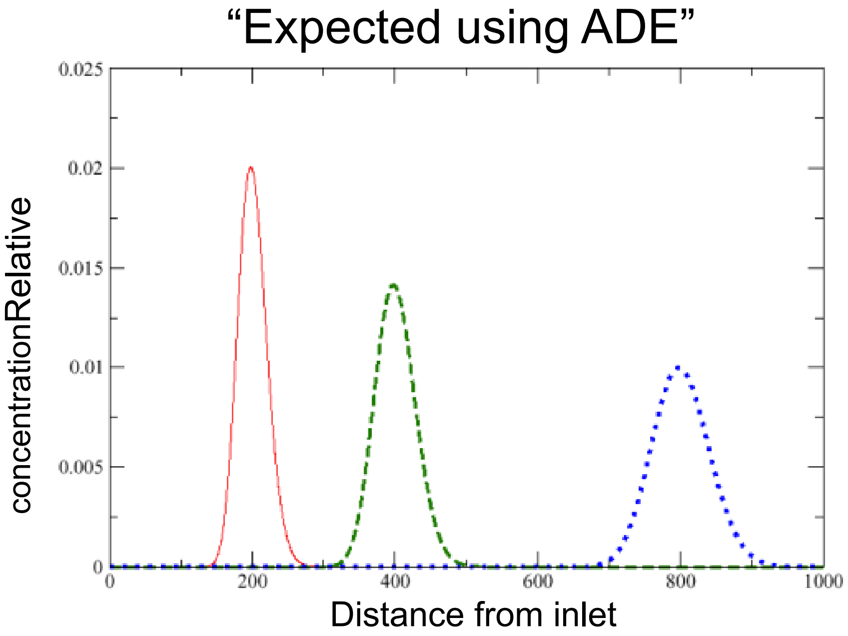
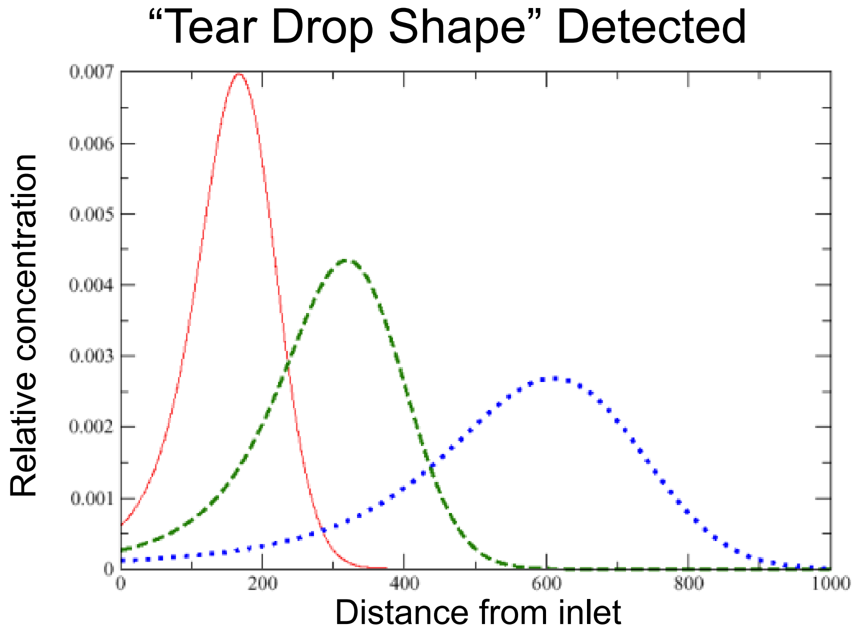
a) Heterogeneous Advection: Meter Scale Uniform Sand with Random Silt Lenses

(Levy and Berkowitz, 2003)

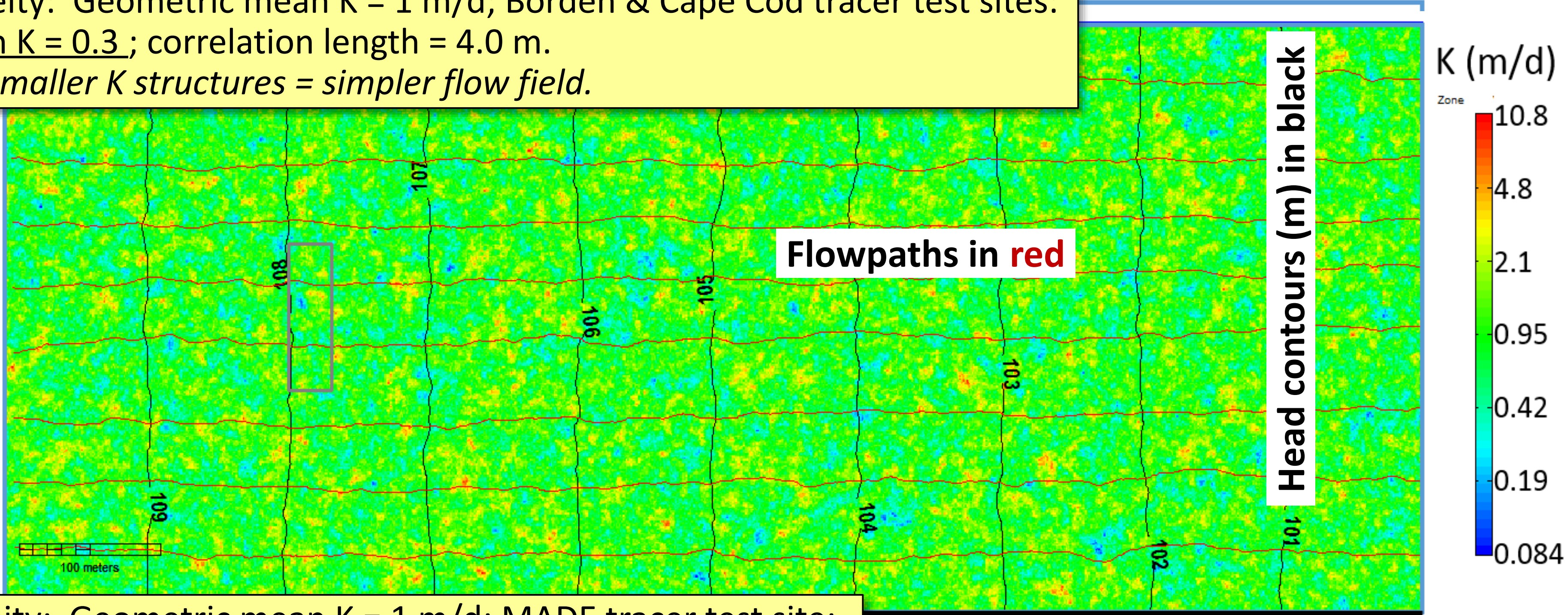
v=35 mL/min



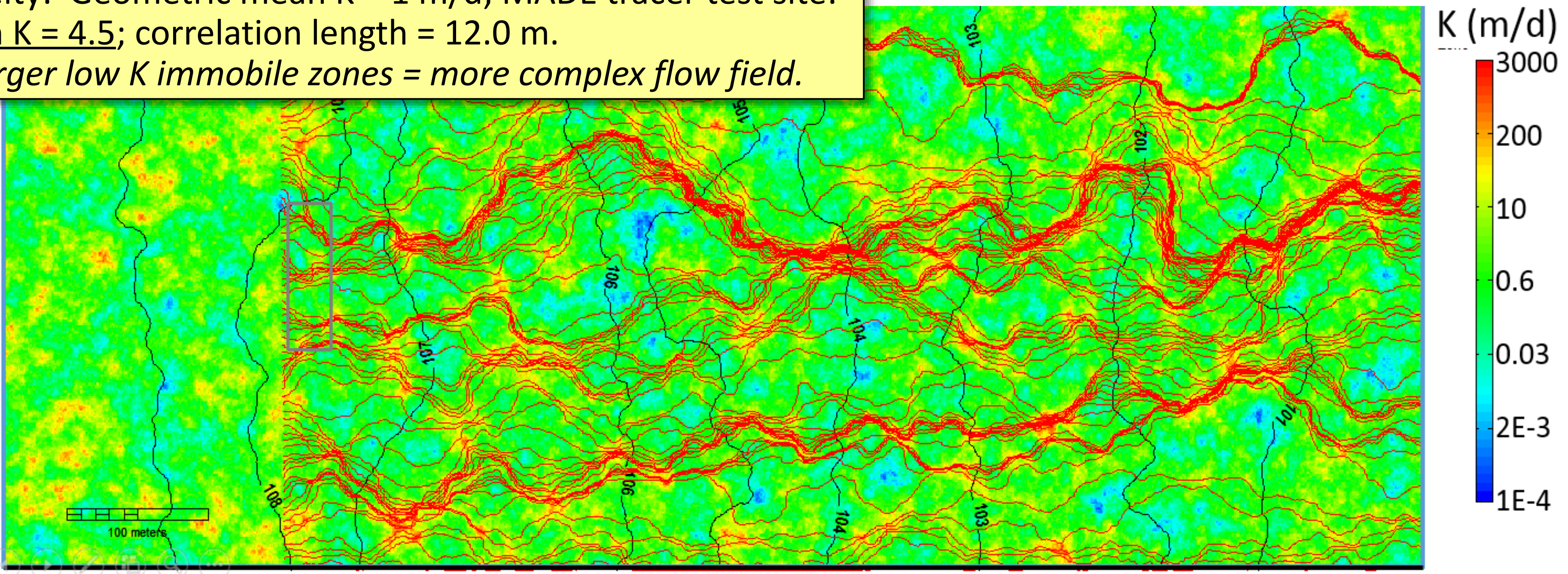




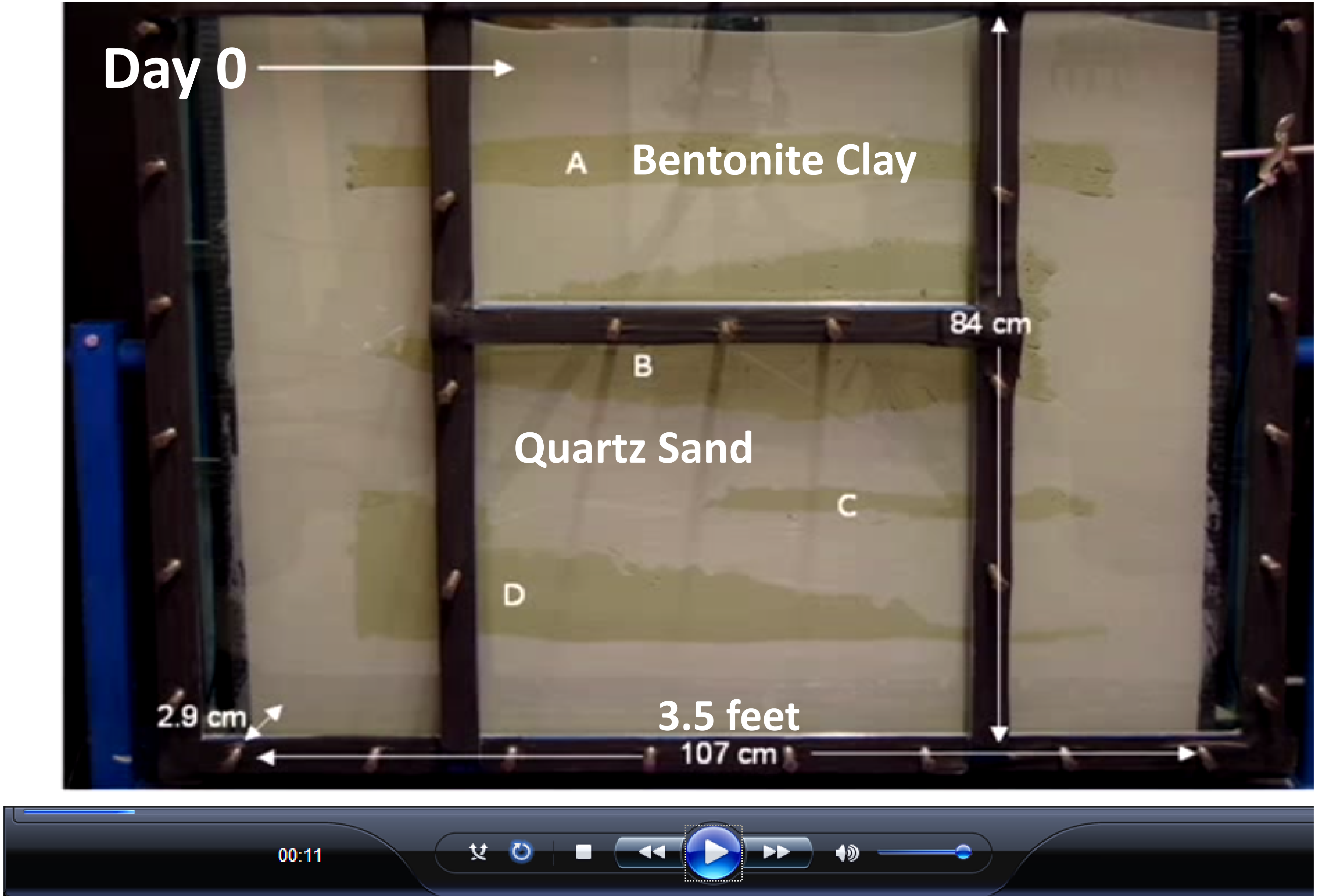
K field heterogeneity: Geometric mean K = 1 m/d; Borden & Cape Cod tracer test sites:
Variance (σ^2) of ln K = 0.3 ; correlation length = 4.0 m.
Smaller K range, smaller K structures = simpler flow field.



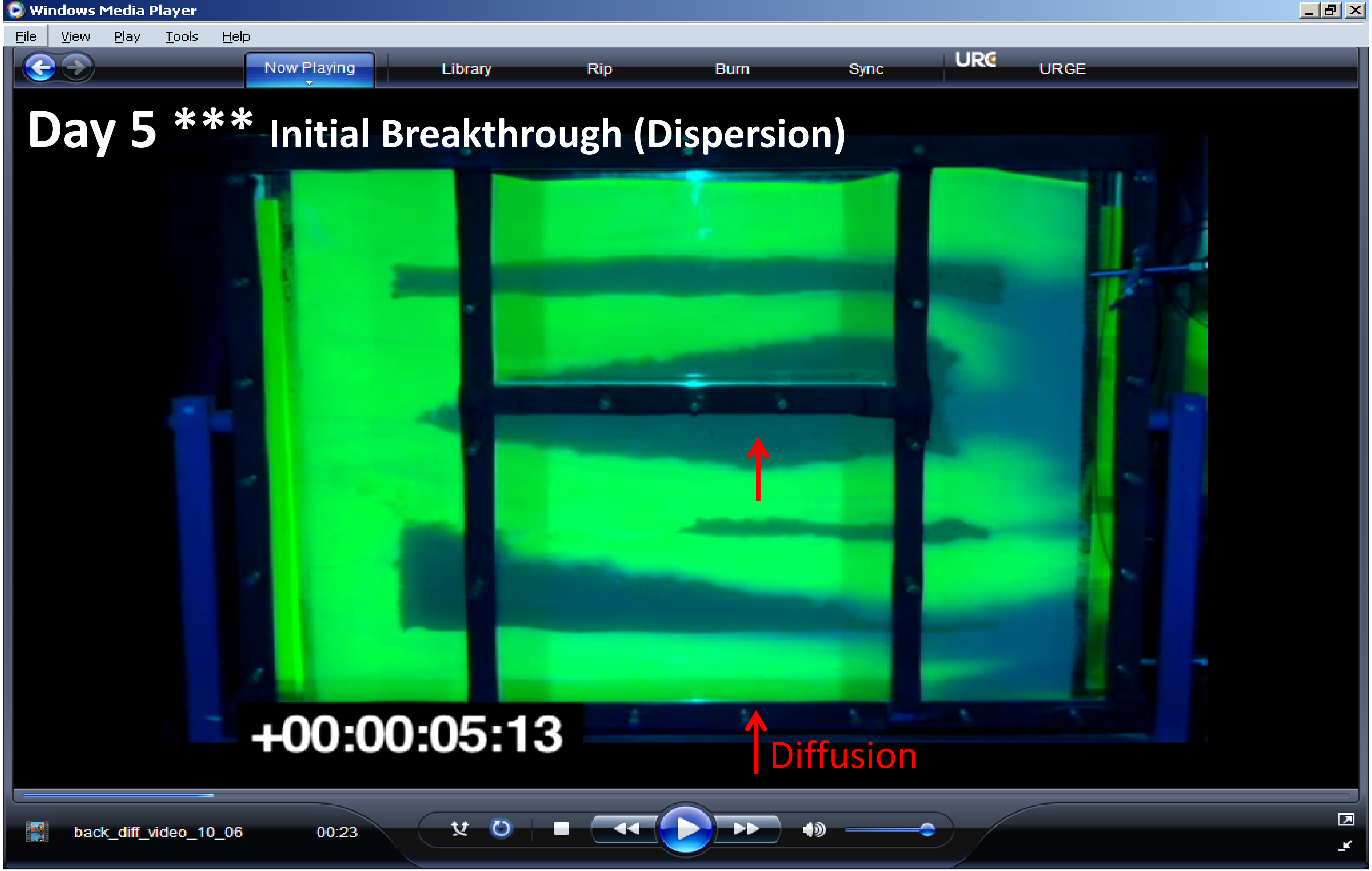
K field heterogeneity: Geometric mean K = 1 m/d; MADE tracer test site:
Variance (σ^2) of ln K = 4.5; correlation length = 12.0 m.
Larger K range, larger low K immobile zones = more complex flow field.



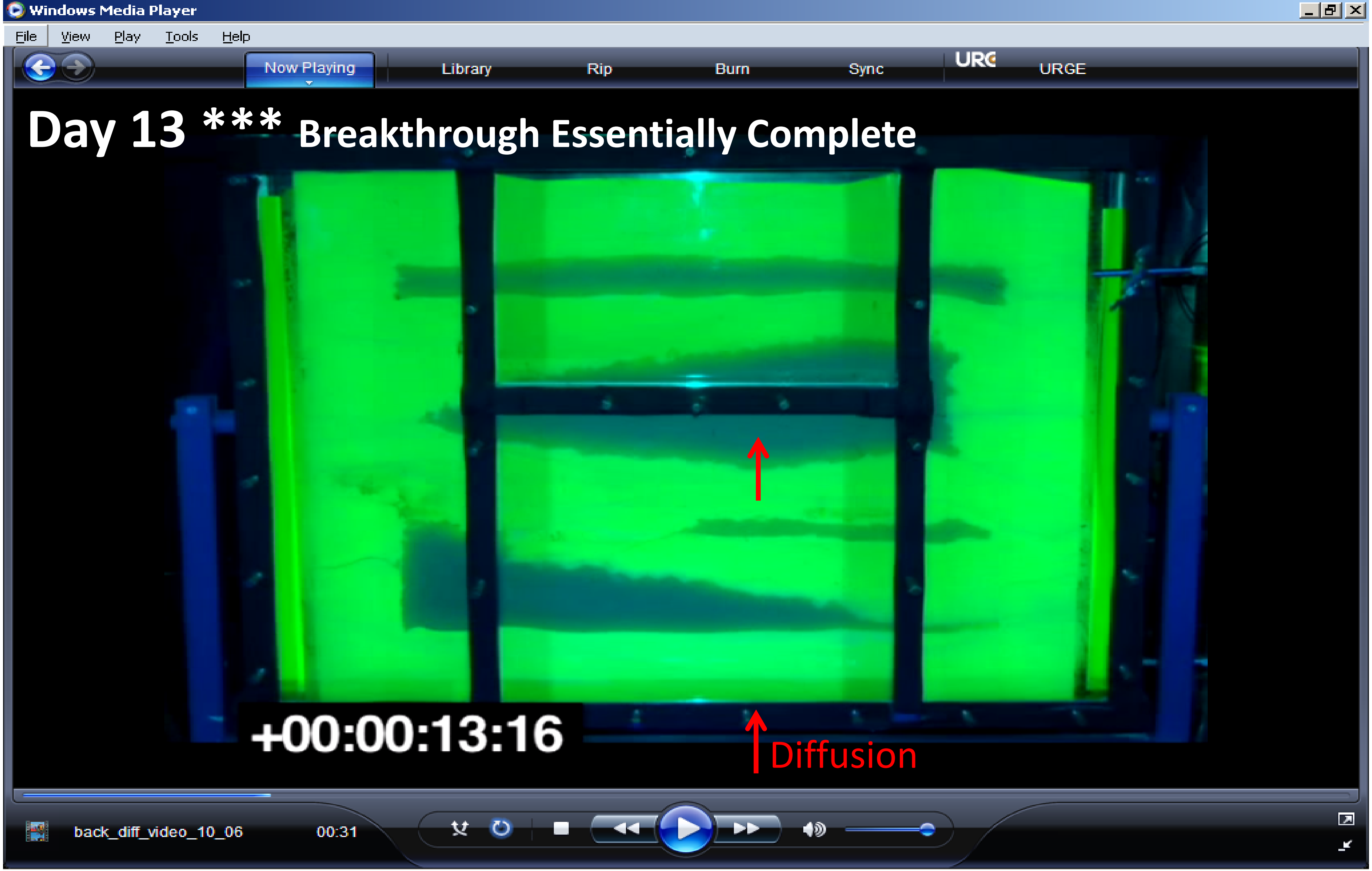
b) Diffusive Mass Transfer and Back Diffusion (Doner and Sale, 2008)



Day 5 *** Initial Breakthrough (Dispersion)



Day 13 *** Breakthrough Essentially Complete




Windows Media Player
File
View
Play
Tools
Help
Now Playing
Library
Rip
Burn
Sync
URGE
Day 24 *** Flushing After 1 Day (Sweeping High K Zones)
+00:00:24:21
Diffusion
back_diff_video_10_06
00:42


Windows Media Player
File View Play Tools Help
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Library
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Sync
URGE
Day 26 *** Flushing Day 3 (Sweeping High K Zones)
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Diffusion and Back-Diffusion
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01:01
Adobe Acrobat Standard - [SethPitkinTriad.pdf]

Extended ADE (HET-TRANS) Model for Highly Heterogeneous Aquifers

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

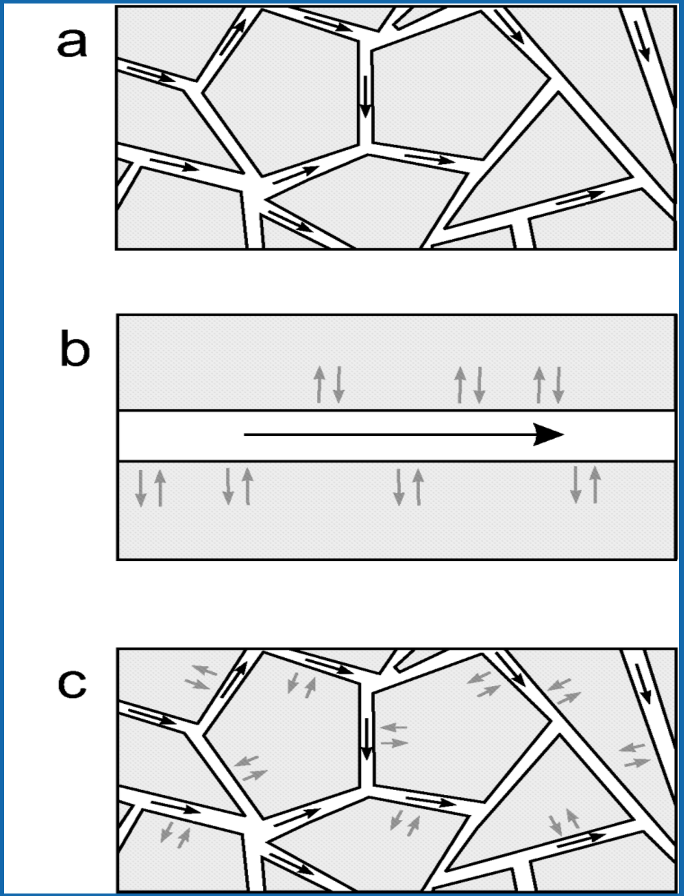
Burnell et al. (2017; 2018)

Notes:

1. M(t) is a memory function for mobile and immobile heterogeneity using probability density functions

2. Includes different degradation rates in mobile and immobile zones

3. Reduces to standard ADE for homogenous media



Berkowitz et al., (2008)

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

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

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

(Burnell et al. 2018)

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

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

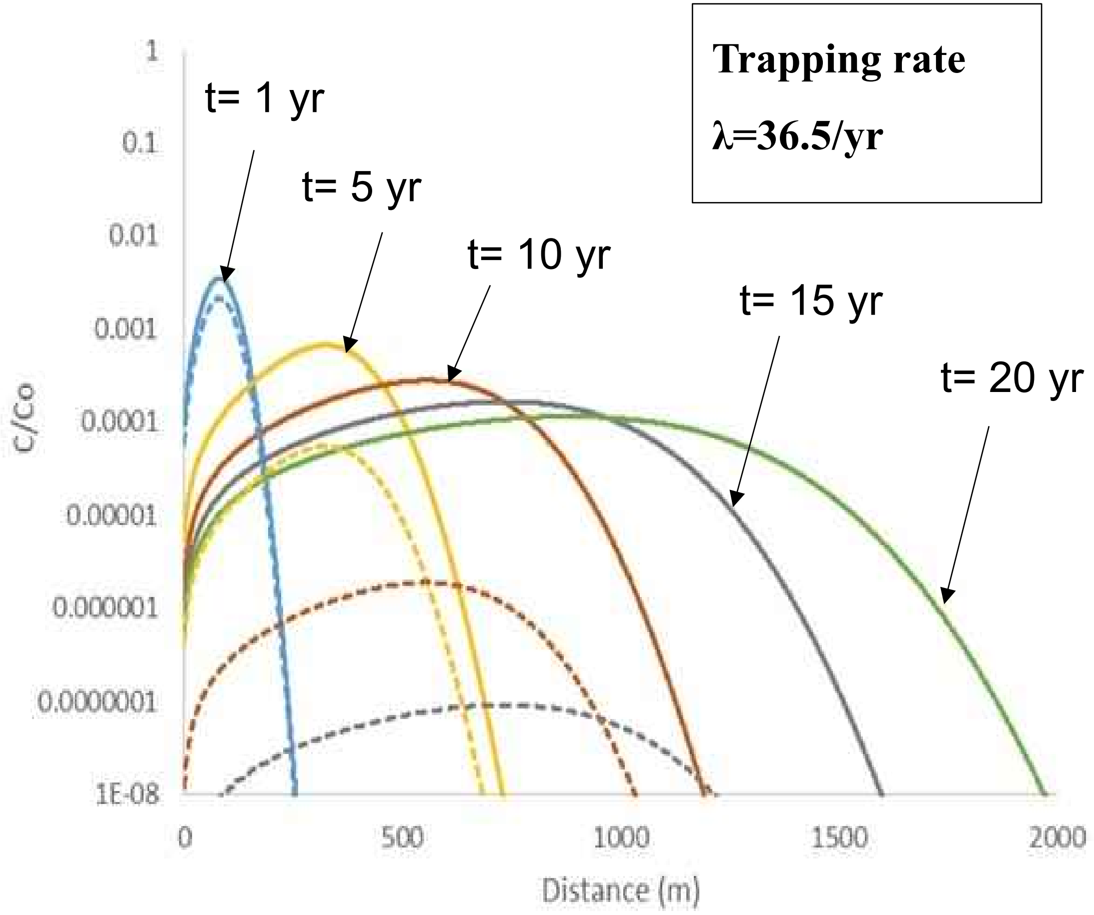
$$\delta = 0.5 \text{ (diffusive scaling)}$$

<u>Heterogeneous advection and matrix diffusion</u>

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

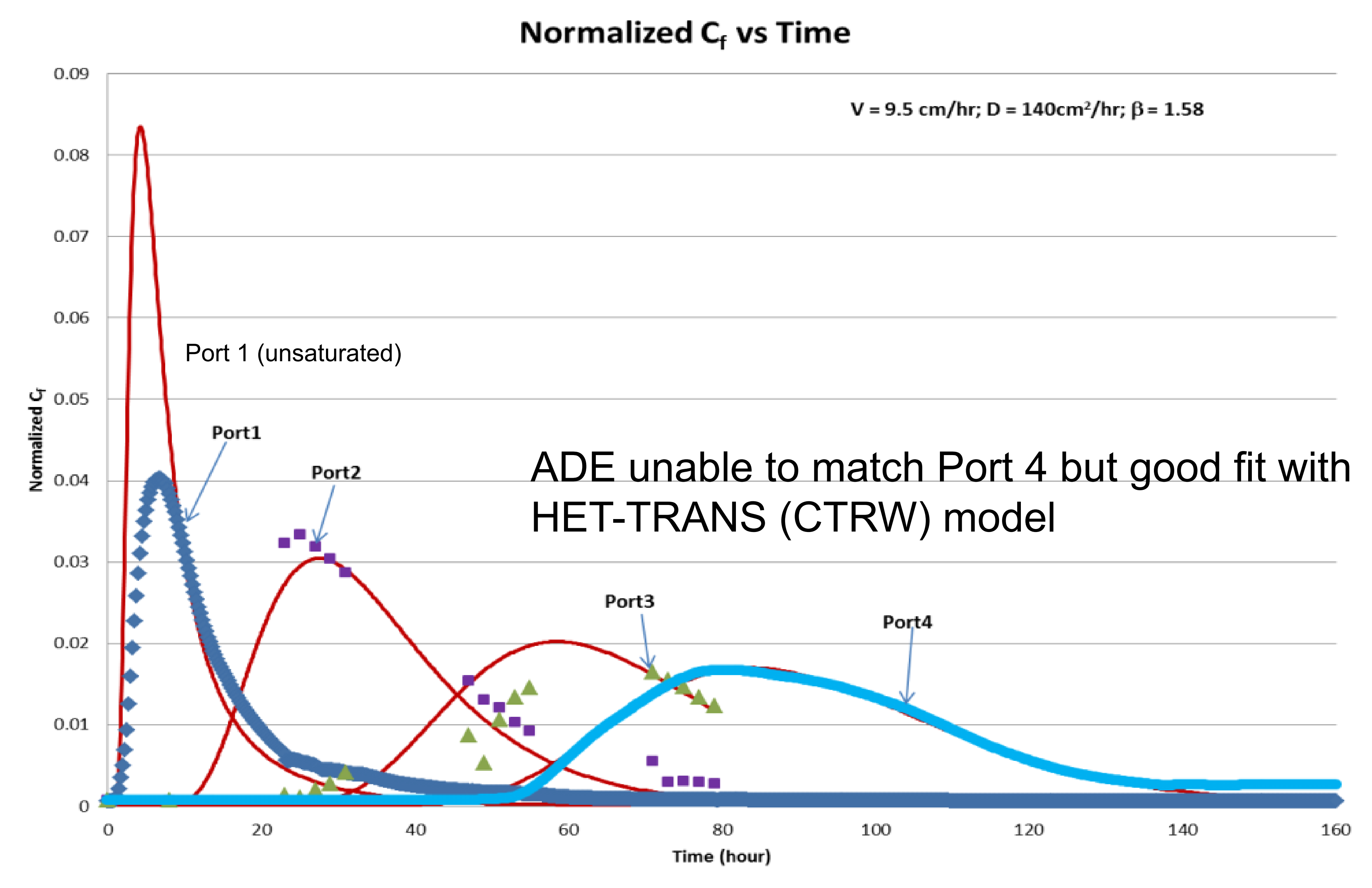


"Tear drop" shape and slowing down from low back-diffusion rates

Dashed line indicates reaction

Burnell et al. (2017)

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



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

EPA Cincinnati, OH Laboratory

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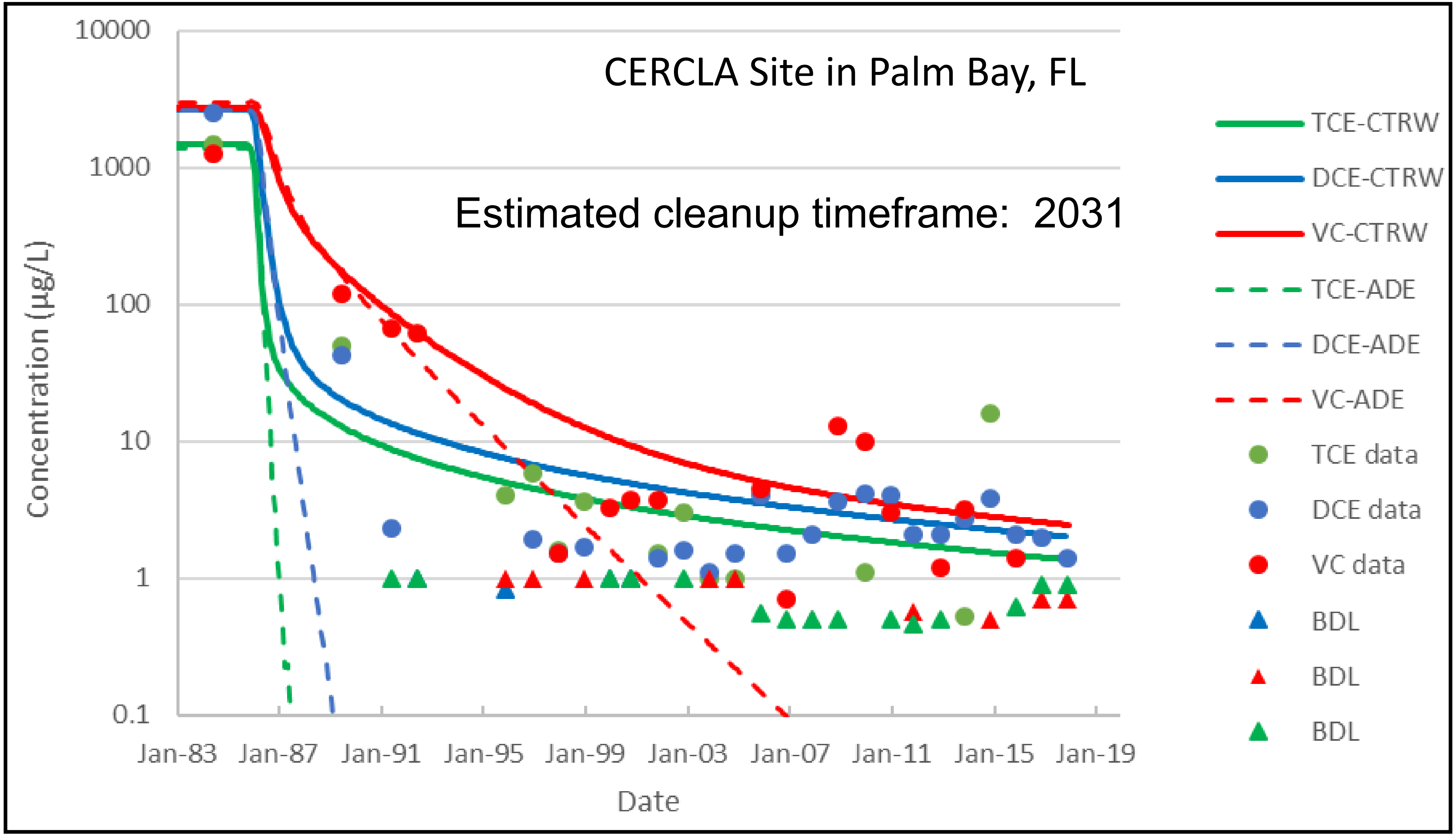
Match of Transient Model to TCE, cis-1,2-DCE, and VC Data at GS-35D (300 ft Downgradient From Source)

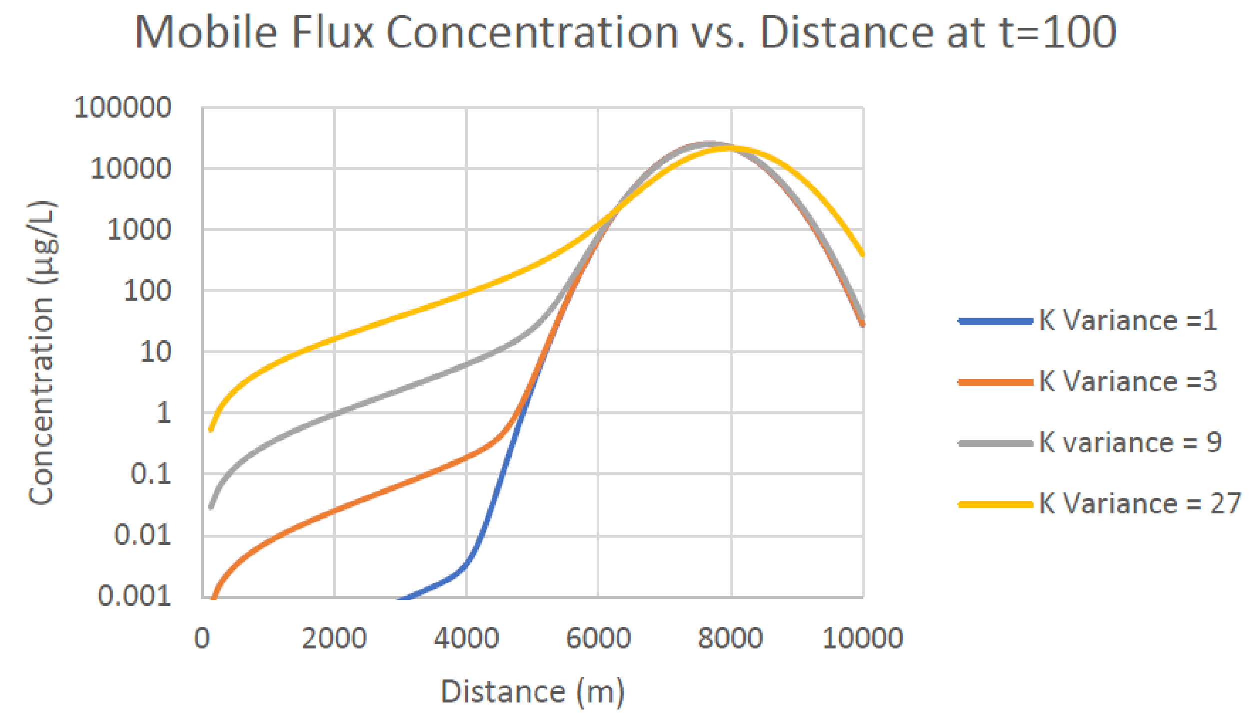


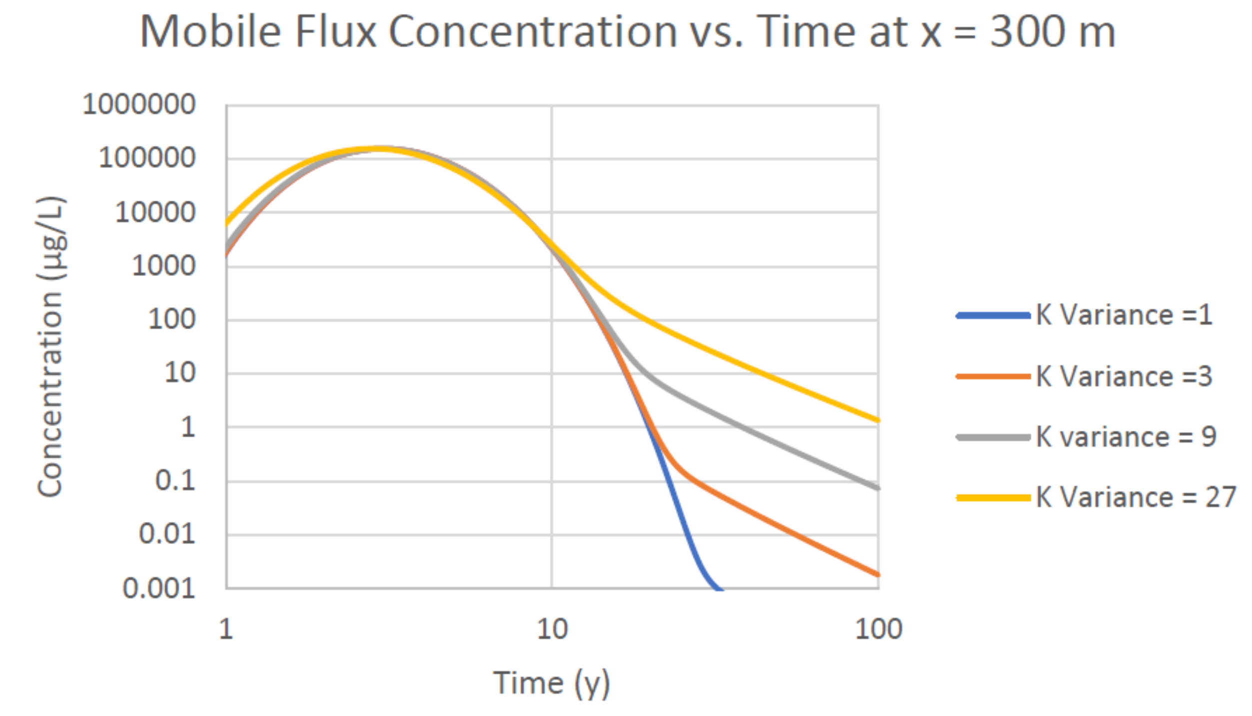
Sensitivity of Log K Variance (σ^2_{lnK})

1) Estimated from K data measurements (slug test, pump tests, and HRSC) for degree of heterogeneity

2) Log K Variance >1 leads to emergence of preferential transport

3) Higher Log K Variance causes wider distribution of plume velocities





Increased log K variance causes higher concentrations remaining (in low K zones) upgradient of plume center of mass

Increased log K variance causes increased tailing with longer cleanup times particularly for COCs with low cleanup standards
(e.g. PFAS, 1,4 dioxane, VC)

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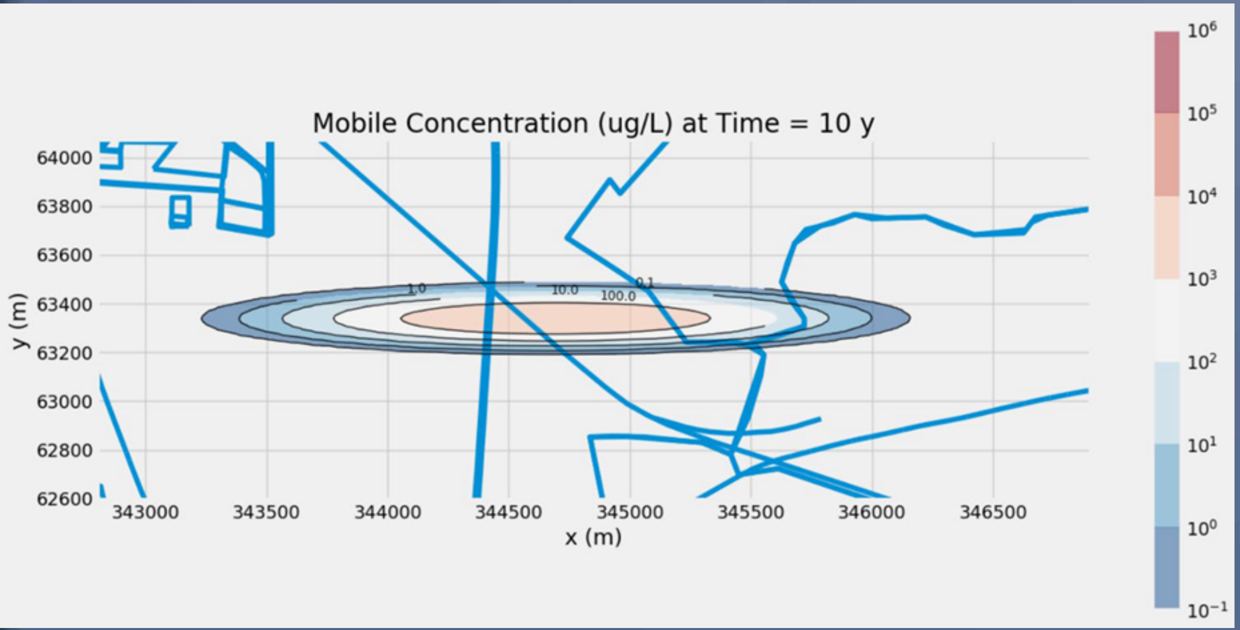
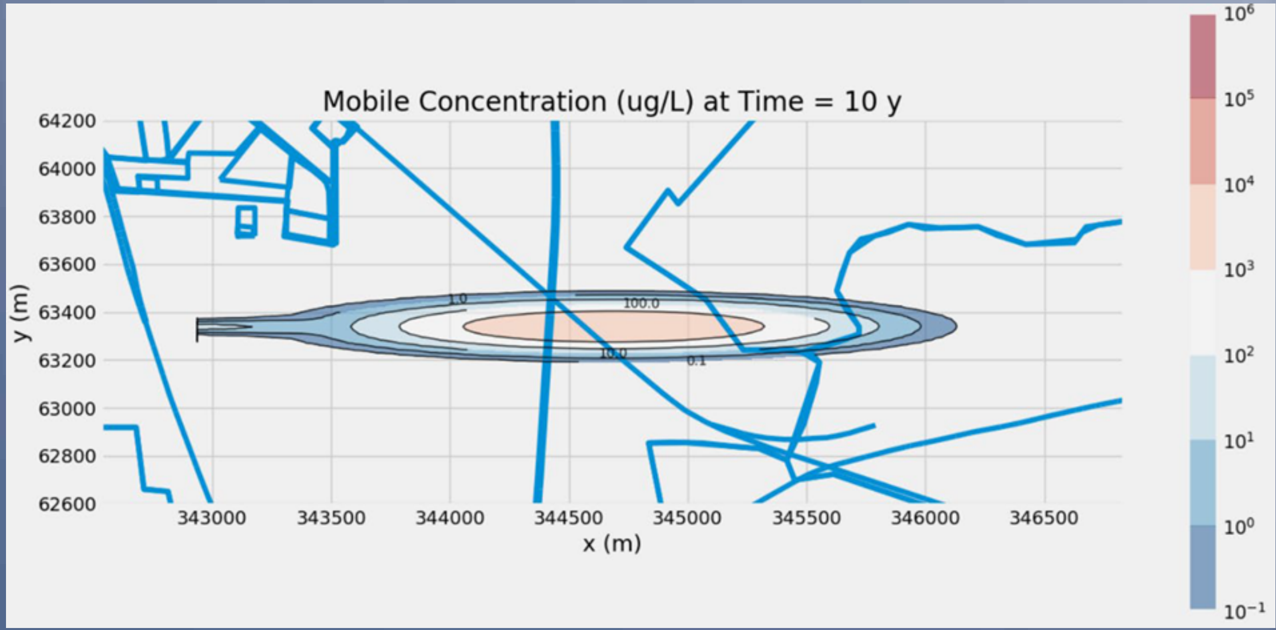
Sensitivity of Log K Variance (σ^2_{lnK}) on Plume Extent During Advection (No back-diffusion)

log K variance = 0.1



log K variance = 10



For relatively homogenous media (log K variance < 1), limited mass is left in the source zone

Plume migrates downgradient as a “slug” (standard ADE)

For highly heterogeneous media (log K variance > > 1), greater mass remains in the source zone (potential for “plume detachment”)

Elevated source zone concentrations from slow advection in low K zones (not necessarily from residual NAPL)

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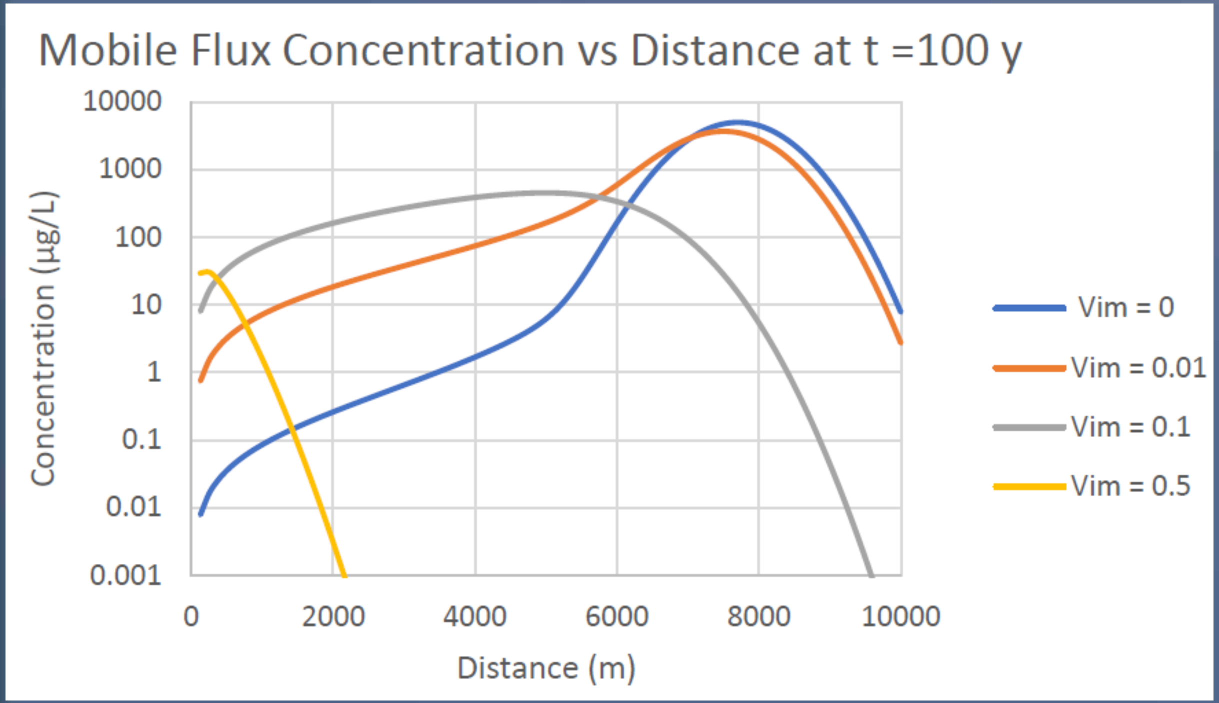
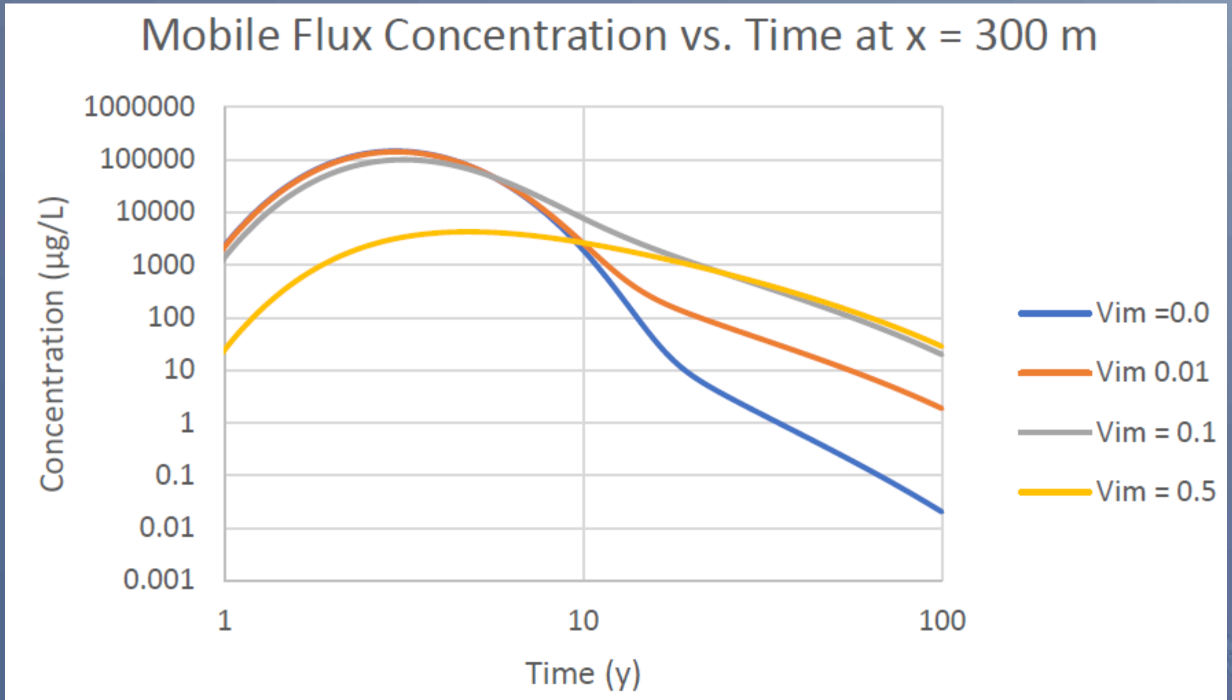
Sensitivity of Immobile Zone Volume Fraction (ϕ_{im})

- Can be estimated from site characterization (soil logs, cross-sections, and HRSC)

- Greater immobile zone volume fraction leads to greater trapping of contaminants in immobile zones



Increased immobile zone volume fraction causes:
1) slower plume migration rate
2) higher concentrations left behind plume front



Increased immobile zone volume fraction causes:
1) increased tailing
2) longer times to reach cleanup standards

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Immobile Zone Heterogeneity: Back-Diffusion Power Law Exponent (δ)

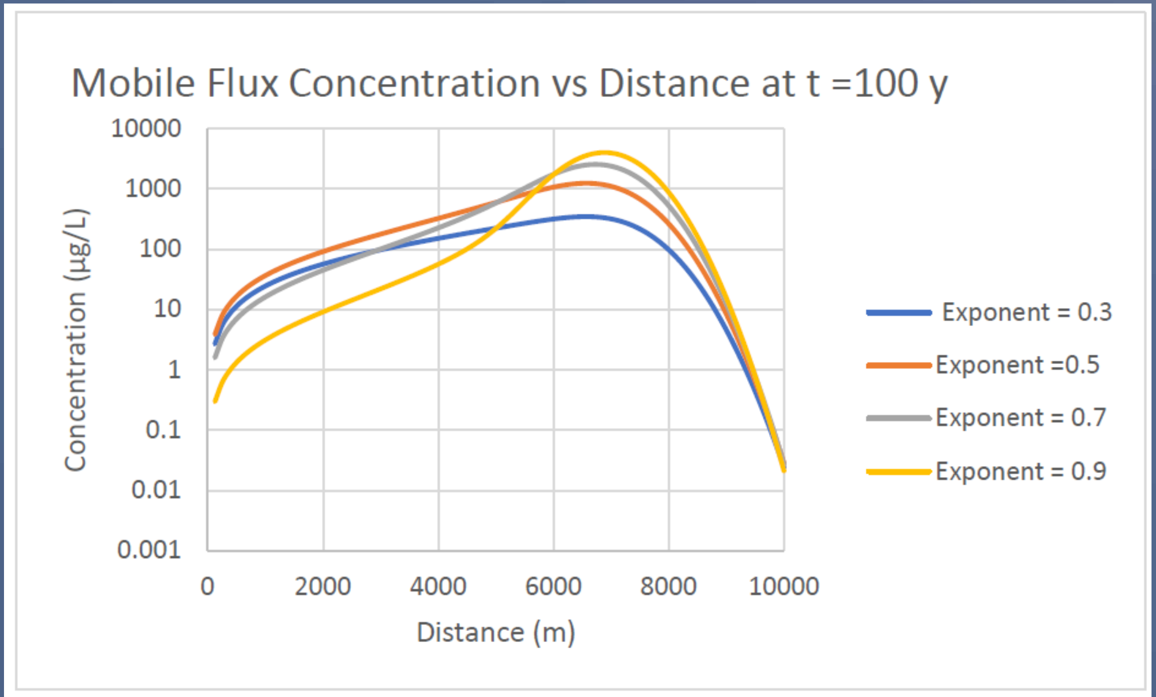
- Can be estimated from lab diffusion studies and tails in monitor wells

- Multiple rates of diffusion occur in heterogeneous immobile zones

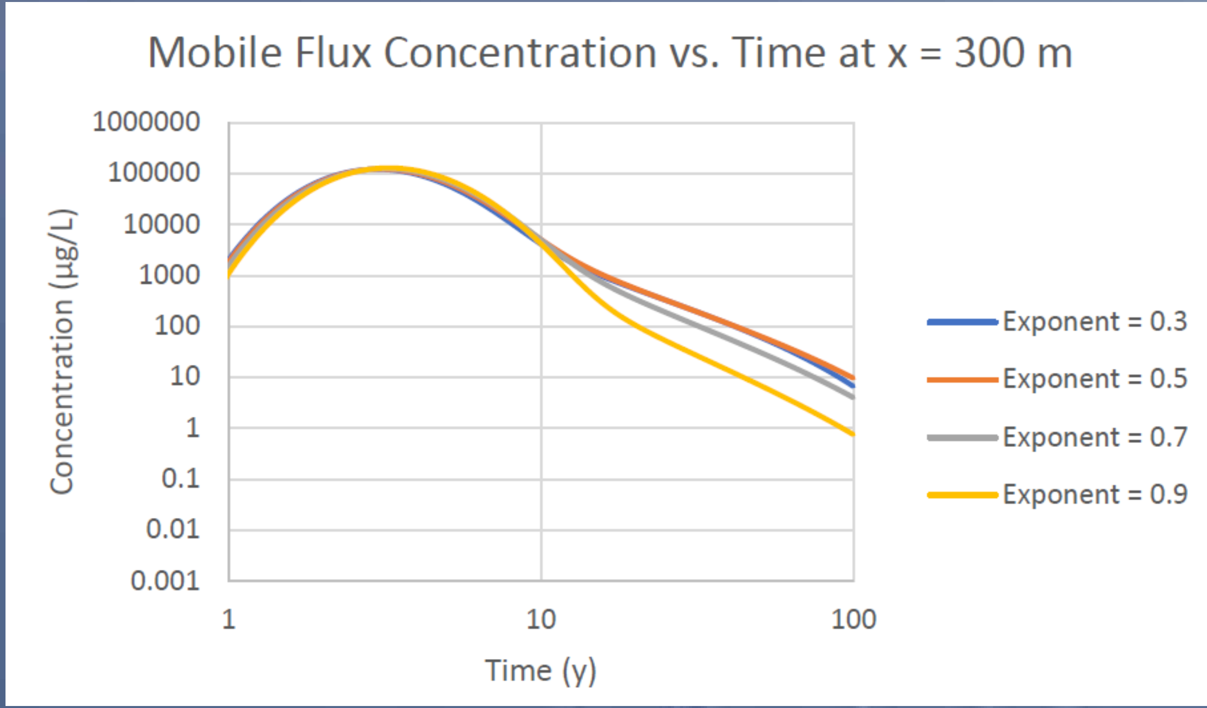
- Lower power law exponent (increased heterogeneity) indicates slower back-diffusion rates

<u>Back-diffusion time pdf:</u>

$p_f(t) \sim 1/t^{1+\delta}$ $0<\delta<1$



Increased immobile zone heterogeneity (smaller δ) causes lower peak concentrations with higher dispersed concentrations upgradient of plume front



Increased immobile zone heterogeneity (smaller δ) causes more tailing with longer times to reach cleanup standards

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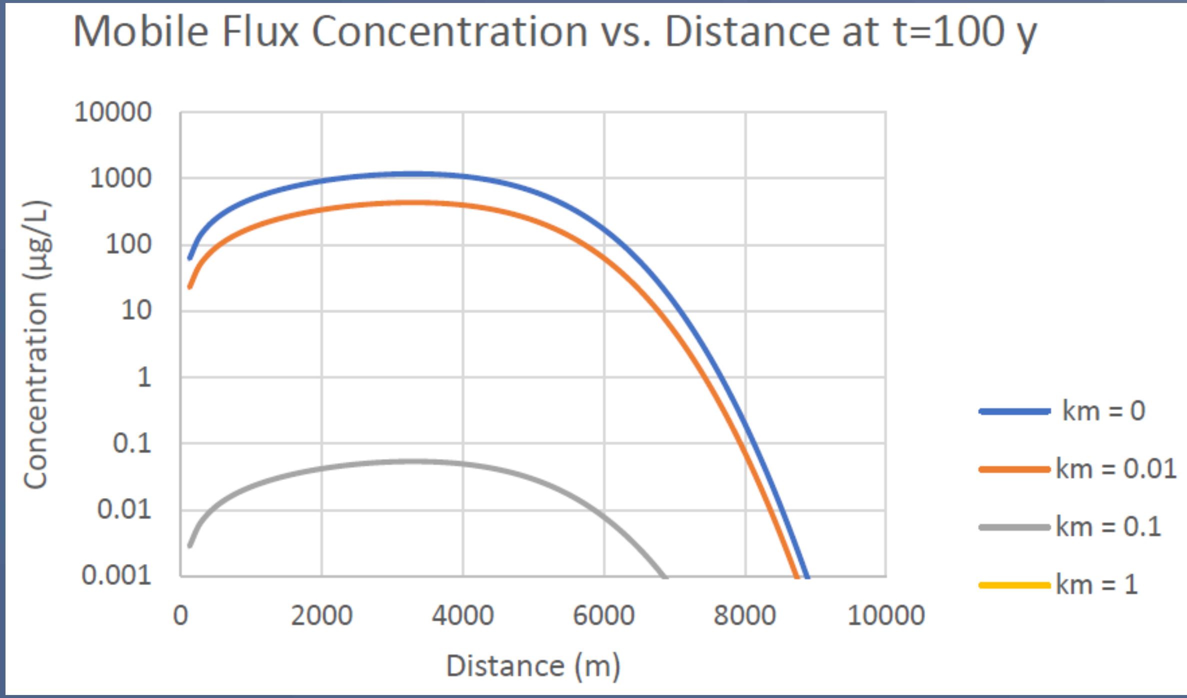
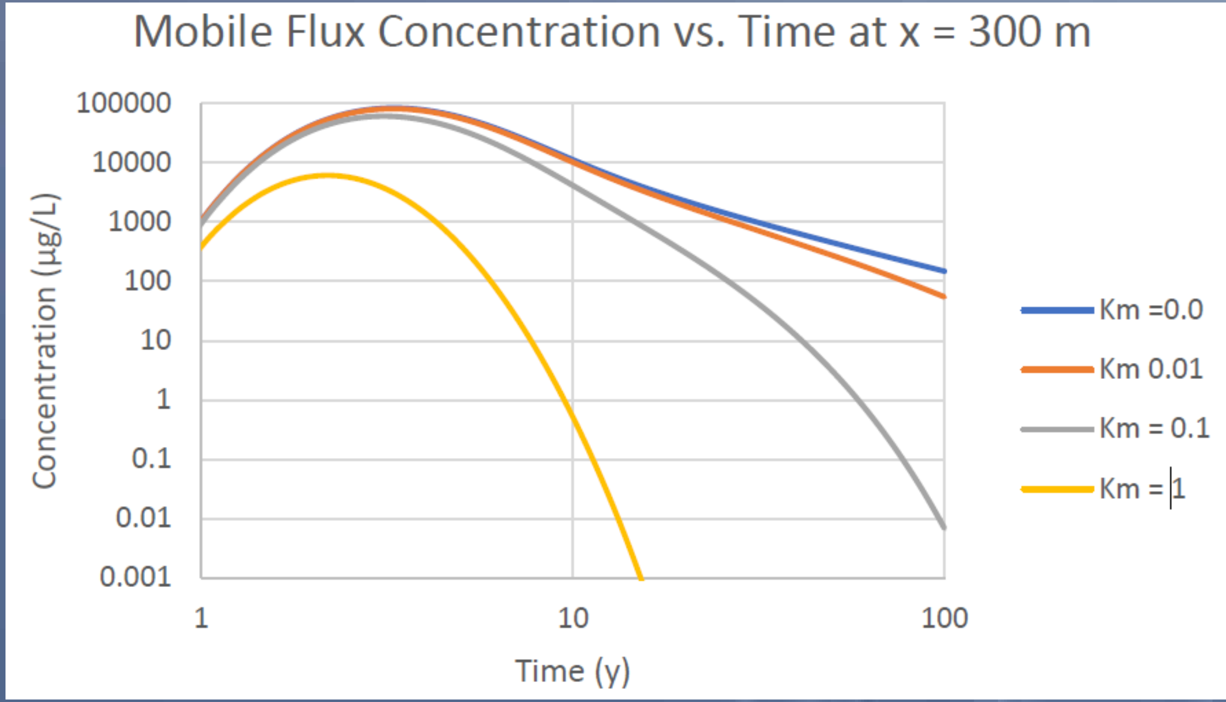
Sensitivity of Mobile Zone Degradation Rate (k_m)

Abiotic and biotic rates can be estimated from lab studies and field data

Degradation reduces plume mass over time with decrease in cleanup time





Lower degradation rate causes slower decrease in plume concentration

No spatial variability in degradation rate causes uniform decrease in concentration throughout plume

Lower degradation rate causes increased tailing and longer cleanup time for COCs with low cleanup standard

Apparent peak occurs earlier (preferential removal of lower velocity plume particles)

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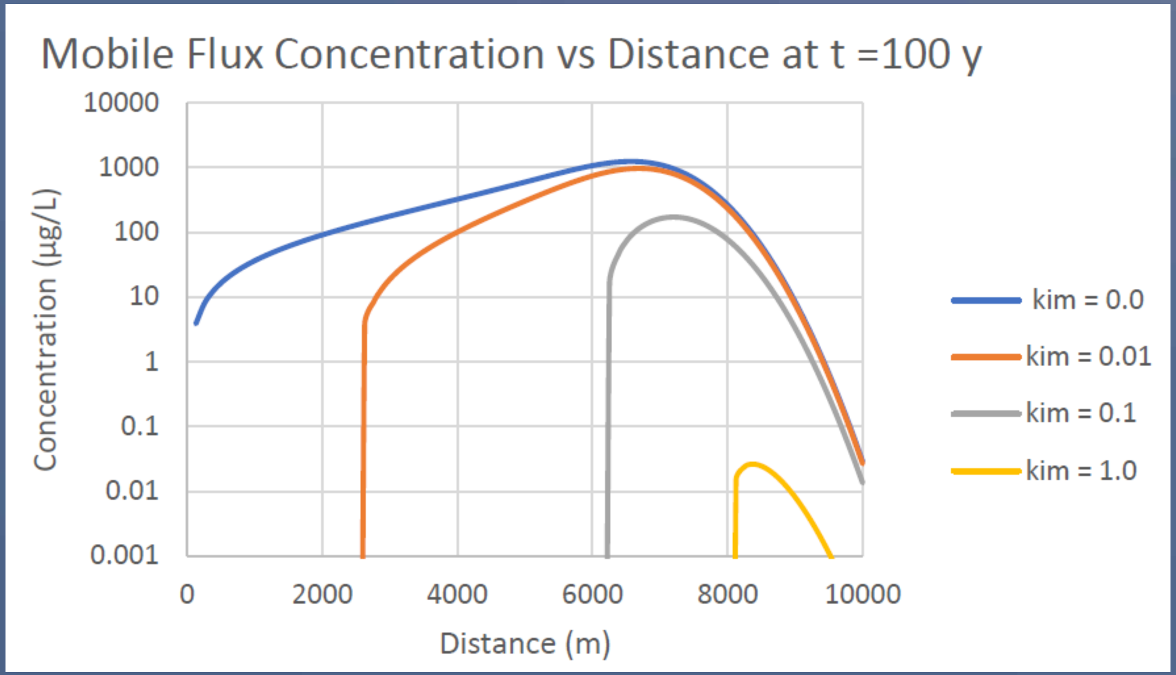
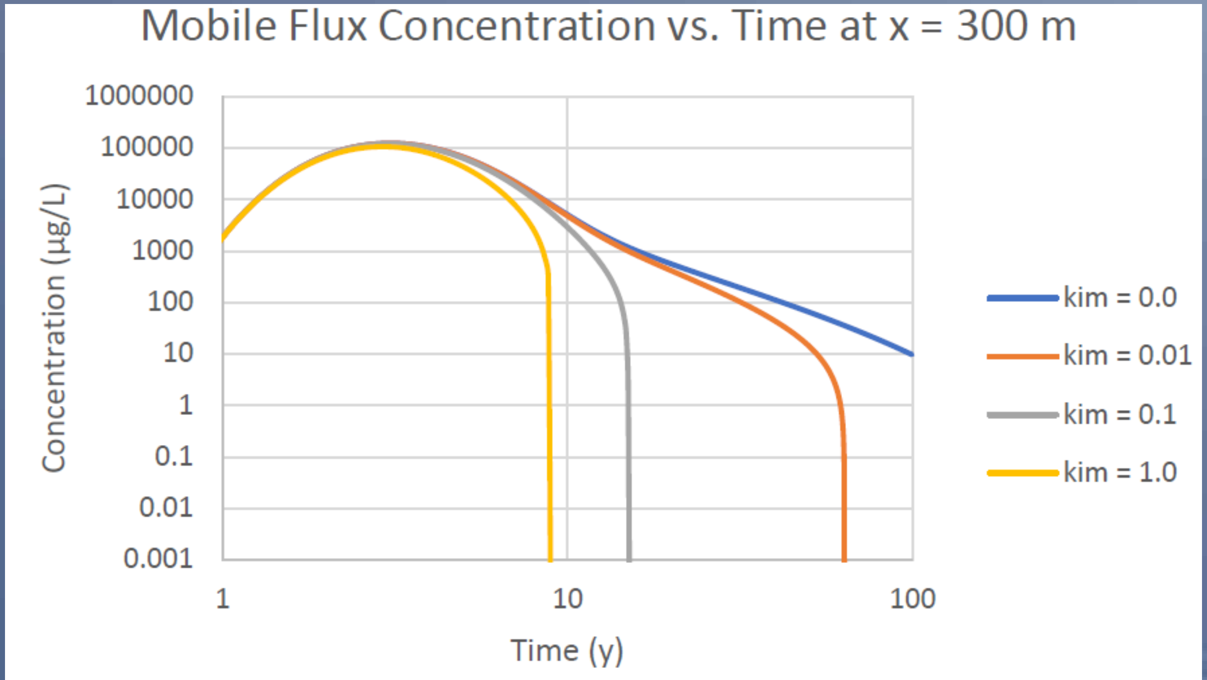
Sensitivity of Immobile Zone Degradation Rate (k_{im})

- Lower biodegradation rates may occur in immobile zones (limited inaccessibility of microrganisms)

- Different degradation rates should be estimated for mobile and immobile zones (lab and field data)





Increased immobile zone degradation rate causes less mass to occur upgradient of plume front

More rapid immobile zone degradation causes lower concentrations with less dispersion about peak

Lower immobile zone degradation rate causes increased tailing and longer cleanup time

Smaller effect on peak arrival time than mobile zone k_m

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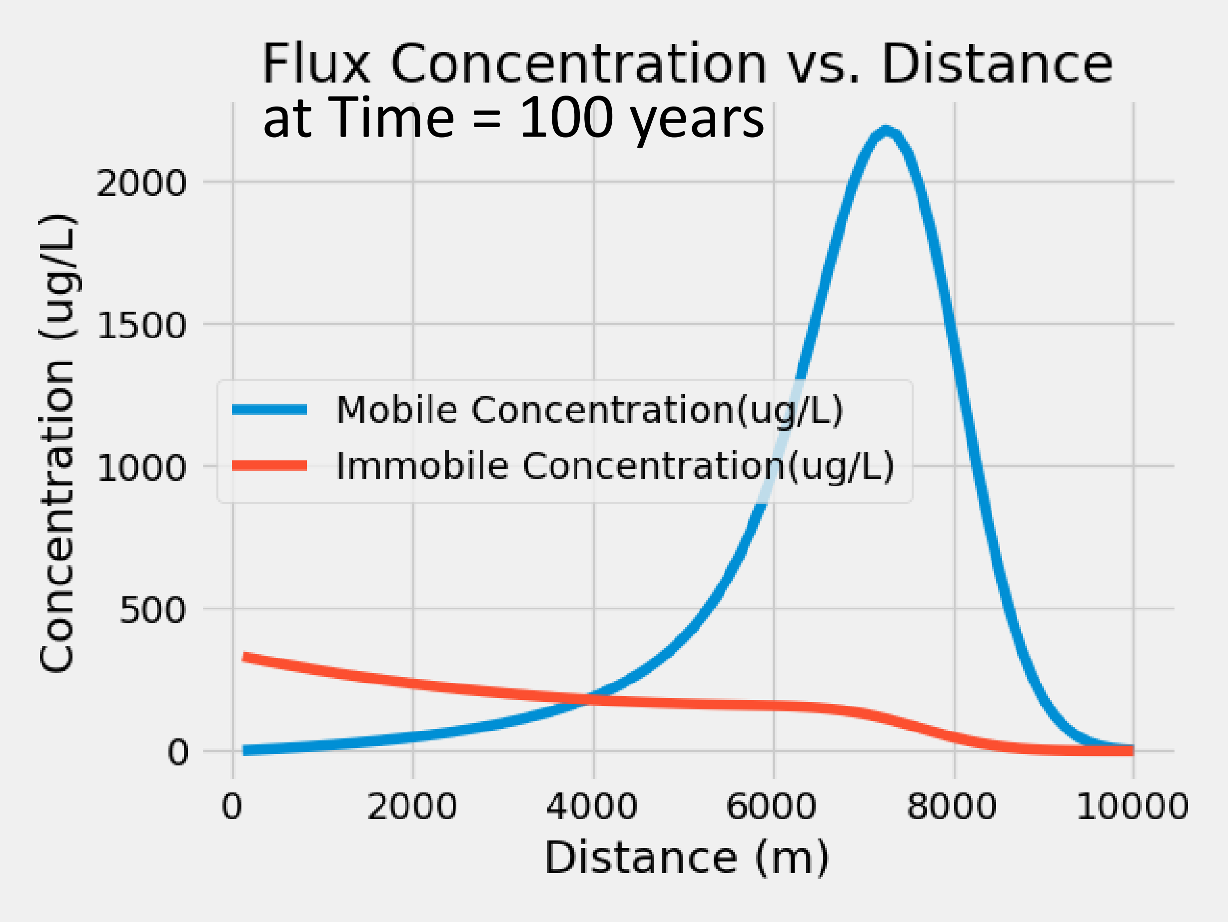
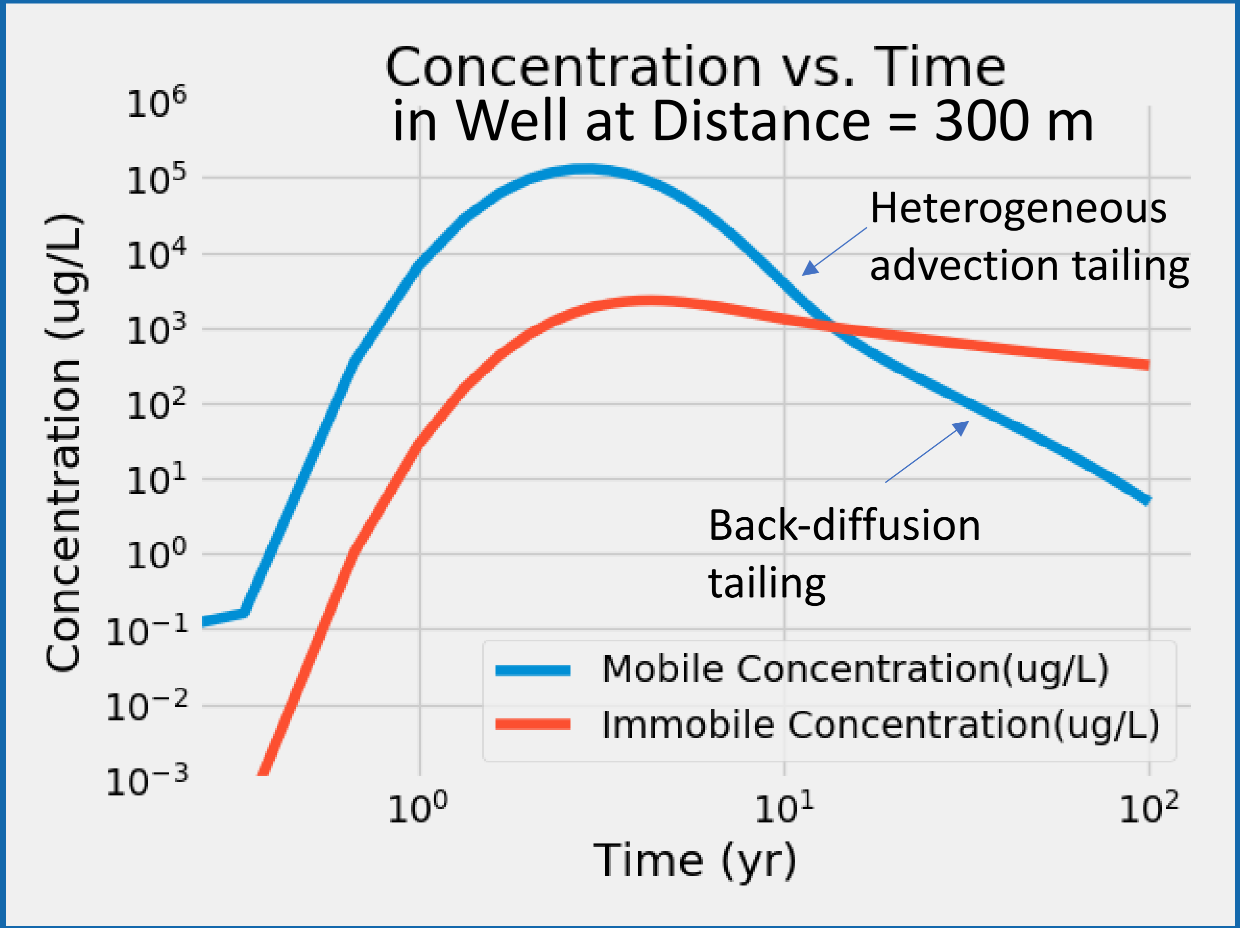
Where and When Will Back-Diffusion Occur? HET-TRANS Model Calculation of C_m and C_{im}





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.

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

- By more fully representing heterogeneity and immobile zone degradation, HET-TRANS model showed:
  - increased heterogeneity may cause "plume detachment" with elevated concentrations in source zones
  - zones of back-diffusion may vary spatially and temporally during different phases of LTM
  - distinct tailing patterns can occur from heterogeneous advection, back-diffusion, and reaction

- Compounds with low standards that degrade slowly (e.g. PFAS, 1,4 dioxane, VC) are more likely to have long tails that persist above cleanup target levels

- CTRW models (HET-TRANS) may help to improve estimate of cleanup timeframe

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Acknowledgements

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- Lenny Konikow, USGS
- 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.

Questions: Dan.Burnell@Tetratech.com