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A Practical Model for Plume Transport, Reaction, and Back-diffusion in Heterogeneous Media for Estimating Cleanup Timeframe

Daniel K. Burnell and Jie Xu
Tetra Tech

Lawrence S. Sims
L.S. Sims & Associates

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

- Most sites are highly heterogeneous: Variance of ln K > 1 (Fogg, 2016)
- Large and dilute plumes at many sites with non-gaussian (anomalous) distribution and non-Fickian spreading rates (~ t^{β})
- Long asymmetric tails in tracer test breakthrough curves or wells during remedial performance monitoring
- Concentration rebound frequently observed after remediation
- Causes: 1) multi-scale heterogeneity causing broad range of velocities with preferential pathways; 2) multi-rate back-diffusion from heterogeneous immobile zones; 3) non-linear sorption-desorption
- **Question:** Are there better models for simulating these important mechanisms for better estimate of cleanup time?

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Presentation Outline

- I. Multi-scale heterogeneity, flaws in standard ADE, and need for new modeling approach for important sub-grid (e.g. pore-scale) mass transfer mechanisms

- II. New Extended ADE (CTRW) Model for heterogeneous advection, back-diffusion, and multi-species (e.g. TCE, RDX, radionuclides) sequential reaction

- III. Examples of analytical screening level model: a) verification using numerical model; b) demonstration to estimate cleanup timeframe at CERCLA site in Palm Bay, FL

- IV. Summary and Conclusions

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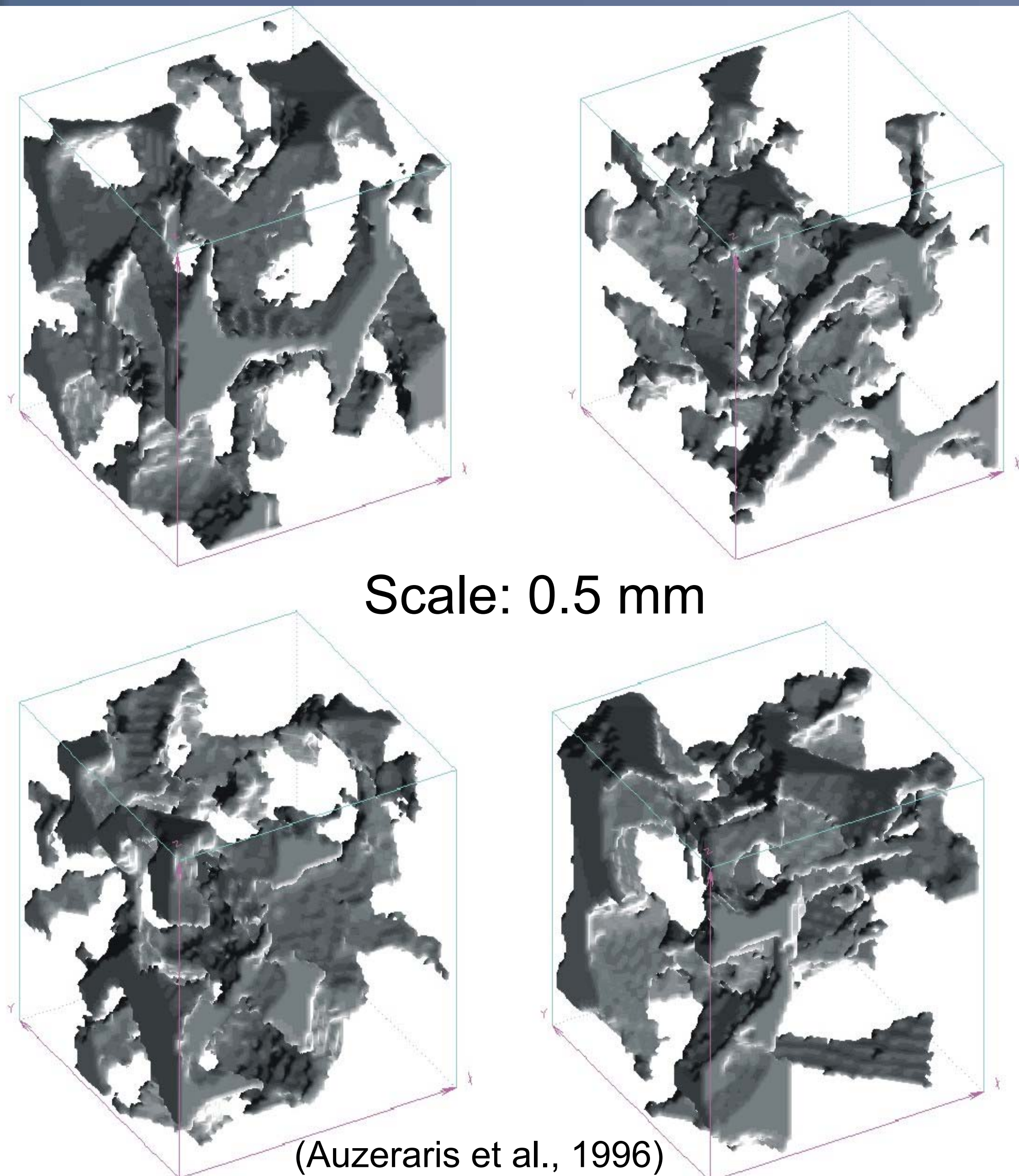
I. Pore and Field-Scale Heterogeneity

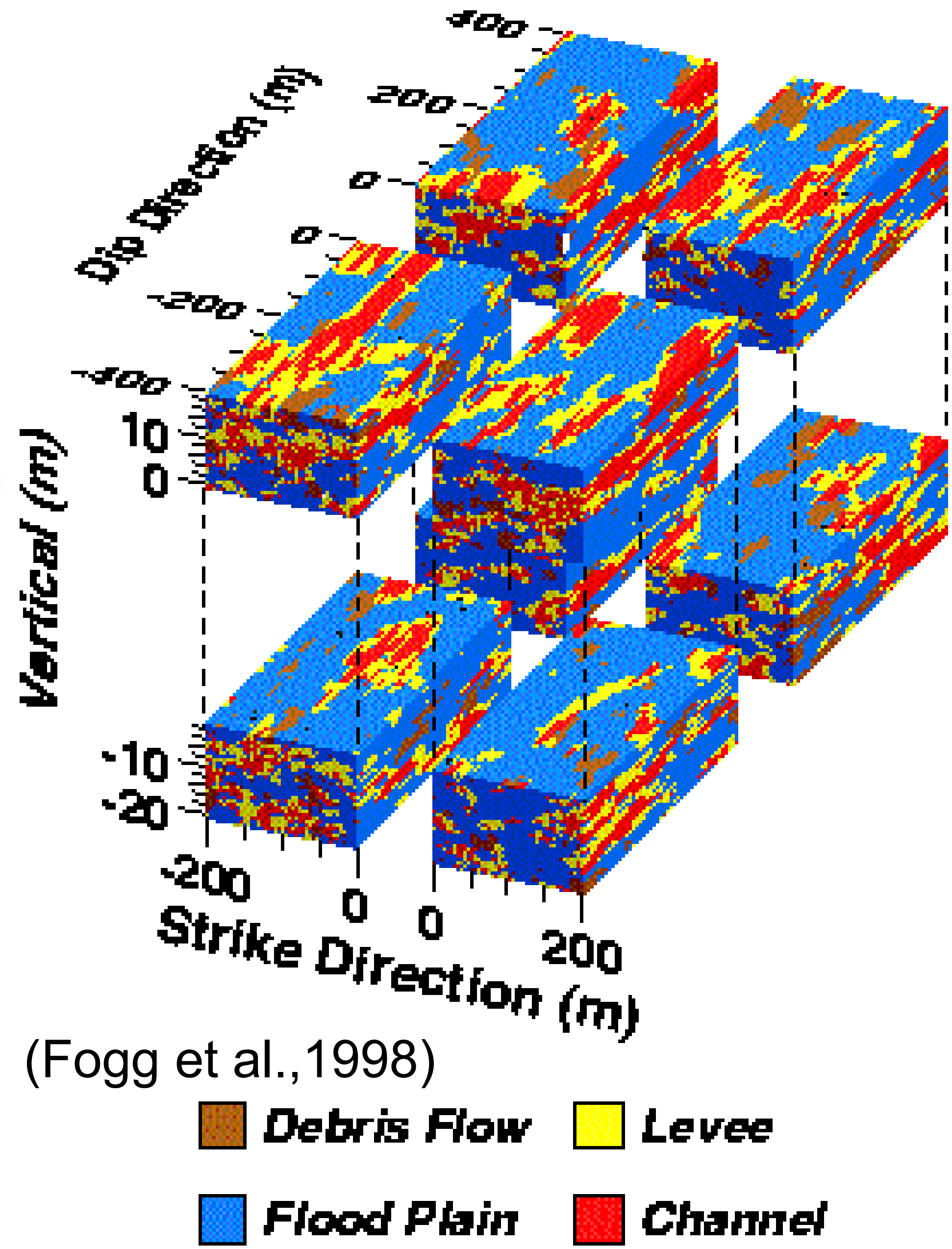
X-ray images of pore space in sandstone



Scale: 0.5 mm

(Auzeraris et al., 1996)

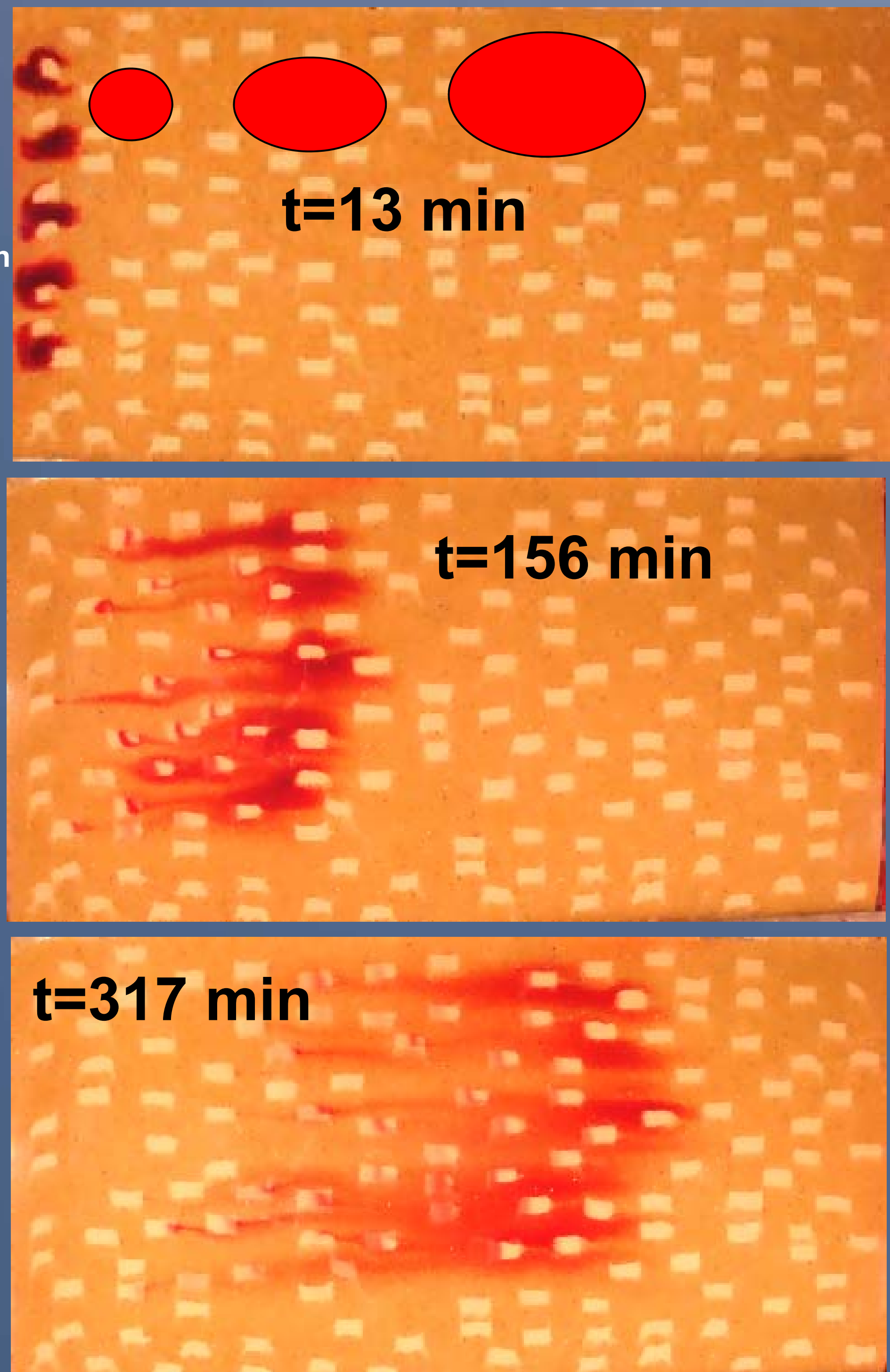
Fluvial depositional environment



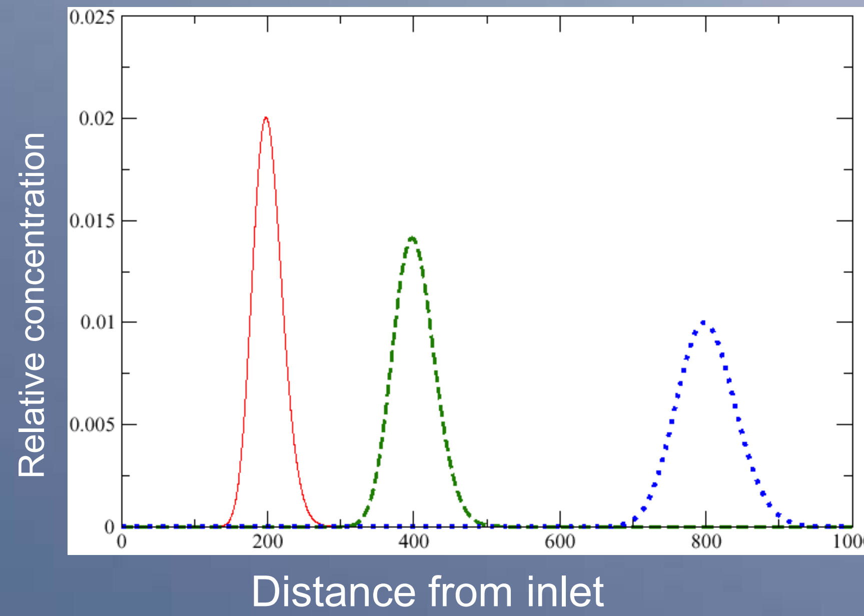
(Fogg et al.,1998)

a) Heterogeneous Advection: Meter scale uniform sand with random silt lenses

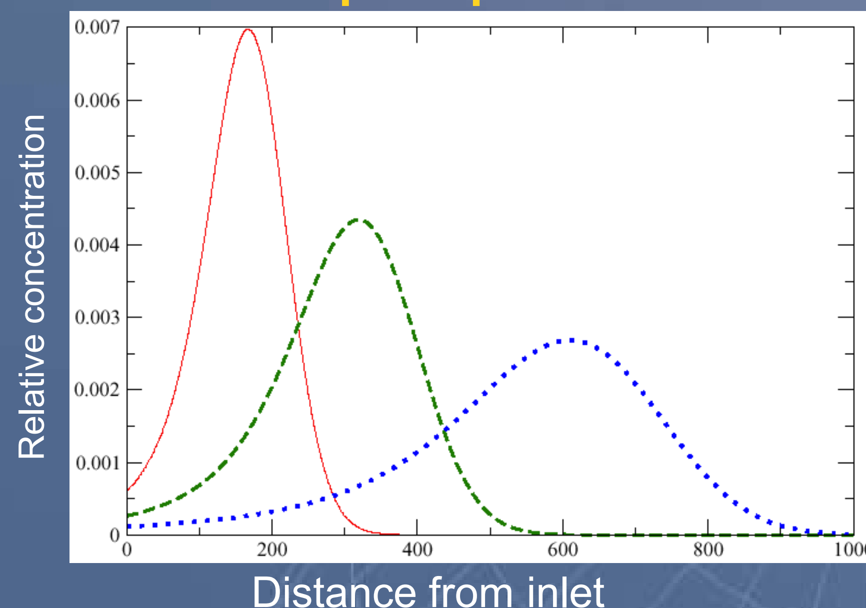
v=35 mL/min



"Expected using ADE"



"Tear Drop Shape" Detected



(Levy and Berkowitz, 2003)

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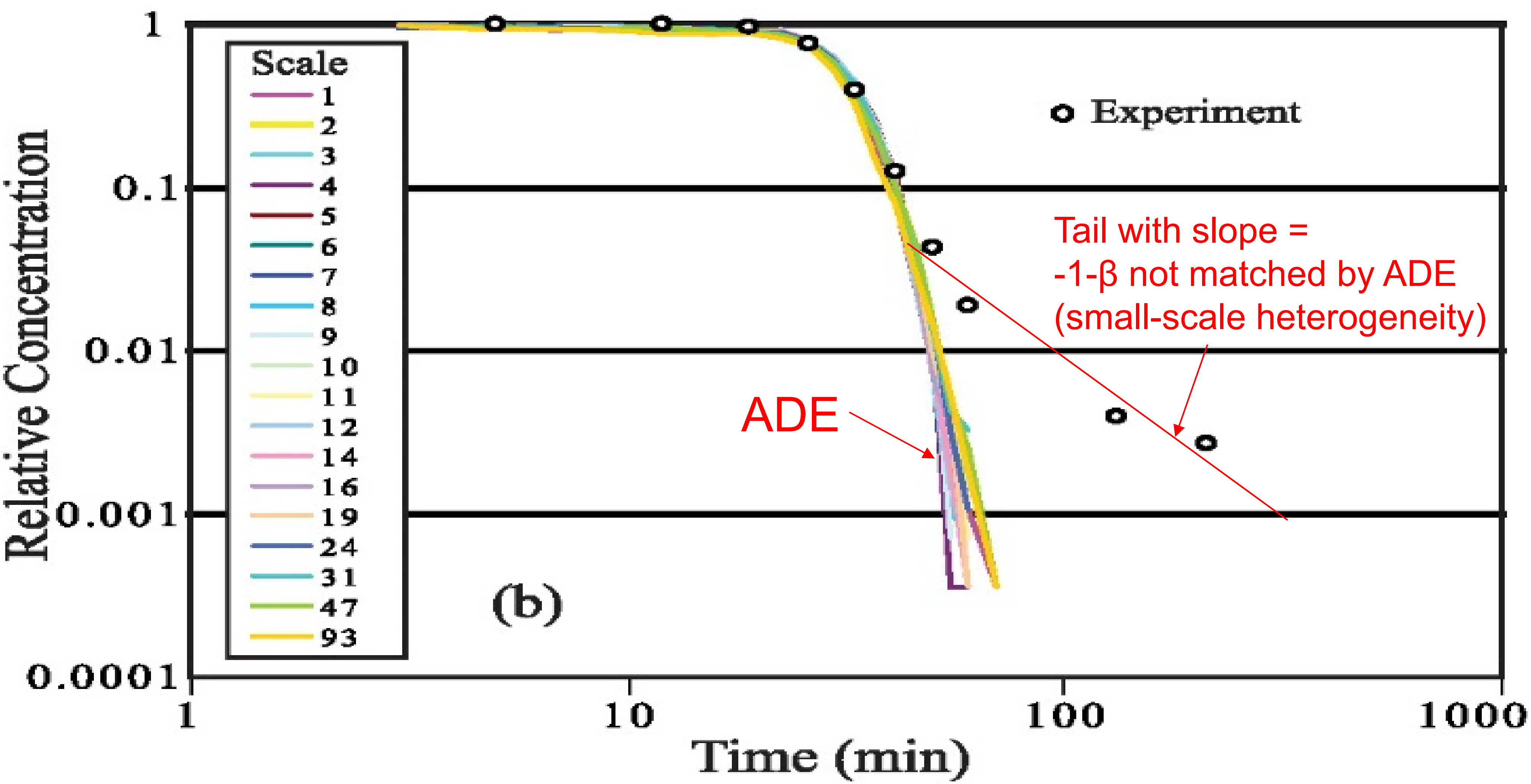
Observed Tailing in Breakthrough Curve: Poor ADE fit (Major et al., 2011) for Extensively Sampled Sandstone Slab



30.5 cm x 30.5 cm homogenous SS: 8649 air permeability measurements and tracer test

Note: Power law exponent β represents degree of heterogeneity; related to variance of hydraulic conductivity

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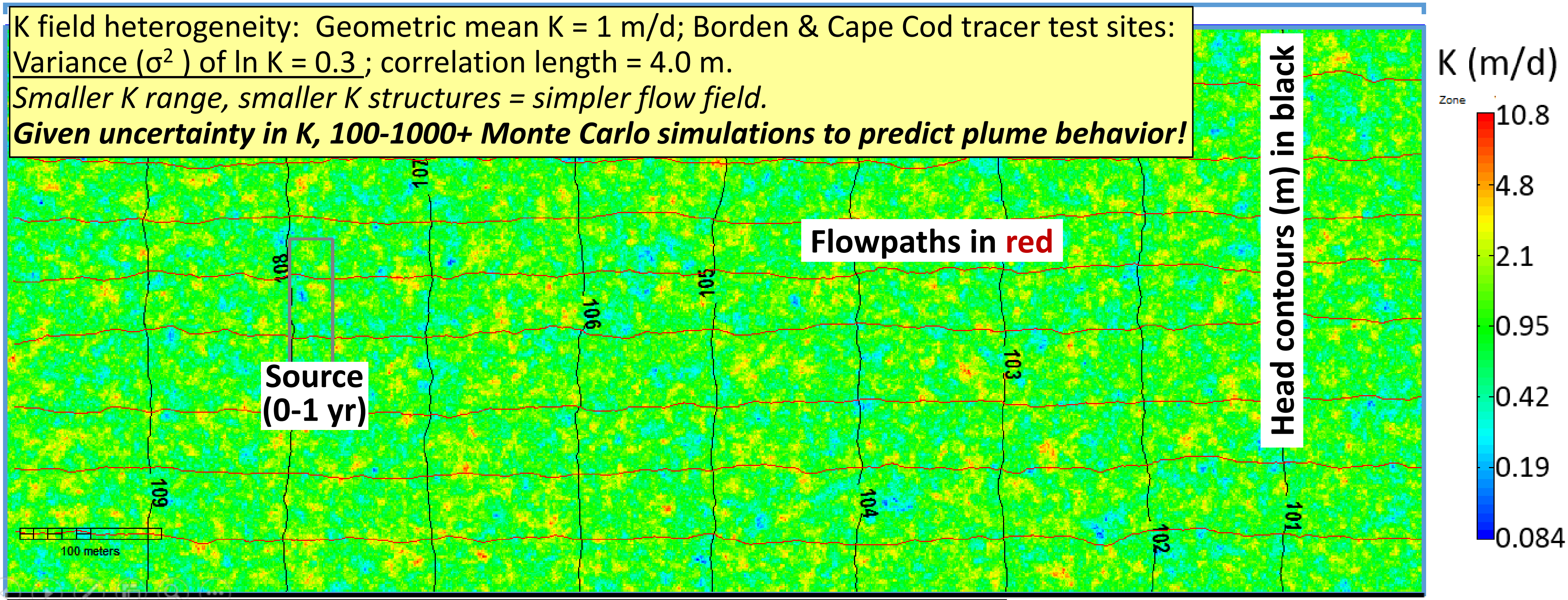
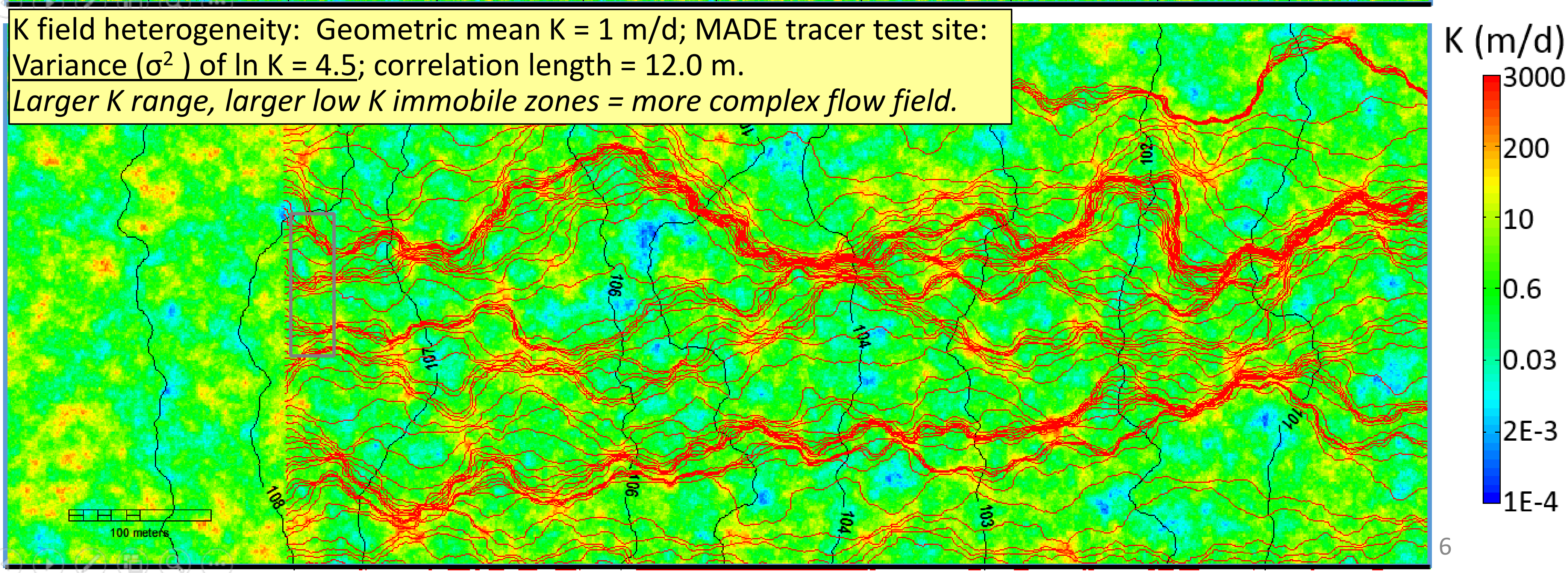
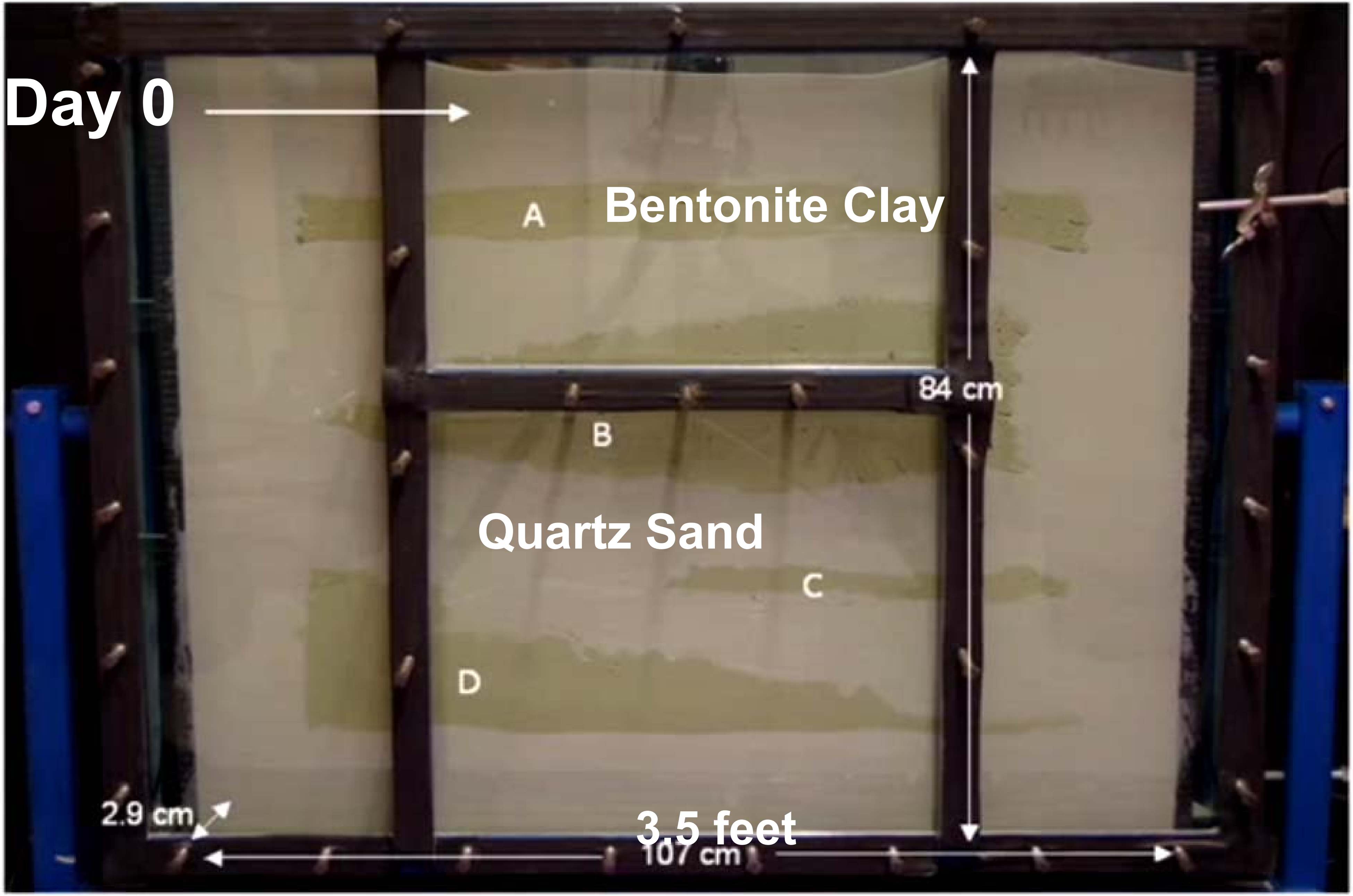
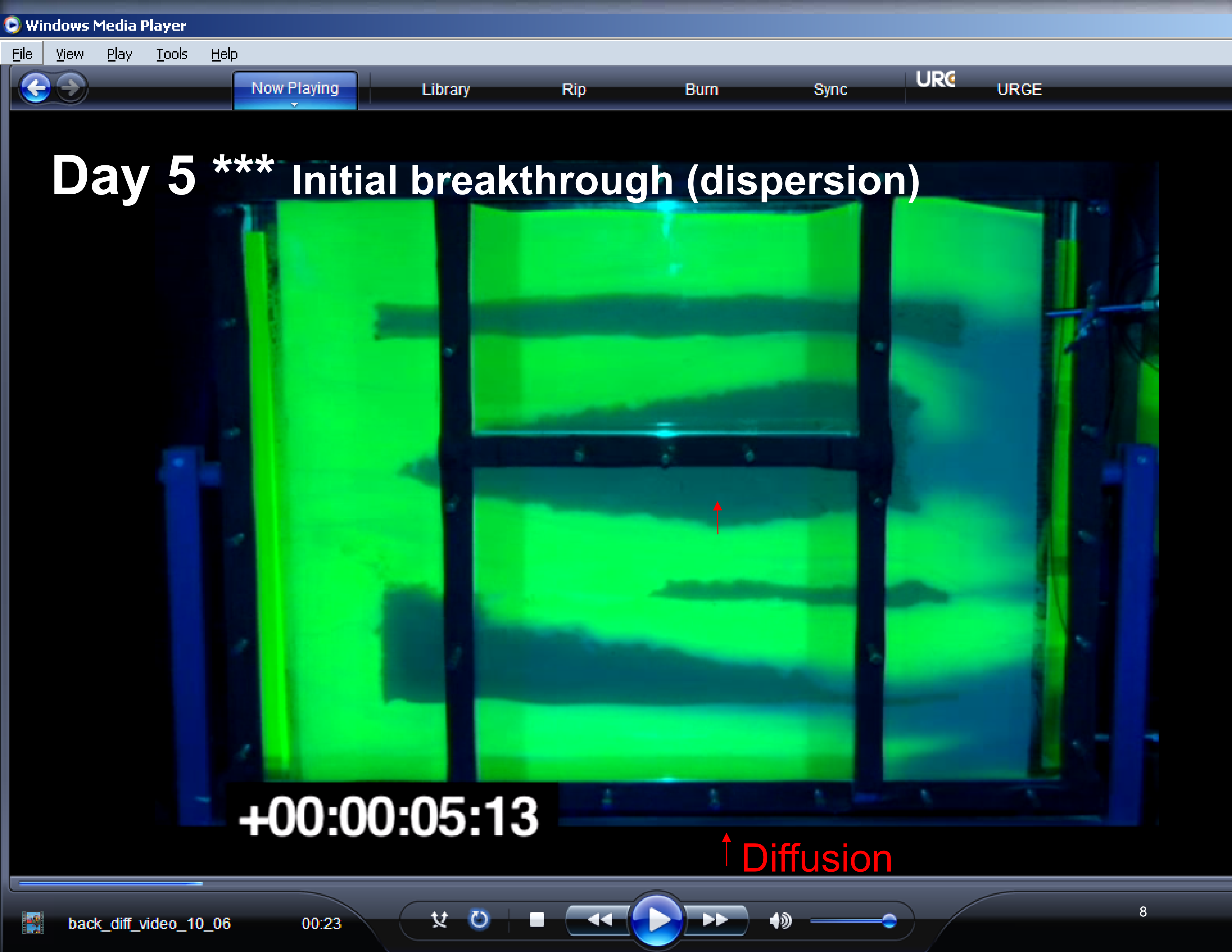

K field heterogeneity: Geometric mean K = 1 m/d; Borden & Cape Cod tracer test sites:
Variance (σ²) of ln K = 0.3 ; correlation length = 4.0 m.
Smaller K range, smaller K structures = simpler flow field.
Given uncertainty in K, 100-1000+ Monte Carlo simulations to predict plume behavior!
Flowpaths in red
Head contours (m) in black
Source
(0-1 yr)
100 meters
109
108
107
106
105
104
103
102
101
K (m/d)
Zone
10.8
4.8
2.1
0.95
0.42
0.19
0.084


K field heterogeneity: Geometric mean K = 1 m/d; MADE tracer test site:
Variance (σ²) of ln K = 4.5; correlation length = 12.0 m.
Larger K range, larger low K immobile zones = more complex flow field.
100 meters
108
106
104
103
102
K (m/d)
3000
200
10
0.6
0.03
2E-3
1E-4

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




Windows Media Player
File
View
Play
Tools
Help
Now Playing
Library
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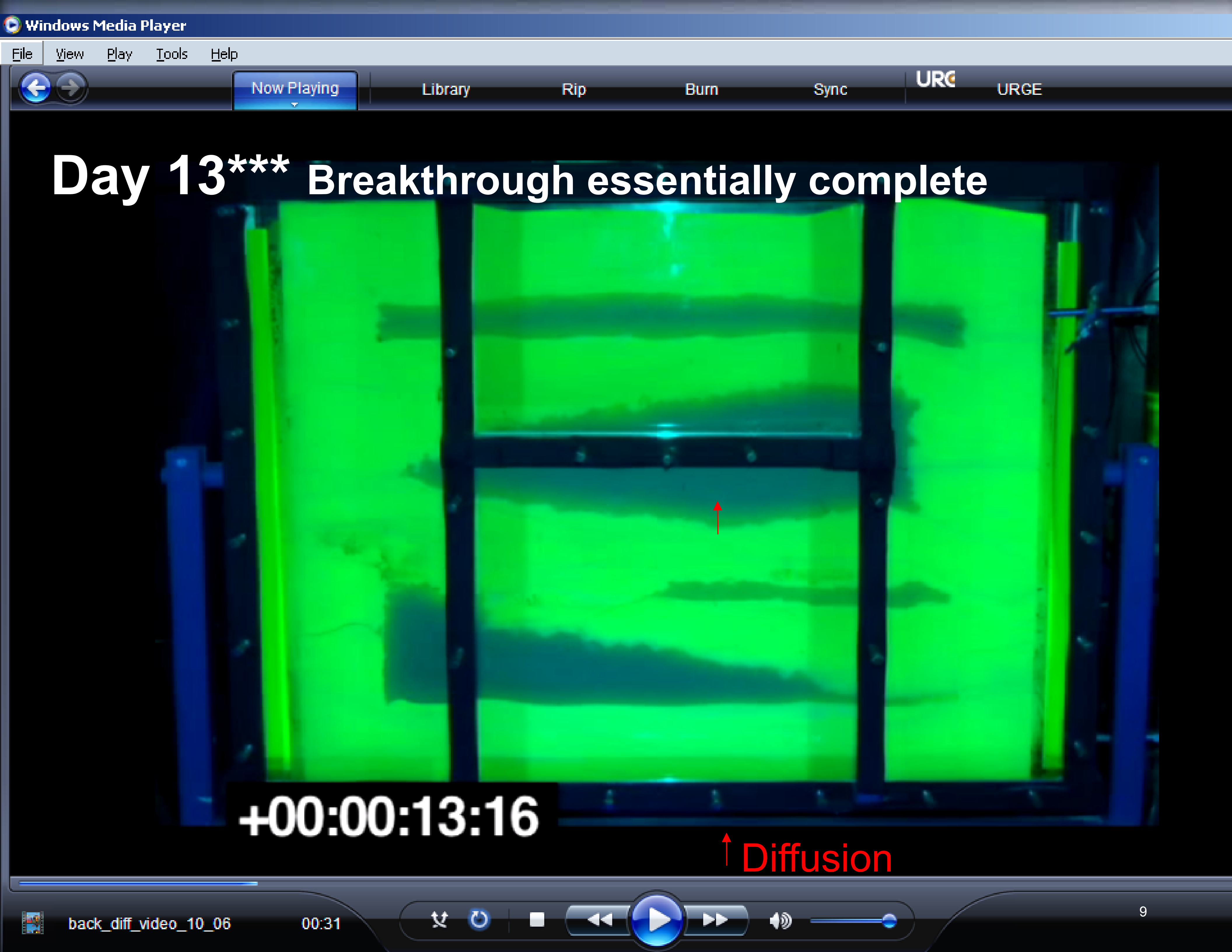
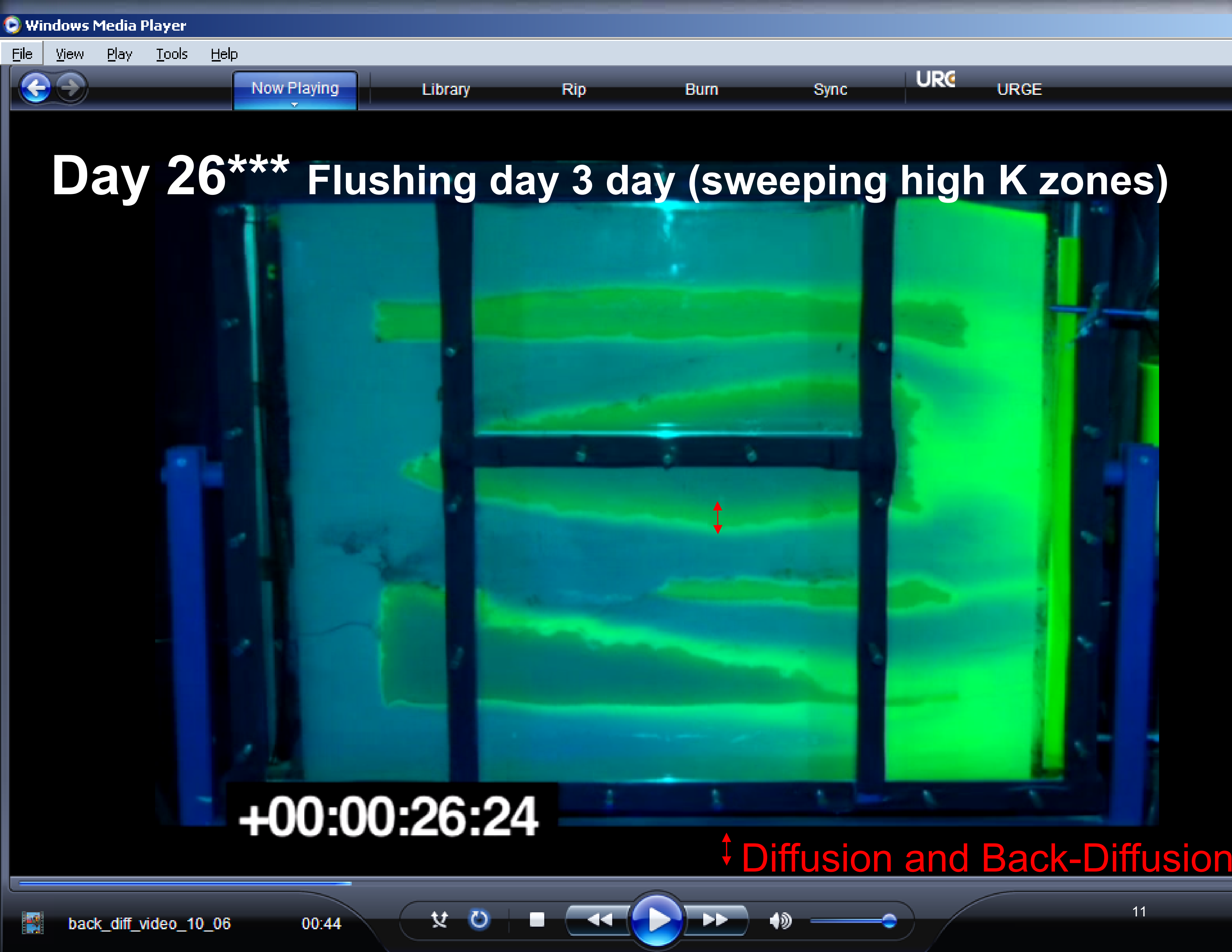
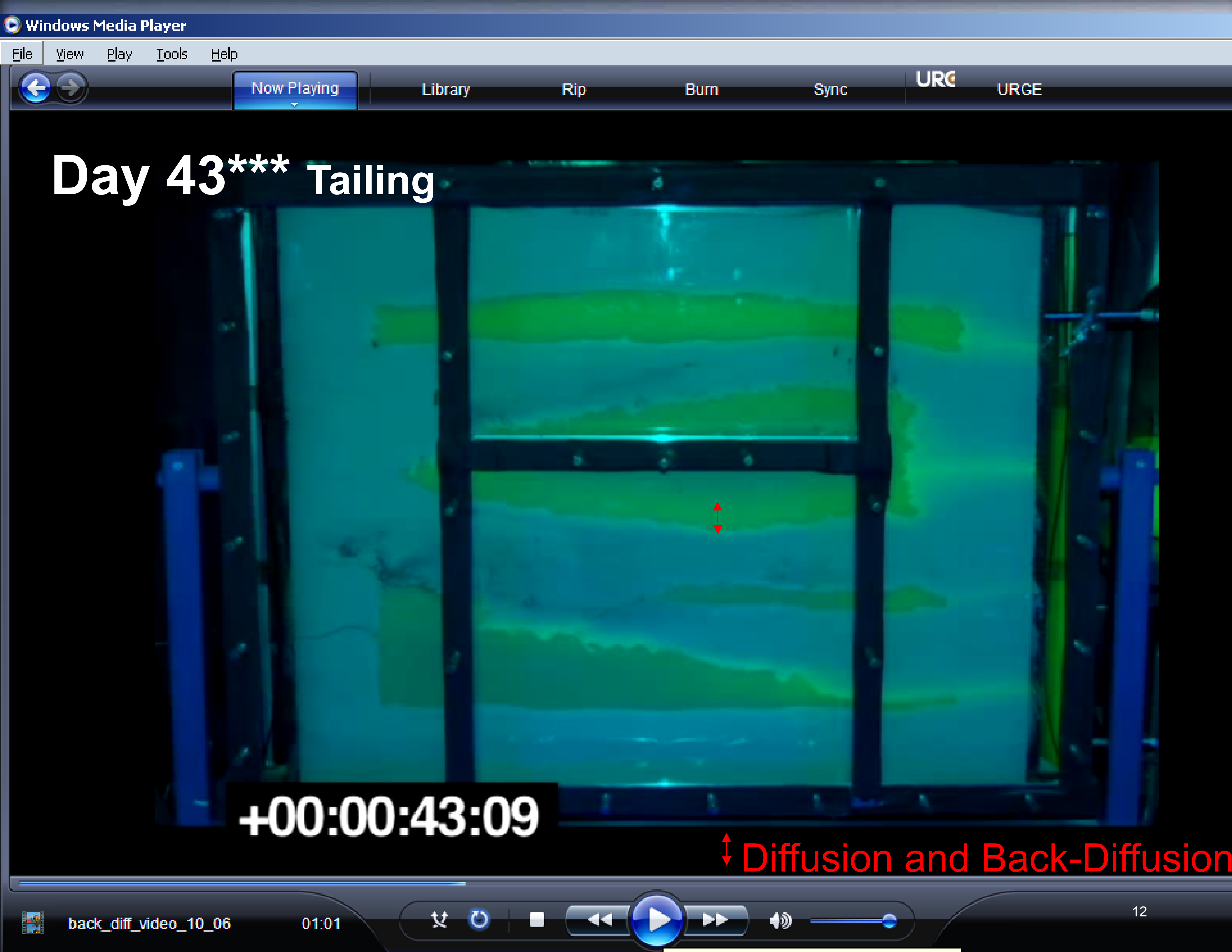
Burn
Sync
URGE
Day 5 *** Initial breakthrough (dispersion)
+00:00:05:13
Diffusion
back_diff_video_10_06
00:23
8


Windows Media Player
File
View
Play
Tools
Help
Now Playing
Library
Rip
Burn
Sync
URGE
Day 13*** Breakthrough essentially complete
+00:00:13:16
Diffusion
back_diff_video_10_06
00:31
9


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
10



Windows Media Player
File View Play Tools Help
Now Playing
Library
Rip
Burn
Sync
URGE
Day 26*** Flushing day 3 day (sweeping high K zones)
+00:00:26:24
Diffusion and Back-Diffusion
back_diff_video_10_06
00:44
11


Windows Media Player
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Library
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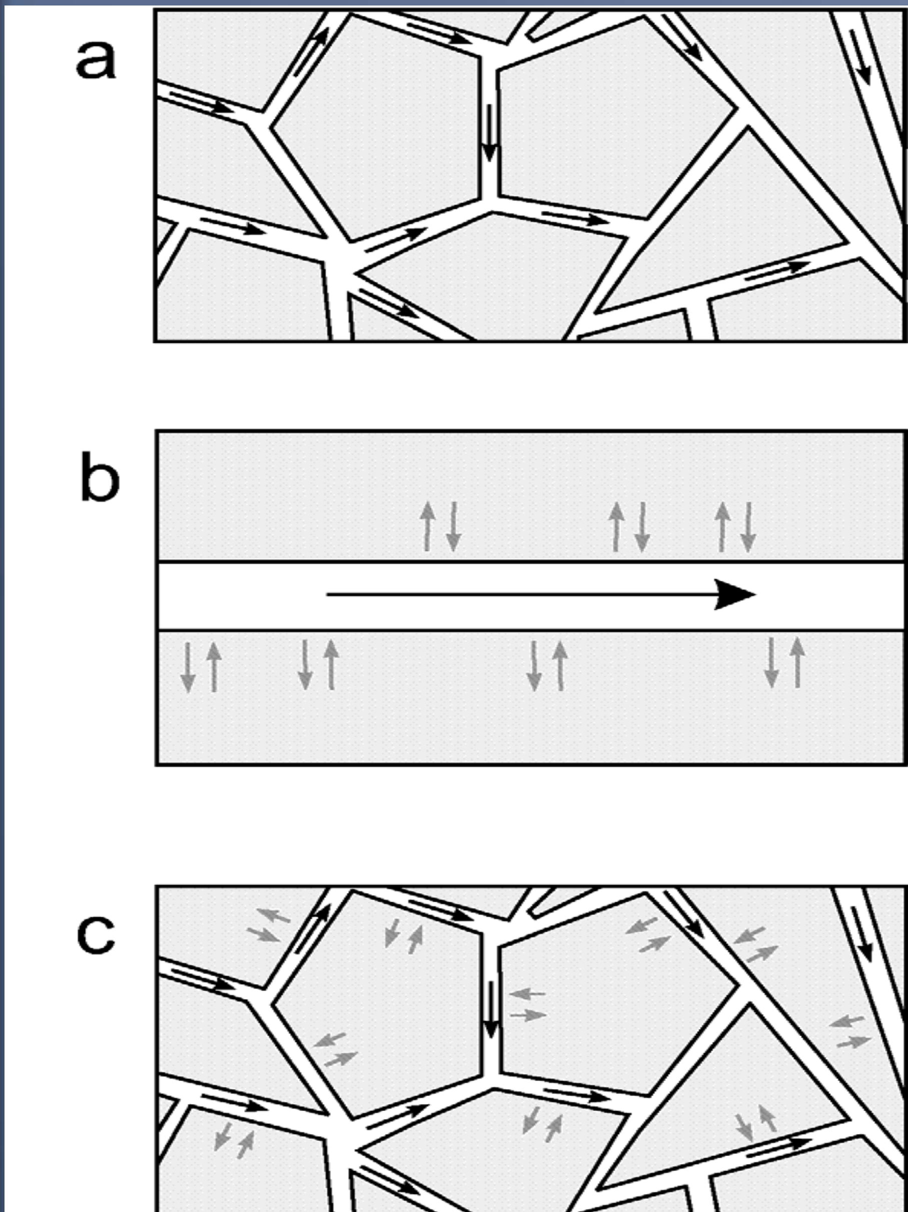
Burn
Sync
URGE
Day 43*** Tailing
+00:00:43:09
Diffusion and Back-Diffusion
back_diff_video_10_06
01:01
12

II. Extended ADE (CTRW) Modeling Approach



Berkowitz et al., (2008)

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

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

Matrix diffusion: immobile zone back-diffusion time pdf :

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

Heterogeneous advection and matrix diffusion

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

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Approach for Advective Heterogeneity Using Travel Time pdf: $\psi(t) \cong \dfrac{\tau^{\beta}}{t^{1+\beta}}$

- $\tau = \frac{l}{v}$ is the homogeneous advection time over K correlation length l
- β represents degree of heterogeneity (lower β is greater heterogeneity)
- Tracer test: breakthrough curve tail: β = (-1 – slope) in log-log plot of C vs t
- Based on Monte Carlo simulations of ln K variances $\sigma^2_{\ln K}$, the heterogeneity parameter β can be estimated using K data:

$\beta = 2.07\ (\sigma^2_{\ln K})^{-0.143}$ $\sigma^2_{\ln K} \leq 7$ (Burnell et al. 2018)

$0 < \beta < 2$ For $\beta \geq 2$, standard ADE can be used.

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Approach for Simulating Back-diffusion

Well known that back-diffusion also causes long concentration tails

Many studies show diffusion is anomalous with slower spreading rates not proportional to time due to immobile zone heterogeneity (wide distribution of diffusion rates)

Given uncertainty in immobile zone characterization, need stochastic approach:

1) capture rate $\lambda = \frac{N}{\tau}$ where τ is the advection time and N is number of immobile zones over K correlation length ℓ
2) power law pdf of back-diffusion rates $p_{im}(\mathrm{t}) \cong \frac{\tau_{im}^{\delta}}{t^{1+\delta}}$

where $\tau_{im} \approx b^2/D^*$ is the homogeneous diffusive time over immobile zone with half-thickness b and diffusion coefficient D^*

Diffusive power law exponent δ is obtained by diffusion testing of cores or late time tails of breakthrough curves (typically δ=0.5)

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Extended ADE (CTRW) Governing Equation for Heterogeneous Advection and Back-diffusion

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

Memory function M(t) encodes advective heterogeneity

- M(t) related to velocity and residence time pdf: $\psi(t) \cong \frac{\tau^\beta}{t^{1+\beta}}$

$$\tilde{M}(u) \equiv \bar{t}u\frac{\tilde{\psi}(u)}{1-\tilde{\psi}(u)}$$

- Single parameter β represents subscale heterogeneity

Various Memory Functions

ADE:	$\tilde{M}(u) = 1$	$(\beta=2)$
Power Law:	$\tilde{M}(u) \propto u^{1-\beta}$	$(0<\beta<2)$
Multi-rate mass transfer (MRMT) (matrix diffusion)	$\tilde{M}(u) = [1+\tilde{\varphi}(u)]^{-1}$	

III. Analytical CTRW Model Benchmark and Application

- New analytical solutions for heterogeneous advection, mobile-immobile mass transfer, and reaction for simple flow fields (Burnell et al., 2017; 2018)

- Flexible analytical modeling approach for different transport scenarios (using memory kernels) and transient sources: run times are minutes!

- Case 1: Analytical solutions and benchmark with particle tracking simulation

- Case 2: Application at Harris CERCLA site, FL

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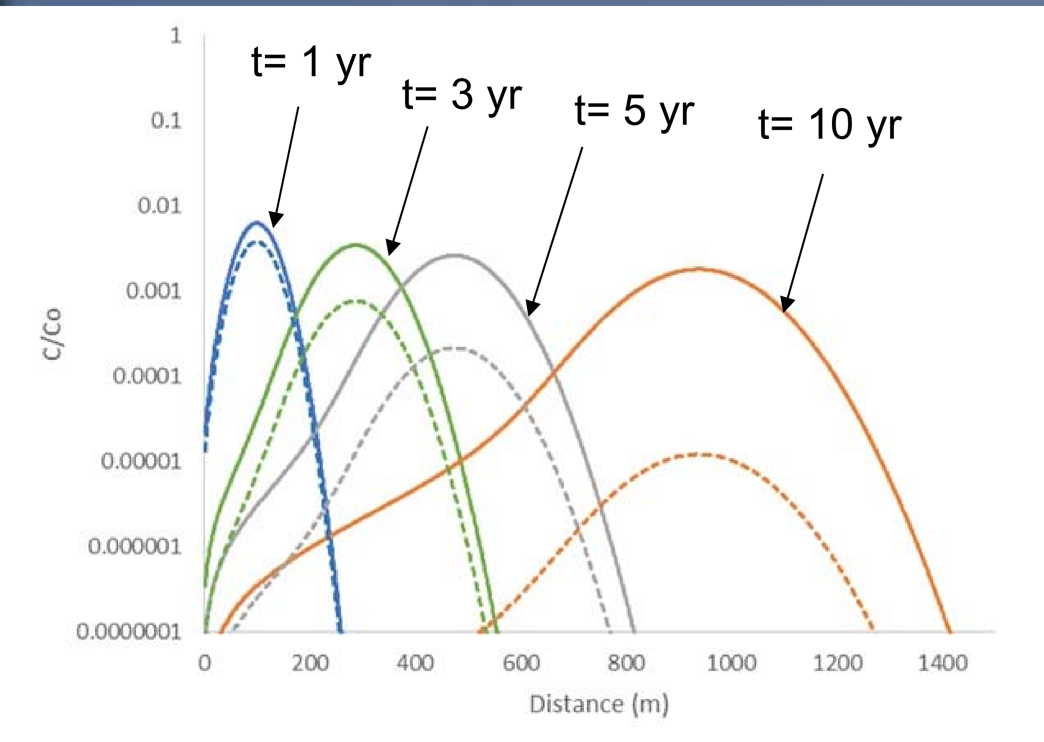
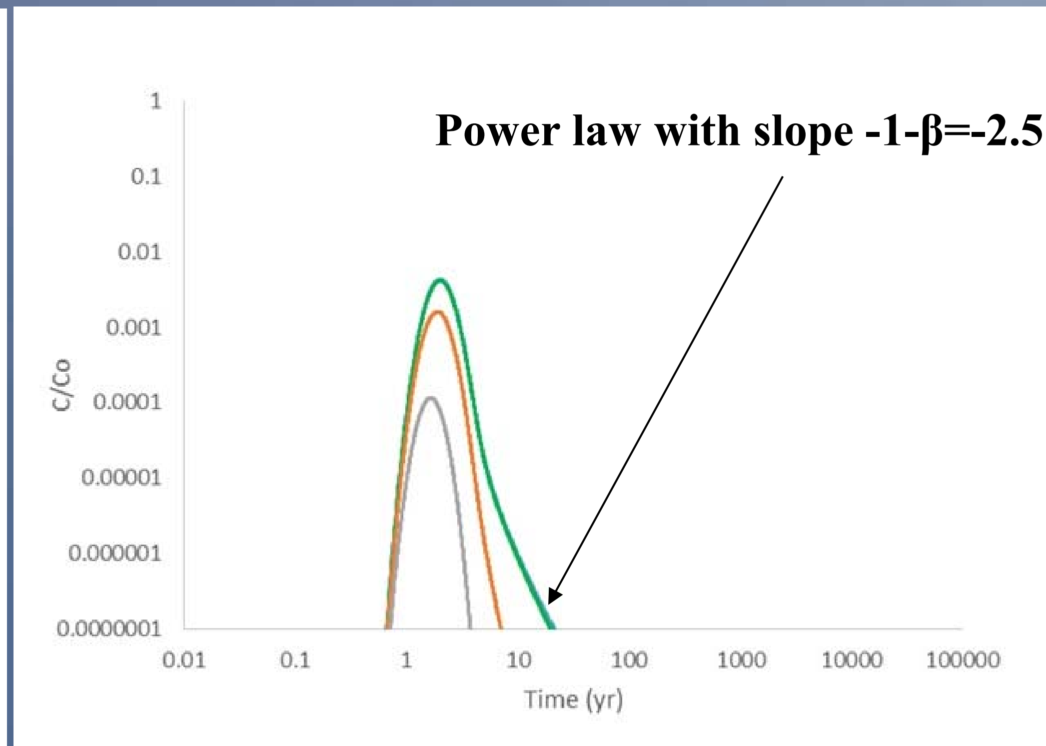
Heterogeneous Advection: Pulse Source with β = 1.5 ($\sigma^2_{\ln K}$=8), v=180 m/yr, D=900 m/yr^2, and First-Order Reaction

Plume spatial profile



Solid: No reaction
Dashed: Reaction: (**k=0.5 y^{-1}**)

Plume breakthrough curve (x=200 m)



Various degradation rates
(**k=0, 0.01, 0.5, 2 yr^{-1}**)

1) "Tear drop" shape of non-Fickian spreading observed in spatial profile
2) May appear Fickian in breakthrough curve (reaction cuts off power law behavior)

Burnell et al. (2017)

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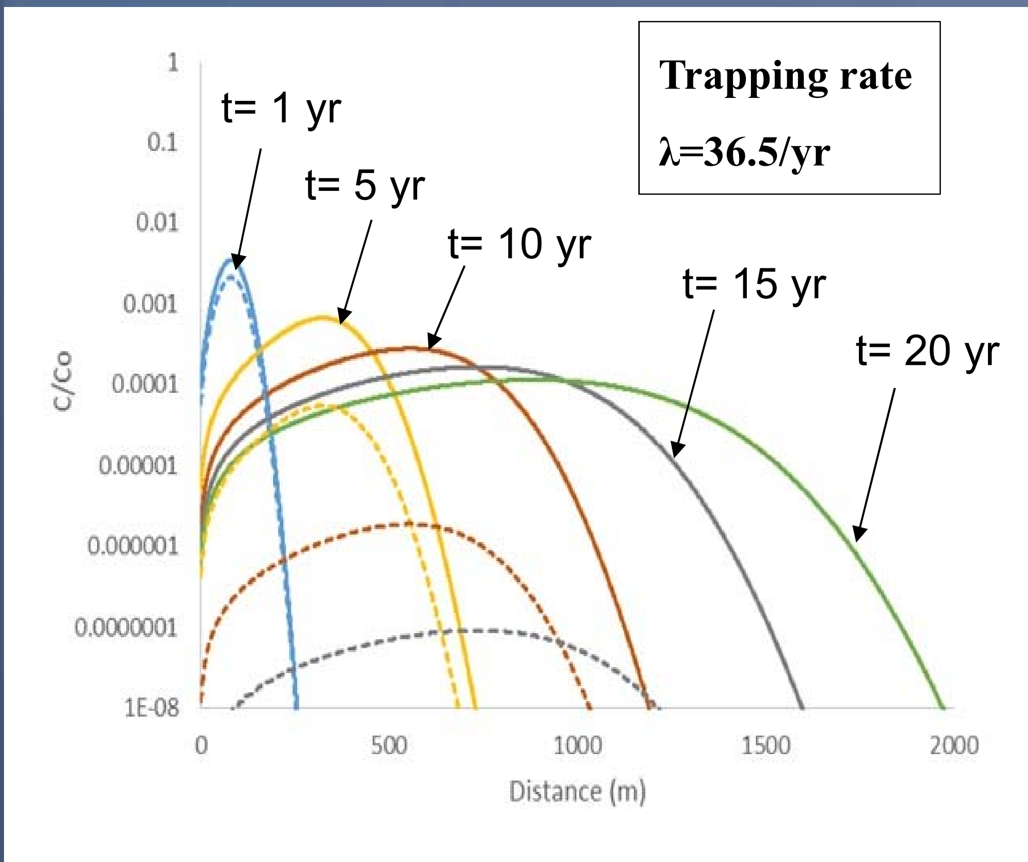
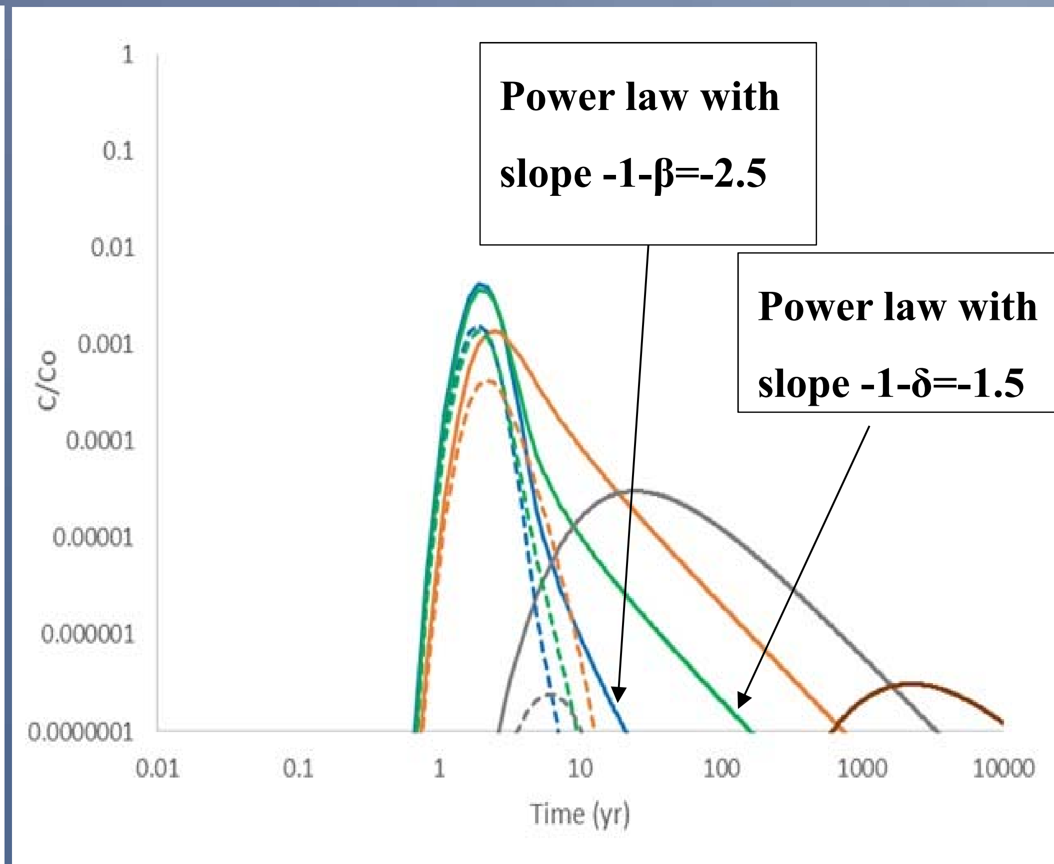
Analytical Solution for Pulse Source: Heterogeneous Advection (β = 1.5), Matrix Diffusion (δ=0.5), and First-Order Reaction

Plume spatial profile



Plume breakthrough curve



Plume slows down because of low remobilization rates

Trapping Rates λ= 0, 3.7, 37, 370, 3700 yr^{-1}

Burnell et al. (2017)

Reaction rate k= 0.5 yr^{-1} (dashed)

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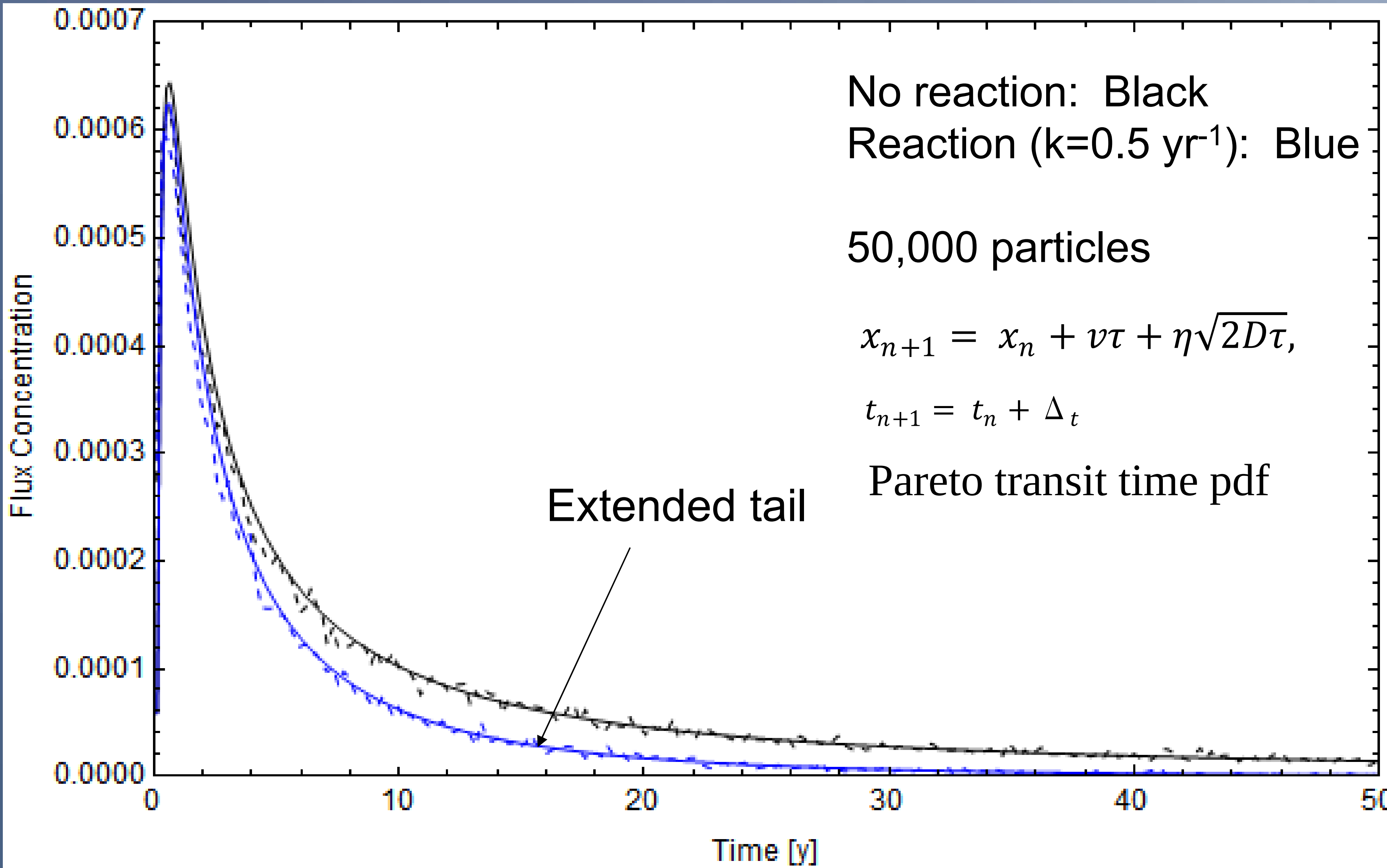
Verification of Analytical Solution with Particle Tracking (dashed) at x= 20 m (β=0.5 and λ=0 yr^{-1})



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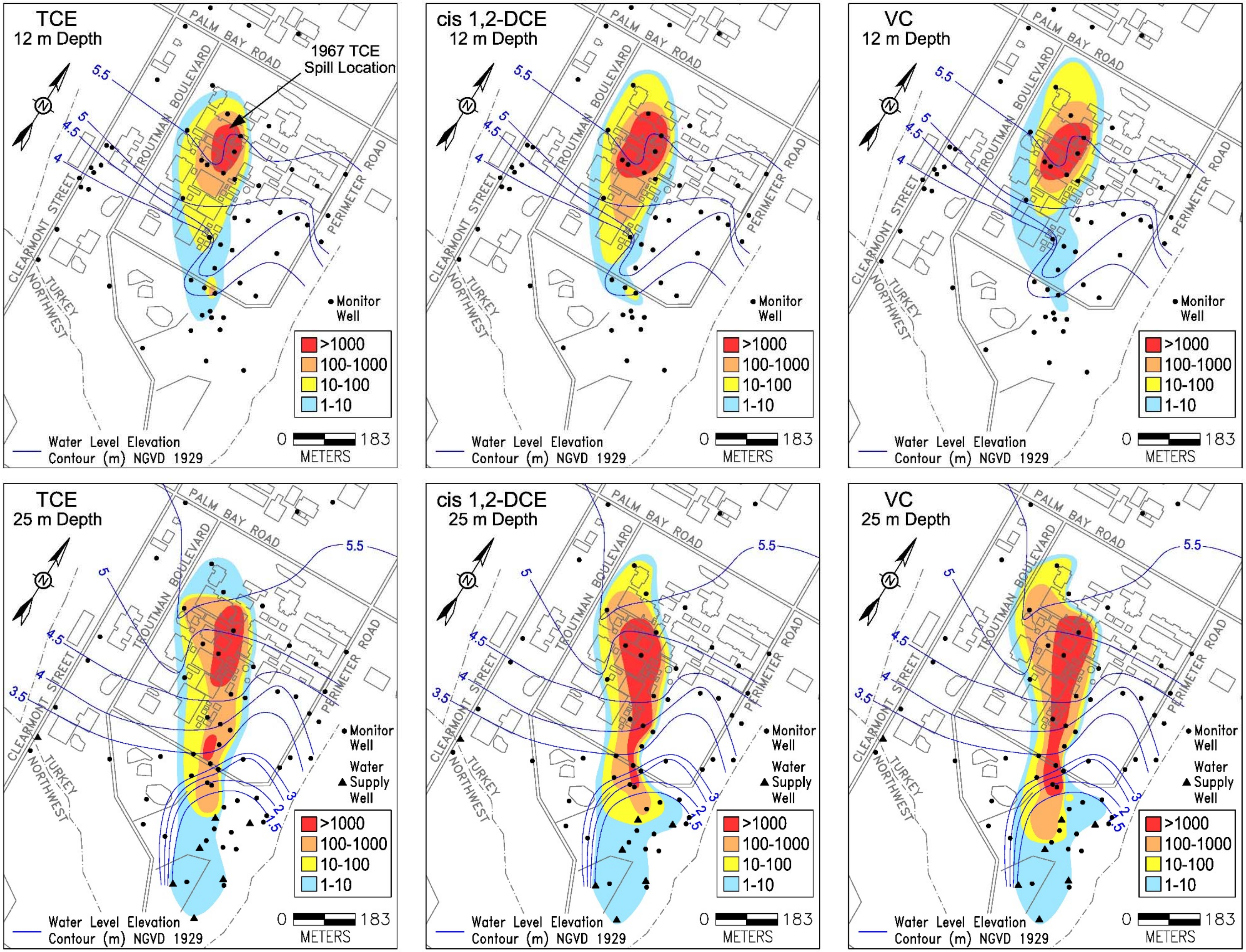
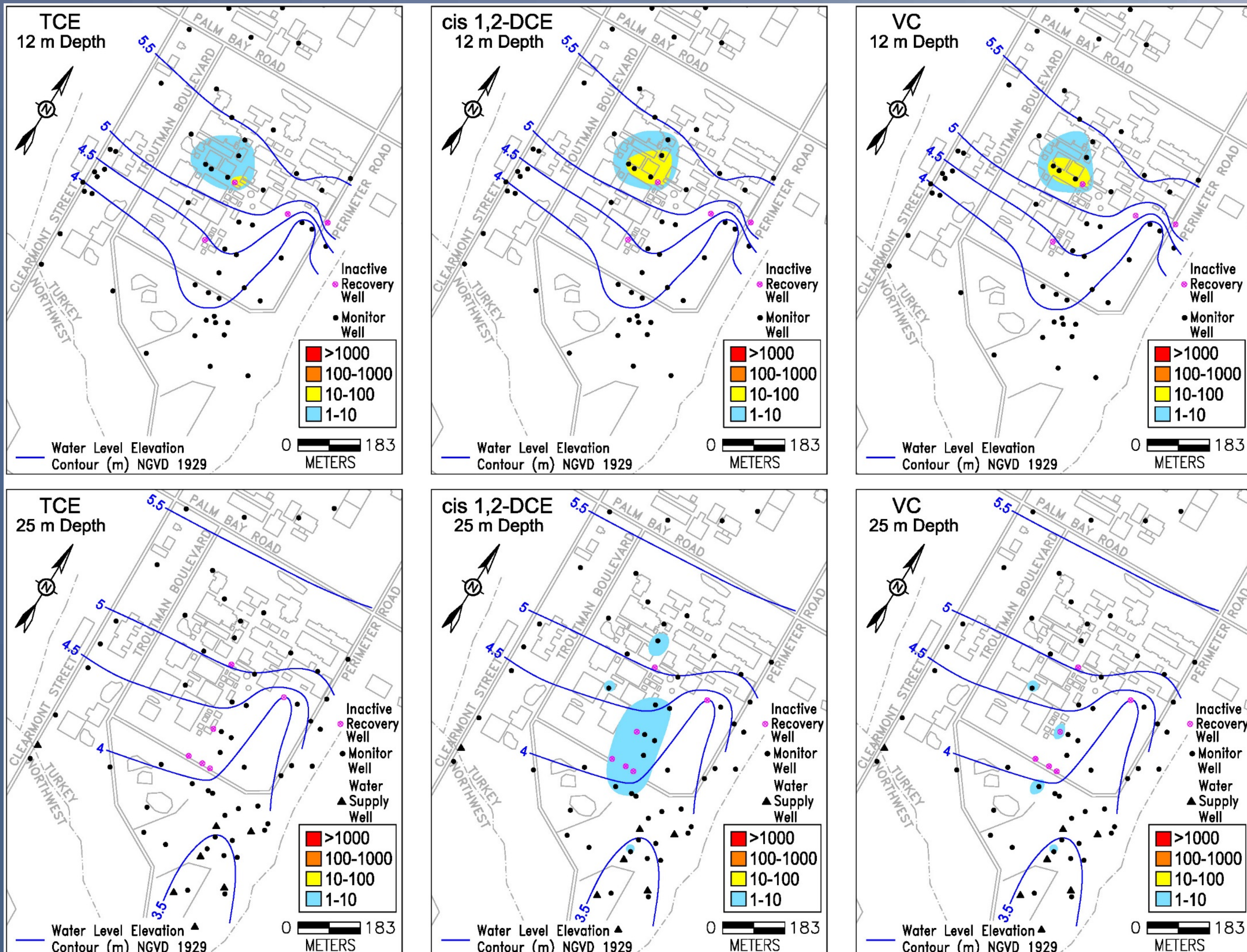
Example 2: TCE, DCE, and VC Plumes in 1984 at CERCLA Site in FL



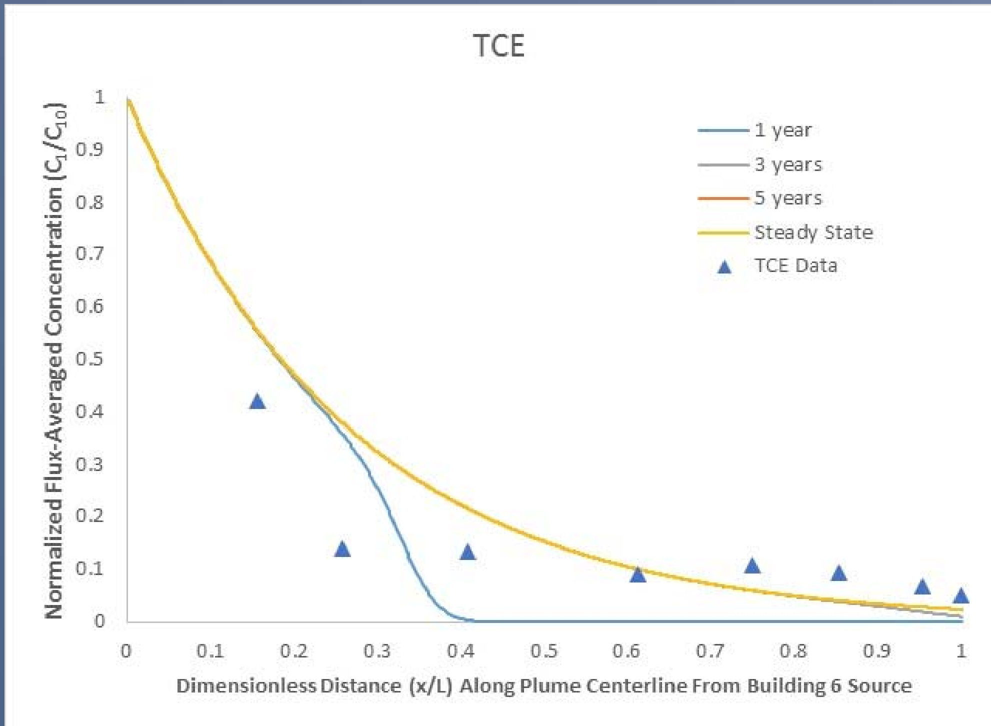
TCE, DCE, and VC Plumes in 2017 at CERCLA Site in FL

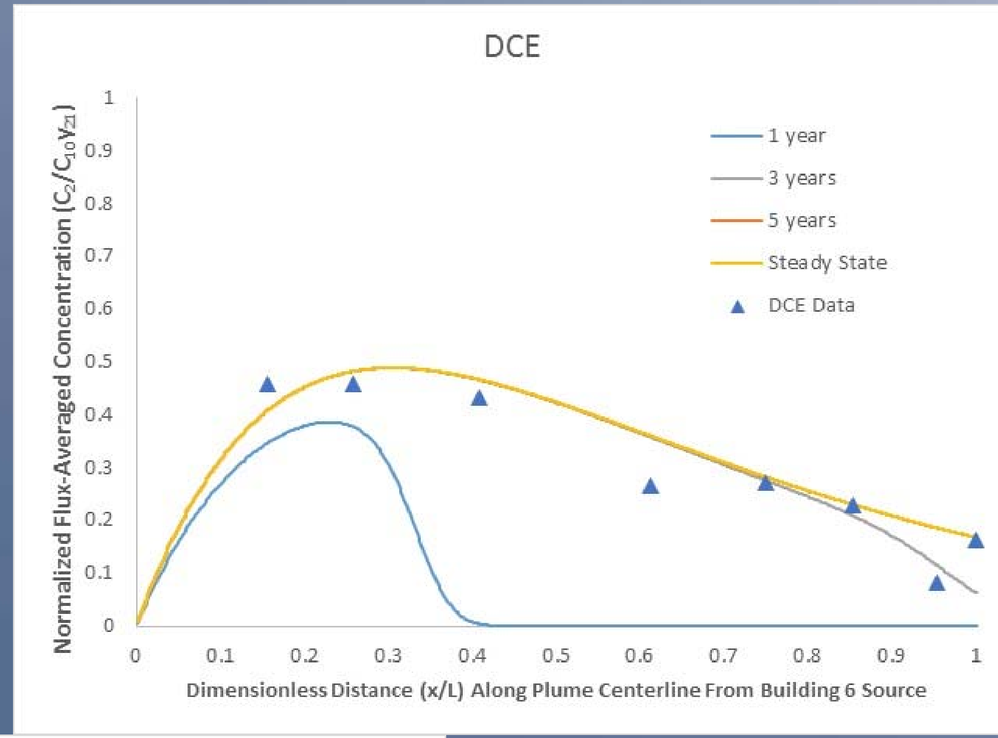


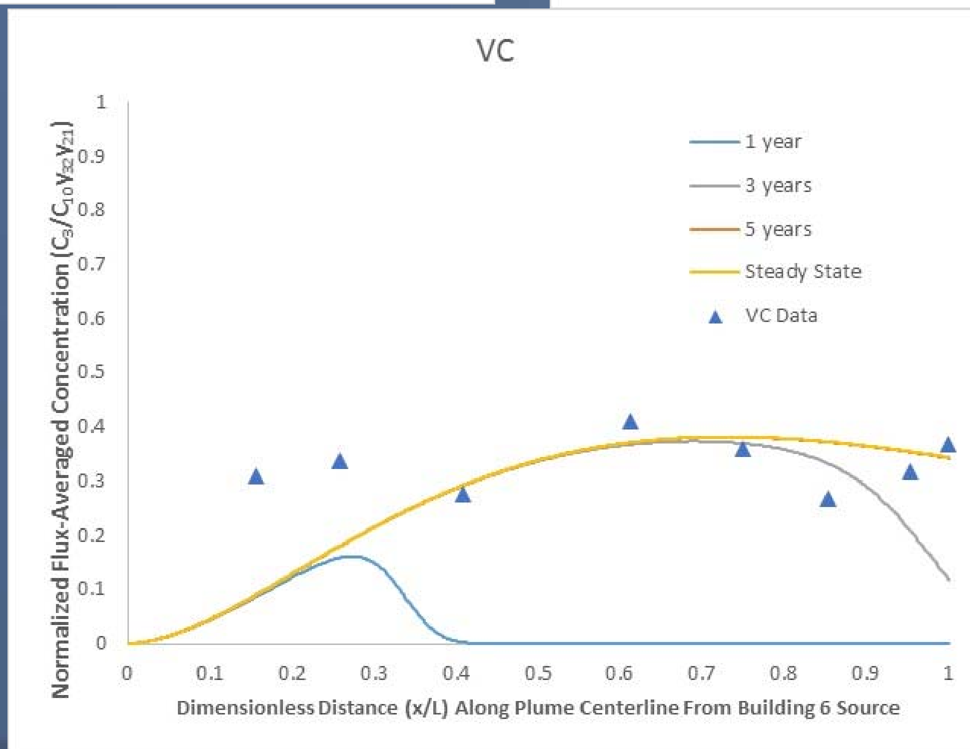
Extended ADE (CTRW) Model Parameters, CERCLA Site, Palm Bay, FL

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
<u>Heterogeneous Advection Time pdf:</u> $\psi(\mathrm{t}) \cong \frac{\tau^\beta}{t^{1+\beta}}$	
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 $\sigma^2_{\ln K} = 3.4$	0.1 day
Power Law Exponent (β) for degree of heterogeneity using <u>advection travel pdf:</u> $\psi(\mathrm{t}) \cong \frac{\tau^\beta}{t^{1+\beta}}$ (Edery et al. 2014; Burnell et al. 2018)	$\beta = 2.07(\sigma^2_{\ln K})^{-0.143}$ $=1.74$
<u>Back-diffusion Time pdf:</u> $p_{im}(\mathrm{t}) \cong \frac{\tau^\delta_{im}}{t^{1+\delta}}$	
Diffusive Trapping rate $\lambda = \frac{N}{\tau}$ where N=average # of immobile zones over K correlation length ℓ	$\lambda=0.08\ yr^{-1}$
Power Law Exponent (δ) for degree of immobile zone heterogeneity	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	5 yr
Retardation Factors (R_1,R_2, and R_3)	1.0
Parent Rate Constant (k_1) $\mathrm{k} \sim \frac{N'}{\tau}$ (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







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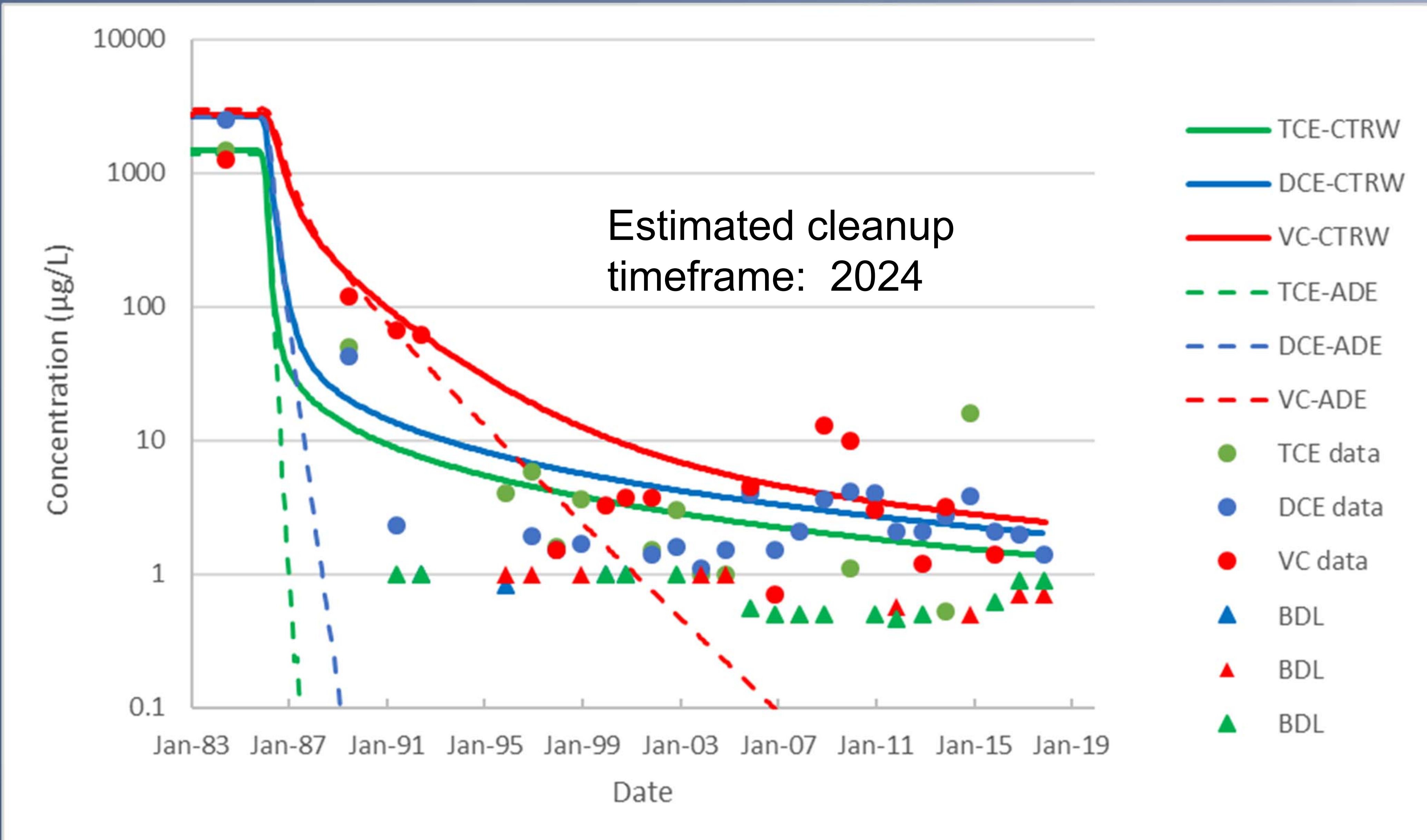
Match of Transient Model to TCE, cis 1,2 DCE, and VC Data at GS-35D (300 ft downgradient from source)



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IV. Summary and Conclusions

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

- Many studies show that standard ADE is scale dependent and does not capture observed long tails in breakthrough curves (leads to under-predicted cleanup timeframe)

Better models are available!

- Extended-ADE (CTRW) model: 1) practical tool for heterogeneous advection, reaction, and back-diffusion; 2) parsimonious (minimal parameters) with success in many experiments; 3) natural extension of ADE that upscales pore-scale processes; 4) yields simple analytical solutions (Burnell et al. 2017) for cost-effective modeling of MNA cleanup timeframes; 5) rapid computational time vs. Monte Carlo approach

- For complex flow fields and reactions, CTRW numerical approach can be applied through integration with MODFLOW

Acknowledgements

- Brian Berkowitz Weizmann Institute of Science
- Scott Hansen Los Alamos National Laboratory
- Leonard Konikow USGS (CTRW integration with MODFLOW)
- Jeffrey Yang USEPA

Recent Papers

1) 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.

2) Burnell, Xu, Hansen, Sims, and Faust, 2018. Practical Modeling Framework for Non-Fickian Transport and Multi-Species Sequential First-Order Reaction, *Groundwater*, Accepted, July issue.

Questions

Dan.Burnell@Tetratech.com

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