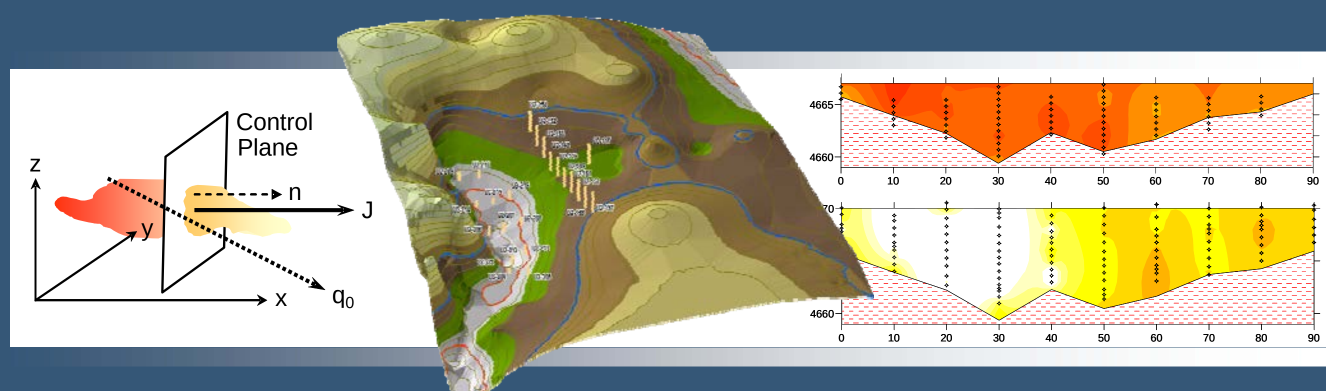
Triad Conference – June 10, 2008

Flux-Based DNAPL Site Assessment & Remediation: Overview of Concepts

Suresh Rao, School of Civil Engineering, Purdue University



Office of Research and Development
National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, Ada, Oklahoma

Without Whom this Wouldn’t be Possible!

- Nandita Basu & Irene Poyer, Purdue University
- Michael Annable, Kirk Hatfield & James Jawitz University of Florida
- Lynn Wood & Michael Brooks, US EPA-Ada
- Ronald Falta, Clemson University
- J. Christ, US Air Force Academy
- Linda Abriola, Tufts University
- Charles Werth, University of Illinois-Urbana/Champaign
- Greg Davis, Colin Johnston & Brad Patterson, CSIRO-Perth
- Ravi Naidu, Megh Mallavarupu & Subhas Nandy CRC-CARE & University of South Australia

DNAPL Site Investigations

A Decade^{+} of Progress

- 1995 — **Can't find it!**
- 1997
- **Can't deplete it!**
- 1999
- 2001 — **No benefit!**
- 2003
- 2005 — **Back Diffusion!**
- 2007
- 2009 — **Flux-based Assessment & Management?**

Hill AFB 1994-1996; Dover AFB 1997-1999
Rao et al. (WRR, 1997); Jawitz et al. (EST, 1998); McCray and Brusseau (EST, 1998); Falta et al. (WRR, 1999); Brooks et al. (JCH, 2004); Childs et al. (JCH, 2006)

Sages (FL) 1998; Bachman Road (MI) 2000
Jawitz et al. (EST, 2000); Mravik et al. (EST, 2003); Ramsburg et al. (EST, 2005)

Partial source removal debate: Theory
Sale and McWhorter (WRR, 2001); Rao and Jawitz (WRR, 2003); Parker and Park (WRR, 2004); Jawitz et al. (WRR, 2005)

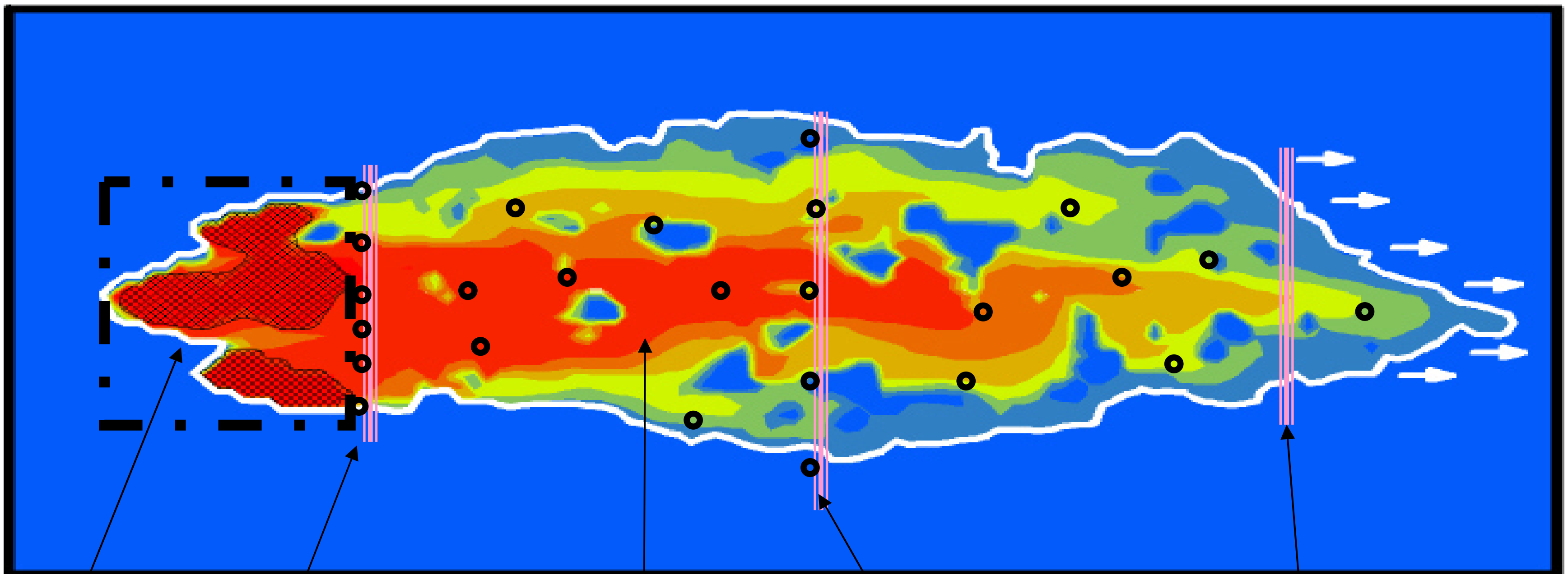
Partial source removal and flux: Lab and field data
Fure et al. (JCH, 2006); Basu et al. (WRR, 2008 in press); Basu et al. (JCH, 2008 in press); Kaye et al. (JCH, 2008 in press); Chen and Jawitz (EST, in review 2007); Brooks et al. (In review, JCH, 2007)

Frequently Asked Questions

- How much data needed before remediation?
- What types of data best serve CSM & design?
- Are high costs justified in terms of reduced uncertainty?
- What are the short-term benefits of source clean up?
- What is the likely plume response to source clean up?
- How to select target (interim) endpoints?
- How to determine long-term stewardship needs?
- Is there a simplified modeling & decision framework?
- How does all this fit into the TRIAD framework?

DNAPL Site Monitoring:

Enhancing Archived Site Data



Source Mass
M_0 and M_{now}

Source Control Plane
$M_d(t)$

Plume Mass (Parent + Products)
$M_p(t)$ & $\lambda(t)$

Plume Control Plane

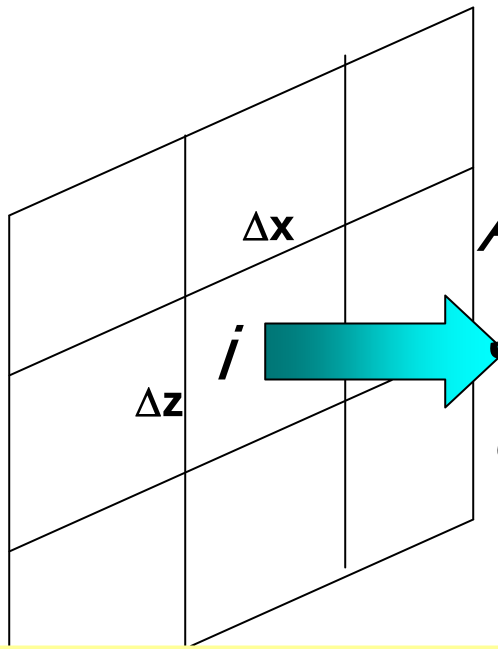
Pump & Treat Wells or Interception Trench or Stream etc.
$E(t)$

Contaminant Fluxes & Mass Discharge at Control Planes

$$M_d = \Sigma J_i A_i$$

- J_i = Local mass flux (ML^2T^{-1})
- q_i = Local Darcy flux (LT^{-1})
- C_i = Local conc. (ML^{-3})
- A_i = Area of element i (L^2)
- M_d = *Source strength* (MT^{-1})
- K_s = Satd. Hyd. Cond (LT^{-1})
- j = Hydraulic gradient (-)

Control Plane (CP)



$$A_i = \Delta x \, \Delta z$$

$$J_i = q_i \, C_i$$

$$q_i = -K_s \, j$$

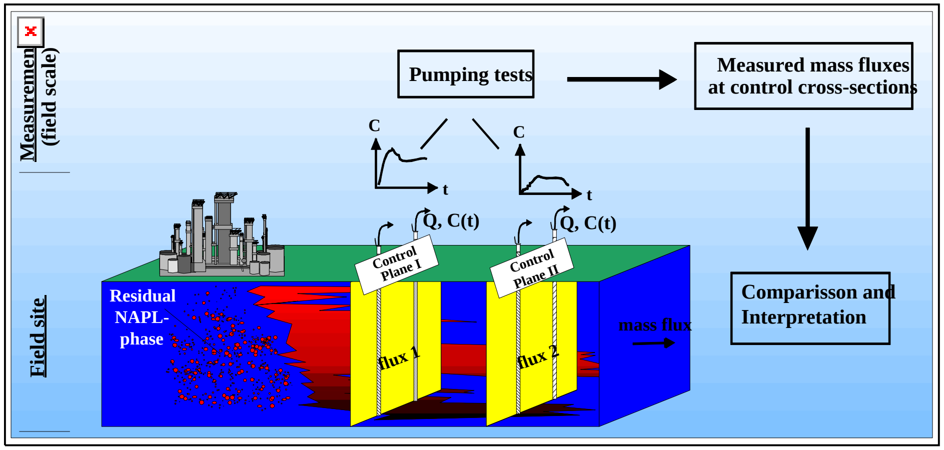
Control plane area should be just large enough to completely inscribe the dissolved plume width

Cleanup to the Extent Necessary (CUTEN or Q10)

- Source Strength
- Source Longevity
- Degradation Rate
- Receptor Loading

Key measures for:
Site characterization
Remediation design &
Performance Assessment

$$M_{CP(2)} = M_{CP(1)} \exp\left(-\frac{\lambda x}{v}\right)$$



Contaminant Mass Discharge Estimates

Site	Contaminant	(M_D; g/day)
Simpson County, NC*	MTBE	<1- 2
Vandenberg AFB, CA*	MTBE	~1-7
Port Hueneme, CA*	MTBE	150
Elizabeth City, NJ*	MTBE	4
Testfeld Sud, Germany*	BTEX	~2
	PAHs	~30
Landfill Site, Germany*	TCE	~3
Alameda Naval Station, CA*	*cis*-1,2-DCE	31
Nekkar Valley, Germany*	PCE	77
Dover AFB, DE*	total chlorinated	280
St. Joseph, MI*	total ethenes	425
Hill AFB, UT	TCE	104
Manufacturing Plant, US	TCE	365
Ft Lewis, US	total ethenes	~850
Site-1, Australia	total ethenes	104
Site-2, Australia	TCE	<10

* adapted from: Einarson & Mackay (2001); *ES&T*, 35(3):67A-73A

Characterization of DNAPL Sources

What We Need

Source Longevity (Source Strength Function)

- present source mass
- source depletion behavior

Source & Flux Distribution (Source Architecture)

- identification of hotspots, targeted treatment

What We Have

Temporal Data

Concentration in select source zone monitoring wells over time

Spatial Data

1. Mass discharge at the source control plane at a point in time
2. Plume Mass

Source Depletion

$$C_s(t) = \frac{C_0}{M_0^{\Gamma}} \left\{ \frac{(\Gamma - 1) V_d A C_0}{M_0^{\Gamma}} t + M_0^{1-\Gamma} \right\}^{\frac{\Gamma}{1-\Gamma}}$$

Falta et al. 2005a

where,

$C_s(t)$ and C_0 =

flux-avg. conc. at source CP at time = t; and t=0

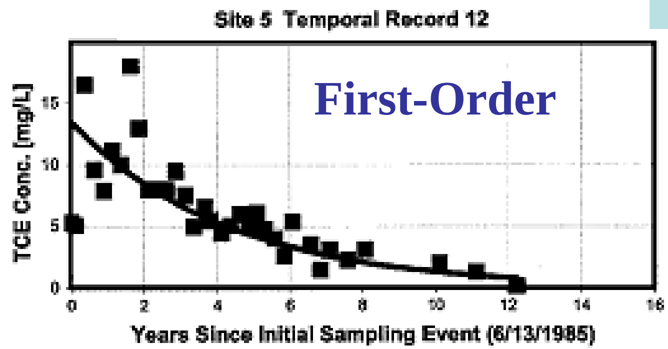
M_0 = initial source mass

V_d = Darcy flux

A = Source CP Area

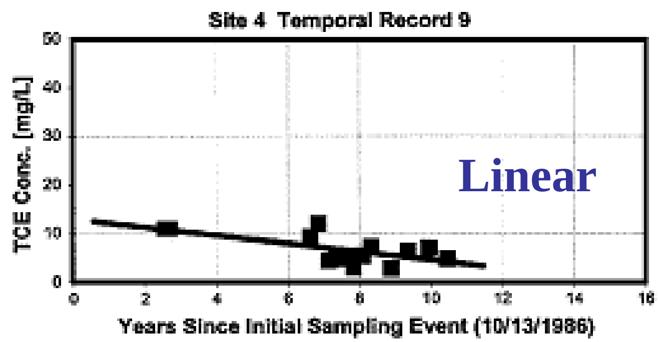
Γ = empirical constant

Simple Cases



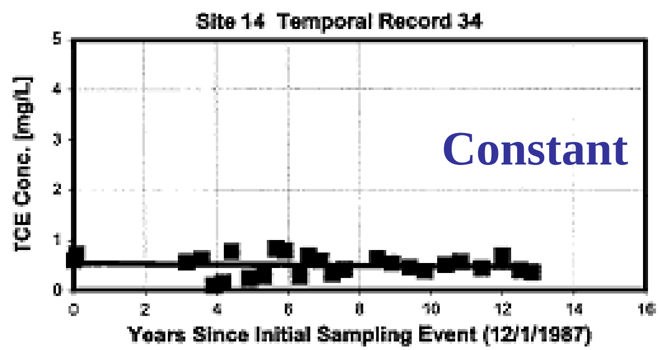
Γ=1

$$C_s(t) = C_0 e^{-\frac{V_d A C_0}{M_0} t}$$



Γ = 0.5

$$C_s(t) = C_0 - \frac{V_d A C_0^2}{2M_0} t$$



Γ = 0

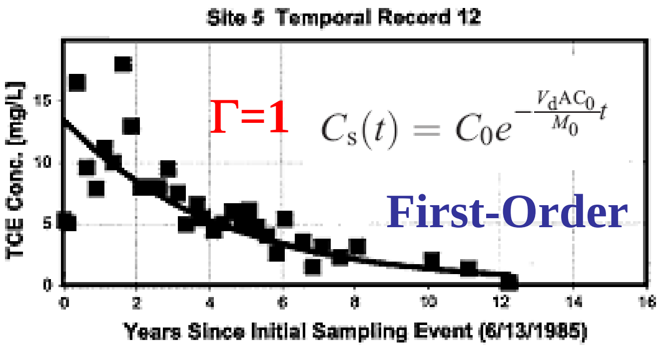
$$C_s(t) = C_0$$

Newell et al., 2006, *Jour. Env. Eng.*
Suarez et al., 2004, *Remediation.*

PURDUE UNIVERSITY

Source Mass Estimation

Fit monitoring well data to standard functions to estimate a value of Γ



Method A: Requires only MW data

1. **Monitoring well data over time fitted with an exponential to estimate k.**
2. **Now,**

$$M_{t=a} = V_d A C_{t=a} / k$$

3. **Here, a = time from which sampling data available**
4. **Thus:**

$$M_{t=now} = M_{t=a} \exp\left(-kt_d\right)$$

Method B: Requires mass discharge (M_D) and plume mass (M_P)

$$M_D(t) = M_{D,0} \exp\left(-\frac{M_{D,0}}{M_0} t\right)$$

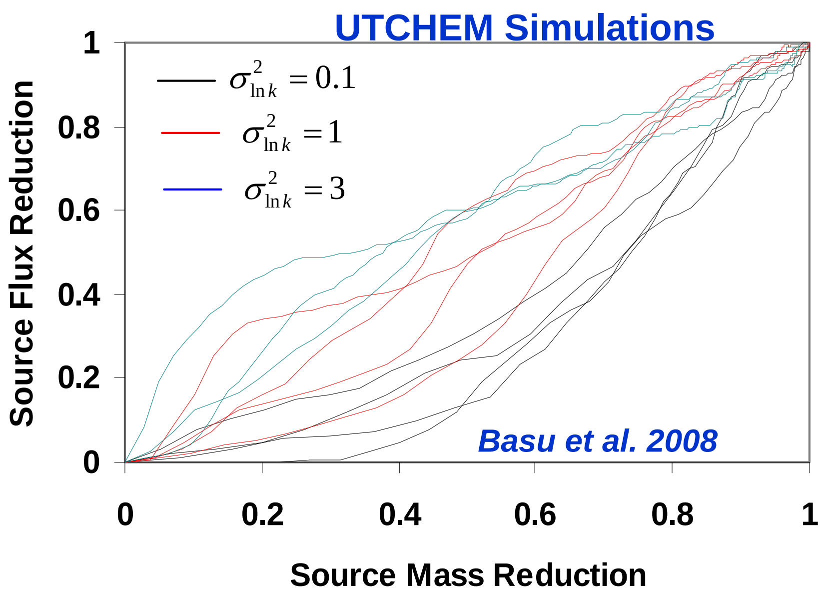
$$M_P(t) = \int_0^t M_{D,0} \exp\left(-\frac{M_{D,0}}{M_0} t\right) dt$$

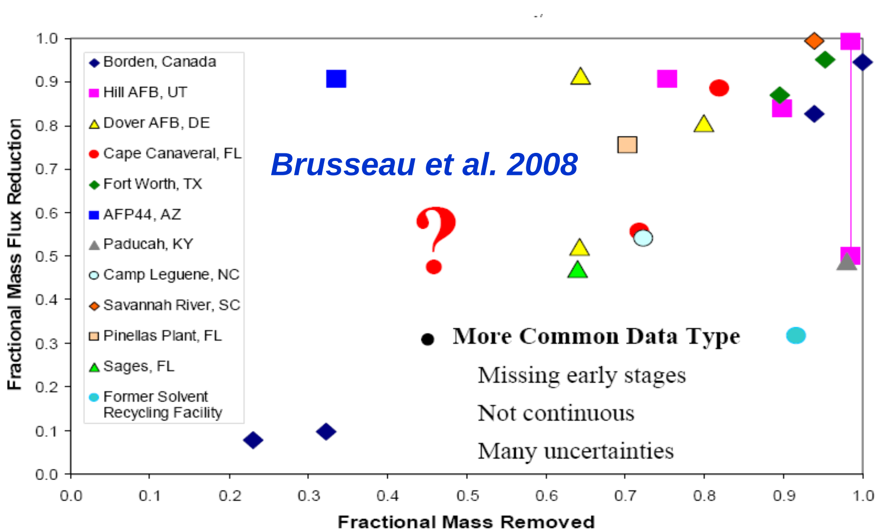
Two equations and two unknowns – solve for $M_{D,0}$ and M_0

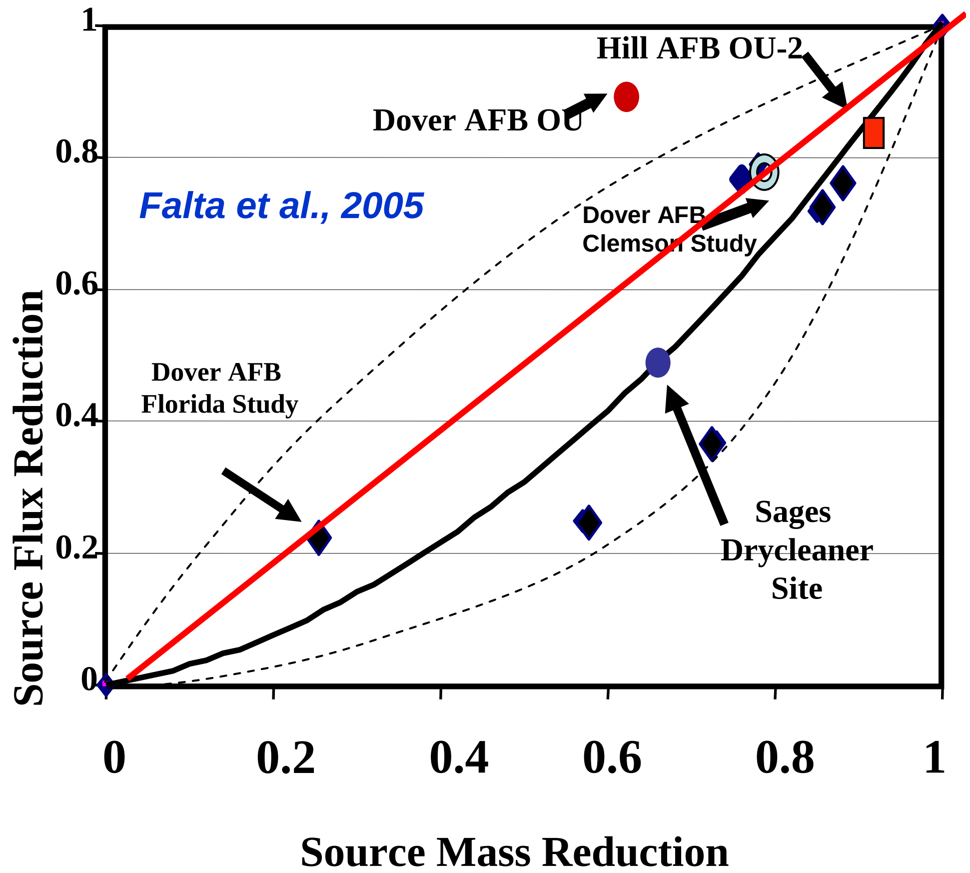
Estimate present source mass using

$$M_{t=now} = M_0 \exp\left(-\frac{M_{D,0}}{M_0} t\right)$$

Source Mass & Source Strength







Exponent Γ is a function of DNAPL source architecture, hydrogeologic heterogeneity & correlation between the two.

PURDUE UNIVERSITY

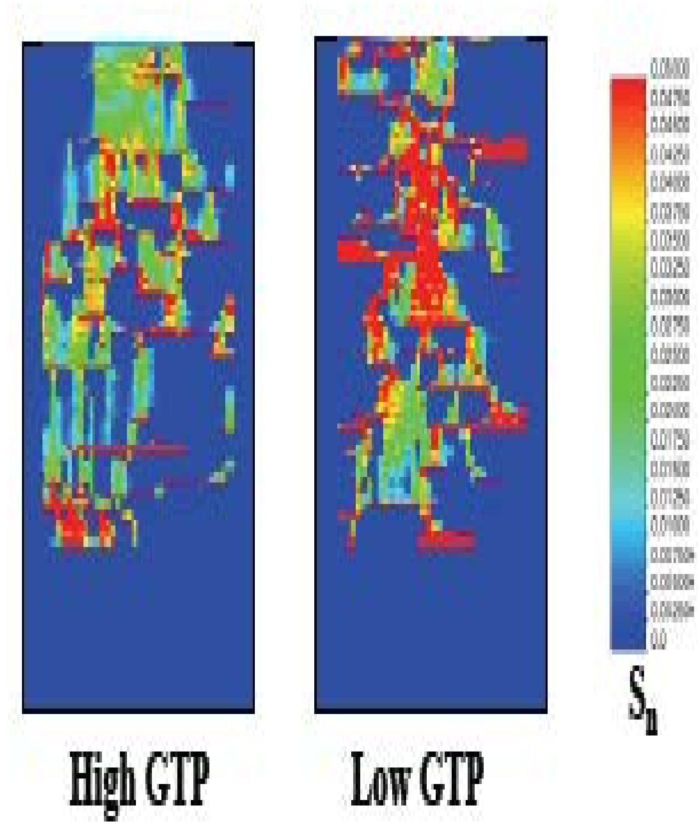
Source Zone Architecture

Eulerian Approach

- Ganglia to Pool mass ratio (GTP)

(Christ el al., EHP 2005)

  - Ganglia: regions of residual NAPL saturation
  - Pool: regions of DNAPL saturation higher than maximum residual DNAPL saturation

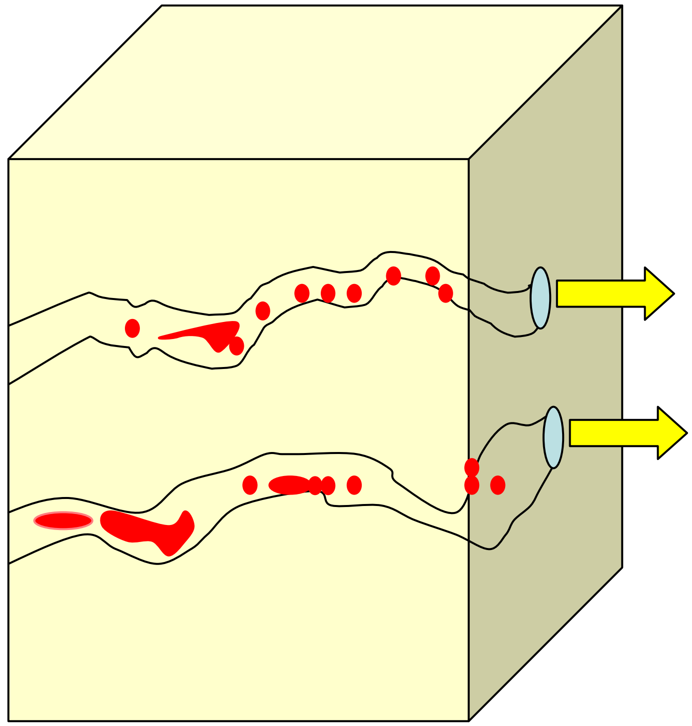


Source Zone Architecture

Lagrangian Approach

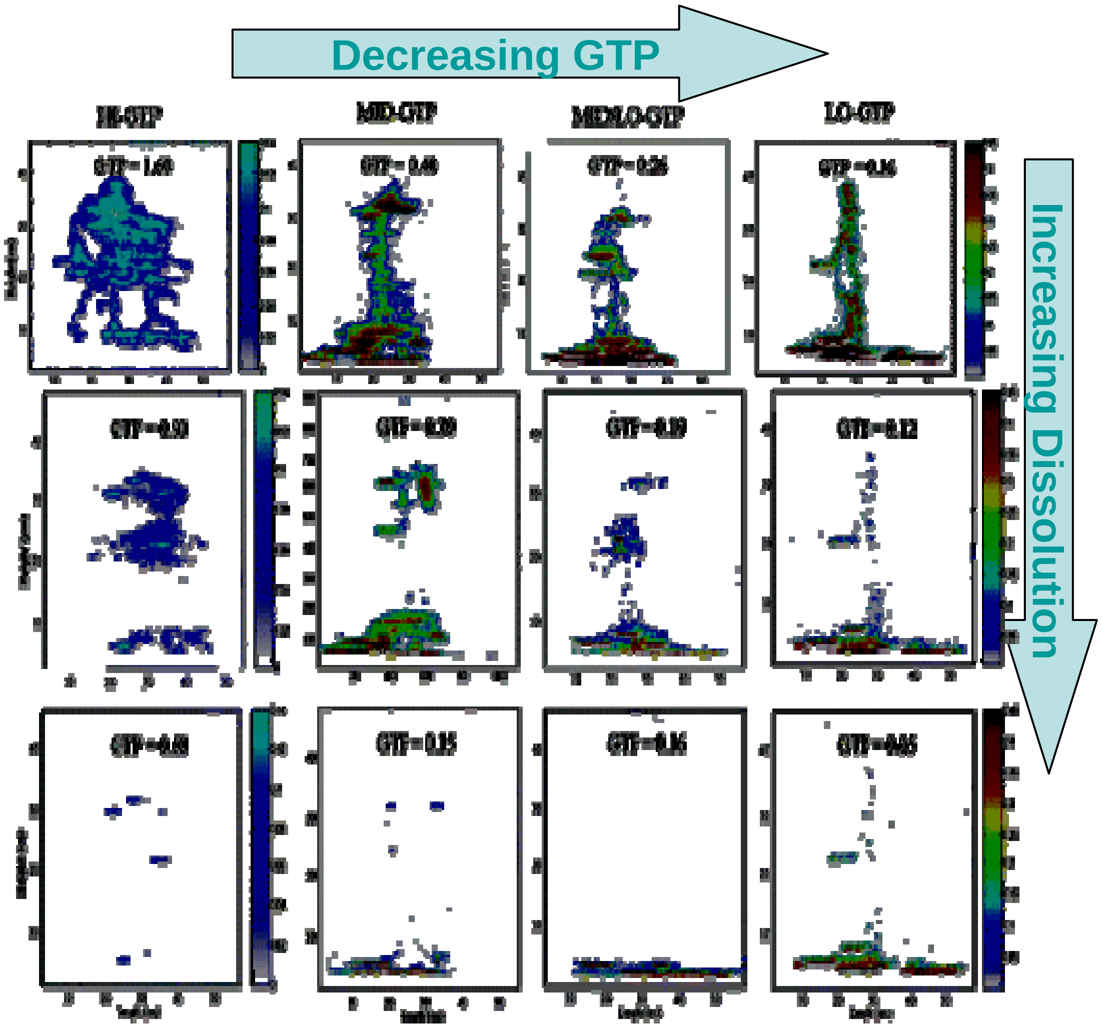
Reactive Travel Times

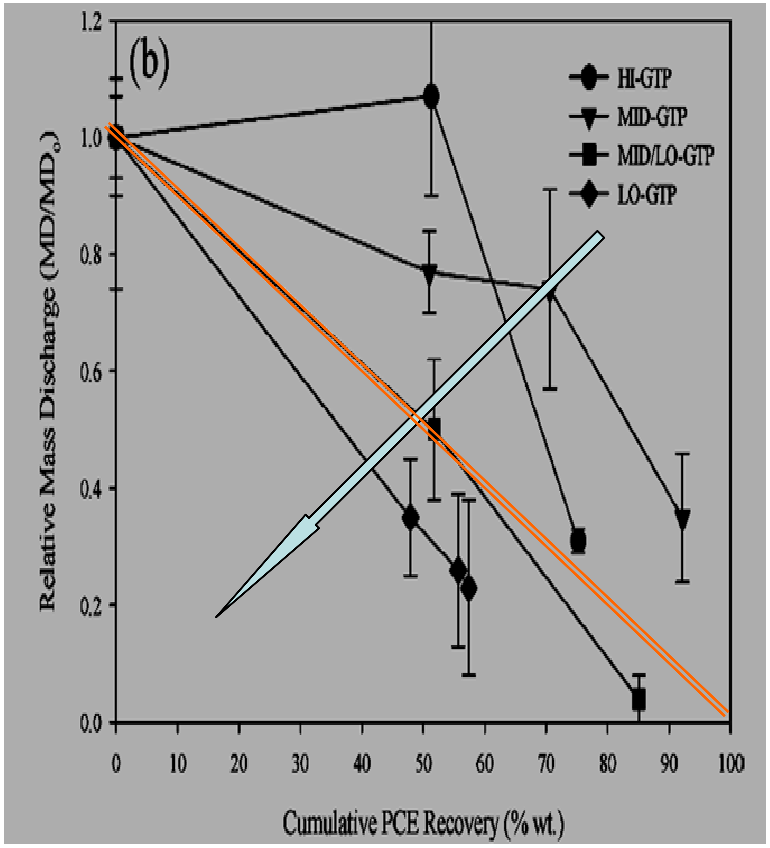
- Source zone conceptualized as a network of stream tubes, each characterized by velocity (travel time) and NAPL saturation.
- The domain described by mean and variance of travel time and NAPL saturation distribution, measured by non-reactive and reactive tracers, respectively.
- The measured parameters are used to predict change in the mean contaminant flux in time over the source control plane



Source Depletion Dynamics:

Surfactant Flushing in 2-D Flow Chambers





Suchomel & Pennell, ES&T, 2006

Simplified Source Depletion Models

$C_f(T)$ = f (HS, DS)

$C_f(T)$ = Flux-avg. Concentration at Source Control Plane

HS = Hydrodynamic Structure

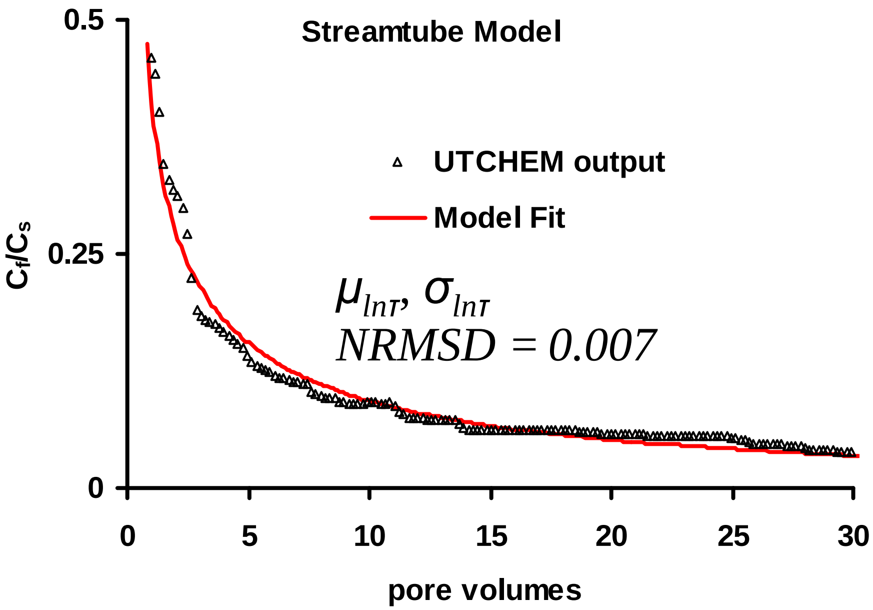
DS = DNAPL Structure

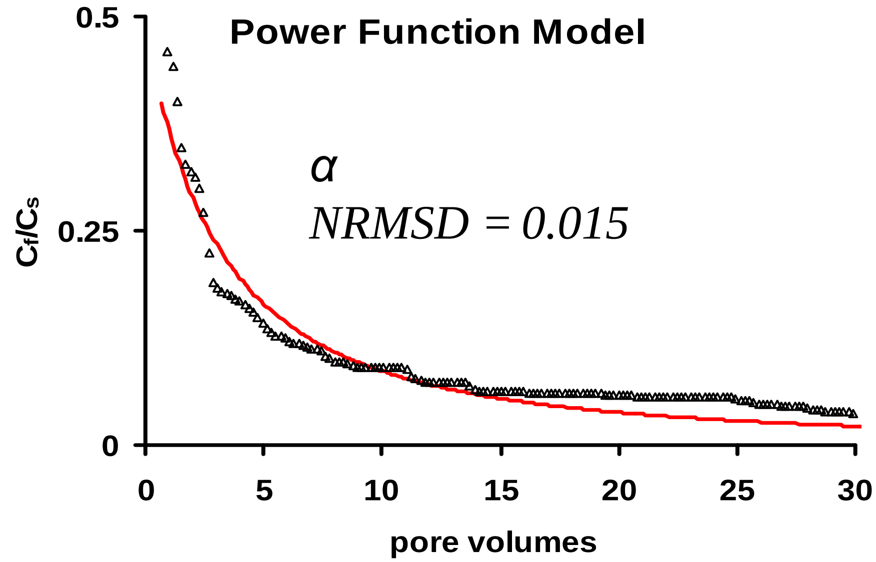
Streamtube Model (Jawitz et al. 2005)	$$\frac{C_f(T)}{f_c C_s} = \frac{1}{2} - \frac{1}{2}\operatorname{erf}\left[\frac{\ln T - \mu_{\ln\tau}}{\sigma_{\ln\tau}\sqrt{2}}\right]$$	$\mu_{ln\tau}$= Mean of Hydrodynamic Field and DNAPL Architecture $\sigma_{ln\tau}$= Variability of Hydrodynamic Field and DNAPL Architecture
Power Law Model (Zhu and Sykes 2005)	$$\frac{C_f(T)}{f_c C_s} = \left[\frac{M(T)}{M_o}\right]^{\beta}$$	M_0 – Initial Mass of NAPL β - Variability Index
Damkohler Model (Parker and Park 2005)	$$\frac{C_f(T)}{C_s} = 1 - \exp\left[-\left(\frac{\kappa_o L}{\bar{K}_s}\right)\left(\frac{M(T)}{M_o}\right)^{\beta_2}\right]$$	M_0 = Initial Mass of NAPL, κ_0 β_2 = Mass Depletion Exponent

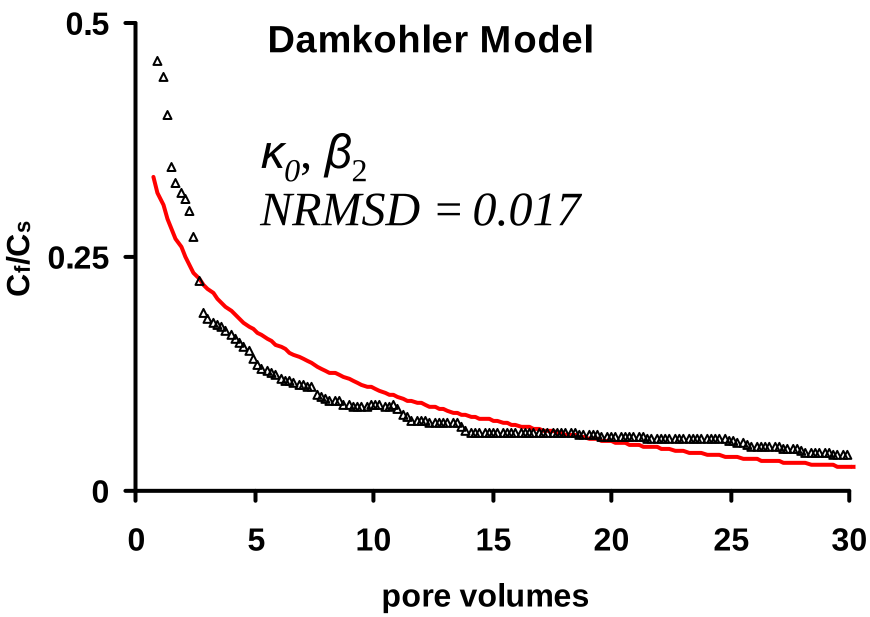
Basu et al., 2006, JCH

PURDUE UNIVERSITY

Dissolution Profile Fitted to Source Depletion Models







Conclusion

All source depletion models *fit* dissolution behavior effectively

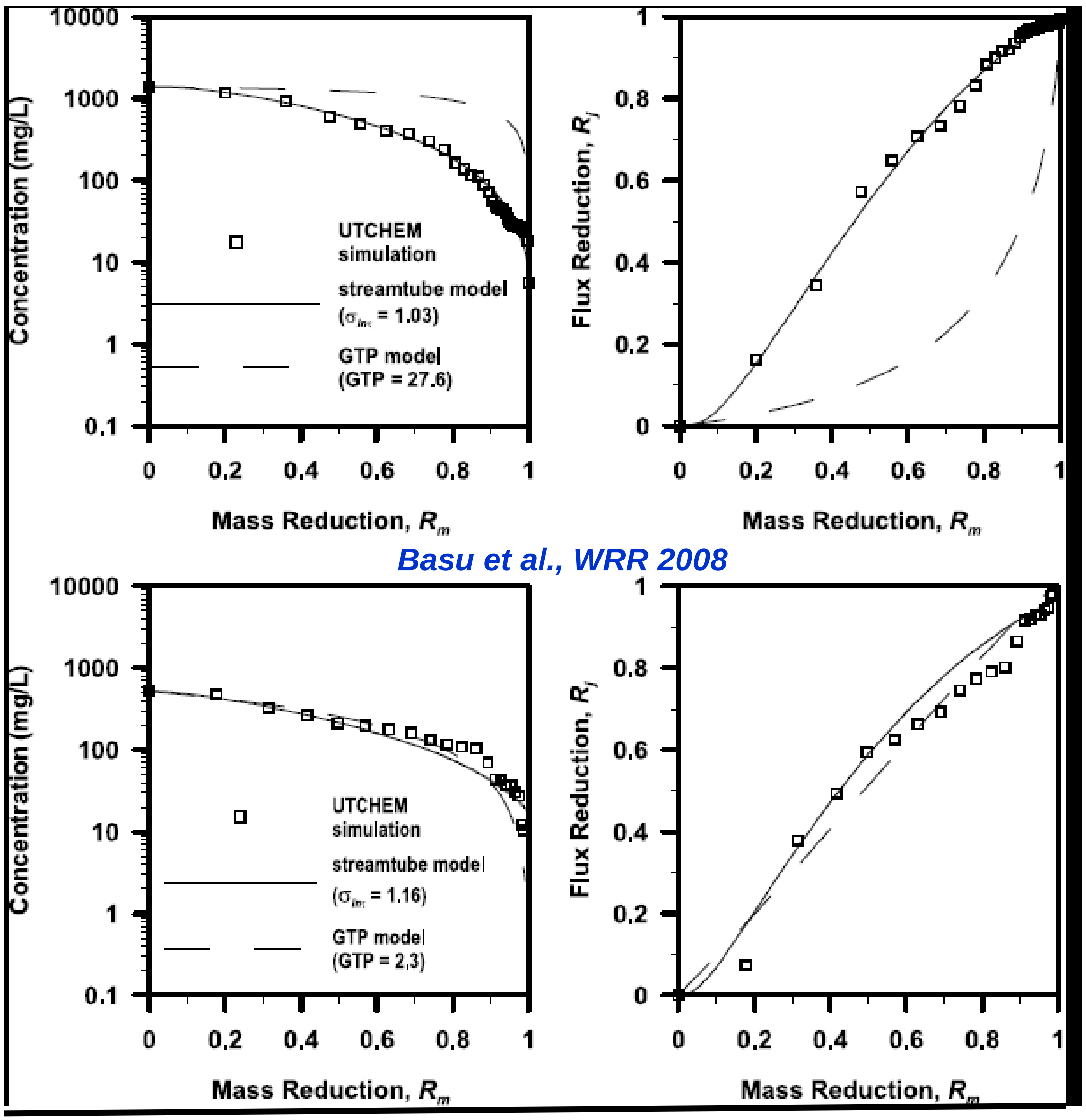
BUT, can we estimate parameters of any of these models independently and *predict* the dissolution profile *apriori*?

- YES, the streamtube model can be parameterized using tracer tests –

Basu et al., JCH, 2008

PURDUE UNIVERSITY

Predicting Source Depletion: Simplified Models

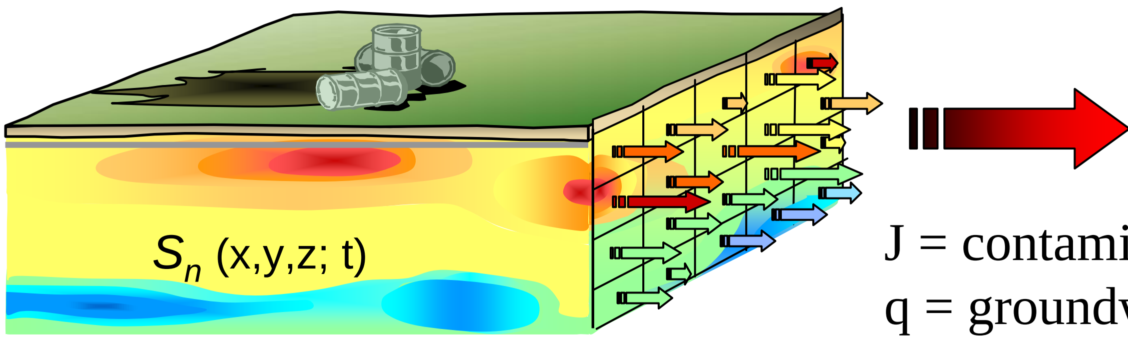


- GTP can be measured in lab. Field methods need to be developed.
- Tracer tests for calibrating stream-tube modeling demonstrated at lab & field scales.
- Eulerian vs. Lagrangian approaches, $$$!!!
- Γ=1 may be an adequate approximation??

PURDUE UNIVERSITY

Spatially Distributed vs. Integrated Parameters

Transition from local parameters (S_n, K, C) to integrated system behavior [J(g/m^2/day); M_D (g/day)]



J (y,z;t) =

q(y,z;t) C(z,y;t)

J = contaminant mass flux (g/m^2/day)
q = groundwater flux (cm/day)
C = dissolved concentration (mg/L)

M_D (g/day)= mass discharge $= \int J\,dA$

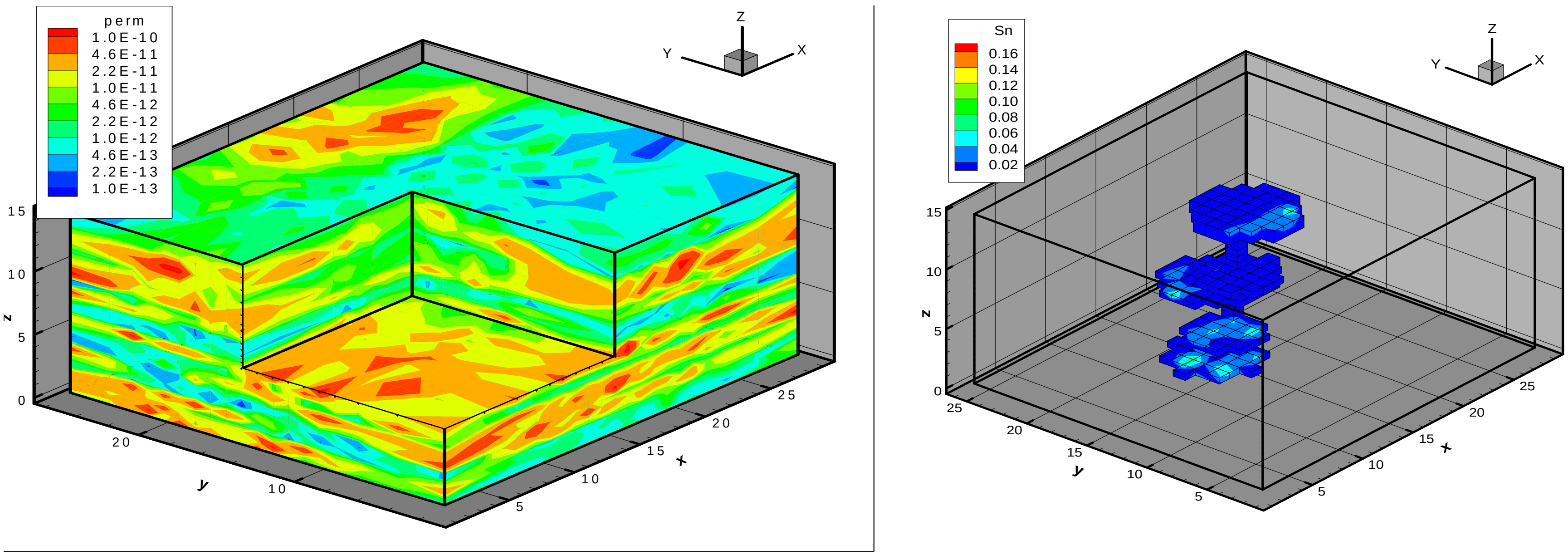
Relationship between mean values:

Total DNAPL mass [$m(t)$] & Source Strength [$M_D(t)$]

Source Mass & Flux Distributions

- How does source mass change with time?
- How does the flux distribution change?

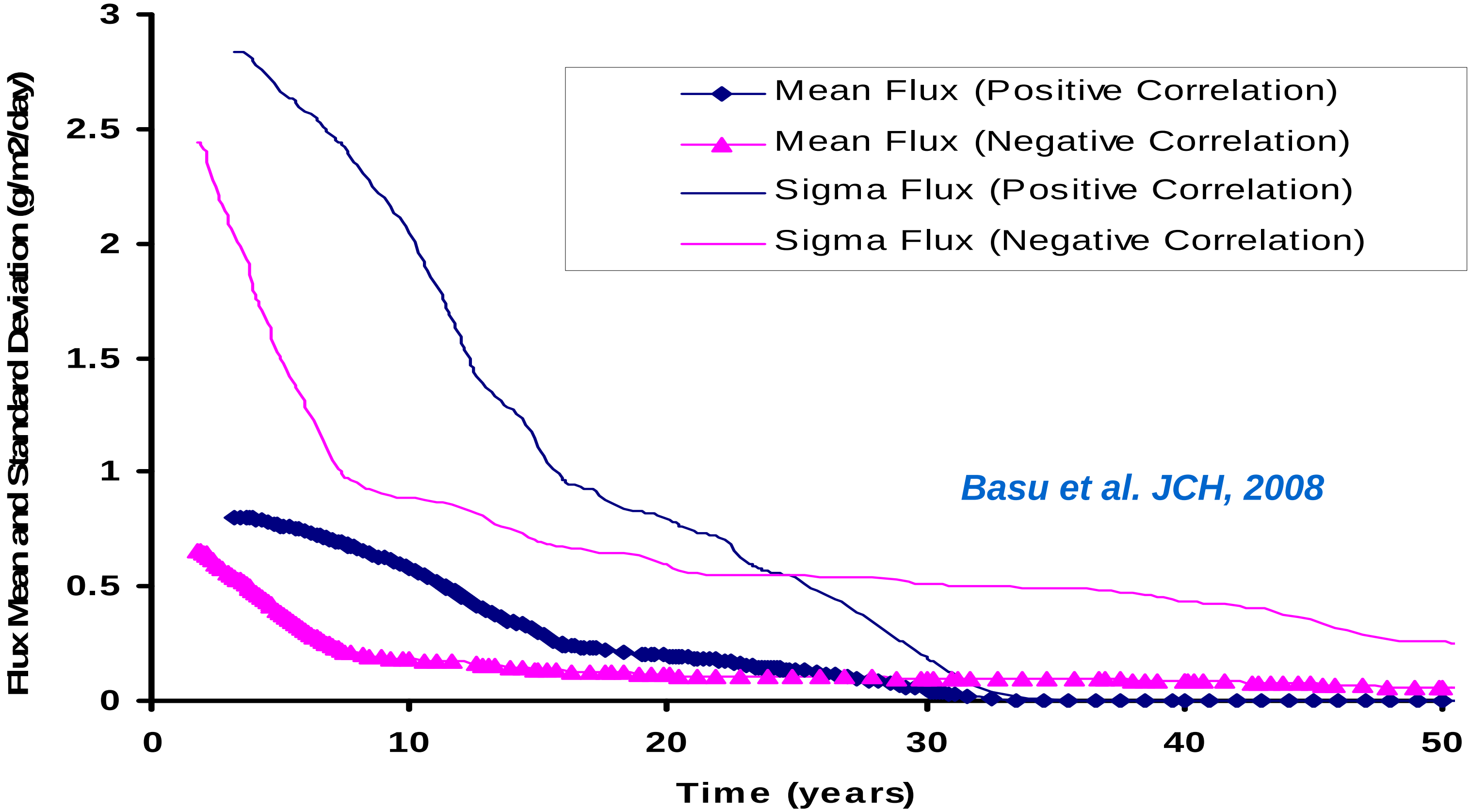
T2VOC Numerical Simulations



Basu et al. JCH, 2008

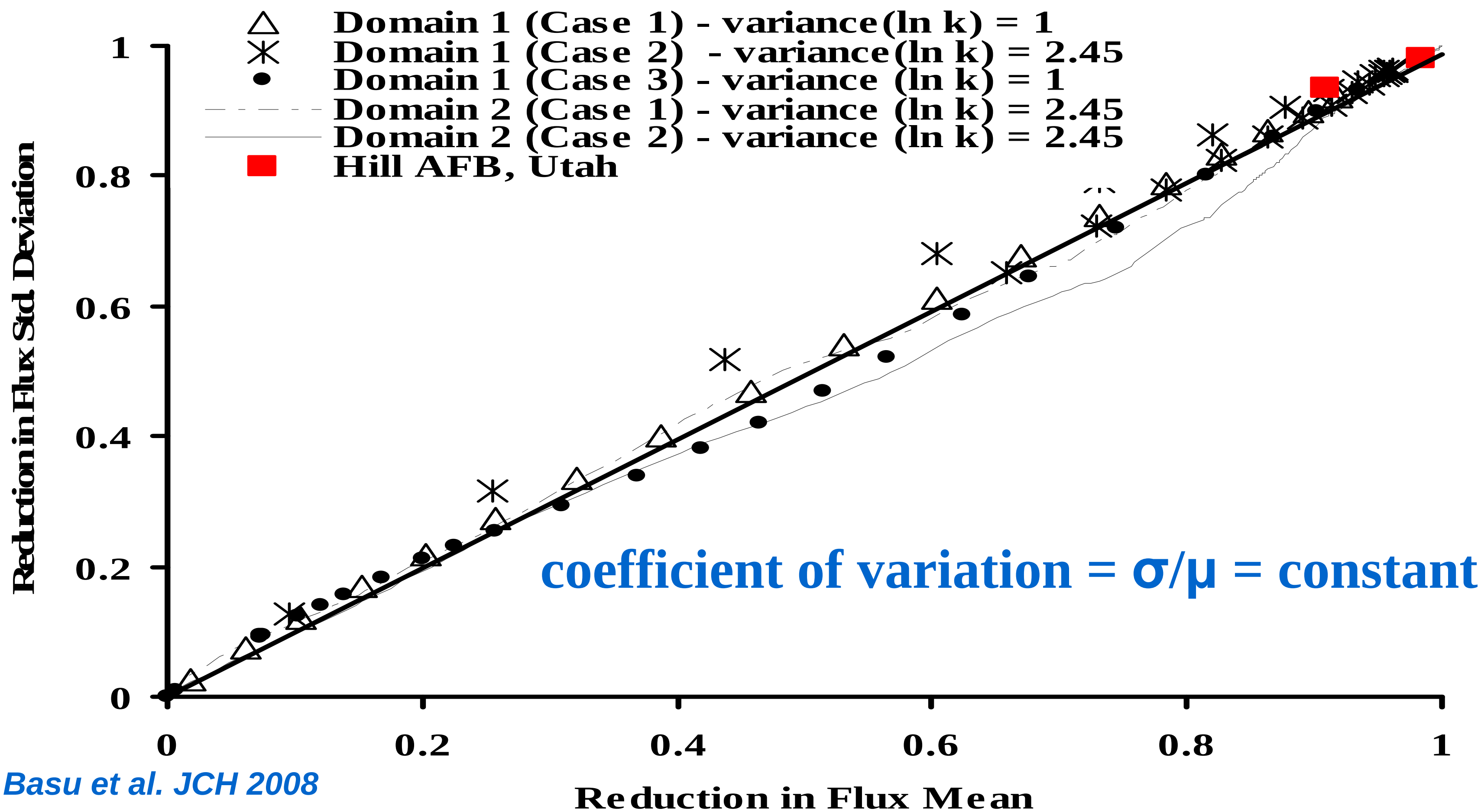
PURDUE UNIVERSITY

Flux Statistics at Source Control Plane



Both mean and standard deviation of contaminant flux distribution decrease with mass depletion from DNAPL source

Flux Statistics at Source Control Plane

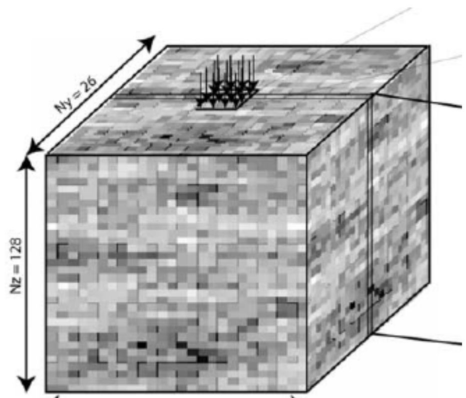


Basu et al. JCH 2008

Numerical simulations are for emplaced NAPL.

Will this be also valid for spills?

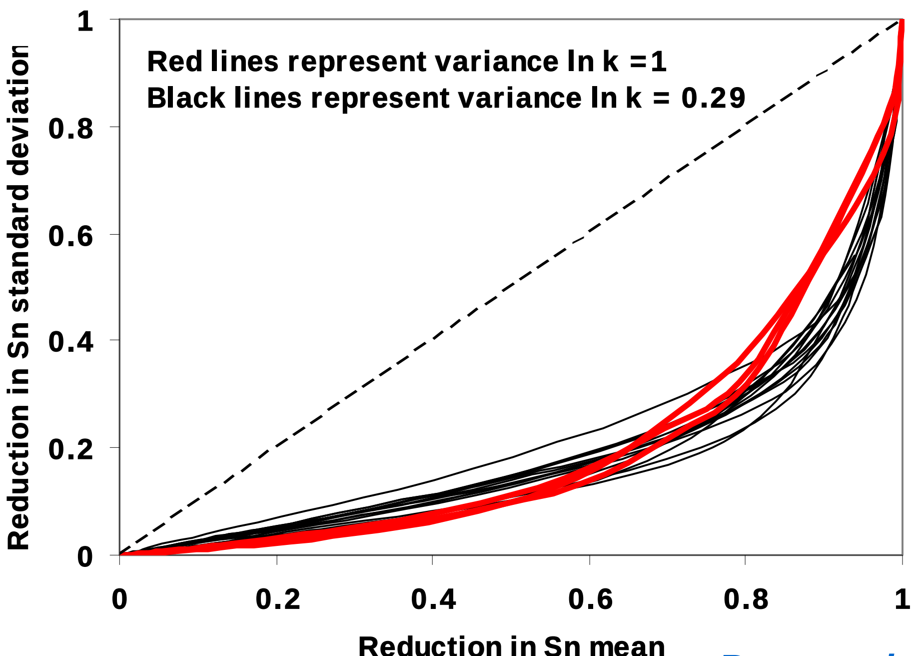
DNAPL Spill & Dissolution Simulations: Evolution of Source Architecture



Simulation data provided courtesy of:

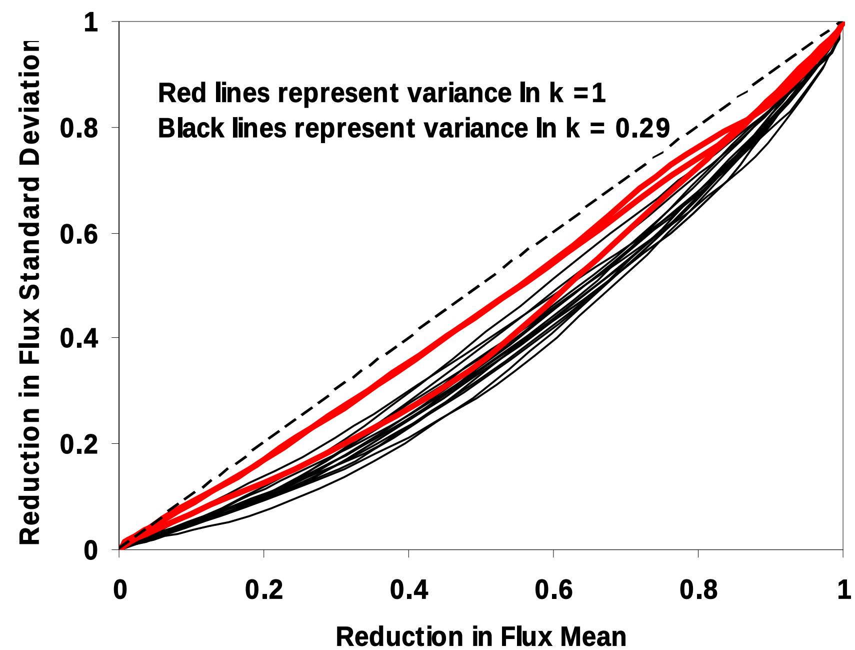
J A Christ (USAFCE) &

L M Abriola (Tufts University)

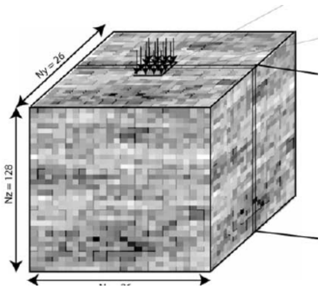


DNAPL Mass

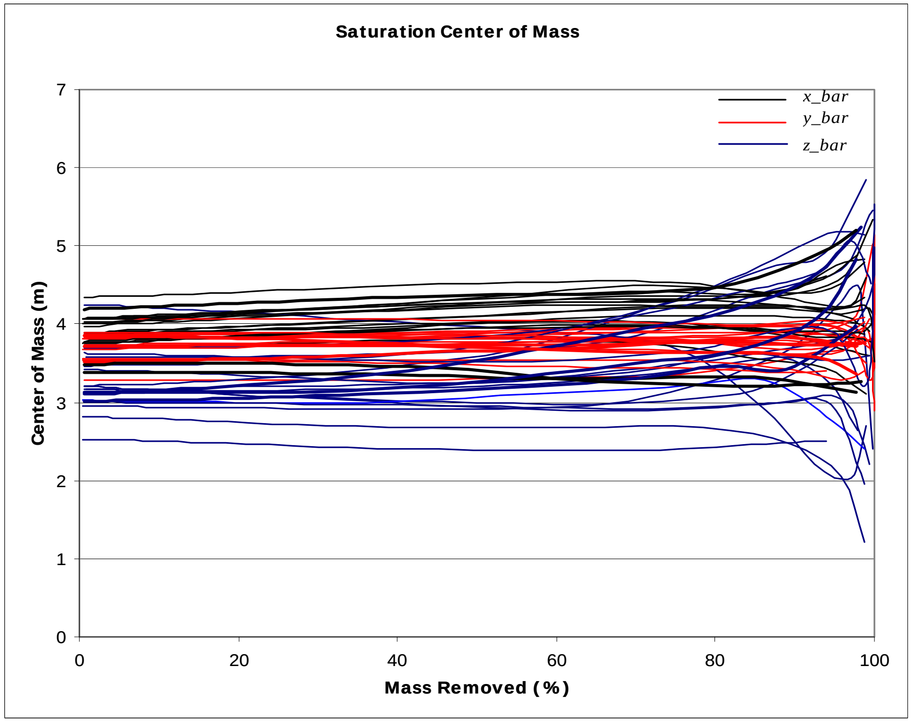
Basu et al. JCH 2009?

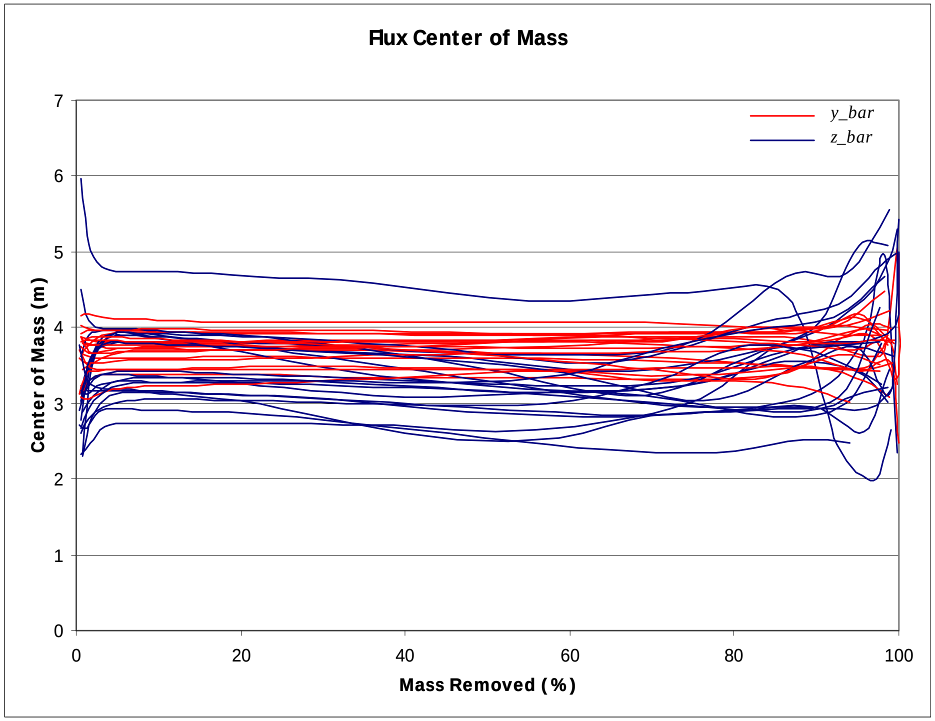


Contaminant Flux



Temporal Evolution Of Source & Flux Centroids

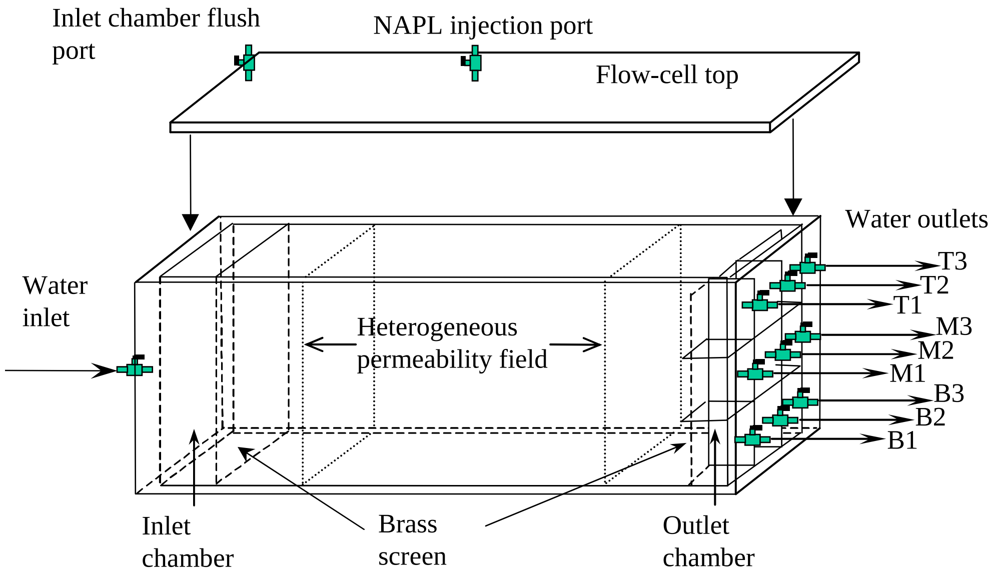




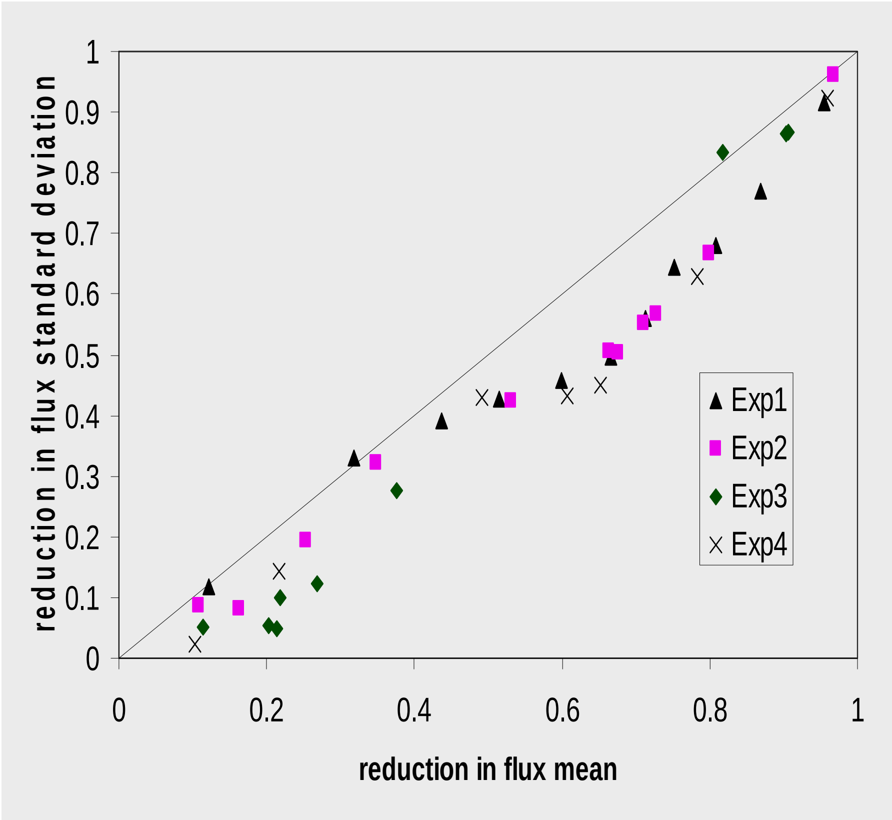
Source Mass **Contaminant Flux**

Basu et al. JCH 2009?

Lab Data: Flux Architecture Dynamics

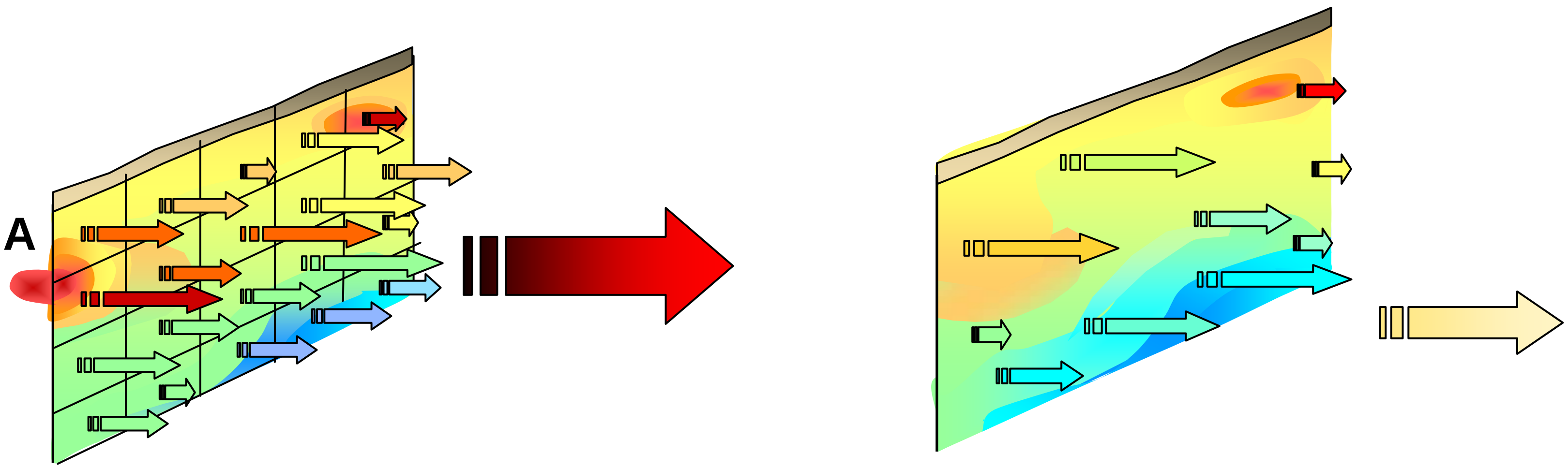


Zhang et al. 2008, JCH



Implication of Results

- Flux distribution is an important metric that can be used for design of optimal remedial system that targets “hotspots”
- Flux distribution more stable over time than source distribution
- The observed stability of flux distribution is an unexpected and interesting result that warrants further investigation
- Stability of flux distribution suggests the ability to characterize flux distributions in time once initial distribution is known.



PURDUE UNIVERSITY

Use the CSM as a Scientific Hypothesis

The CSM is the basis of all site decisions about risk, remediation, closure & reuse. It integrates all available evidence & predicts when more is needed.

Preliminary CSM predicts contaminant distributions →

Develop new SAP to test new predictions

FLUX Characterization

Test predictions: Data confirms or modifies predictions

→ **Mature CSM --the basis for decisions & subsequent activities**

the CSM maturation process

TRIAD Benefits

Improved Site Decision Making:

- Integration of archived site monitoring data with new data collection for enhanced conceptual site model
- Mass discharge at source & plume control planes enables estimation of source mass, source longevity, and natural attenuation
capacity
- Mass discharge serves as a metric for site prioritization, remediation performance, and helps in setting interim cleanup goals
- Groundwater & contaminant flux distribution measured at source control planes allows targeted source treatment & helps formulate cost-effective of site monitoring strategies

Questions

- How much data needed before remediation?
- What types of data best serve CSM & design?
- Are high costs justified in terms of reduced uncertainty?
- What are the short-term benefits of source clean up?
- What is the likely plume response to source clean up?
- How to select target (interim) endpoints?
- How to determine long-term stewardship needs?
- Is there a simplified modeling & decision framework?
- How does all this fit into the TRIAD framework?

Answers?