

Closing the Mass Balance ... The Long and Winding Road

South River Science Team Meeting - July 2010

July 14, 2010

Jim Dyer

DuPont Engineering Research and Technology



The miracles of science™

Key Contributors/Collaborators

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Value of Exercise

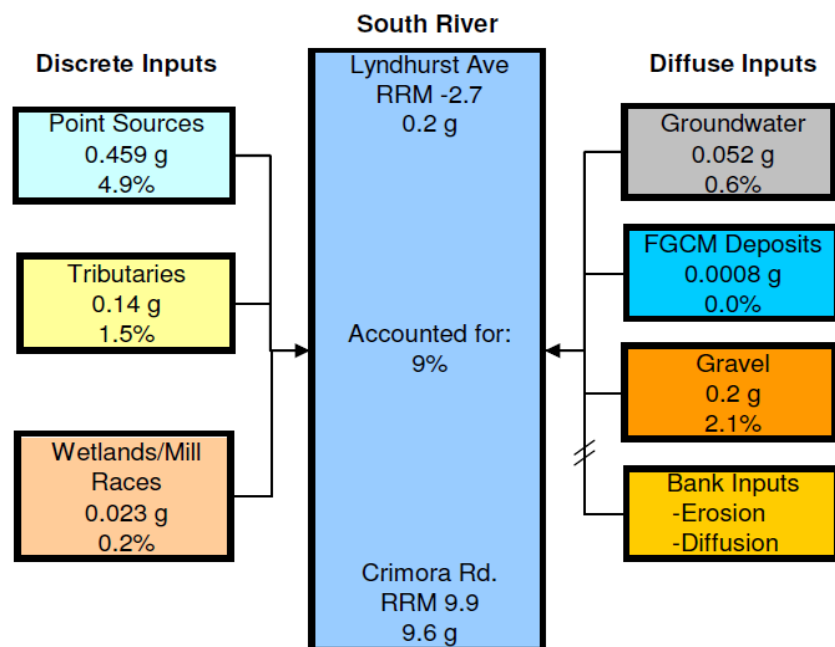
- Providing direction to research studies at Univ. of Waterloo
- Important source of basic data for the “Quantifying Conceptual Aquatic Exposure and Pathway Diagrams” task team
- Facilitating dialogue with Danny Reible and influencing DGT probe field studies
- Tool for helping build consensus on conceptual model

Toward a Hg Mass Balance...

3Q 2008

The Water and Hg "Budgets"
Lyndhurst to Crimora
Morrison & Flanders

Filtered Inorganic Mercury (FIHg)



- Tributaries, millraces, wetlands & bedrock GW are minor sources
- Cannot account for 90% FIHg & 36% FMeHg mass entering 12.3 mi stretch of river with known, quantified sources
- Bank-to-bank sources important

Toward a Hg Mass Balance...

May–August 2008

Benthic Flux Chamber Studies
Landis, Flanders, et al.

Benthic Flux Chamber vs. Avg. Reach-Wide River Flux

FIHg: -65 to 220 vs. 50 to 1,600 ng/m²·hr

FMeHg: -12 to 160 vs. 15 to 60 ng/m²·hr

BFC seepage/advection rate
≪ total GW influx from
water budget



Toward a Hg Mass Balance...

4Q 2008

Simplified, Steady-State Diffusion-Advection Models
Lyndhurst to Crimora
Dyer

$$n_A = \frac{D_{A3}(\rho_{A22} - \rho_{A21})}{z_2 - z_1} \qquad n_A = \frac{D_{A3}}{z_2 - z_1} \left(\frac{[\rho_{A22} \exp(Pe_{A3}) - \rho_{A21}] Pe_{A3}}{\exp(Pe_{A3}) - 1} \right)$$

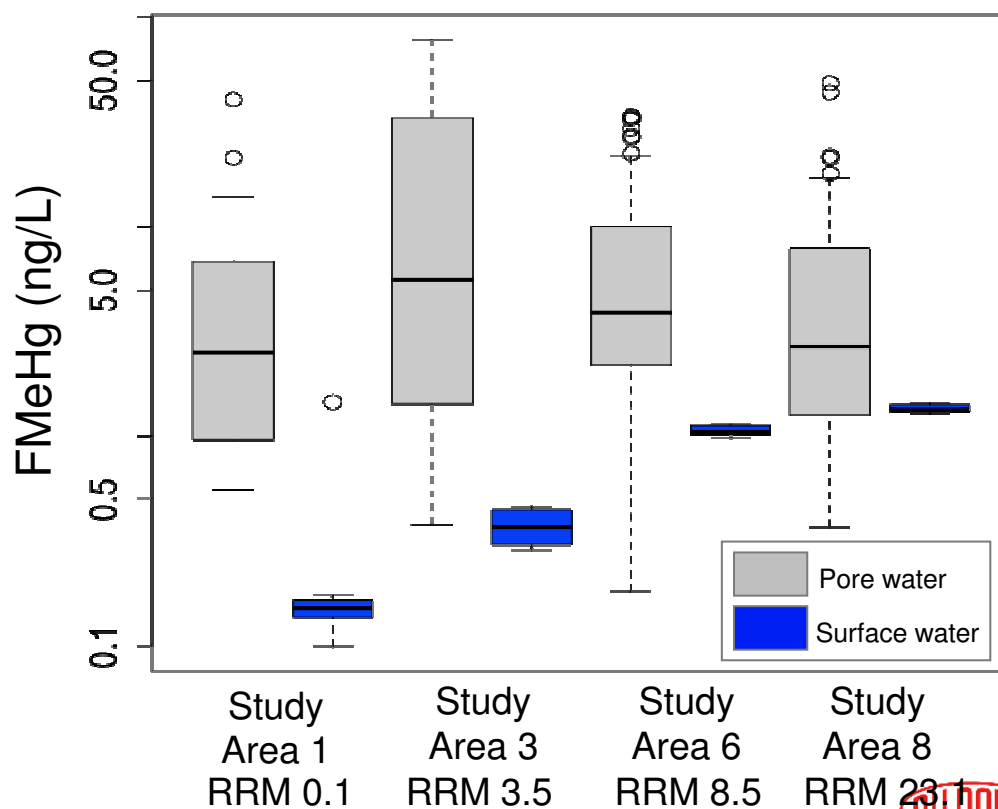
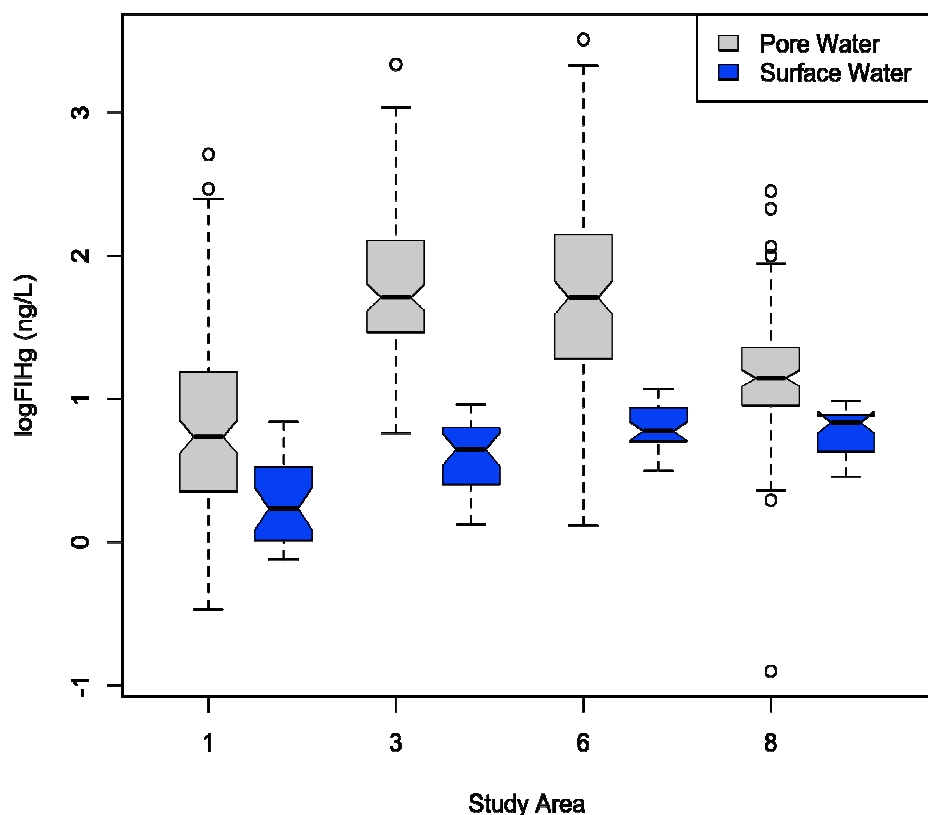
- Diffusion alone cannot account for avg. reach-wide river fluxes, upper-end BFC fluxes, or fluxes seen in filter desorption studies
- Diffusion-advection eqn. suggests advection is important
- For Hg pore water concs. measured up until that time, model predicts advection volumes >> field-measured values
- Model-predicted FIHg fluxes >> BFC-measured values
- **Conclusion: Increase focus on measuring “true” pore water concs.**

Toward a Hg Mass Balance...

June-August 2009

Phase II EcoStudy
Physical Loading Studies by Study Area
Morrison, Flanders et al.

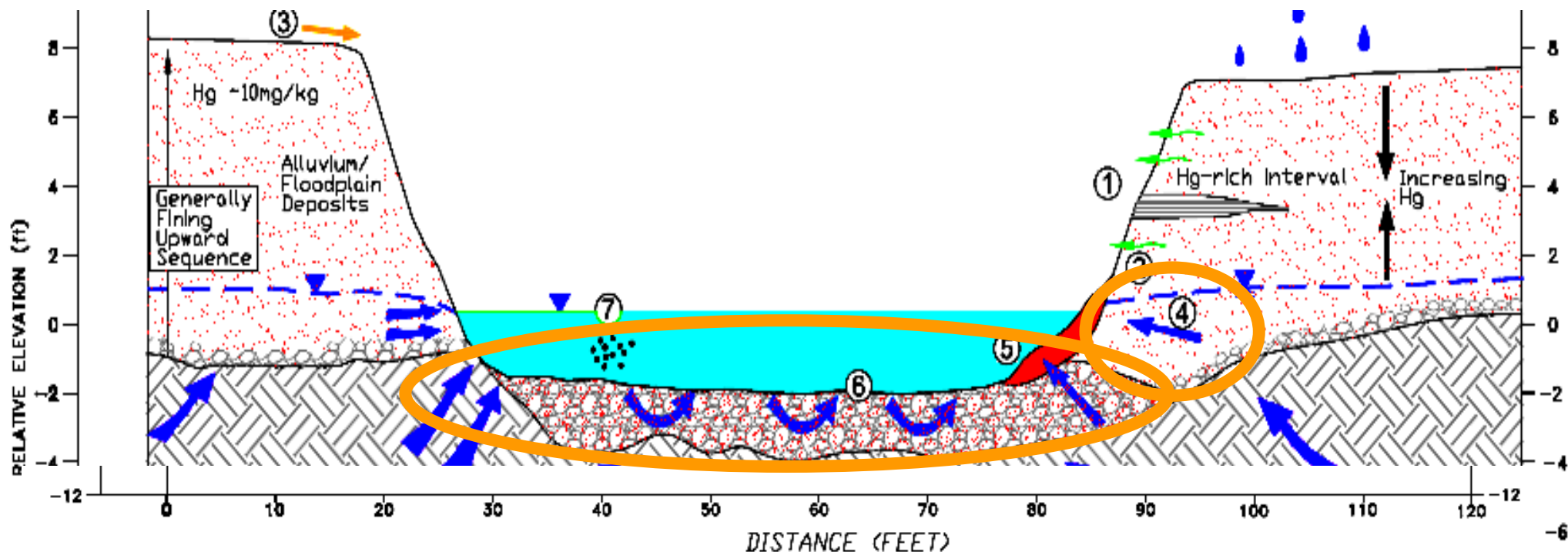
On average, new and more comprehensive data sets show a much greater mass transfer driving force than older, limited data sets



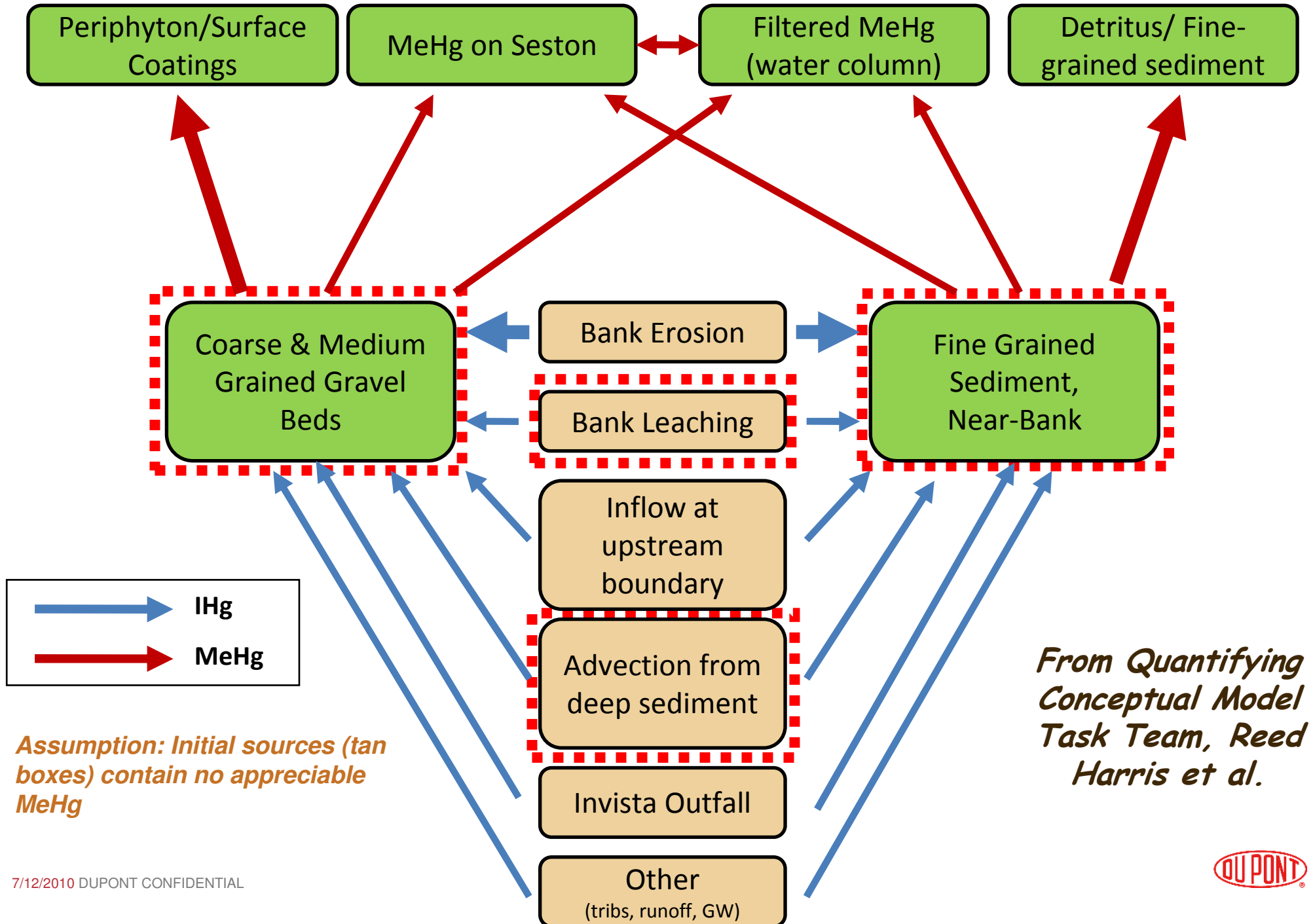
Schematic of Physical Compartments in South River

Nancy Grosso et al.

- 1 Hg release age deposit (floodplain) and eroding banks
- 2 Interflow during precipitation events
- 3 Overland flow / TSS
- 4 Alluvial groundwater advective flux
- 5 Fine-grained channel margin deposit
- 6 Hyporheic flow and stream bed pumping
- 7 Fine-grained particles in gravel bed (embedded reaches)



DRAFT EVERGREEN Conceptual Pathway Model of IHg Sources Feeding MeHg Production in South River



2010 Mass Transfer Studies and Computations

Dyer and Landis

Analyzed pore & surface water data from Phase II EcoStudy

- goal of choosing & applying appropriate mass transfer models that will help quantify conceptual models of FIHg & FMeHg cycling & transport in the river & lead to feasible remedial options

Expanded toolbox of mass transfer (MT) models

- steady-state, water-phase-only models w/ analytical soln.
- transient models w/ analytical soln. & equilibrium partitioning
- transient models requiring numerical soln.

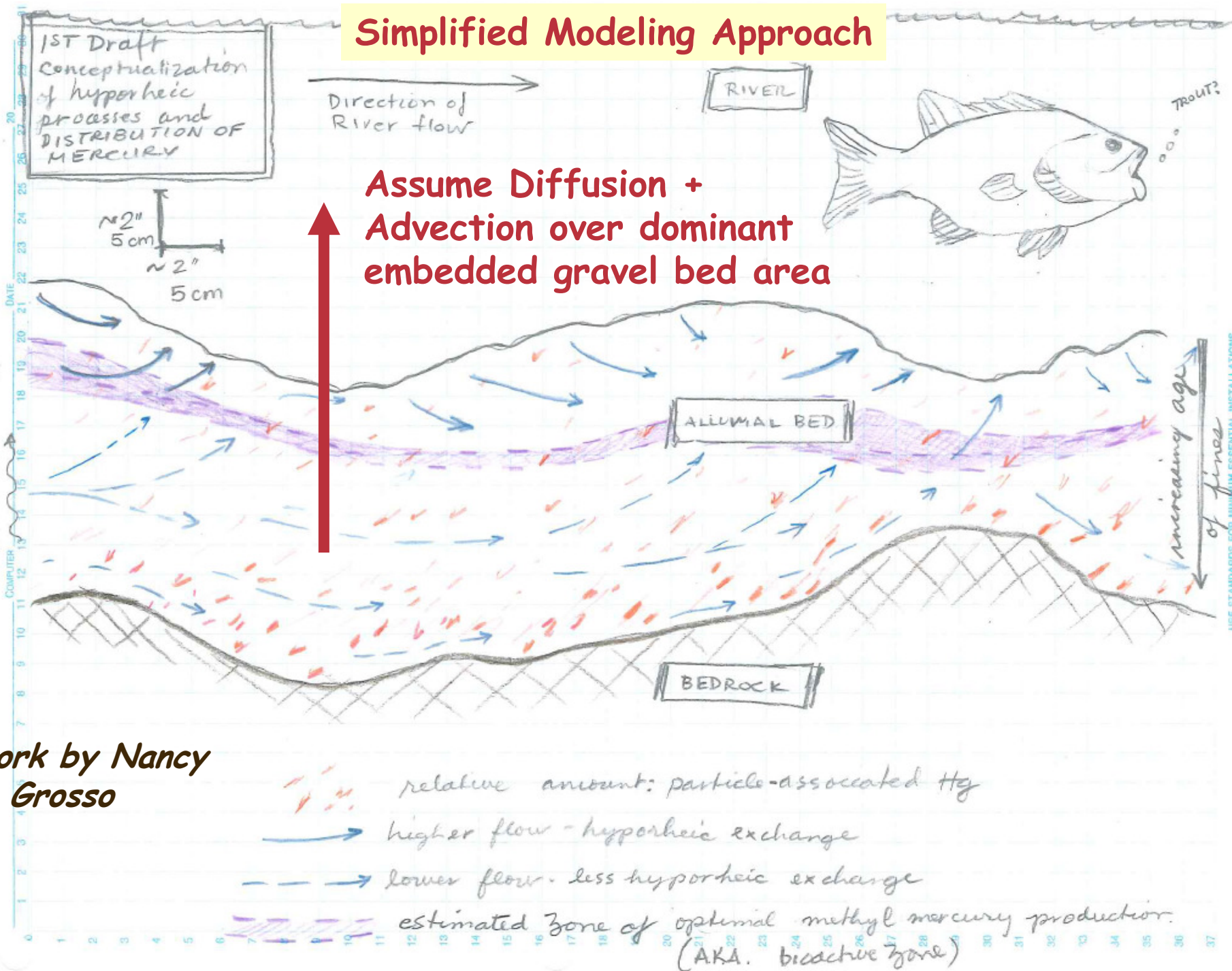
Reconcile model predictions with pore/surface water data from Phase II Study Areas and benthic flux chambers

- can we better explain origin & magnitude of Hg mass flux to river?

Identify additional lab/field studies/pilots with goal of selecting feasible remedial options

Simplified Modeling Approach

Assume Diffusion +
Advection over dominant
embedded gravel bed area

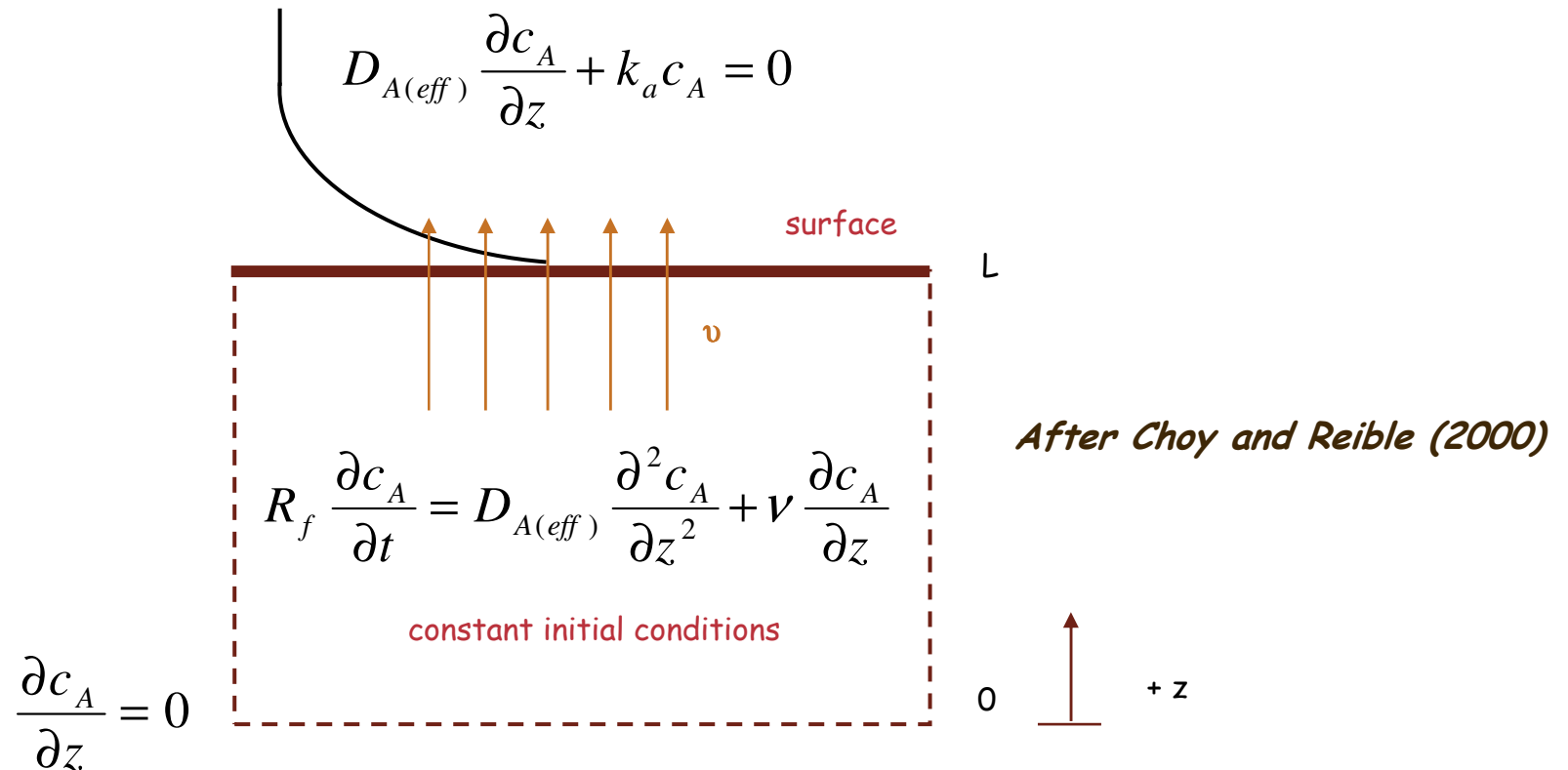


Artwork by Nancy
Grosso

Simplified Mathematical Representation of Transient MT Flux from Alluvial Bed

Diffusion-Advection in a Finite Layer + Mass Transfer Resistance at surface

Uniform initial conc., mass transfer at surface, zero flux at base



Expanded Mass Transfer Model Toolbox

Steady-State Diffusion-Advection

$$n_A = \frac{D_{A(eff)}}{z_2 - z_1} \left(\frac{[c_{A2} \exp(Pe_A) - c_{A1}] Pe_A}{\exp(Pe_A) - 1} \right) \quad \text{Analytical Solution}$$



Transient Diffusion-Advection (Semi-Infinite Medium)

$$c_A(z, t) = c_i + (c_{A0} - c_i) \left\{ \frac{1}{2} \operatorname{erfc} \left\{ \frac{R_f z - vt}{2\sqrt{D_{A(eff)} R_f t}} \right\} + \frac{1}{2} \exp \left(\frac{vz}{D_{A(eff)}} \right) \operatorname{erfc} \left[\frac{R_f z + vt}{2\sqrt{D_{A(eff)} R_f t}} \right] \right\}$$



Transient Diffusion-Advection w/ Mass Transfer Resistance at Surface in Finite Layer (More Realistic)

$$R_f \frac{\partial c_A}{\partial t} = D_{A(eff)} \frac{\partial^2 c_A}{\partial z^2} + v \frac{\partial c_A}{\partial z} \quad z \in [0, L] \quad n_A(t) \Big|_{z=z_i} = -D_{A(eff)} \frac{\partial c_A}{\partial z} \Big|_{z=z_i}$$

Analytical Solution

Numerical Solution Required

Study Area #3

High- & Low-Flow Regimes - June 2009

Steady-State Mass Transfer Coefficient Model

Bed Area (estimated from Arc GIS database)

Gravel + Cobble + Sand $\equiv$ High-Flow Regime = 1737 m²

Silt + Clay $\equiv$ Low-Flow Regime = 408 m²

$\text{Area}_{\text{Pore Water Data}} / \text{Area}_{\text{Surface Water Data}} = 43\%$

Surface Water Data

Upstream Avg.: 186 cfs , 1.57 ng FIHg/L

Downstream Avg.: 184.7 cfs , 2.54 ng FIHg/L

Net Flux FIHg = [(184.7 cfs)(2.54 ng/L) - (186 cfs)(1.57 ng/L)]*43% =
0.2 gm/day

Study Area #3

High- & Low-Flow Regimes - June 2009

Steady-State Mass Transfer Coefficient Model

TK Solver Rule Sheet

Status	Rule
* Unsat	$N = k_a \cdot A_{eff} \cdot \Delta C / 1e06$
* Unsat	$Flux = N/A$
* Unsat	$A_{eff} = A \cdot f$
* Unsat	$Percent = N / Total_Mass \cdot 100$
* Unsat	$Re = \rho \cdot u \cdot L / \mu$
* Unsat	$Sc = \mu / (\rho \cdot Da)$
* Unsat	$k_a = 0.00036 \cdot Re^{0.8} \cdot Sc^{0.33333} \cdot Da / L$
* Unsat	$LOG \Delta C = LOG(\Delta C)$

Study Area #3 - High-Flow Regime - June 2009 Steady-State Mass Transfer Coefficient Model

TK Solver Variable Sheet for High-Flow Regime

Status	Input	Name	Output	Unit	Comment
		N	.019728992	g/day	Mass transfer rate
L	1737	A		m2	Planar bed area
L		Flux	473.253497	ng/m2/hr	Mass flux
		Aeff	1737	m2	Effective mass transfer area
	1	f			Mass transfer area factor
L		Percent	9.86449589		Percent total mass accounted for
L	.2	Total_Mas		g/day	Total mass unaccounted for
L	63.4	ΔC		ng/L	Mass transfer driving force
		Re	37625731.2		Reynold's Number
	1	ρ		g/cm3	Density of water
L	.9	u		ft/sec	water velocity across surface of sediment
	450	L		ft	Characteristic mass transfer length
	1	μ		cp	Viscosity water
		Sc	1754.38596		Schmidt Number
L	.0000057	Da		cm2/sec	Molecular diffusivity
L		ka	.74645662	cm/hr	Estimated mass transfer coefficient based on turbulent flow ma
		LOG ΔC	1.80208926		Log10 mass transfer driving force

Study Area #3

High- & Low-Flow Regimes - June 2009

Steady-State Mass Transfer Coefficient Model

TK Solver Monte Carlo Input Distributions

High-
Flow

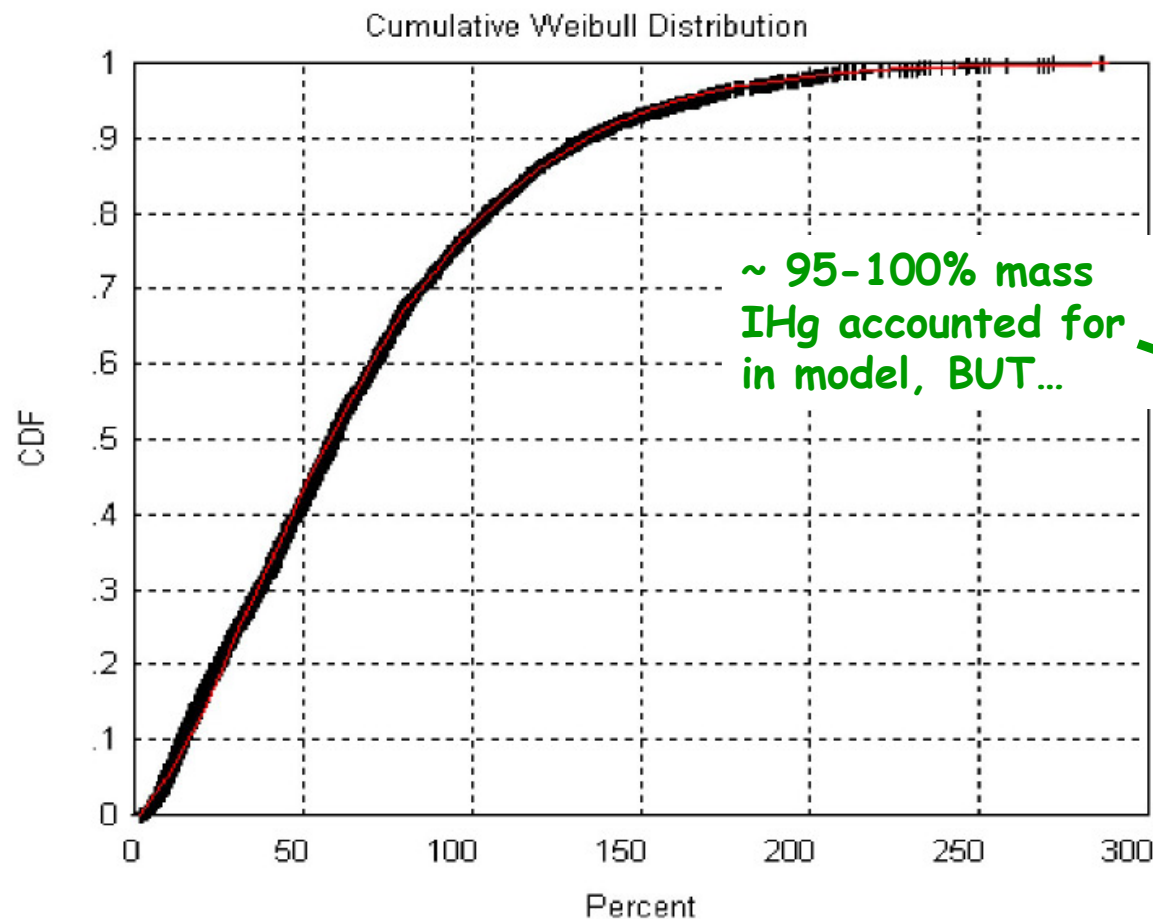
Name	Unit	Description	Distribution
A	m2	Planar bed area	Triangular (1600,1800,1737)
Total_Mass	g/day	Total mass unaccounted for	Triangular (0.15,0.25,0.2)
ΔC	ng/L	Mass transfer driving force	Trapezoidal (6,35,295.2,730.1)
u	ft/sec	water velocity across surface of sediment	Triangular (0.4,3,0.9)
Da	cm2/sec	Molecular diffusivity	Triangular (0.000004,0.00001,0.0000057)

Low-
Flow

Name	Unit	Description	Distribution
A	m2	Planar bed area	Triangular (350,500,408)
Total_Mass	g/day	Total mass unaccounted for	Triangular (0.15,0.25,0.2)
ΔC	ng/L	Mass transfer driving force	Trapezoidal (33,66,468,1084)
u	ft/sec	water velocity across surface of sediment	Triangular (0.1,0.5,0.3)
Da	cm2/sec	Molecular diffusivity	Triangular (0.000004,0.00001,0.0000057)

Study Area #3 - High-Flow Regime - June 2009 Steady-State Mass Transfer Coefficient Model

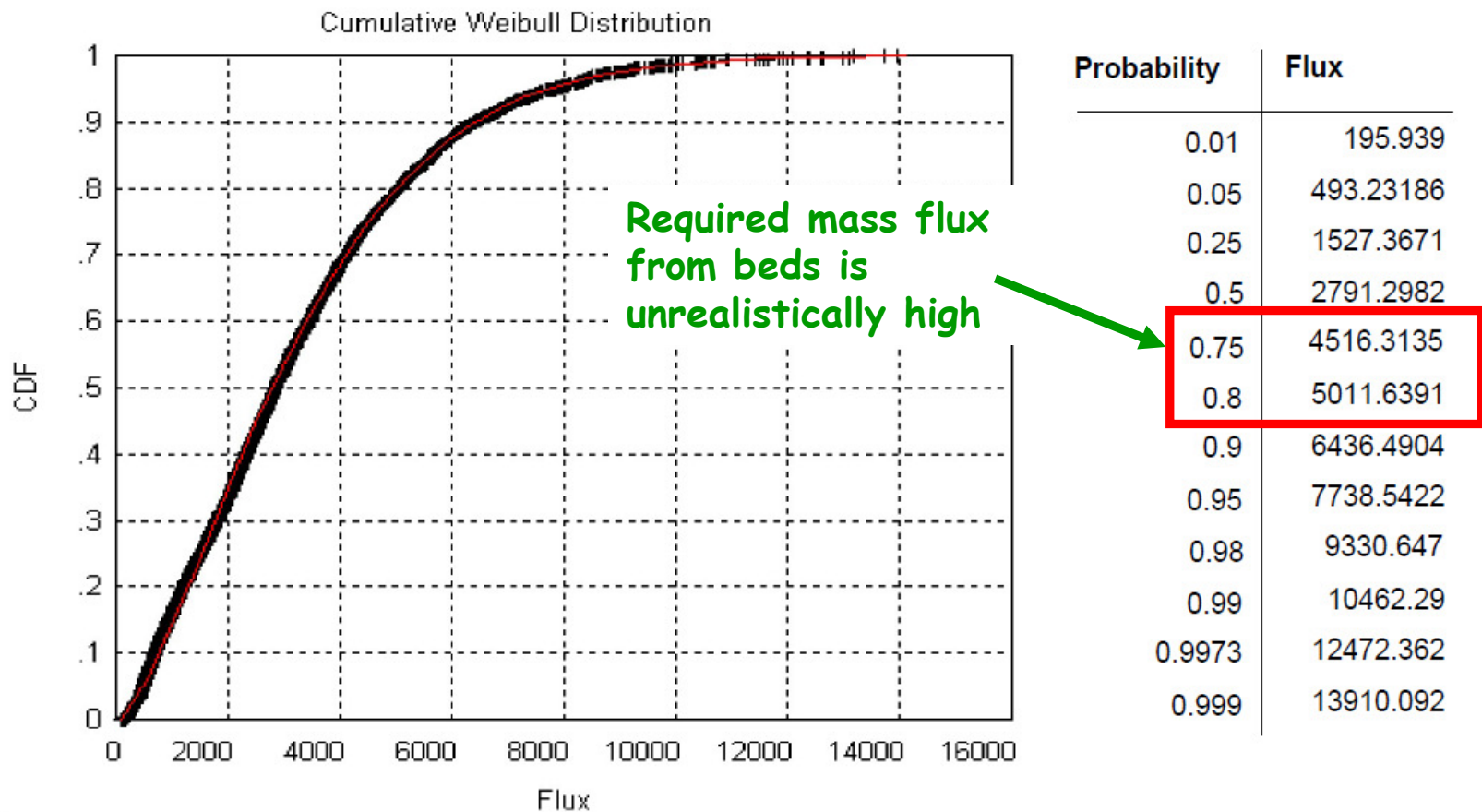
TK Solver Monte Carlo Output - % FIHg Mass Accounted for by Model



Probability	Percent
0.01	3.993413
0.05	10.075004
0.25	31.438708
0.5	57.728205
0.75	93.768458
0.8	104.14083
0.9	134.02293
0.95	161.37833
0.98	194.87902
0.99	218.72011
0.9973	261.11893
0.999	291.48049

Study Area #3 - High-Flow Regime - June 2009 Steady-State Mass Transfer Coefficient Model

TK Solver Monte Carlo Output - Mass Flux (ng/m²/h)



May 25 2010 08:35:07

[Variables]

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Steady-State Mass Transfer Coefficient Model Results for Cases with a Positive Mass Flux into the River

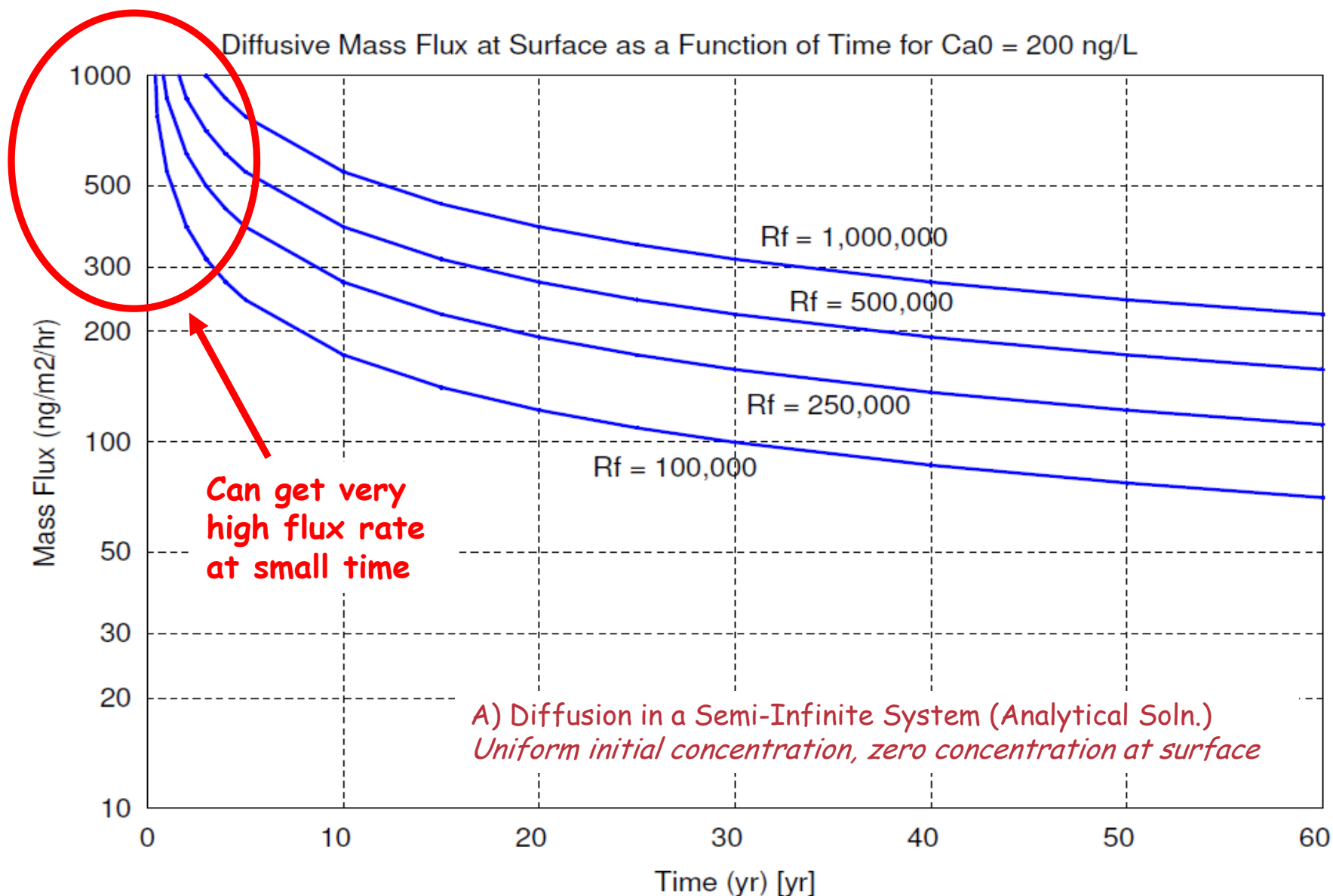
Study Area	Month	FIHg SW Mass Flux Normalized to PW Sampling Area (g/d)	Flow Regime	10/50/90 Values for Fraction of Bed Area Fluxing	75% Probability Value for FIGHg Mass Flux (ng/m ² /hr)	75% Probability Value for % FIGHg Mass Accounted for by Model	Sum of High- and Low-Flow Regimes - % FIGHg Mass Accounted for by Model
1	June	0.015	High	0.5/0.8/1	275	160	172
			Low	1	210	12	
	July	0.09	High	0.5/0.8/1	590	60	61
			Low	1	100	1	
	August	0.022	High	0.5/0.8/1	200	85	89
			Low	1	100	4	
3	June	0.2	High	1	4500	95	105
			Low	1	2000	10	
3	July	0.016	High	1	340	90	125
			Low	1	540	35	
6	August	0.02	High	0.5/0.8/1	375	180	280
			Low	1	1900	100	

Conclusions

Steady-State Mass Transfer Modeling

- Conducted extensive Monte Carlo simulations to understand uncertainties & perform bounding calculations
- Limited number of adjustable parameters for reconciling model with data
- Mass transfer driving force assumed to be at steady state when it probably is not
- Pore water collected at depth, but mass flux measured/calculated at surface
- Assumes dissolved-phase MT only
 - Hg partitioning to solids not included (no Hg sink)
 - colloidal transport not considered
- Model typically predicts much higher mass flux and larger advection rate than measured by BFC when accounting for ~100% mass

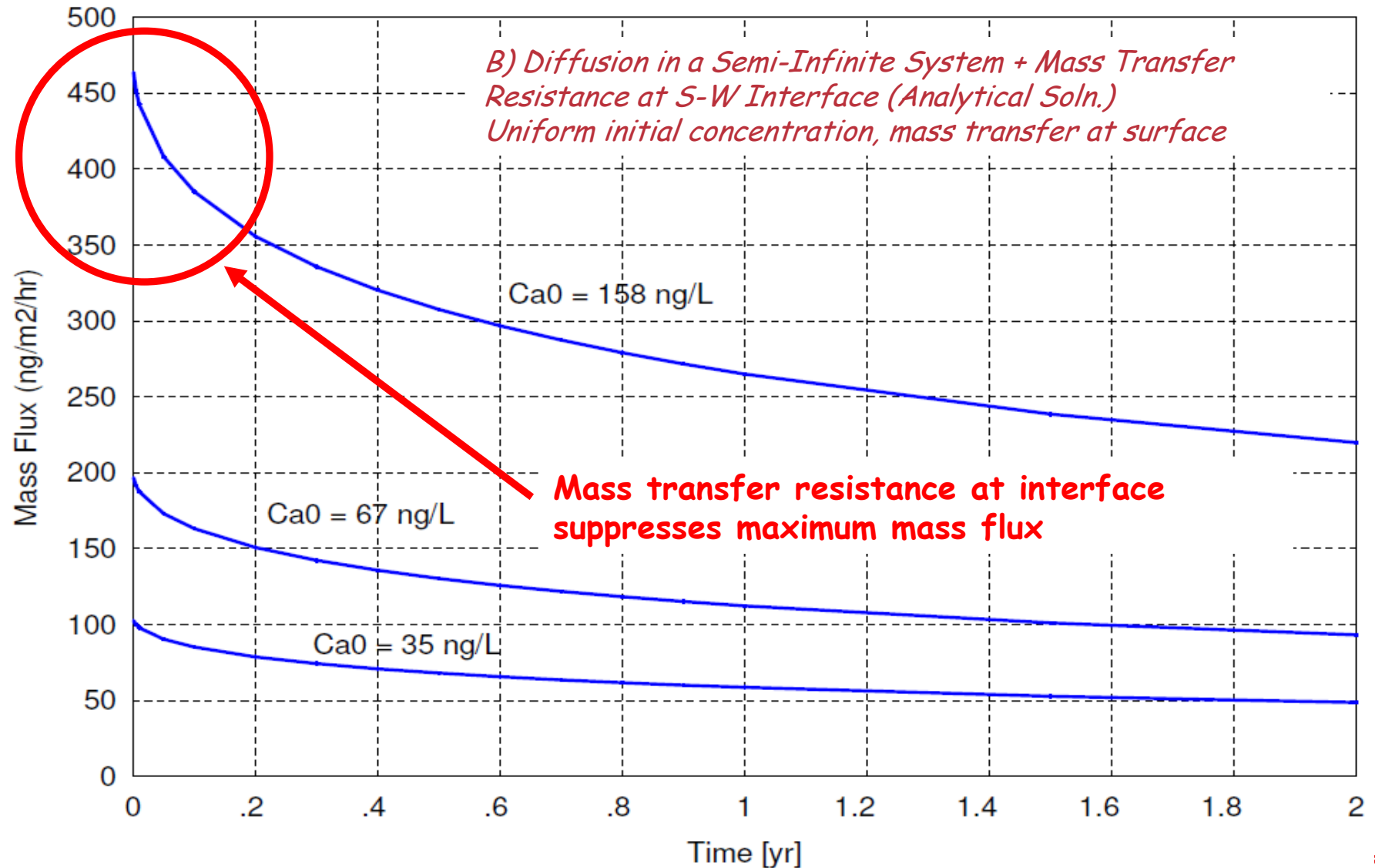
Transient Model Example - Flux Profile Flowing Gravel Bed - Diffusive Flux Only



Transient Model Example - Flux Profile

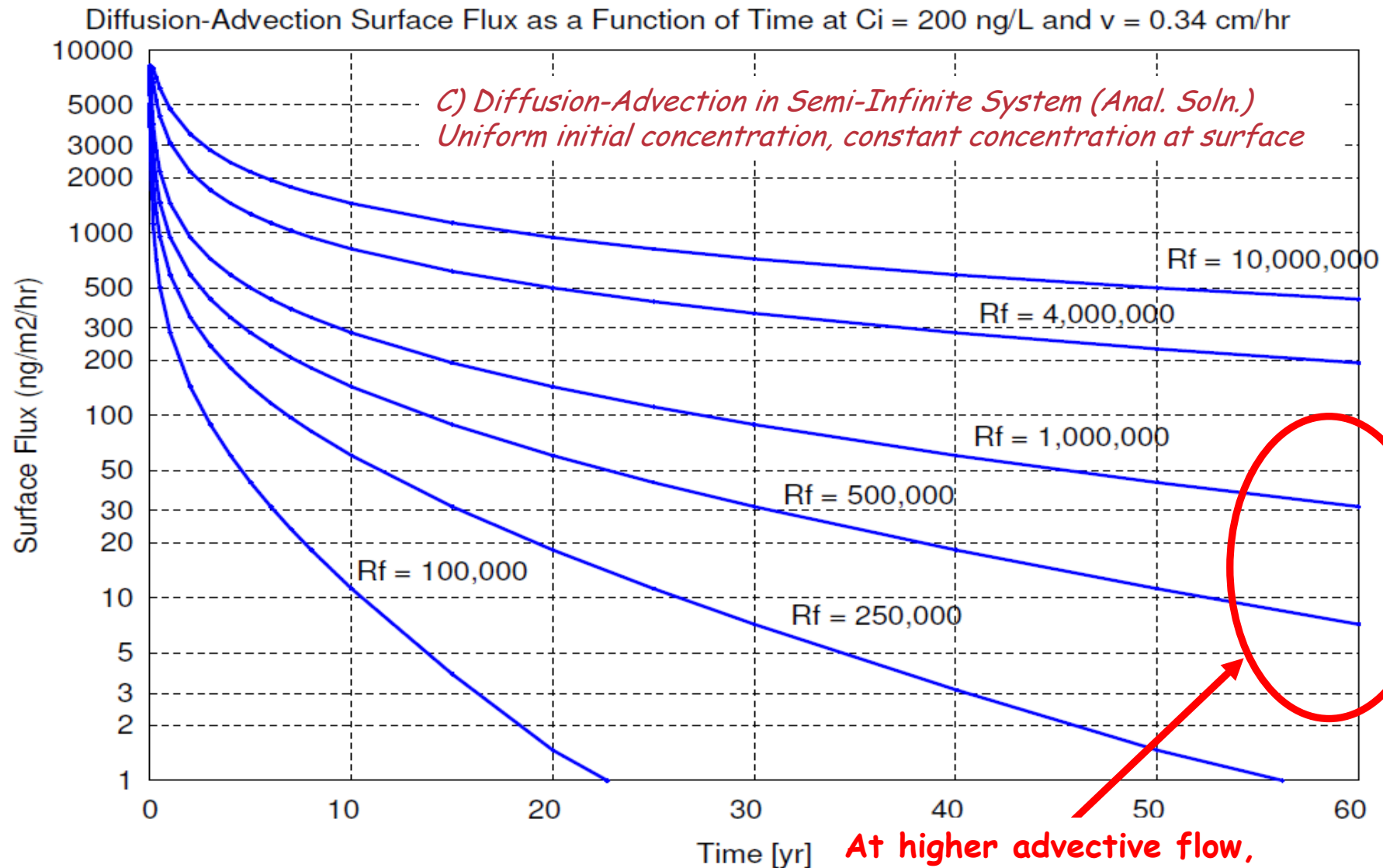
Quiescent Gravel Bed - Diffusion + Surface MT Resistance

Diffusive Mass Flux at Surface with Mass Transfer Resistance for $R_f = 100,000$ and $k_a = 0.3$ cm/hr



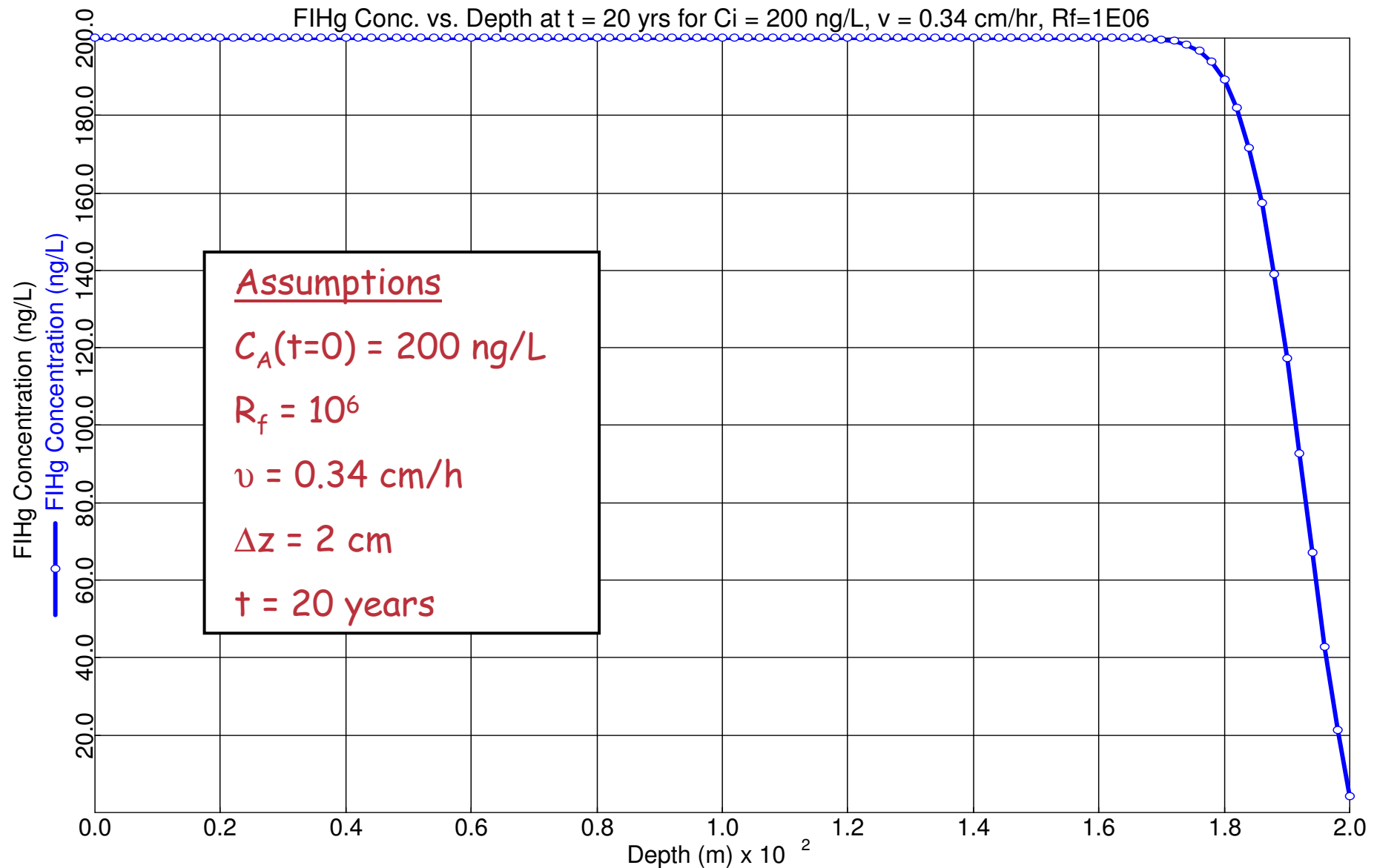
Transient Model Example - Flux Profile

Flowing Gravel Bed - Diffusion + Advection



At higher advective flow,
surface flux drops to BFC-
type values for $R_f < 10^6$

Transient Model Example - Concentration Profile Flowing Gravel Bed - Diffusion + Advection



Conclusions

Transient Mass Transfer Modeling

- Transient models provide picture of how mass flux and Hg concentration change with time, depth, & equilibrium partitioning to sediment
- Retardation factor & time have strong influence on mass flux
- Unclear where we fall on these plots in actual system, but models suggest high flux rates are possible for freshly deposited solids

For $R_f = 10^5$ - 10^6 (reasonable assumption for Hg) + seepage velocity = 0.34 cm/h (avg. GW influx over 12.6 mi per 2008 water budget)

- Calculated mass flux at 60 yr is comparable to flux measured with BFC
- However, at these lower sediment flux rates, the model greatly underestimates the measured net mass flux in the water column

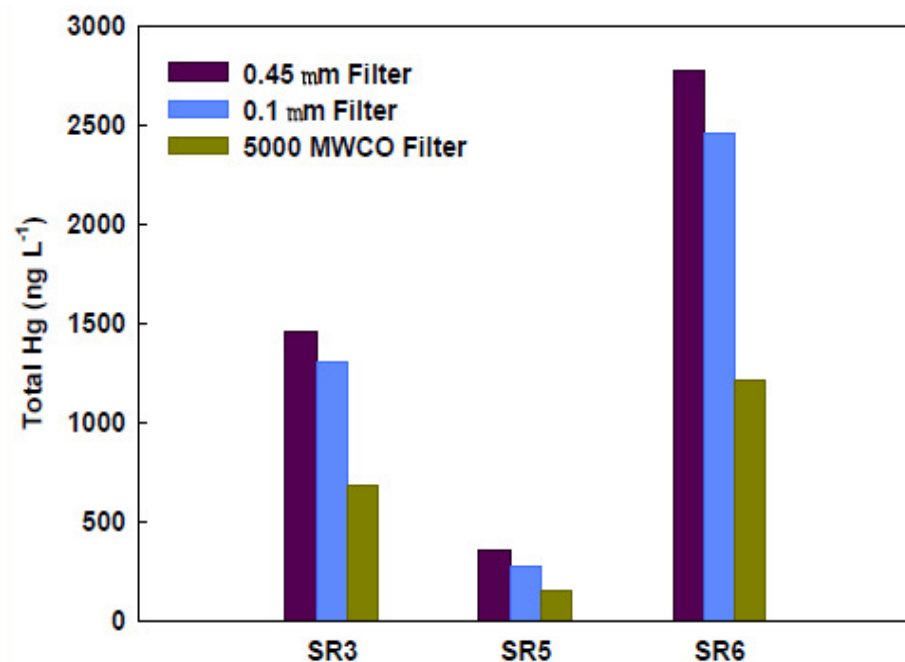
Data from Univ. of Waterloo Points to Potential Importance of Colloidal Transport



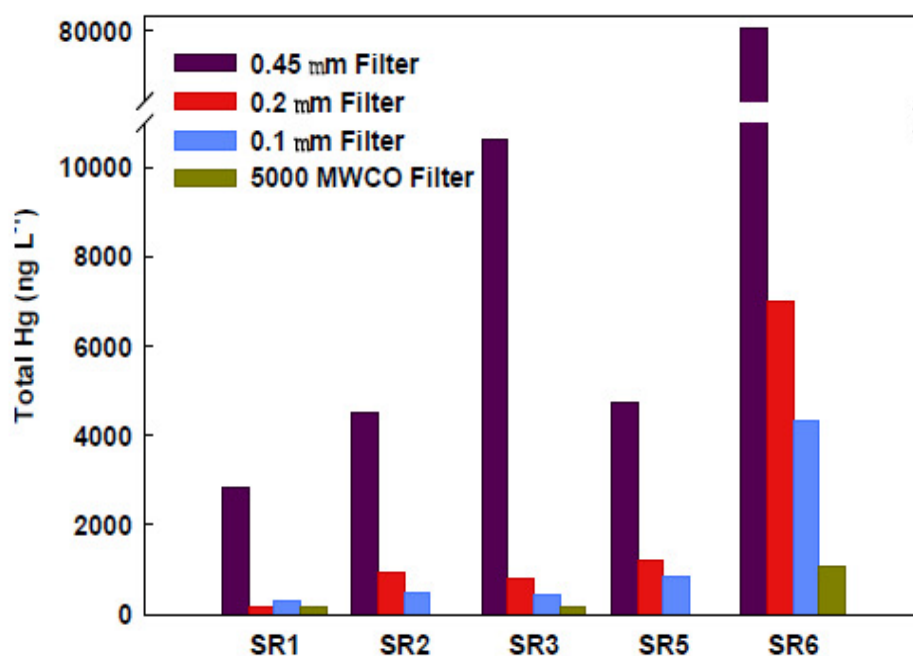
Draft

Filter Comparison

Saturated Control Columns



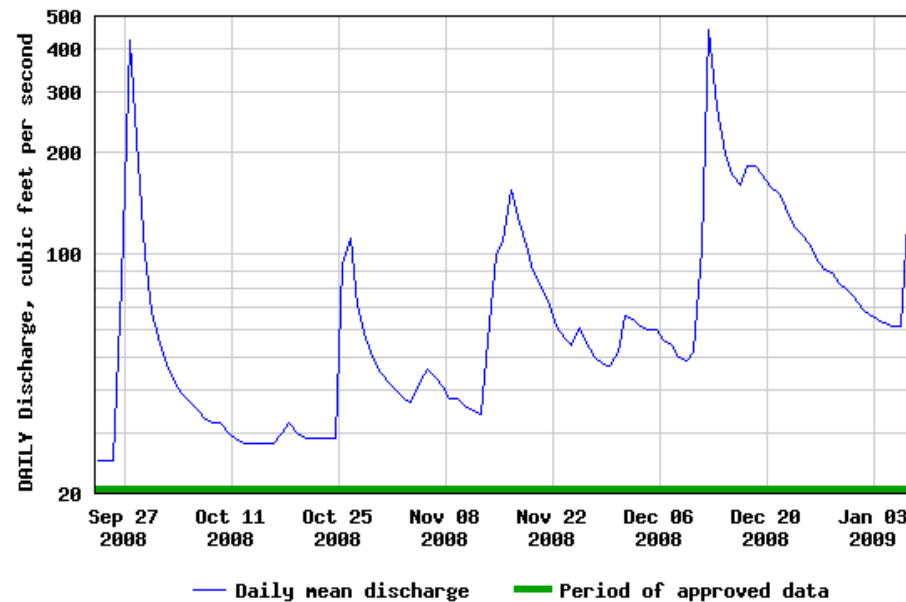
Resuspension Tests



Revised June 7/10



USGS 01626000 SOUTH RIVER NEAR WAYNESBORO, VA

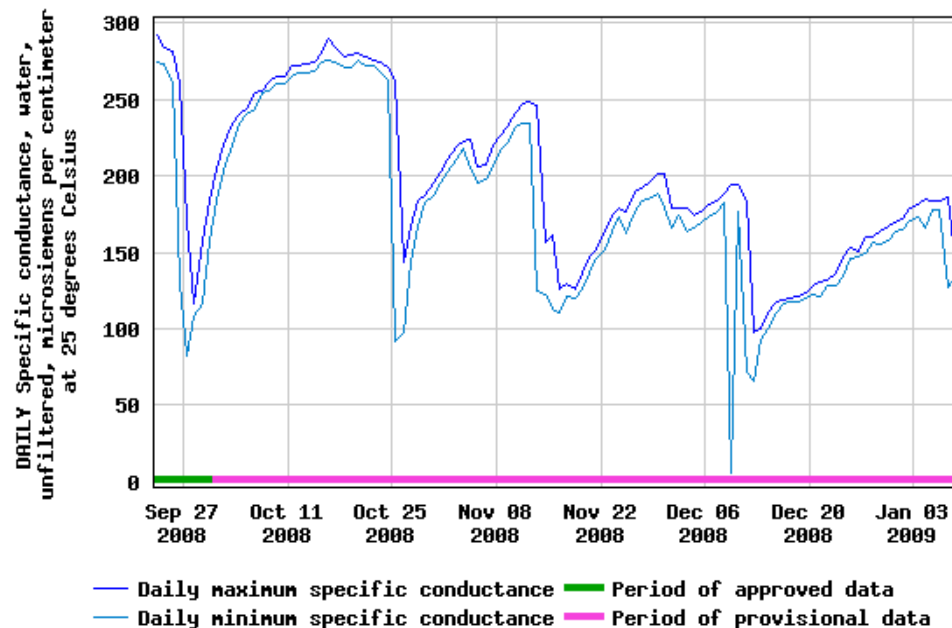


2008 data, but
note that...

Conductivity is
inversely
proportional to
river flow rate



USGS 01626000 SOUTH RIVER NEAR WAYNESBORO, VA



Sharp drop in
conductivity
coinciding with
high-flow events
could potentially
drive colloid
release

Key Learnings from Mass Transfer Studies to Date

This exercise, which started out trying to “close the mass balance,” has identified gaps in our understanding of Hg fate & transport in the South River as well as how these gaps will impact remedial options selection

- potentially important role of colloidal transport
 - may be using incorrect/incomplete model
- insufficient understanding of hydrology in river w.r.t. advection & impact on Hg flux
- understanding of truly dissolved pore water conc. still “in a state of flux”
- difficult to close mass balance using 0.45 μ filtered Hg
 - not truly dissolved, so K_d values are conditional
 - more recent comprehensive data sets focused on filtered Hg only
- DGT probe studies hold promise