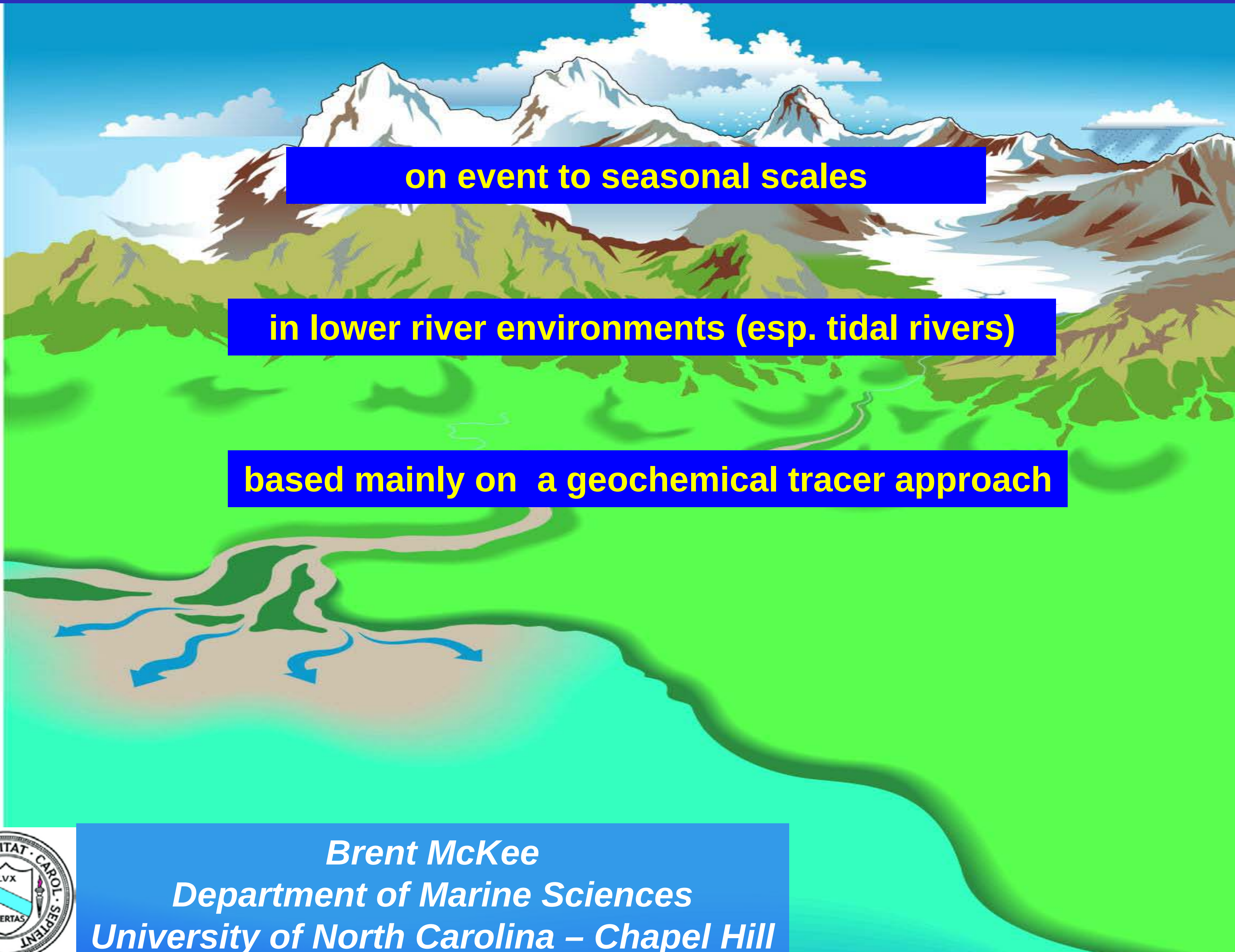
Variable Geochemical Supply to the Ocean



Brent McKee
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University of North Carolina – Chapel Hill

The “Source to Sink” concept has been very important to the geochemical community as well….for many decades

Comparison of that effort to S2S?

Not separate from source to sink for sediment but rather very dependant on larger understanding of particulate S2S …….and hopefully mutually beneficial

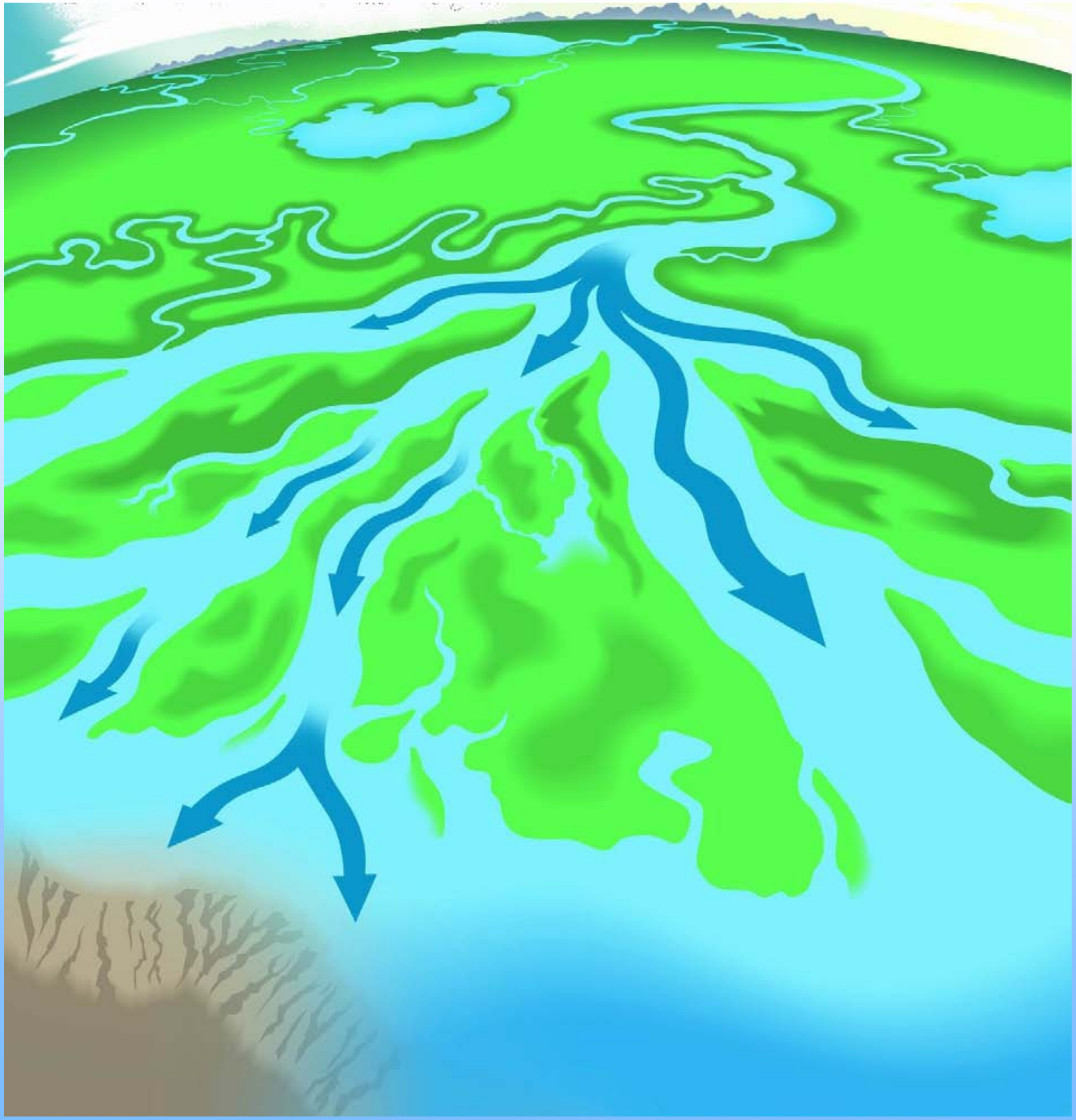
(1) Examine what we know about the variability in concentrations and fluxes of important geochemical materials (carbon, nutrients, trace elements) to the ocean via rivers.

----On event to seasonal scales

(2) Spatially focus on transformations and fluxes in transitional zone between land and ocean (especially in the tidal river)

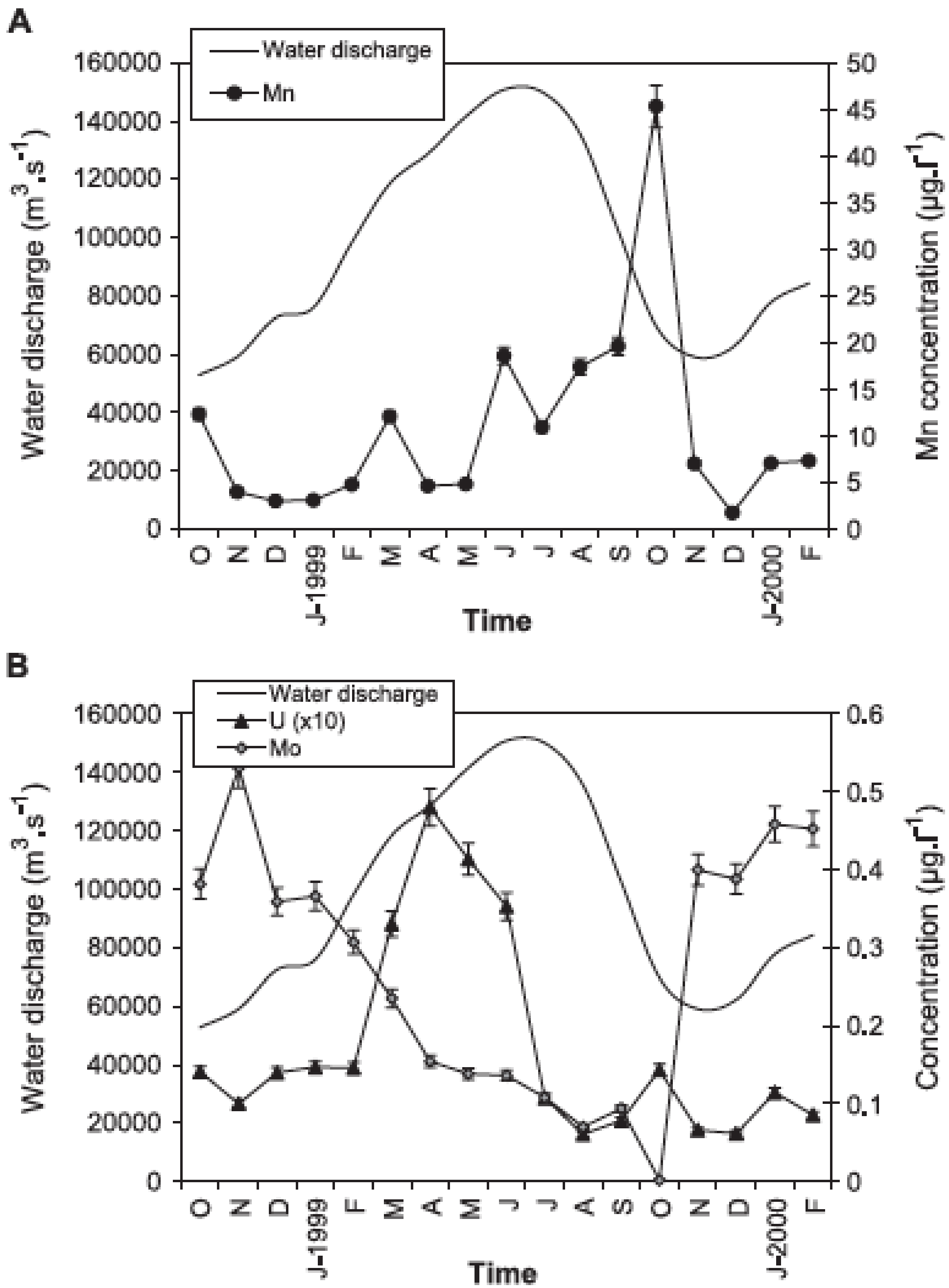
(3) Focus on what is needed to develop some predictive capability regarding geochemical fluxes to the ocean via rivers…..need for a better mechanistic understanding of processes that impact fluxes.

Oceanographer's View of Riverine fluxes to the Ocean



- Many oceanic geochemical budgets calculated based on limited number of riverine flux numbers (often one data point to represent a river)
- These uncertainties deemed to be no worst than uncertainties in other parts of the ocean budget…so good enough
- Therefore no real motivation (no funding) to better constrain riverine variability (spatial or temporal)

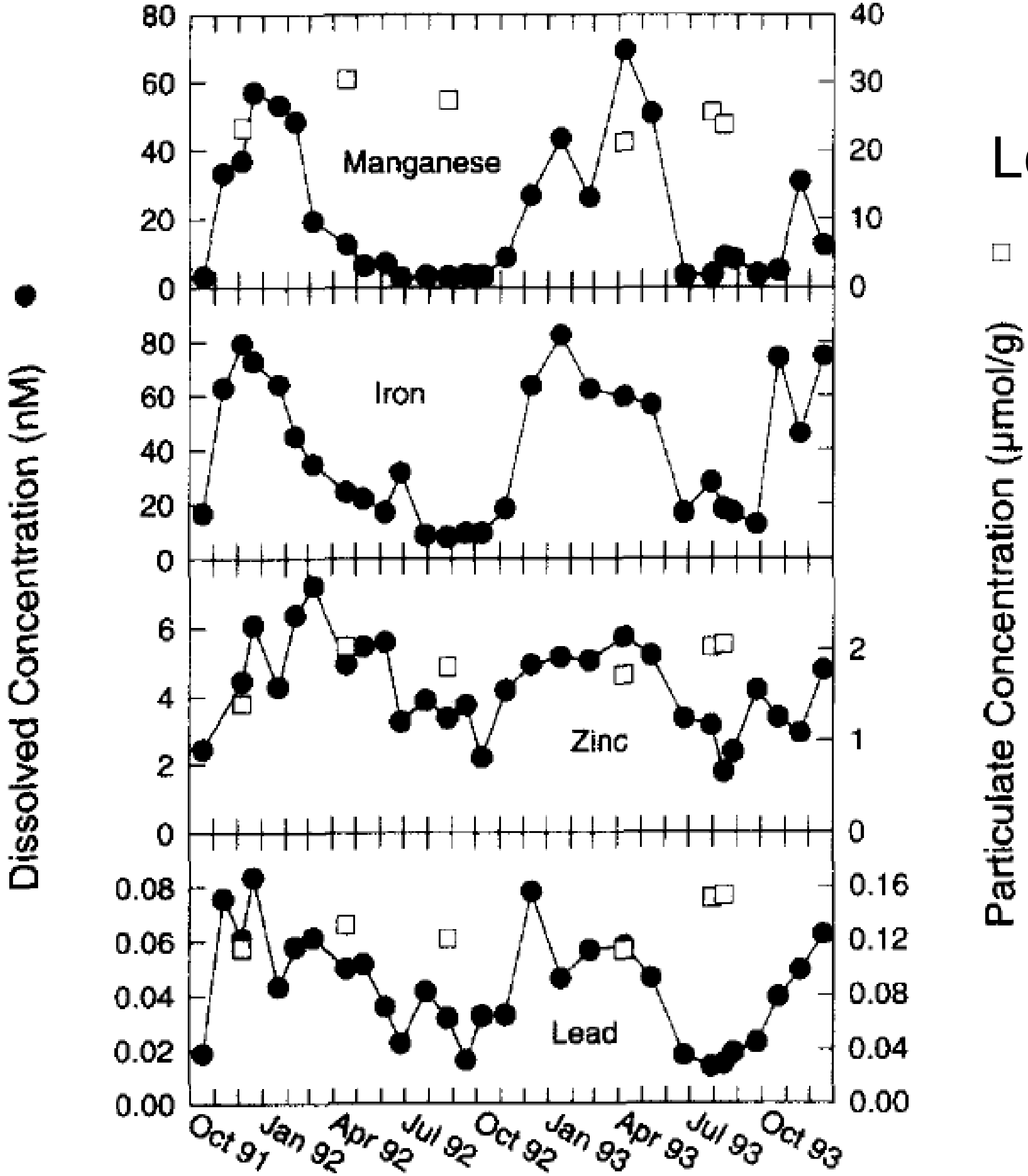
When we do look closer at monthly or seasonal scale changes in riverine fluxes of geochemical constituents……….



Solimões River

Floodplain interactions?

Viers et al. (2005)



Lower Mississippi River

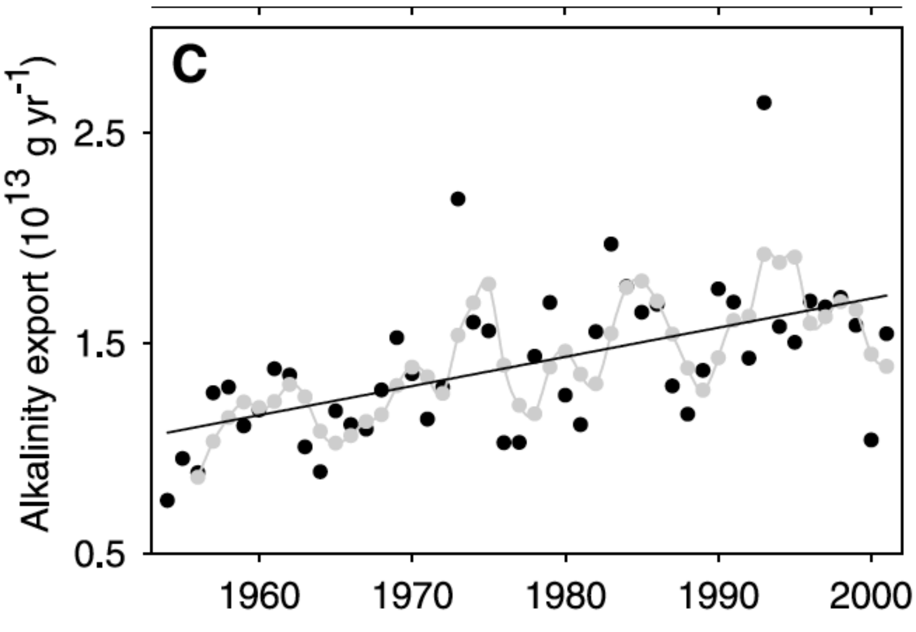
Temperature (microbial activity)?

Deposition/transformation in riverbed sediment?

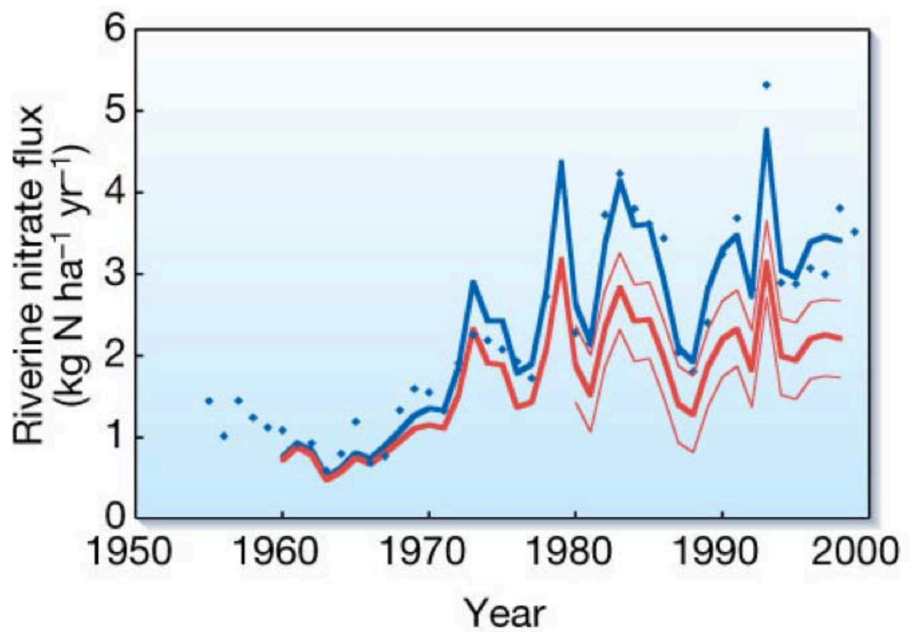
Shiller et al. (1997)

Decadal Scale?

Mississippi River



Raymond and Cole (2003)

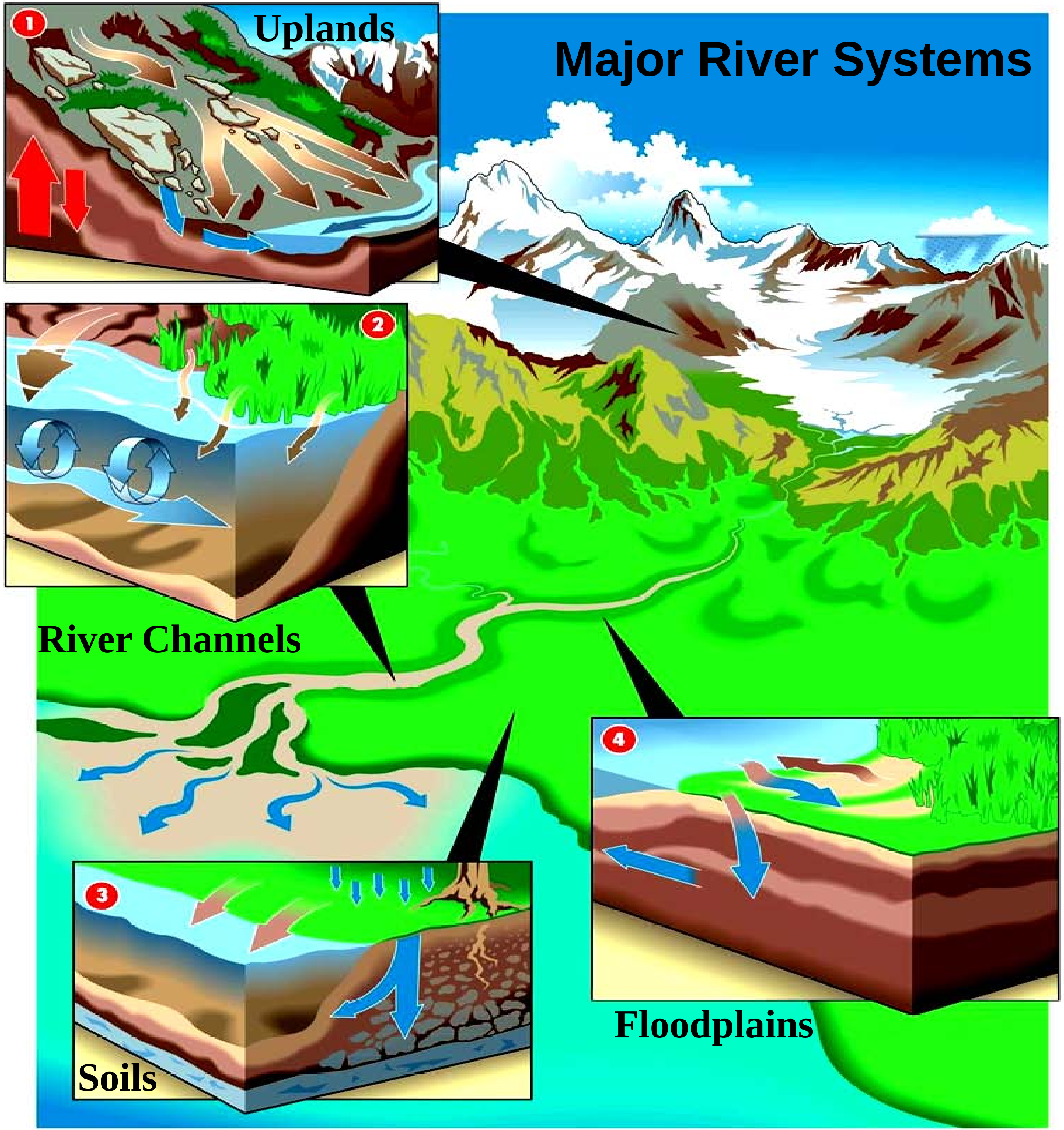


McIsaac et al. (2001)

Climate ?

Anthropogenic ?

Must be able to tie changes in concentrations and fluxes to a mechanistic understanding of processes and transformations



Predict Changes in Riverine Flux?

Strong Interactions Between Subsystems

Non-linear Responses to Change

Observation:

Percentage of Riverine Transport in Particulate Form

<u>Macronutrients</u>:

Phosphorus **~ 85%** *(Meybeck, 1982; Seitzinger et al., 2005)*

Nitrogen **~40-85%** *(Mayer et al., 1998)*

<u>Micronutrients</u>:

Iron, cobalt, chromium, manganese **>90%**

Selenium, zinc, molybdenum, copper **>50%** *(Meybeck et al., 2003)*

<u>Organic Carbon</u>: **~ 65%** *(Seitzinger et al., 2005)*

Post-depositional geochemical transformations from particulate to colloidal/dissolved phase well documented for these constituents

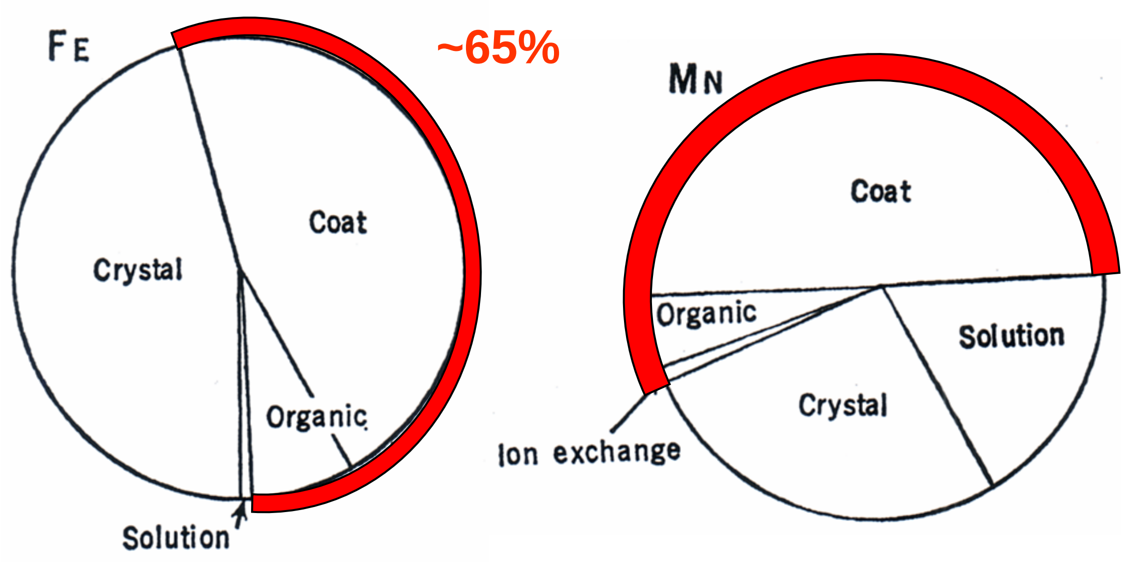
River Chemistry: Micronutrients and toxins

ELEMENT		Required by all life-forms	Required for some life-forms	Moderately Toxic	Highly Toxic
Iron	**Fe**	X			
Manganese	Mn	X			
Copper	Cu	X		X	
Zinc	Zn	X			
Molybdenum	Mo	X			
Vanadium	V		X	X	
Cobalt	Co		X		
Selenium	Se		X	X	
Iodine	I		X		
Silver	Ag		X		X
Lead	Pb				X
Mercury	Hg				X
Chromium	Cr			X	

Biogeochemical Particulate Load in Rivers

How much is reactive or available?

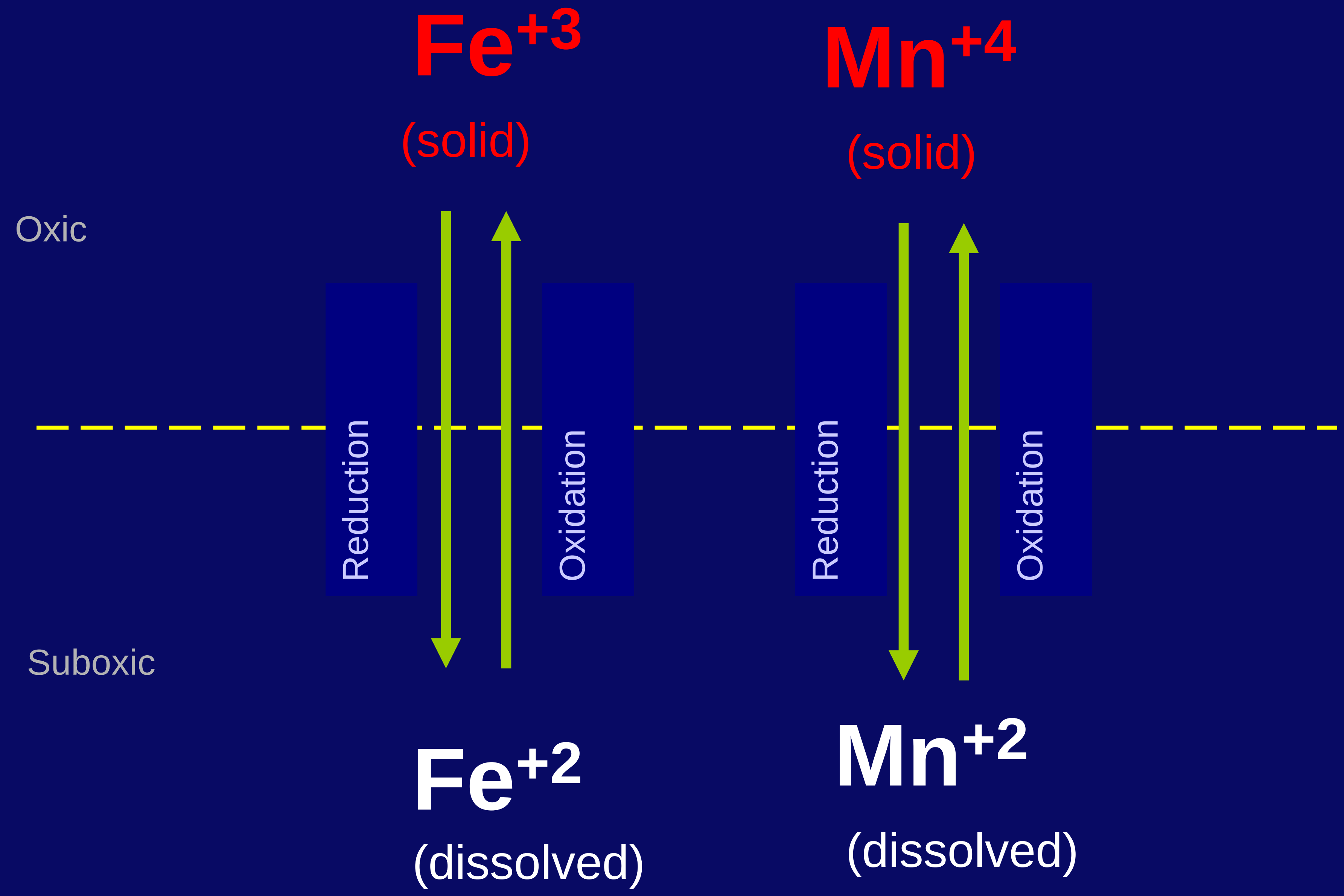
Amazon River



Gibbs, 1973

Mississippi River

<u>Middle Reaches</u>: **~ 40% of particulate Fe** (and **90% of particulate Mn**) transported in a form available for recycling, primarily oxide coatings ***(Hayes, 1993)***



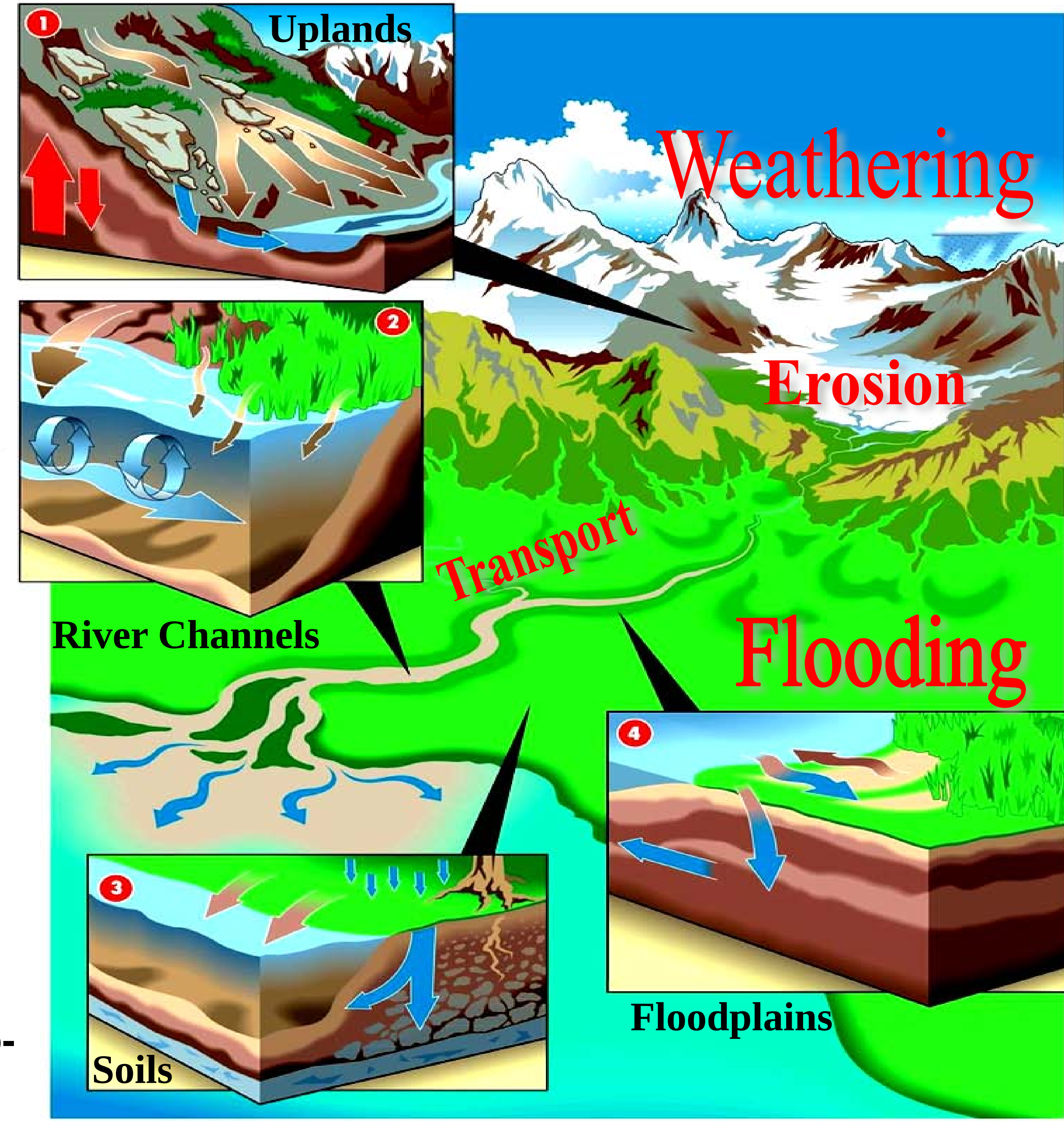
Fe+3
(solid)
Mn+4
(solid)
Oxic
Reduction
Oxidation
Reduction
Oxidation
Suboxic
Fe+2
(dissolved)
Mn+2
(dissolved)

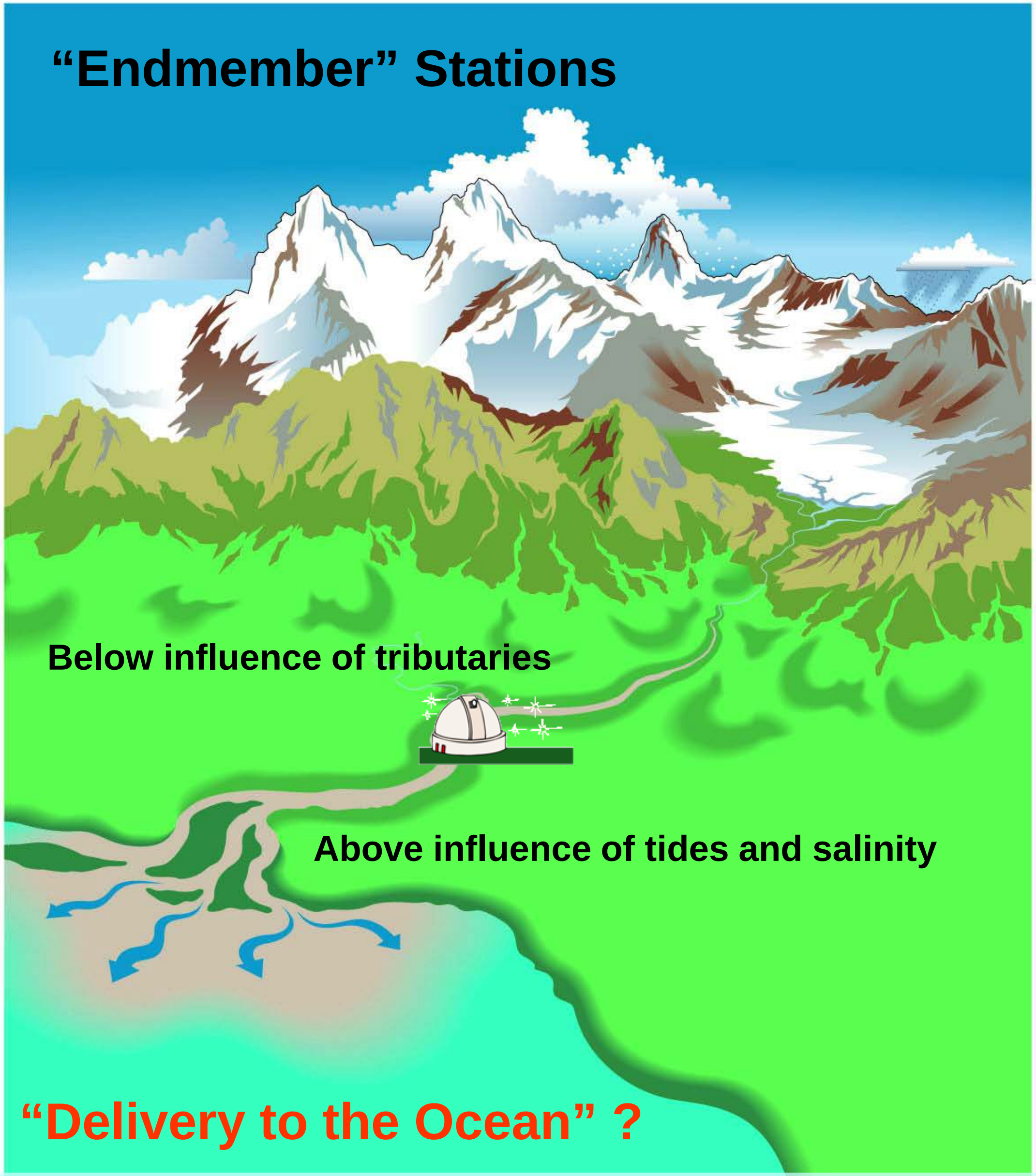
Processes within the watershed sensitive to global change
(Climate, Human)

Therefore, potentially large downstream effects

Transport rates
Composition
Partitioning
(dissolved/particulate)

Carbon, micro- and macro-nutrients, trace elements





Lack of measurements within the tidal river

[and understanding of processes and fates]

Amazon (Obidos) 740km

Changjiang (Datong) 511 km

Mississippi (Tarbert Landing) 495 km

Ganges (Paksay) 390 km

Brahmaputra (Bahadurabad) 348 km

The "Missing Link"

Any Transformation, Loss or Addition that occurs within the lower river is not reflected in traditional flux estimates

What are important processes in the lower river that may affect geochemical fluxes?

- Sources of fine-grained particulates in various compartments (banks, bottom, floodplain)

- Residence time and extent of geochemical transformation within compartments

- Degree of connectivity between compartments

An example of each …….insights gained from systems highly impacted by man!

Haw River (Cape Fear River Basin)

8/26/08 2.4 m^3s^{-1}

TSM = 7 mg l^{-1}

8/28/08 743 m^3s^{-1}

TSM = 235 mg l^{-1}

Source of sediments?

One Quantitative approach (Matisoff et al. 2005)

$$\frac{^{7}Be}{^{210}Pb} \quad \text{ratio}$$

$$A = (^{7}\mathrm{Be})_{\mathrm{sample}}$$
$$A_o = (^{7}\mathrm{Be})_{\mathrm{source}}$$
$$B = (^{210}\mathrm{Pb}_{\mathrm{xs}})_{\mathrm{sample}}$$
$$B_o = (^{210}\mathrm{Pb}_{\mathrm{xs}})_{\mathrm{source}}$$

$$A = A_o\, e^{-(\lambda_{^7\mathrm{Be}} t)}$$
$$B = B_o\, e^{-(\lambda_{^{210}\mathrm{Pb}} t)}$$

Half life ^{7}Be (53 d)
Half life ^{210}Pb (22 y)

Source of both cosmogenic

"age" or residence time in the system:

$$t = \frac{-1}{(\lambda_{^7\mathrm{Be}} - \lambda_{^{210}\mathrm{Pb}})} \ln\left(\frac{A}{B}\right) + \frac{1}{(\lambda_{^7\mathrm{Be}} - \lambda_{^{210}\mathrm{Pb}})} \ln\left(\frac{A_o}{B_o}\right)$$

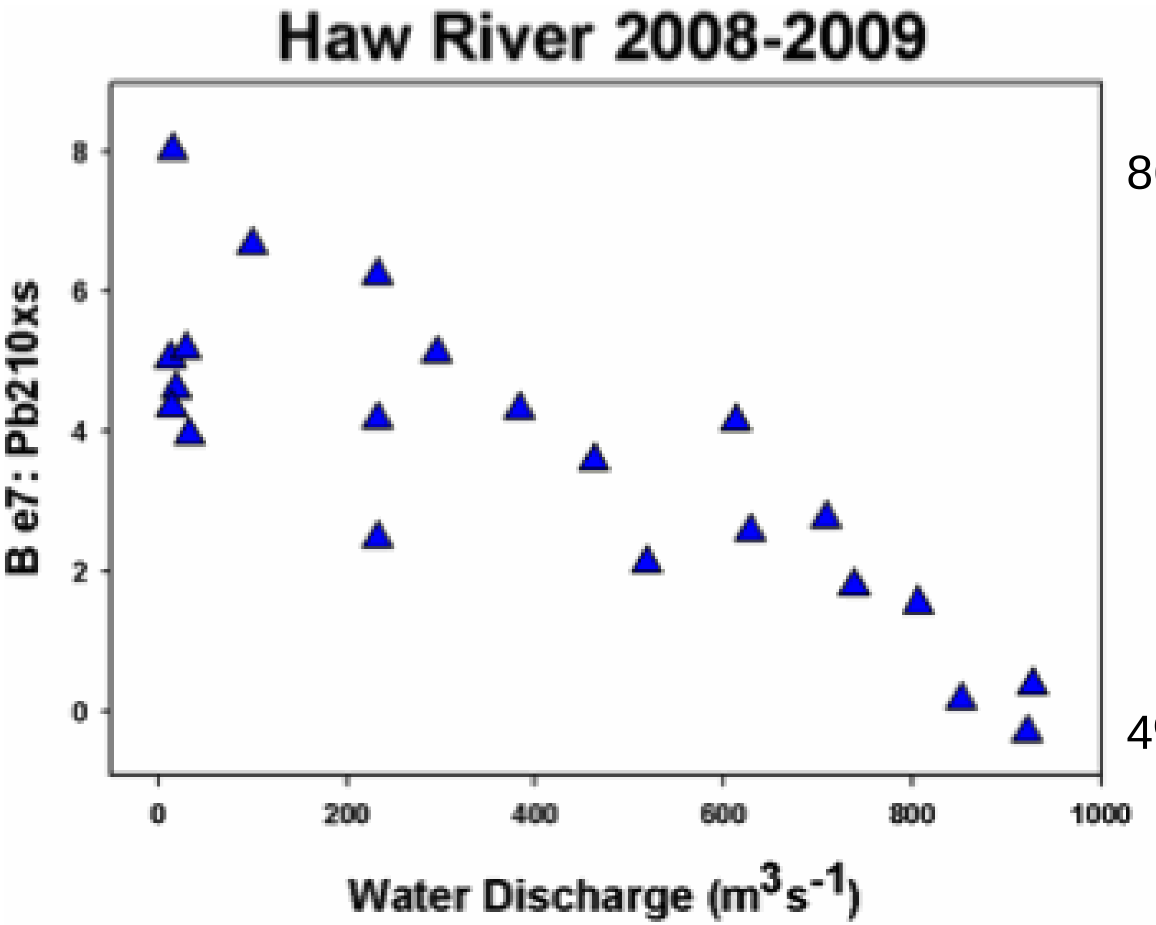
A constant determined by the $^{7}Be/^{210}Pb_{xs}$ in precipitation

OR

Diluted by "old" sediment:

$$\%\ \text{'new' sediment} = 100 \times (A/B)/(A_o/B_o)$$

Decay (age) vs. dilution by "old" sediments

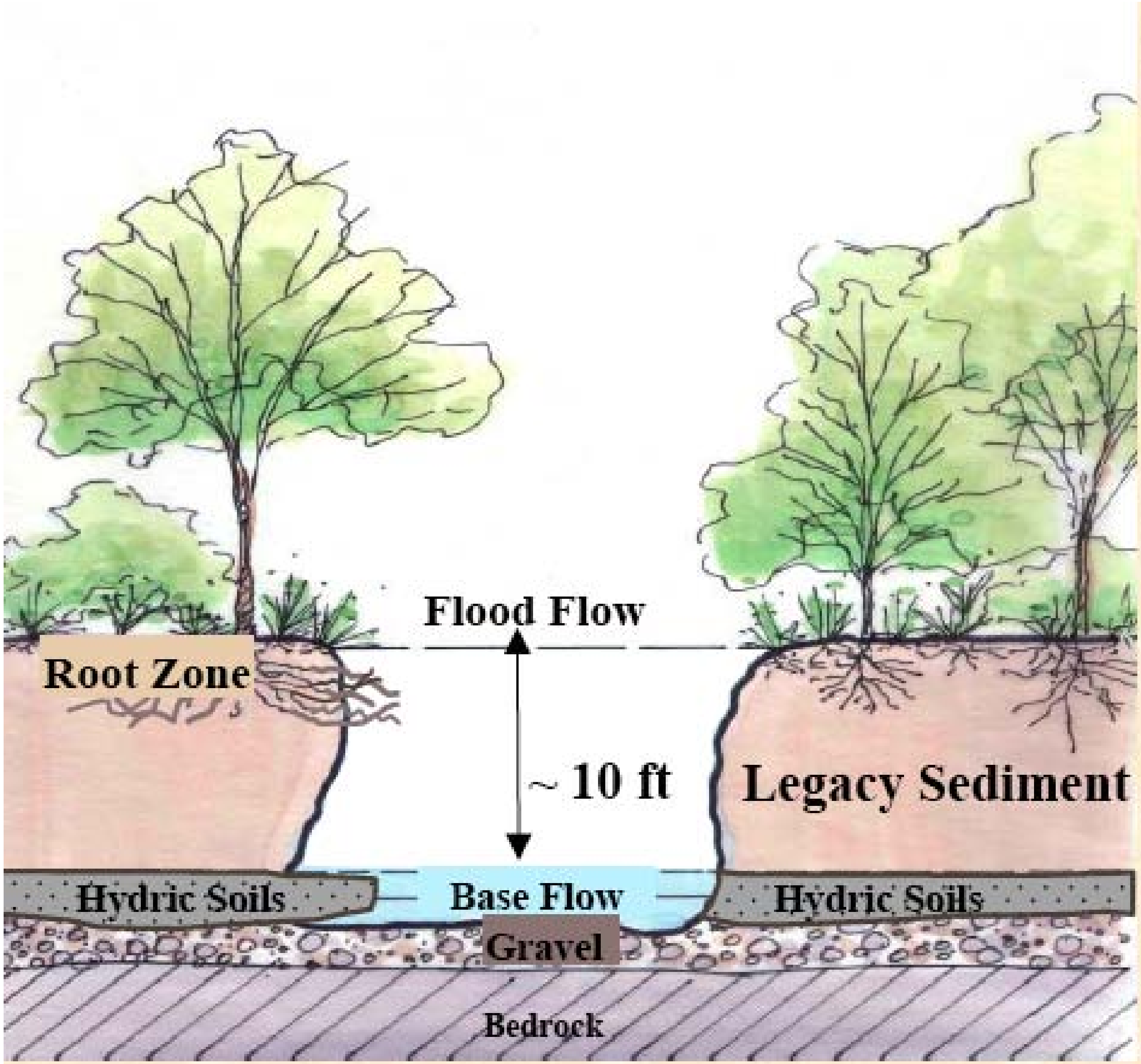


86% new

4% new

Diluted by “old” legacy sediment:

$$\% \text{ ‘new’ sediment} = 100 \times (A/B)/(A_o/B_o)$$


Flood Flow
Root Zone
~ 10 ft
Legacy Sediment
Hydric Soils
Base Flow
Hydric Soils
Gravel
Bedrock

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- **Residence time and extent of geochemical transformation within compartments**

- Degree of connectivity between compartments

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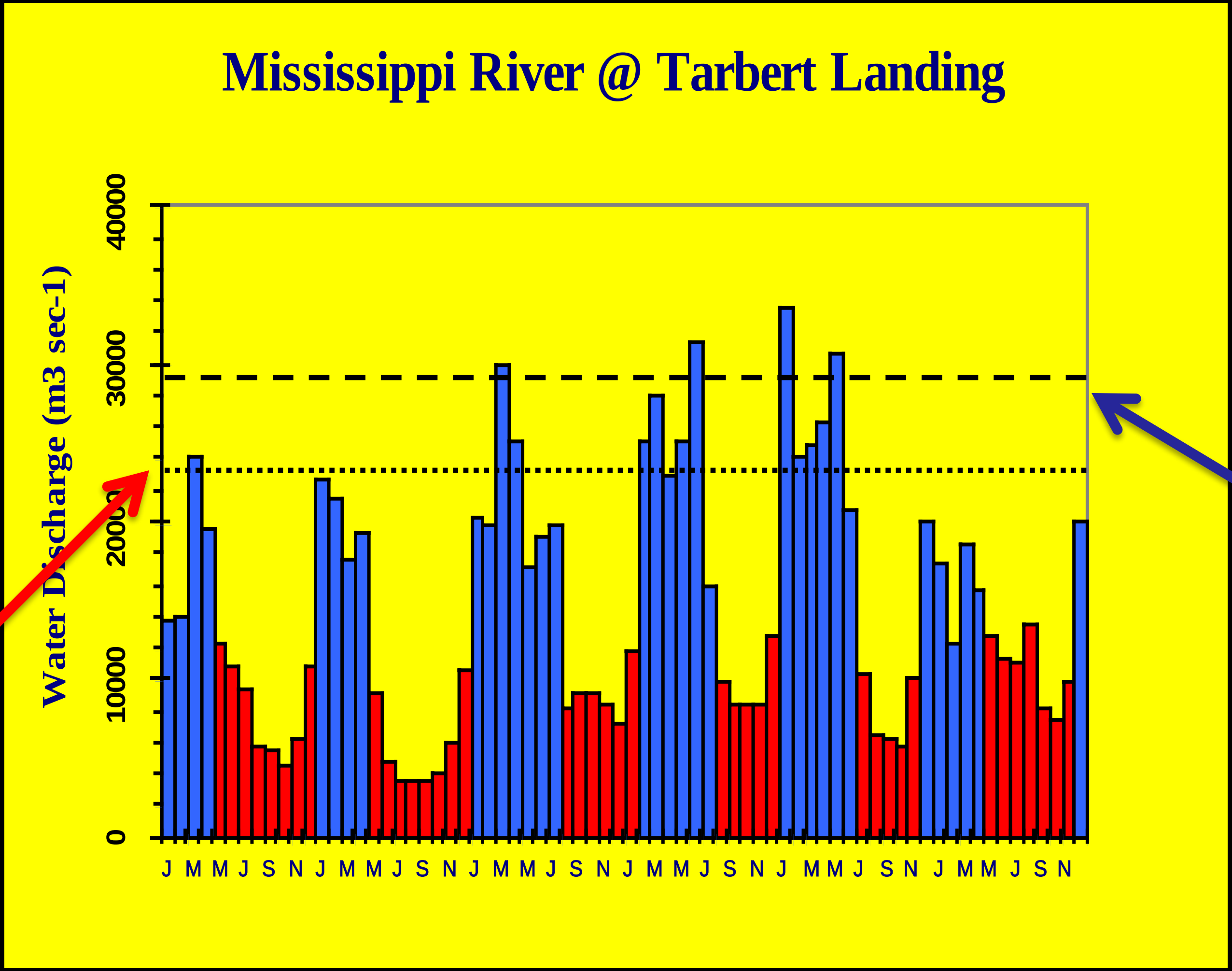
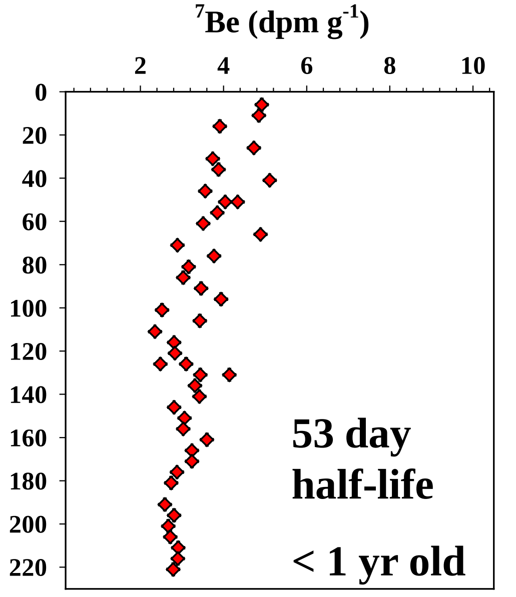
Fine rained riverbed sediments in Lower Mississippi have predictable cycles of deposition and remobilization

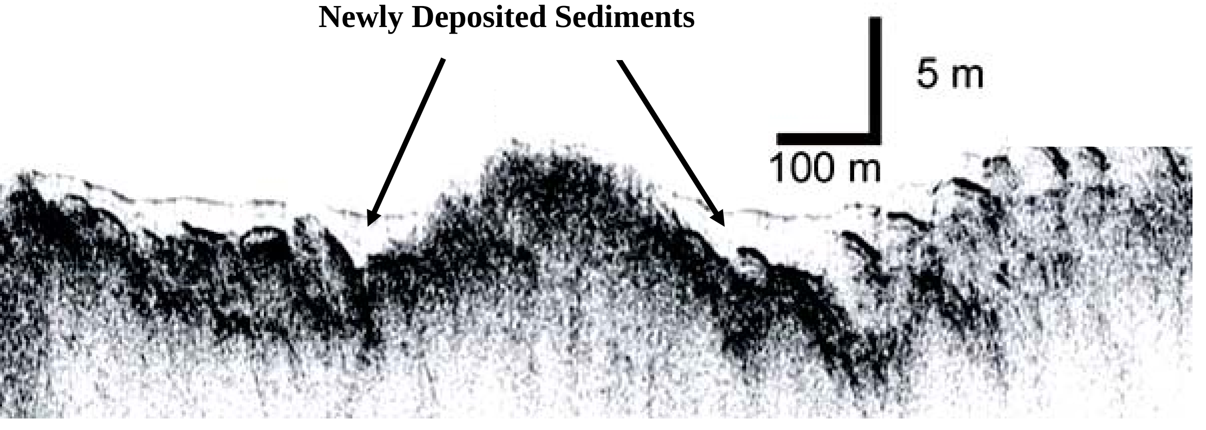


Net deposition and storage < 13,000

Net resuspension and remobilization > 20,000

1-3 m of sediment deposited seasonally in lower river depocenters

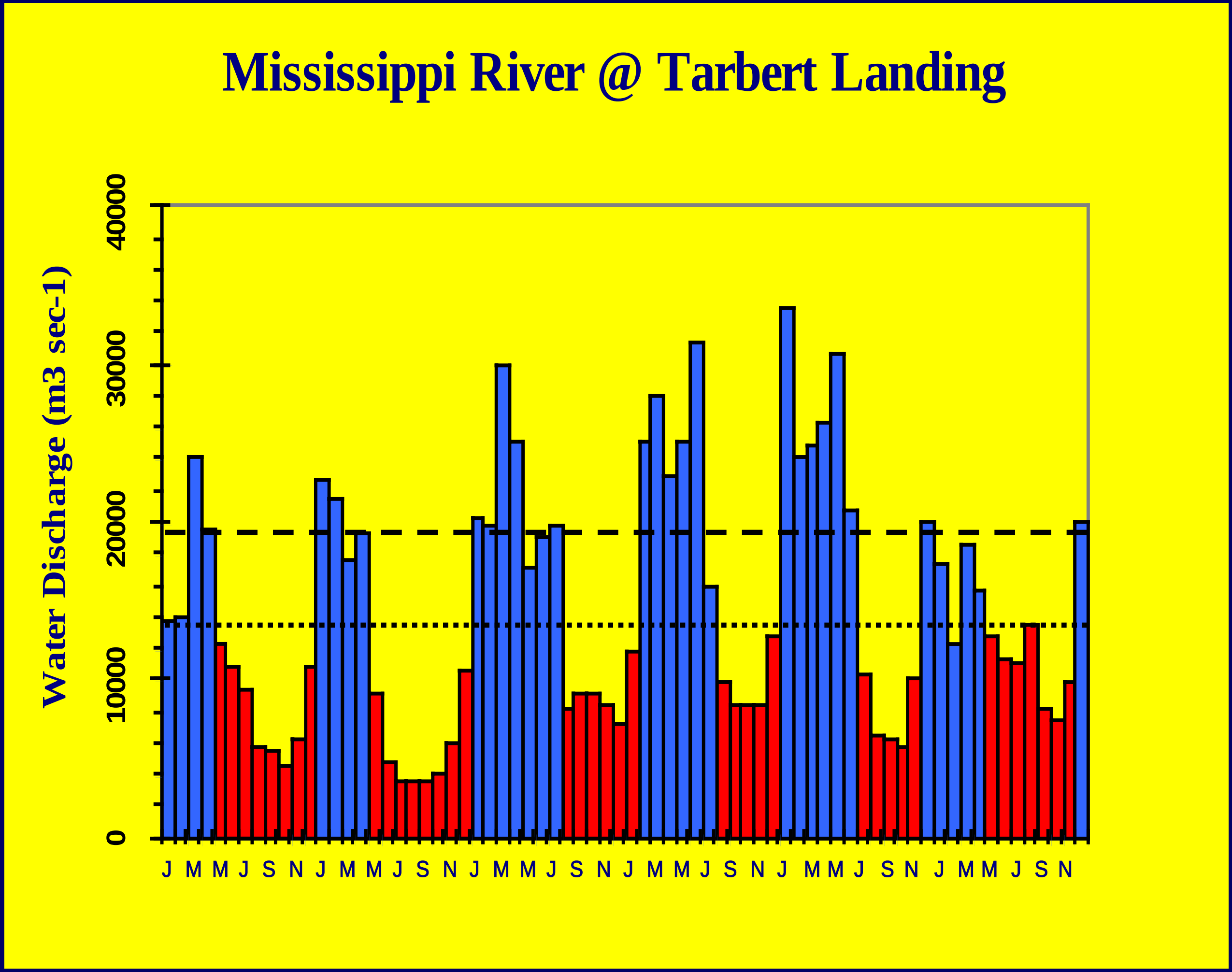




from Allison and Galler

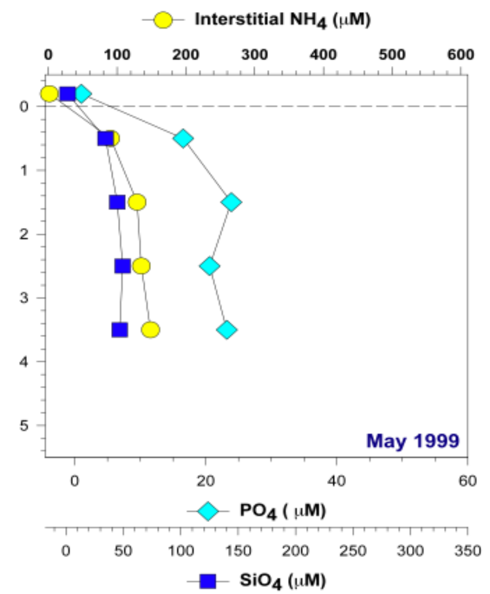
~ 25-30% of Annual Sediment Discharge is Deposited in Lower River during Falling and Low Flow Stages

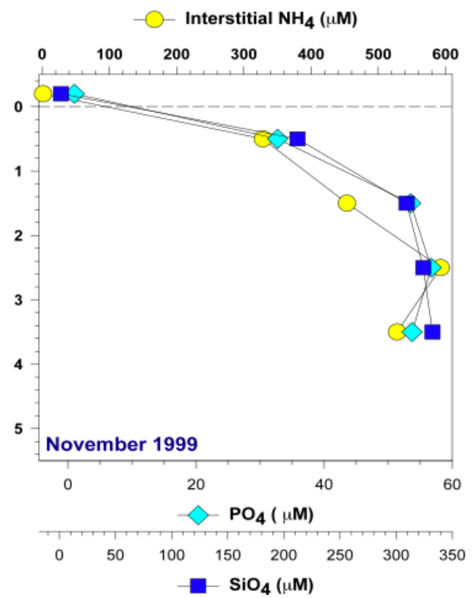
Newly Deposited Sediments Remain on the Riverbed for 5 - 8 months

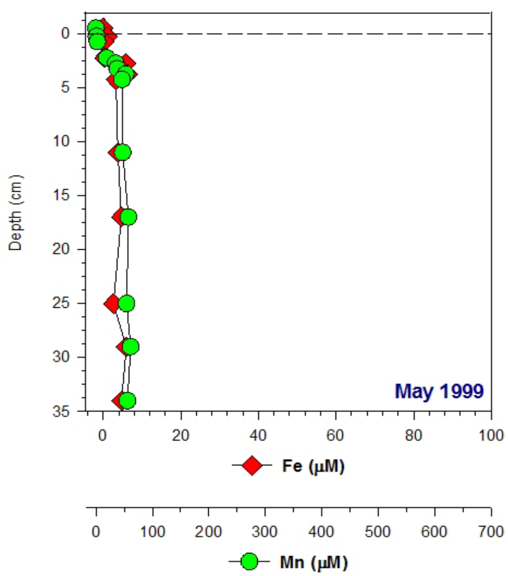


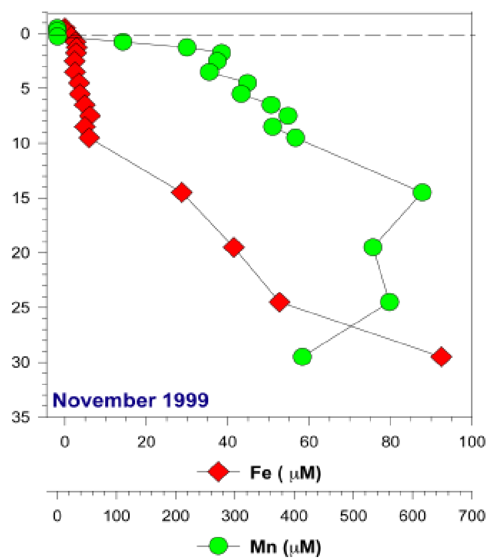
Strong evidence for substantial diagenesis affecting river particulates during seasonal storage

Beginning of depositional period | **End of depositional period**









Strong evidence for substantial Remineralization during seasonal storage

Repeat Cores from Lower River (May and November 1999)

Increases in Porewater Concentrations Over 162 Days:

- **2 fold for PO_4**
- **5-6 fold for NH_4 and SiO_4**
- **15 fold for Mn**
- **20 fold of Fe**

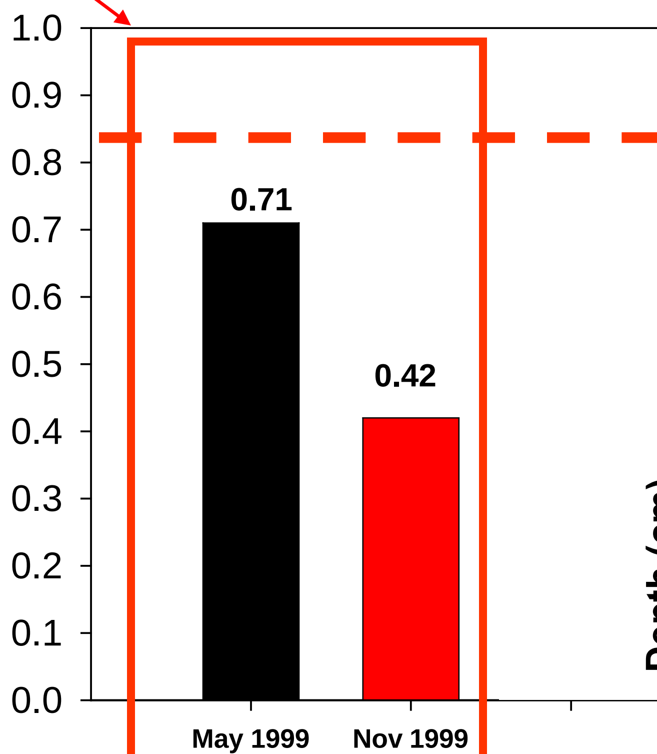
1999: Deposition period early May – late December

Porewater data demonstrates very active remineralization

Mississippi River-Shelf

POC:SA

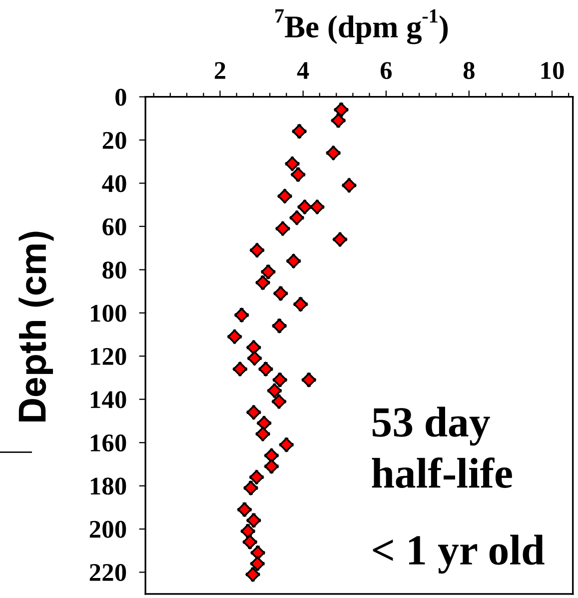
(mg OC m^{-2})



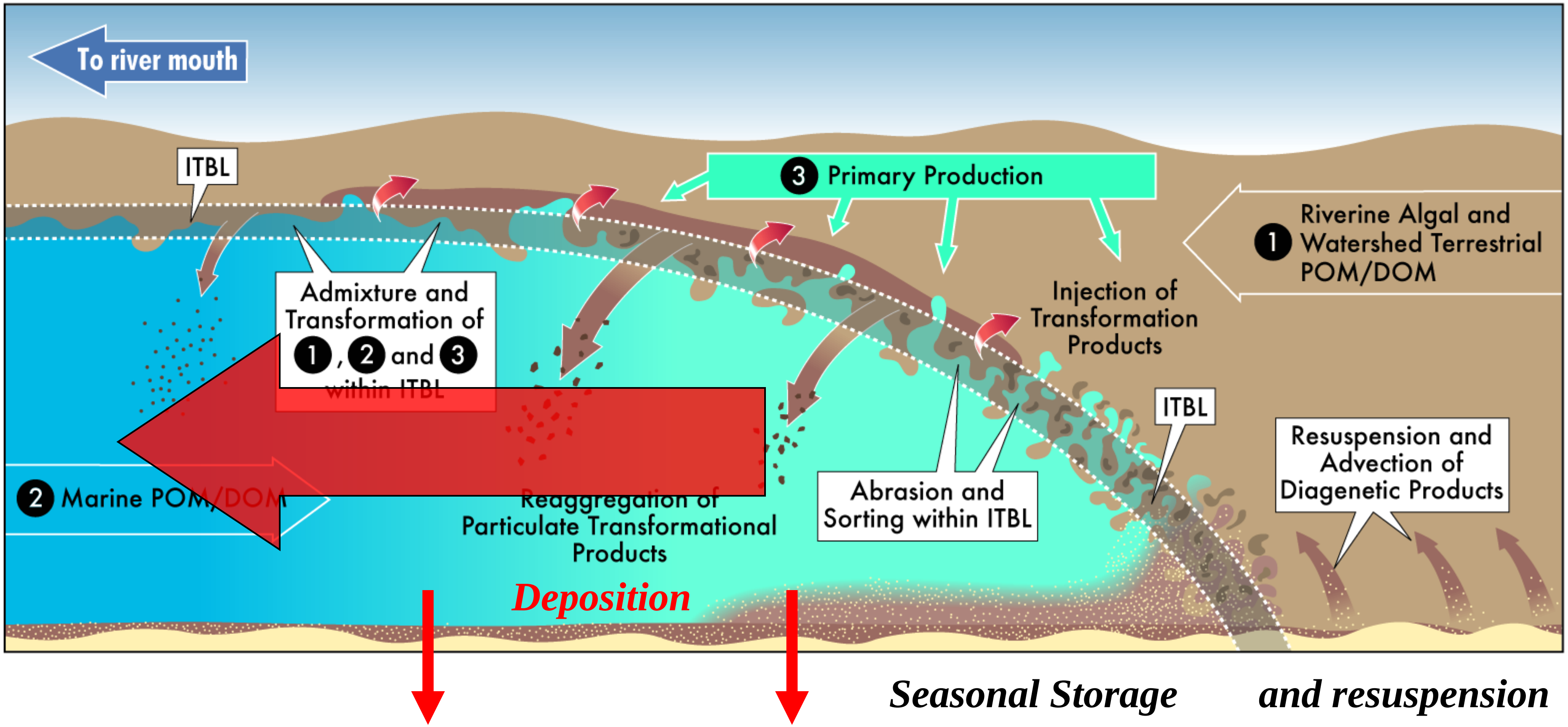
Upper 50 cm of riverbed

(6 months)

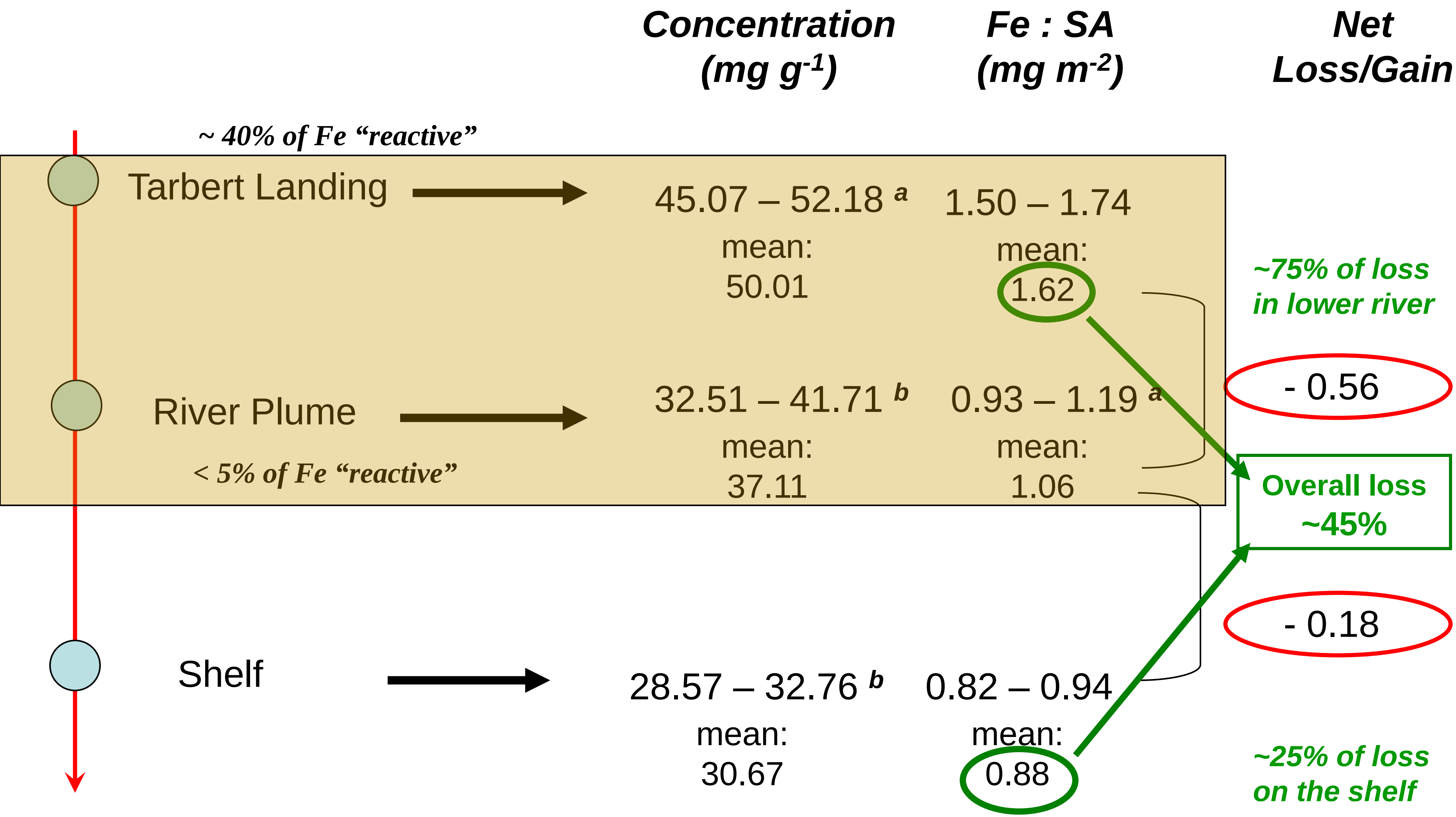
~40% loss



When discharge rises above ~20,000 m^3s^{-1}
…resuspension-remobilization occurs
Materials delivered to the margin



***Particulate Iron**: Mississippi System*



a: Hayes, 1993; b: Trefry et al., 1986

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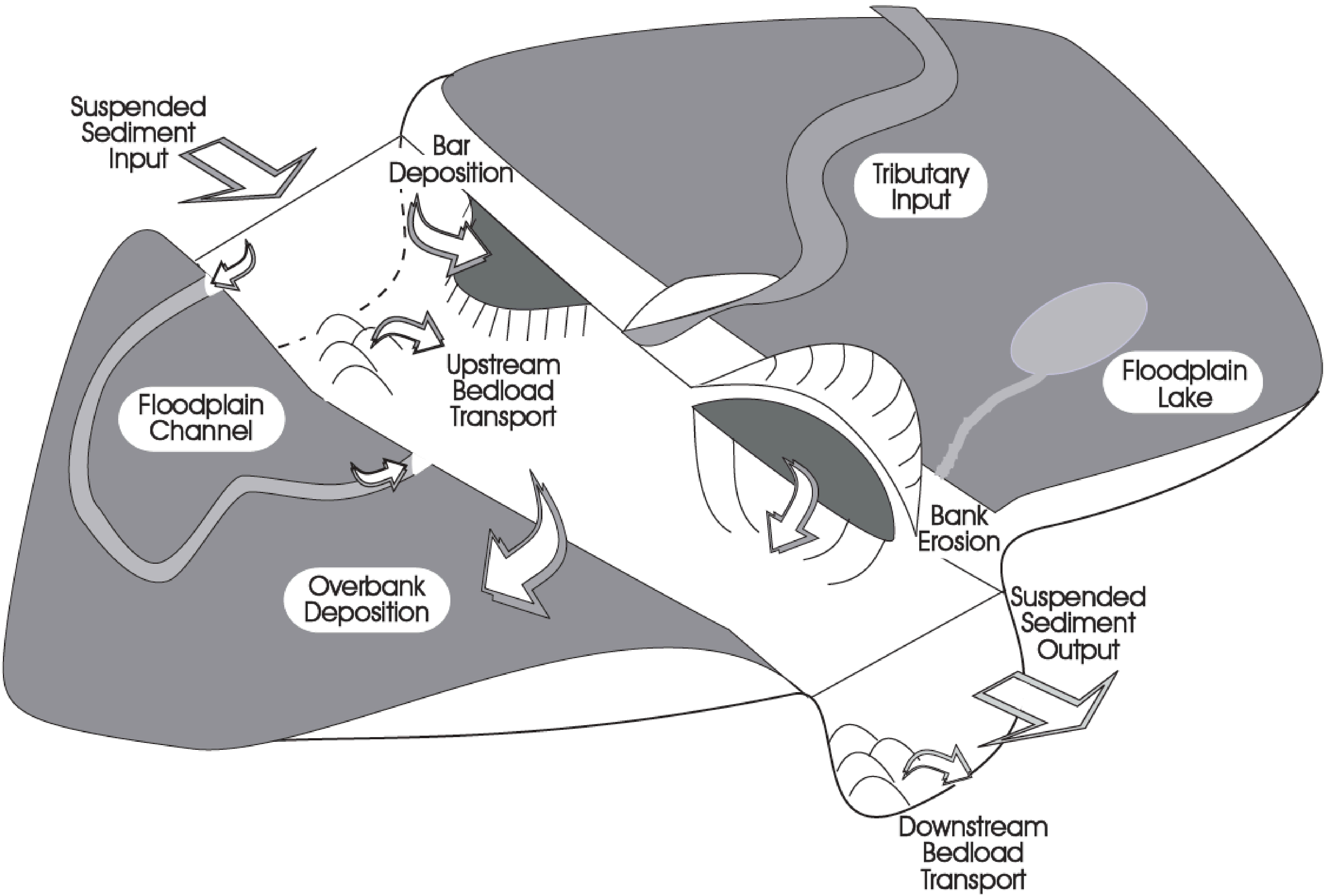
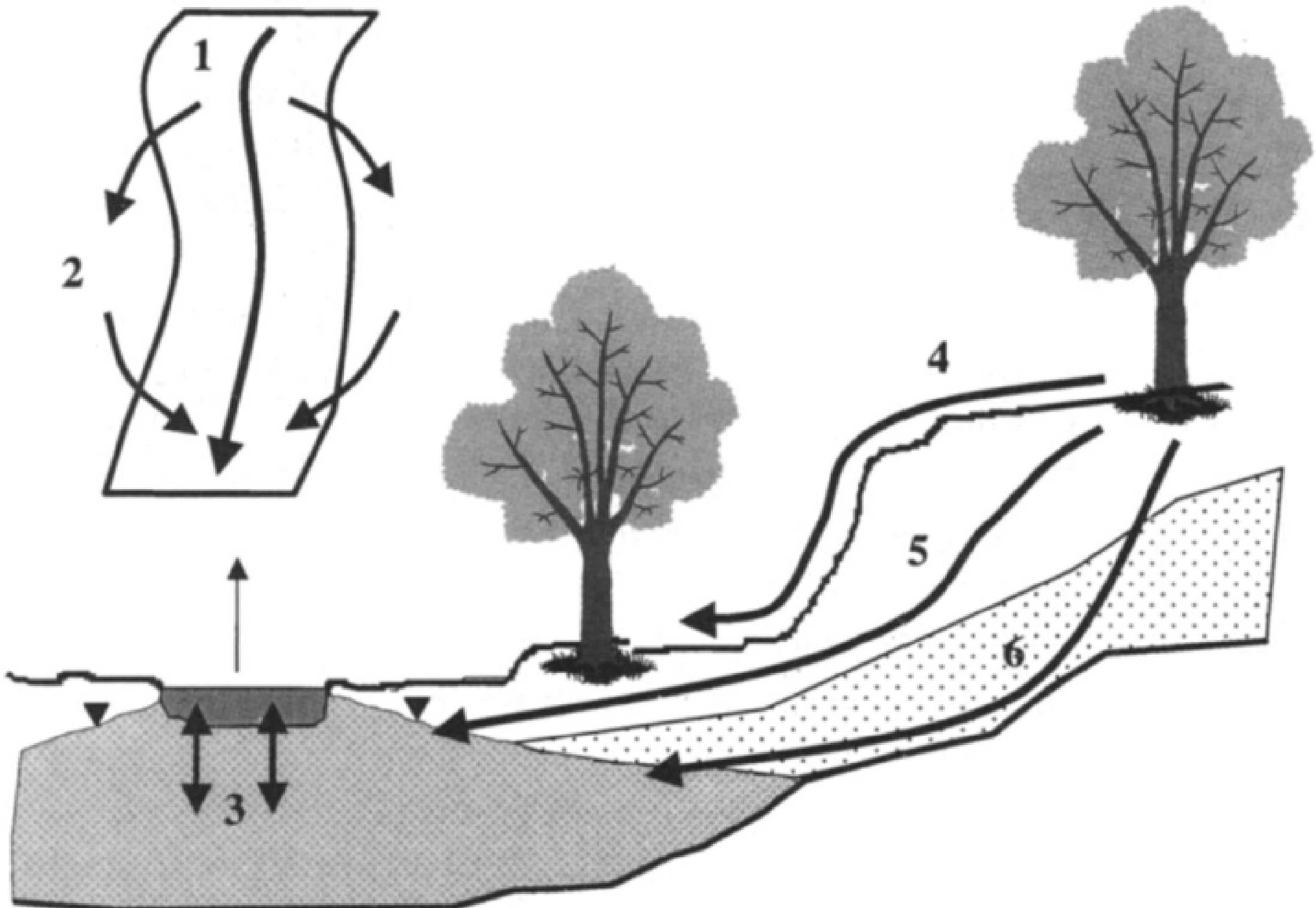
- **Degree of connectivity between compartments**

An example of each …….insights gained from systems highly impacted by man!

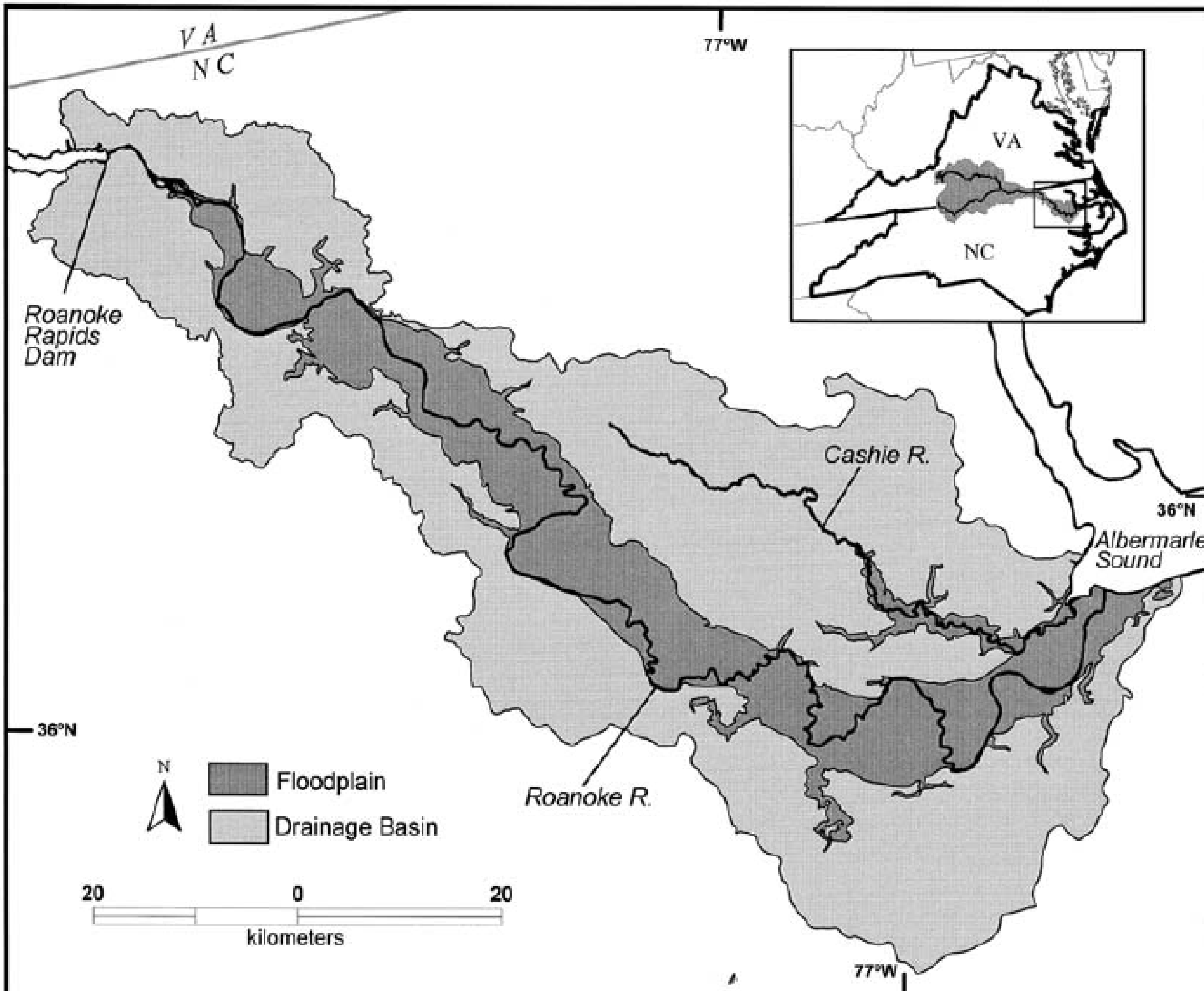
Lateral Connections (floodplain, banks etc)



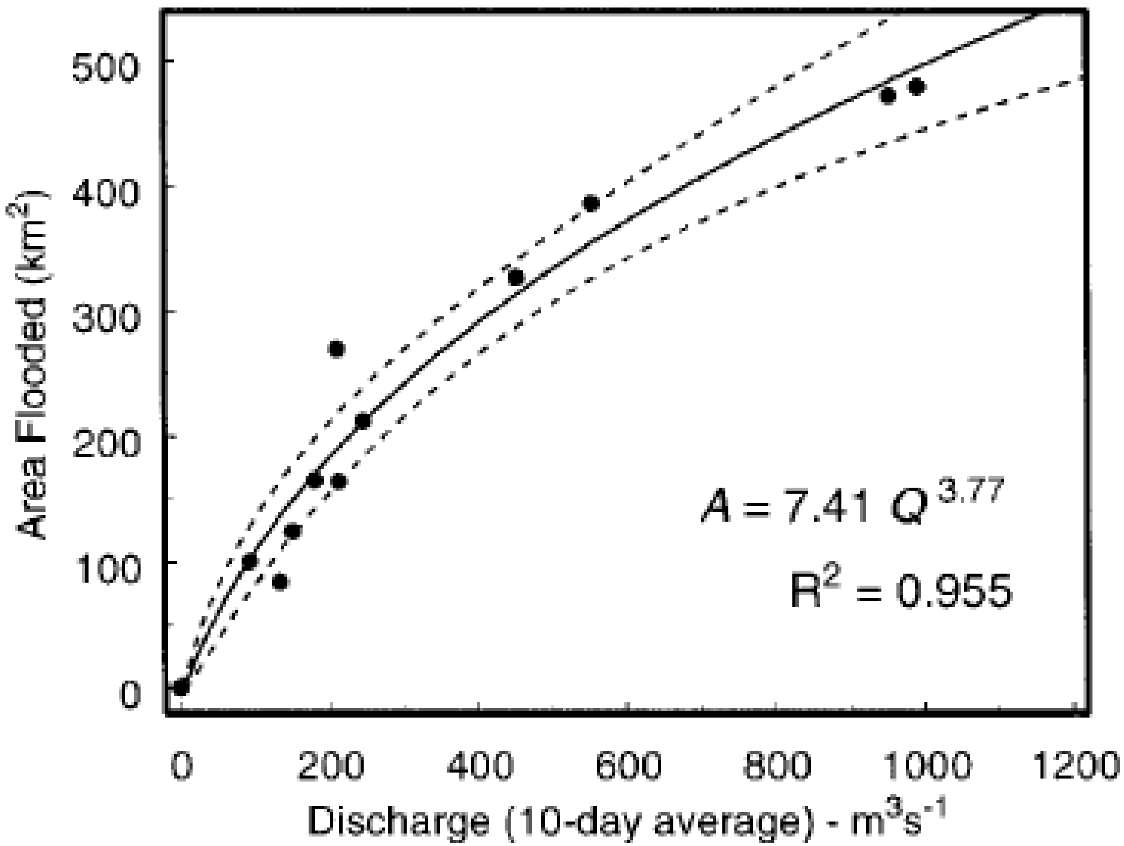
Dunne et al. (1998)



Surface and Groundwater Return



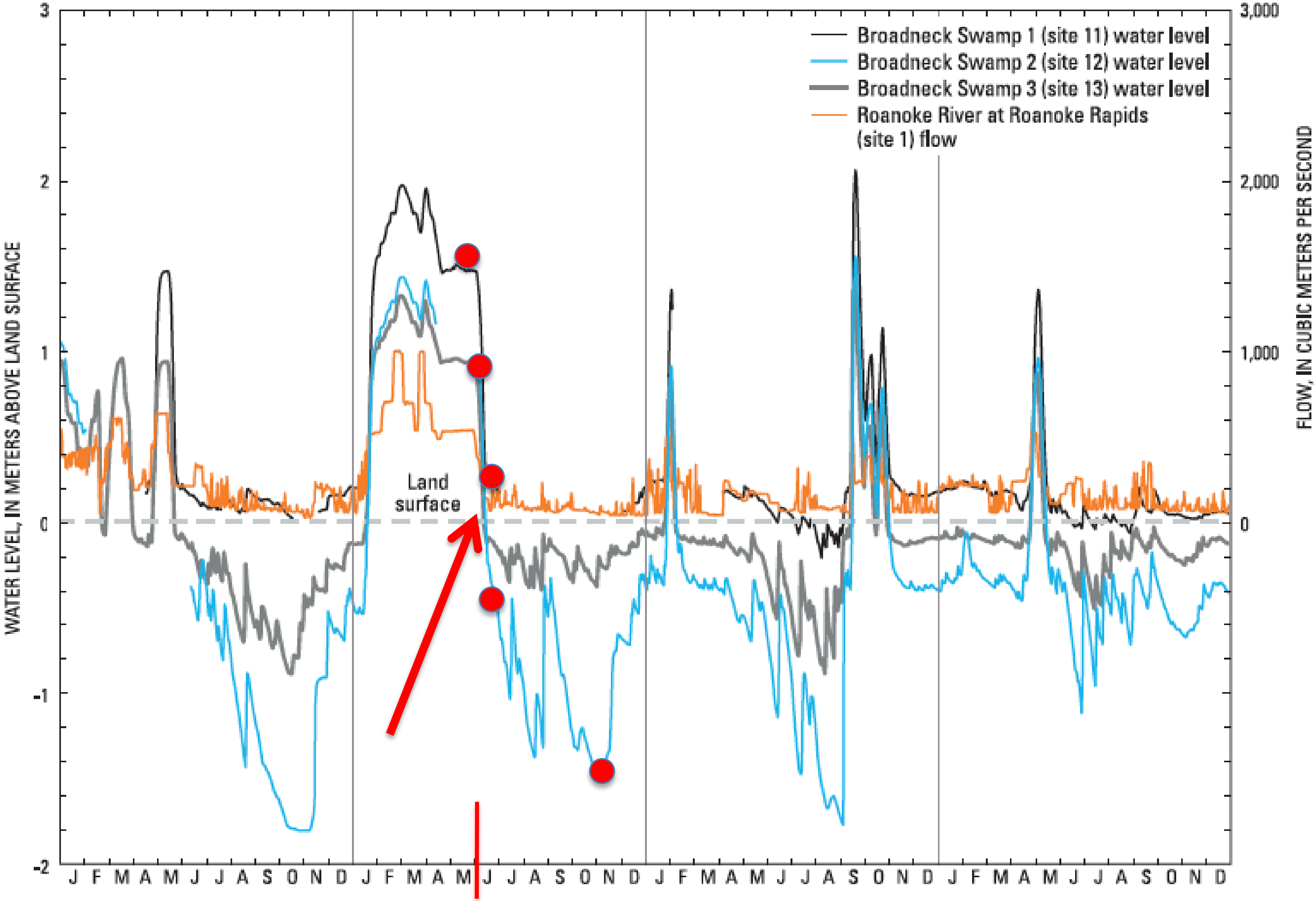
VA
NC
77°W
VA
NC
Roanoke
Rapids
Dam
Cashie R.
36°N
Albermarle
Sound
36°N
N
Floodplain
Drainage Basin
Roanoke R.
20
0
20
kilometers
77°W



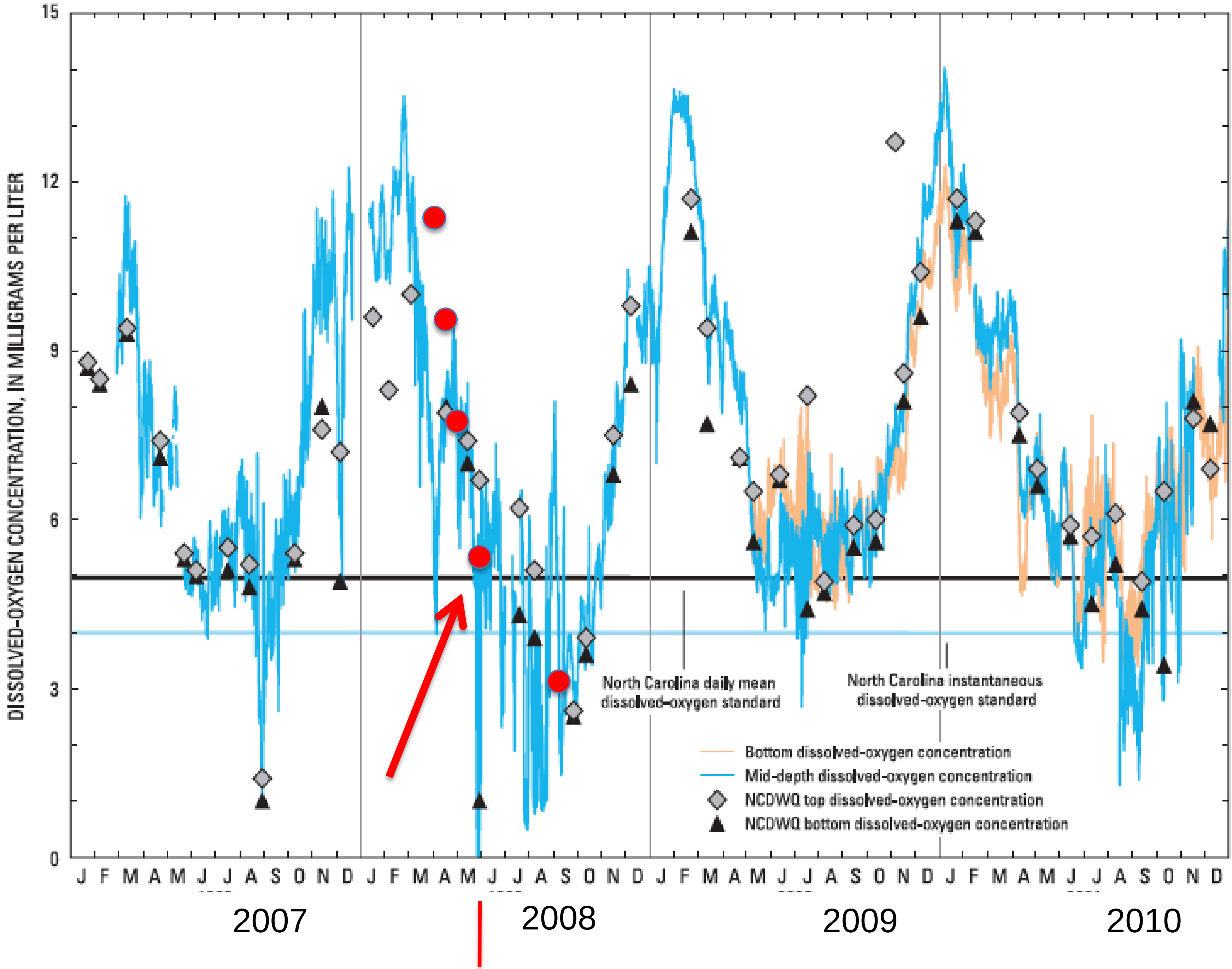
Discharge controlled by Dominion Power

Flooding predictable based on Discharge

Townsend and Foster (2002)



2007 2008 2009 2010



DISSOLVED-OXYGEN CONCENTRATION, IN MILLIGRAMS PER LITER
15
12
9
6
3
0
J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D
2007
2008
2009
2010
North Carolina daily mean dissolved-oxygen standard
North Carolina instantaneous dissolved-oxygen standard
Bottom dissolved-oxygen concentration
Mid-depth dissolved-oxygen concentration
NCDWQ top dissolved-oxygen concentration
NCDWQ bottom dissolved-oxygen concentration

Unfinished Business……

To predict future changes in the geochemical material flux from rivers, we have to have a better mechanistic understanding of processes within the river and downriver transformations