Benthic Sources and Sinks of Nutrients and Trace Elements – An Update

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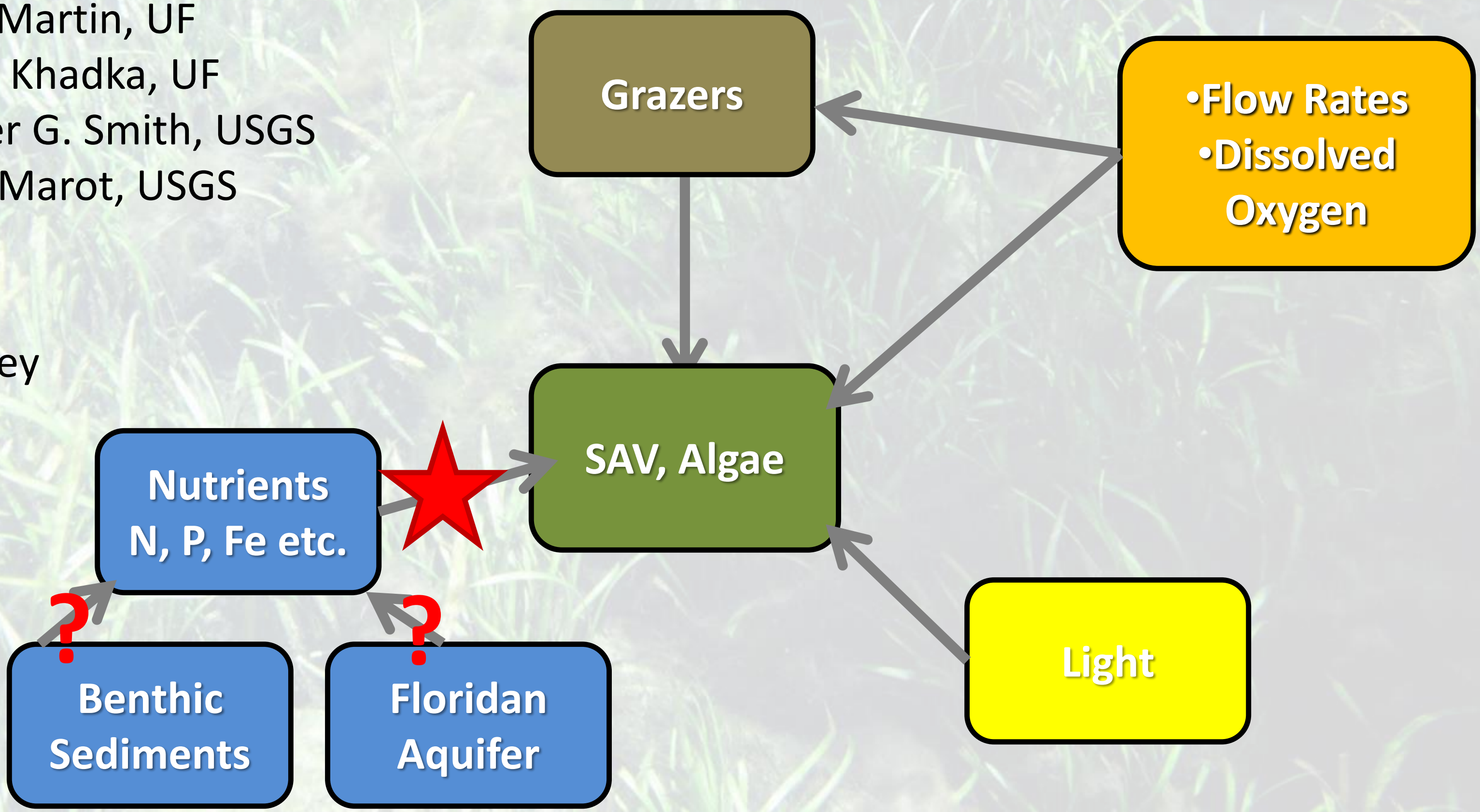
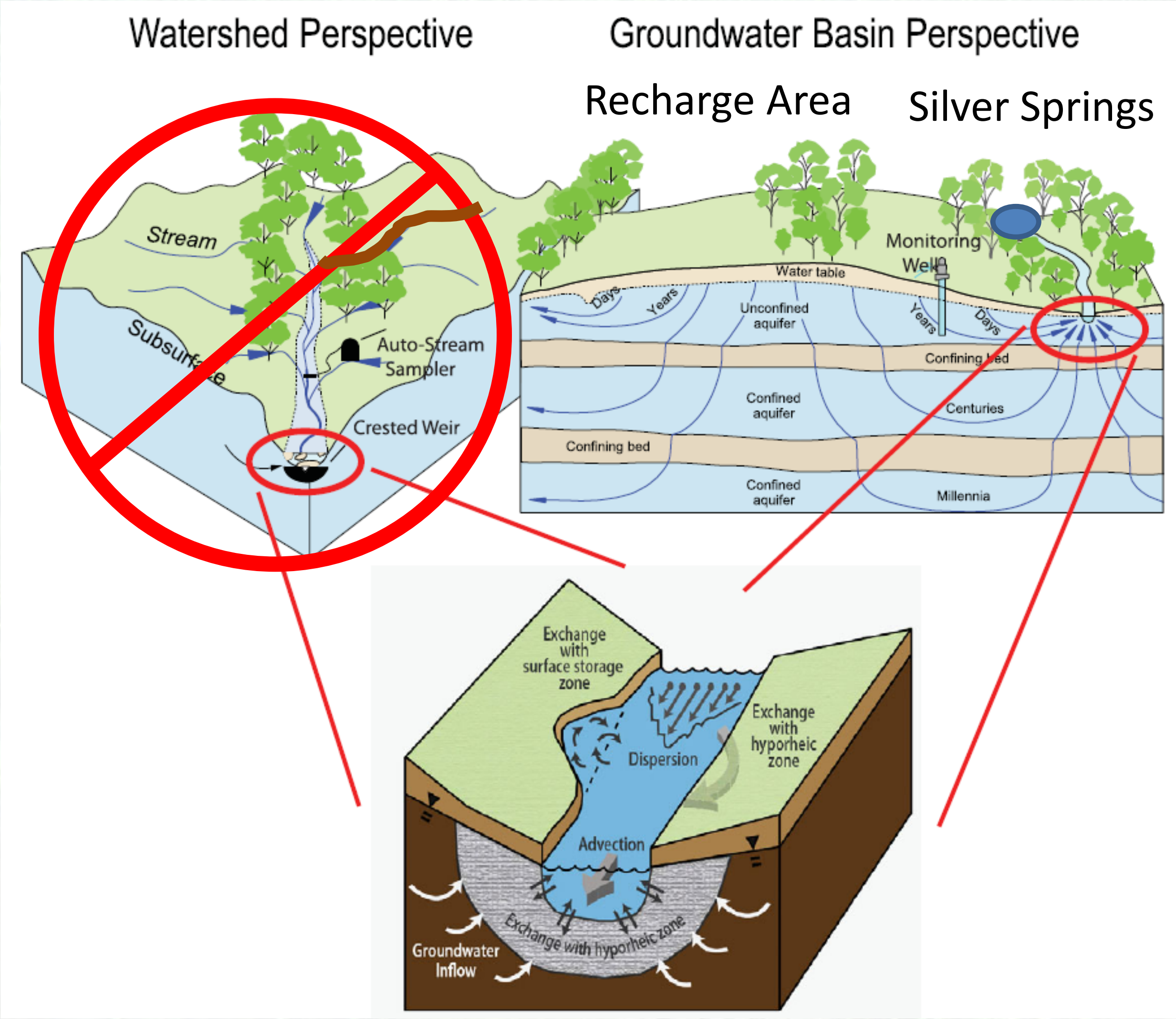
Special thanks to Mike Coveney and Jodi Slater



Modified from M Cohen

Karst River Corridor Science



- Overland flow
  - Negligible in karst settings
  - Maybe in Silver River drainage?
- Large contribution from groundwater
  - What are sources?
  - What are ecosystem impacts?

Harvey and Gooseff, 2015, WRR

Overall Goal

Assess and estimate benthic fluxes (diffusion and advection) of nutrients (C,N,P, S, Fe, Mn) from bottom sediments to/from river

Tasks:

1. Measure sediment thickness ✓
2. Measure physicochemical properties of sediment
   A. C, N, P metal concentrations ✓
   B. Porosity, permeability ✓
3. Measure chemical compositions of pore waters ✓
4. Measure head gradients between pore water and river ✓

Overall Goal

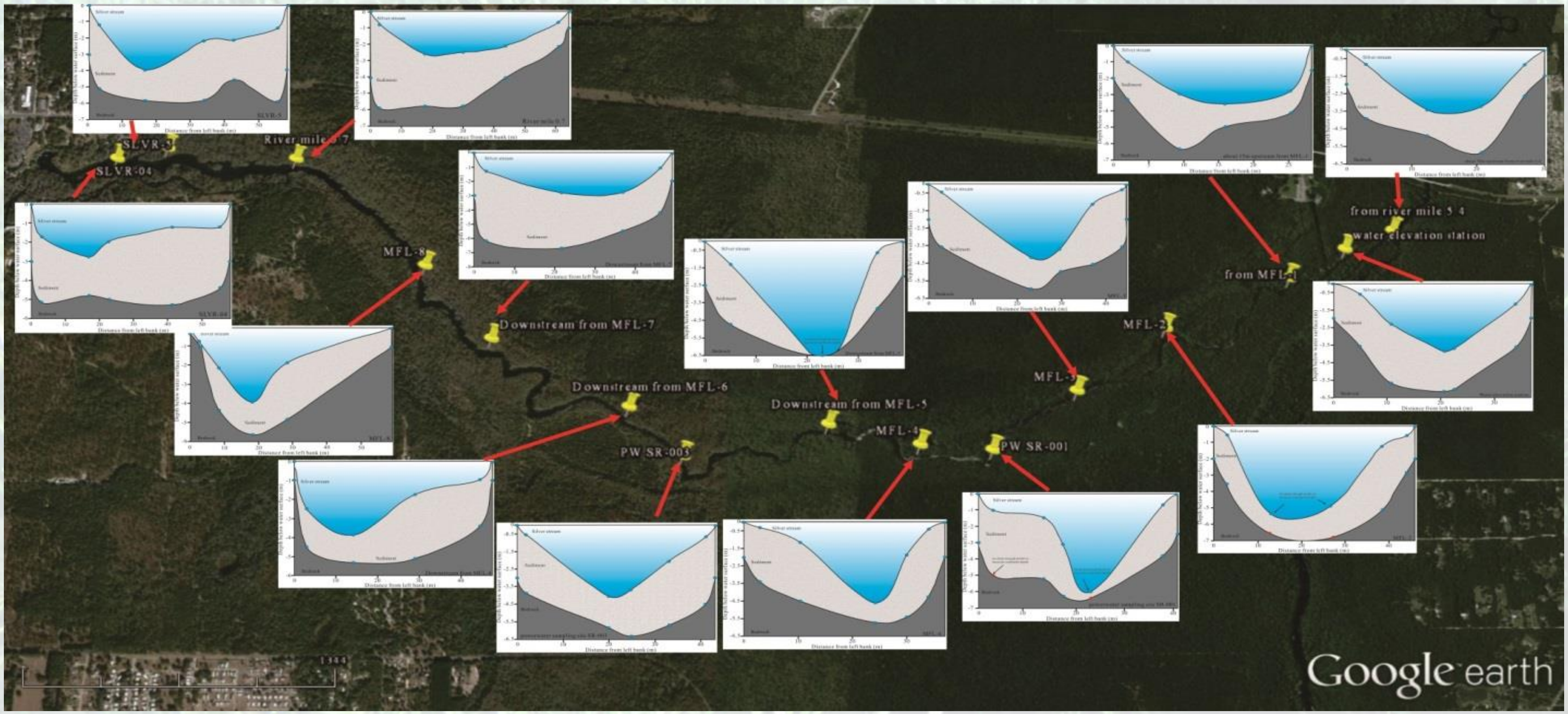
Assess and estimate benthic fluxes (diffusion and advection) of nutrients (C,N,P, S, Fe, Mn) from bottom sediments to/from river

Tasks:

5. Estimate sediment ages/accumulation rates - ongoing (almost ✓; sample analyses ongoing)
6. Estimate diffusive fluxes – ✓ - refining
7. Estimate advective fluxes – ✓ - refining
8. Compare with other fluxes – ✓ - refining

Sample sites

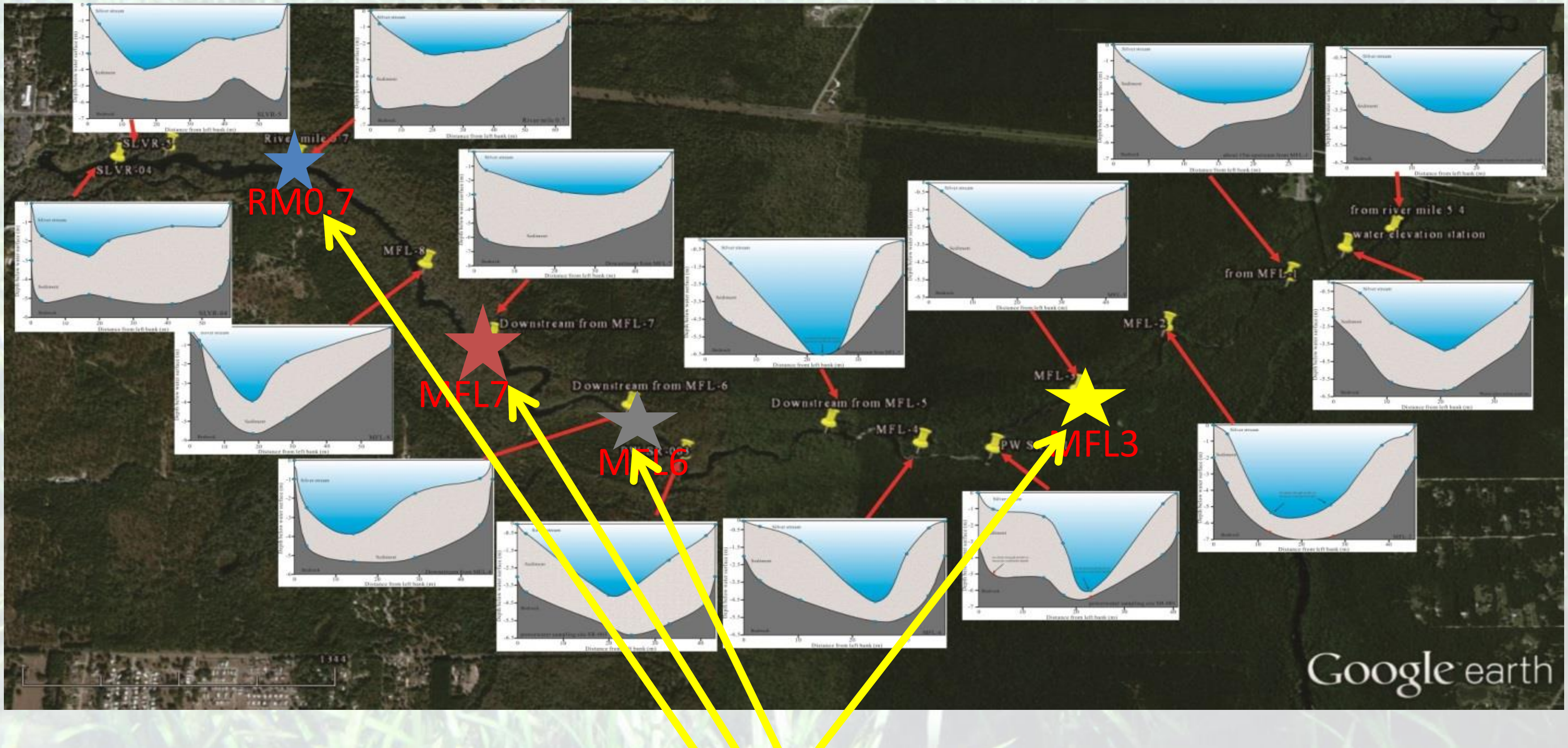
Upstream → Downstream



- 15 transects measured for sediment thickness

Sample sites

Upstream → Downstream

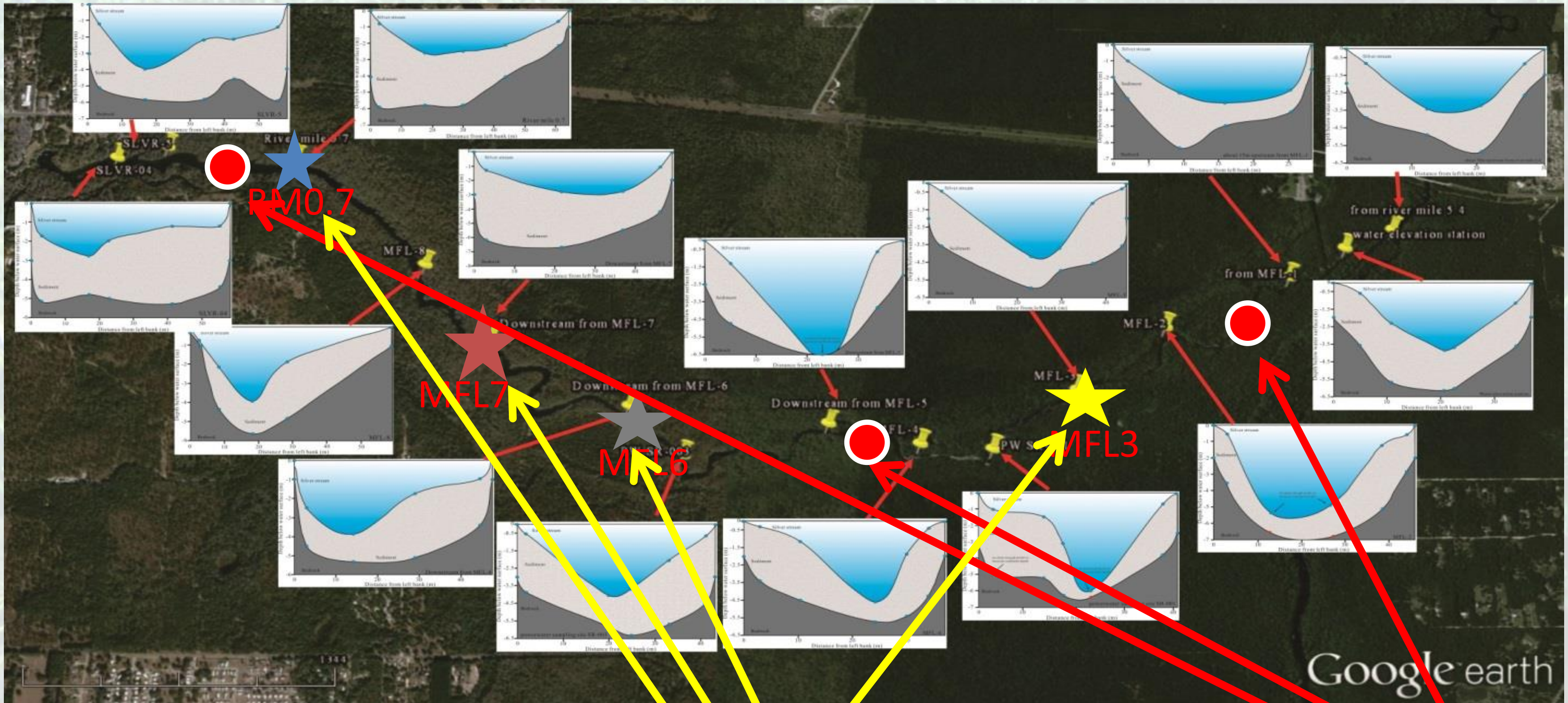


- 15 transects measured for sediment thickness

- Four primary transects
  - Deep and shallow pore water compositions
  - Hydraulic conductivity
  - Coring - stratigraphy
  - Long term head gradients
  - Sedimentation rates

Sample sites

Upstream → Downstream



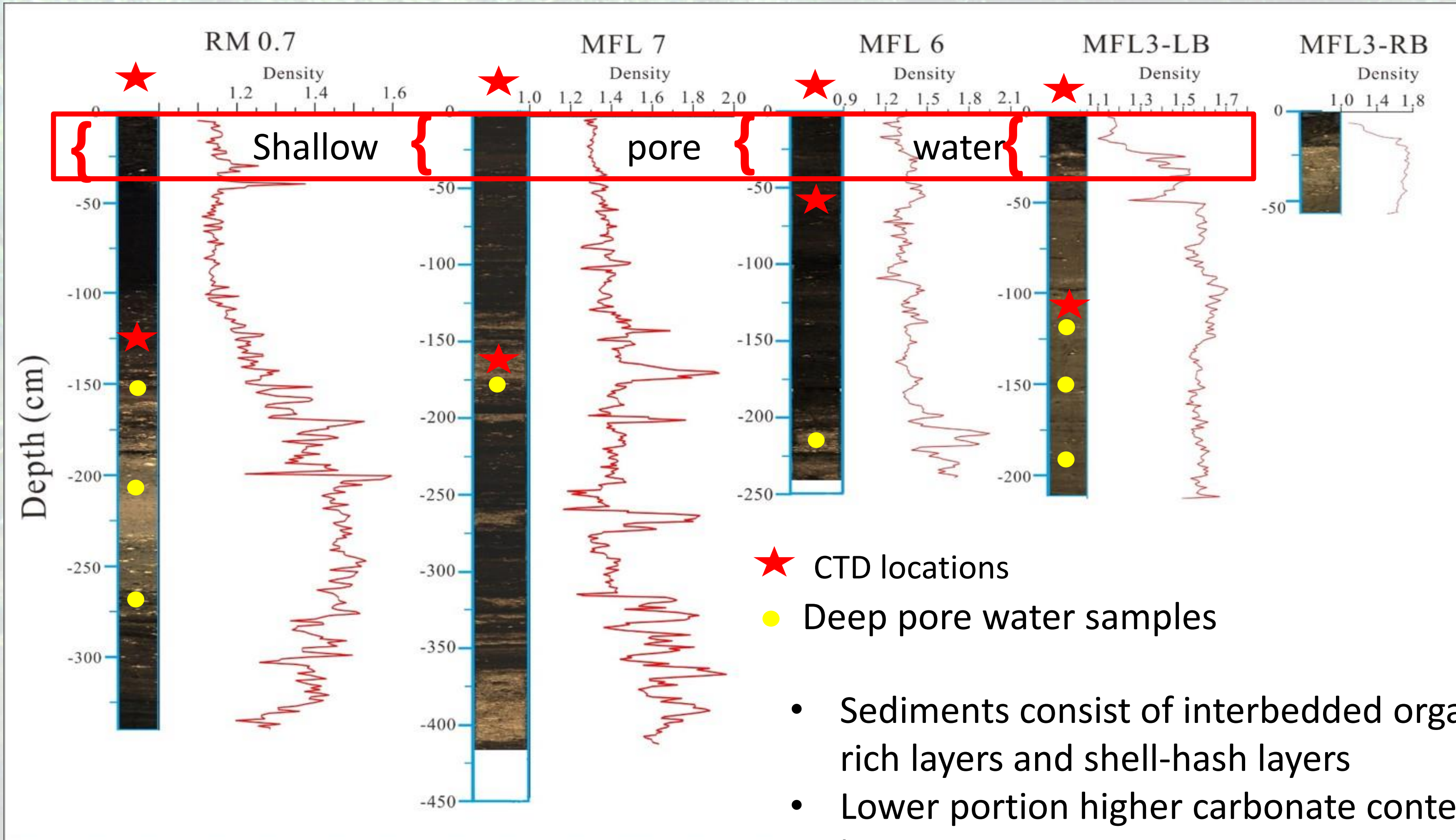
- 15 transects measured for sediment thickness

- Four primary transects
  - Deep and shallow pore water compositions
  - Hydraulic conductivity
  - Coring - stratigraphy
  - Long term head gradients
  - Sedimentation rates

- Three additional pore water sample sites
  - Shallow pore waters only
  - Cohen lab sites

Sediment Stratigraphy

Upstream → Downstream

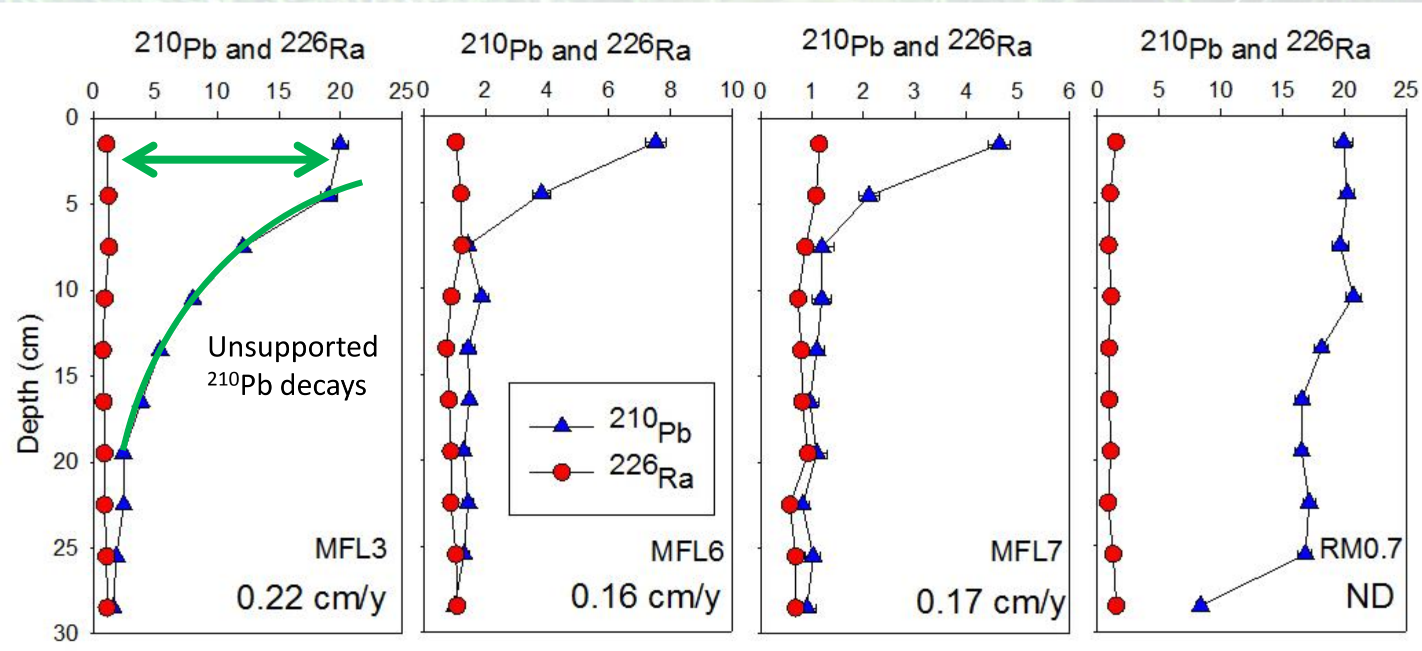


- Sediments consist of interbedded organic C-rich layers and shell-hash layers
- Lower portion higher carbonate content, lower OC contents

Sedimentation Rates - Status

Fairly consistent sedimentation rates except RM0.7

- RM0.7 suggests rapid sedimentation
- Rapid sedimentation (young sediment) suggest river also eroding



- All γ counting
- Provide ^{226}Ra activities
- Slow and difficult

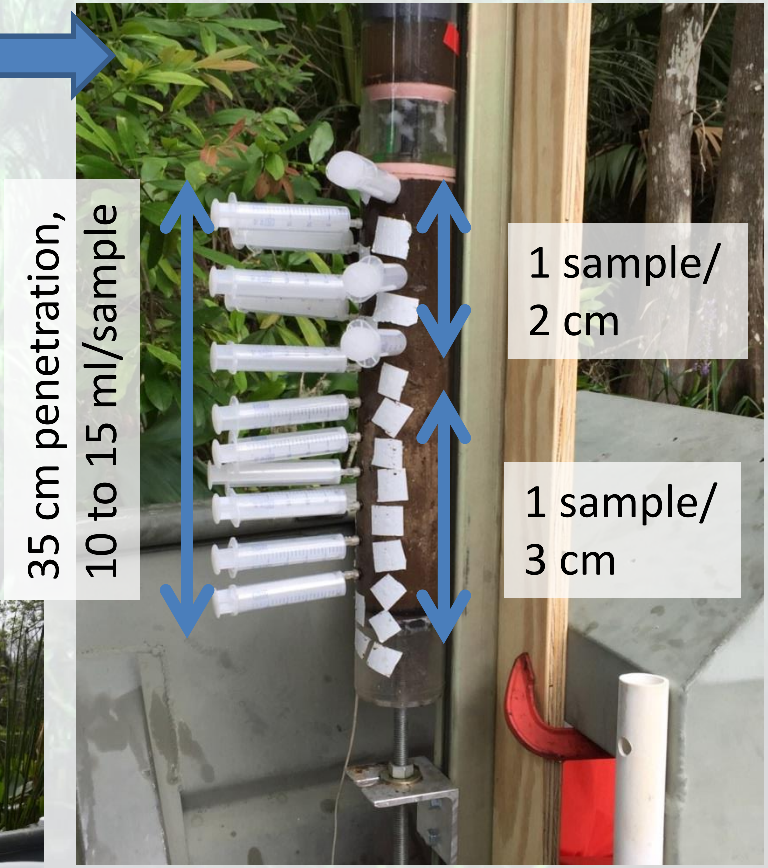
$^{226}Ra \xrightarrow{1699\ yr} {}^{xxx}Y \xrightarrow{minutes}$

$^{210}Pb \xrightarrow[22\ yr]{} {}^{206}Pb$

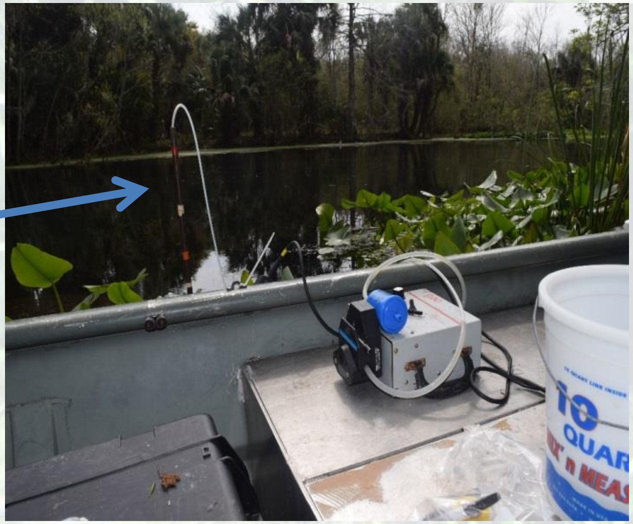
- Recollected three cores - Analyze by α counting
  - Higher resolution (1/cm)
- Collection from 0 to 60 cm at RM0.7

Pore Water Sampling

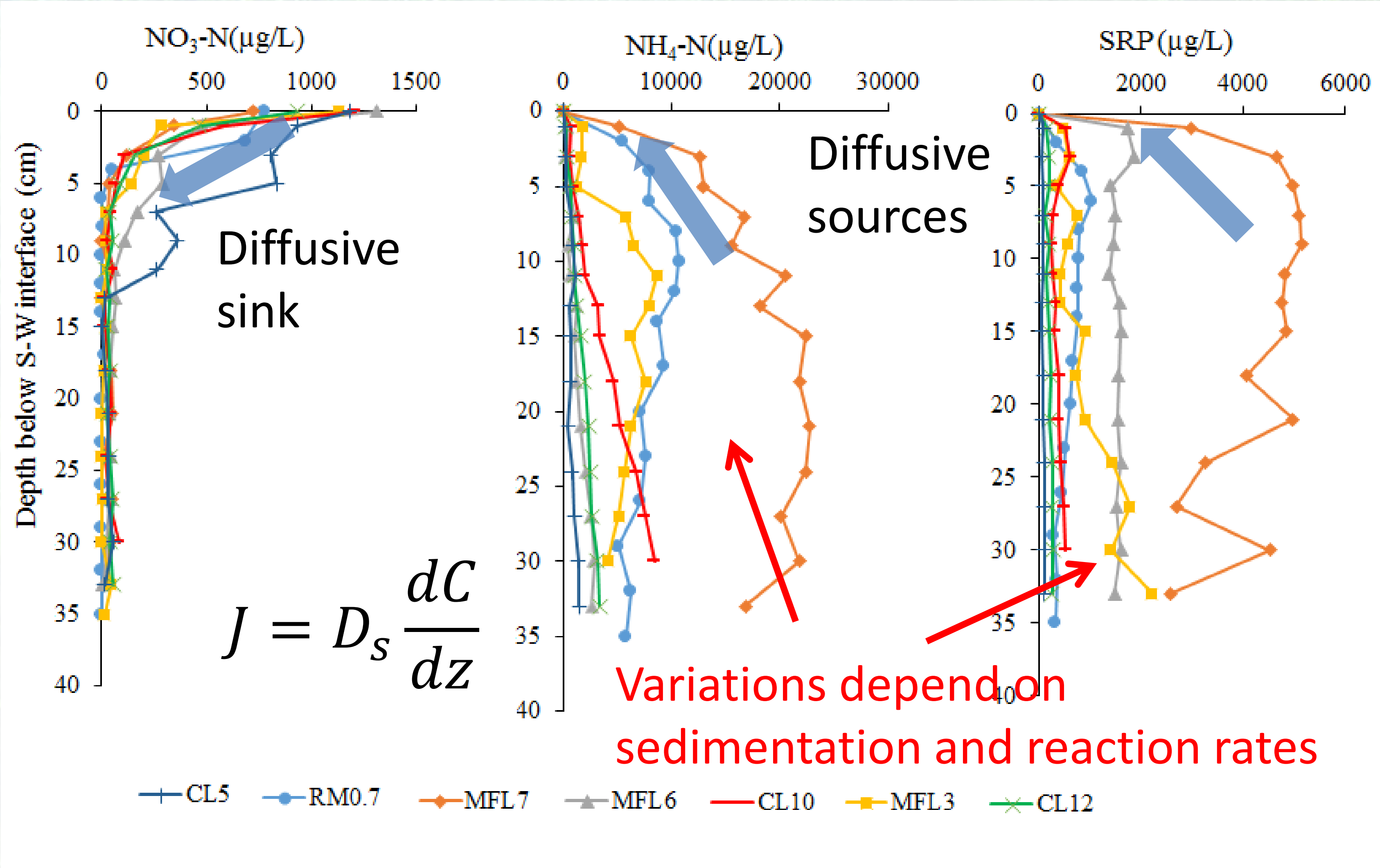
- Whole core squeezers:
  - Shallow high resolution pore water
  - Estimate diffusive fluxes
  - Similar core barrel for ^{210}Pb collection
- Vapor probe:
  - Deep low resolution sampling
  - Provide “end-member” pore water compositions



Pump water from 1 – 2 m depth



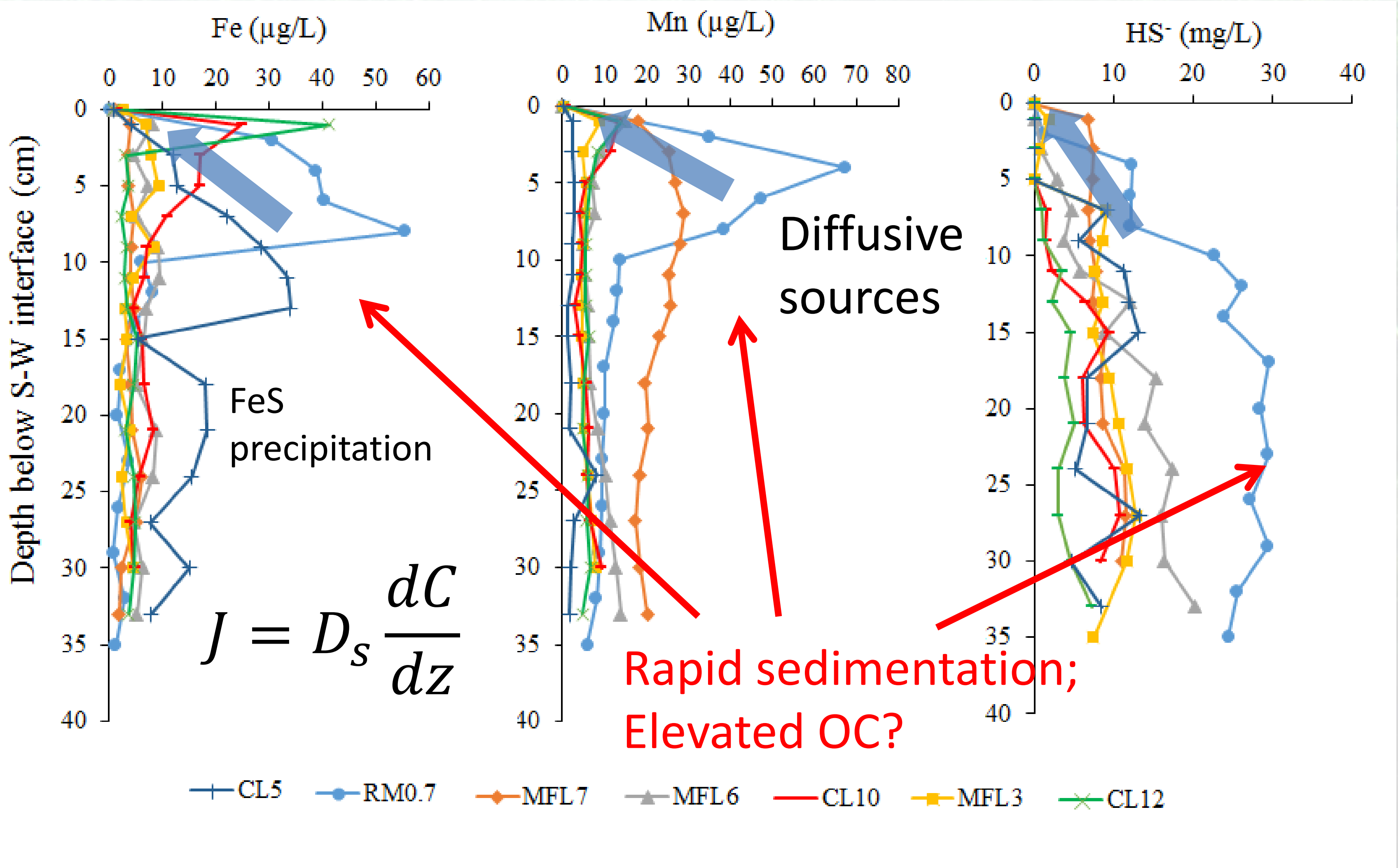
Shallow Pore Water Profiles – Nutrients



$$J = D_s \frac{dC}{dz}$$

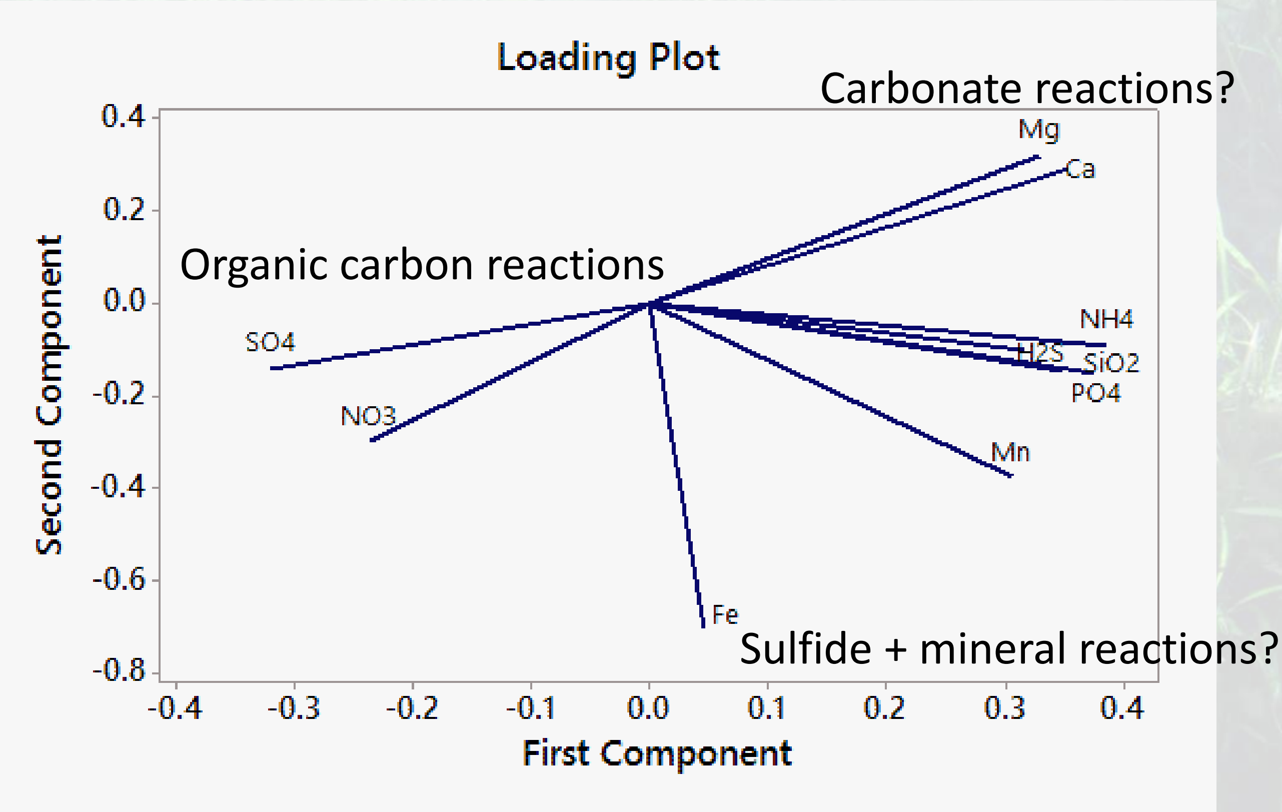
- Loss of NO_3 to sediments - homogeneous
- NH_4 and SRP sources to water column – heterogeneous; depends on sediment compositions and/or sedimentation rates

Shallow Pore Water Profile – Metals and Sulfide



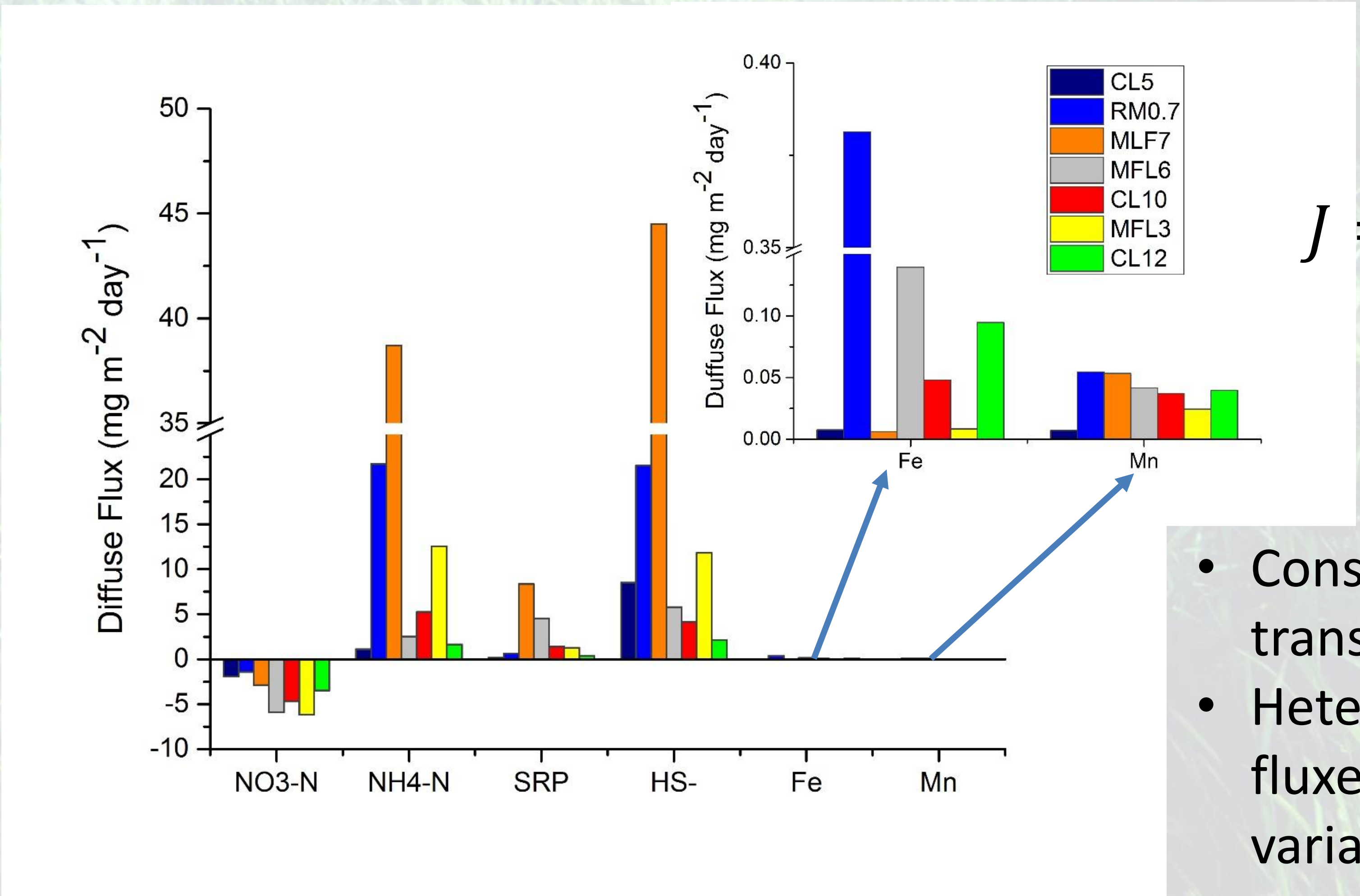
- All sources to water column
- Major variations may relate to sedimentation rate

Pore water Chemistry – PCA



- Redox sensitive solutes and nutrients controlled by 1st component.
- Inverse correlation between oxidized and reduced species
- Fe, Ca & Mg not related
  - Ca and Mg - carbonates
  - Fe –sulfide influence

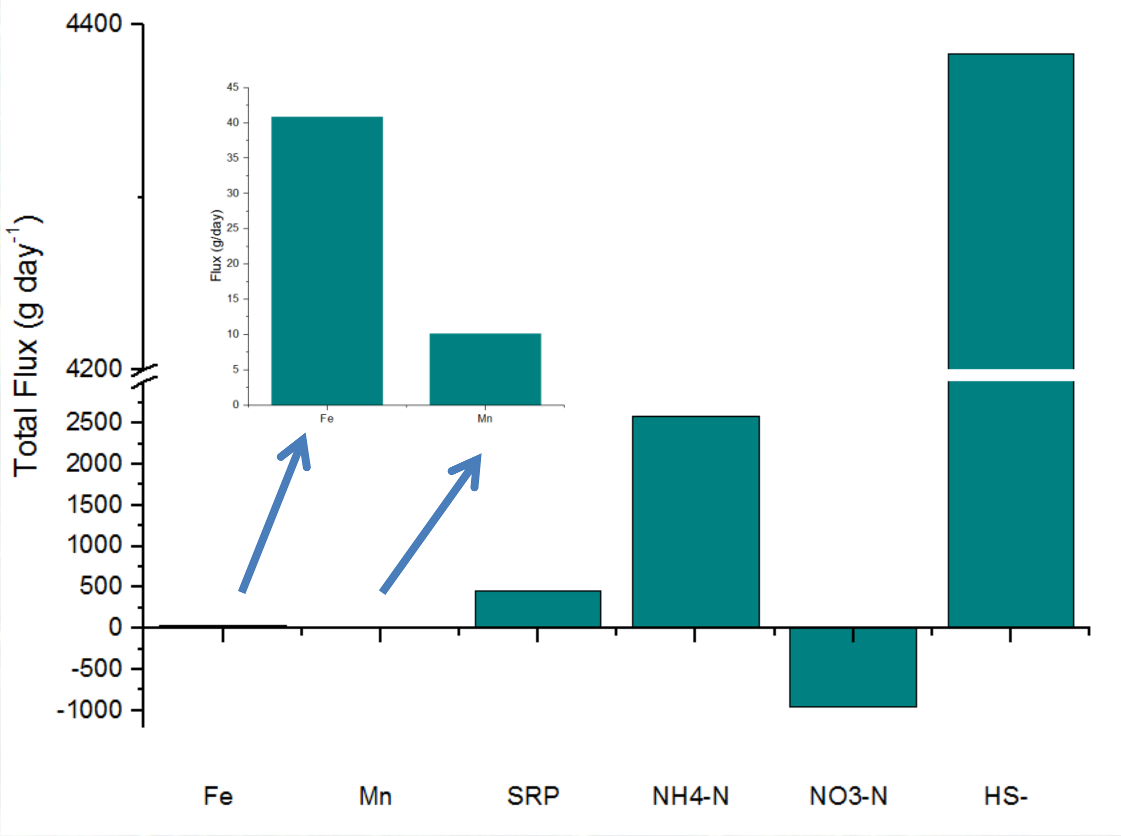
Diffusive Flux Rates – by site



$$J = D_s \frac{dC}{dz}$$

- Considers diffusive transport only
- Heterogeneous fluxes from variations in pore water compositions

Whole River Diffusive Fluxes



Assumes:

- bottom area = 0.23 km^2
- Full range of heterogeneity is captured
- Heterogeneity has normal distribution

Diffuse fluxes vs Silver Spring fluxes

Solute	Diffuse flux (kg/day)	Spring flux (kg/day)	Diffuse flux relative to spring flux (%)
Fe	0.04	0.41	9.89
Mn	0.01	0.41	2.43
SRP	0.46	24.00	1.90
NH_4	2.58	30.94	8.35
NO_3	-0.95	4087.24	0.02
HS^-	4.38	0.00	100.00

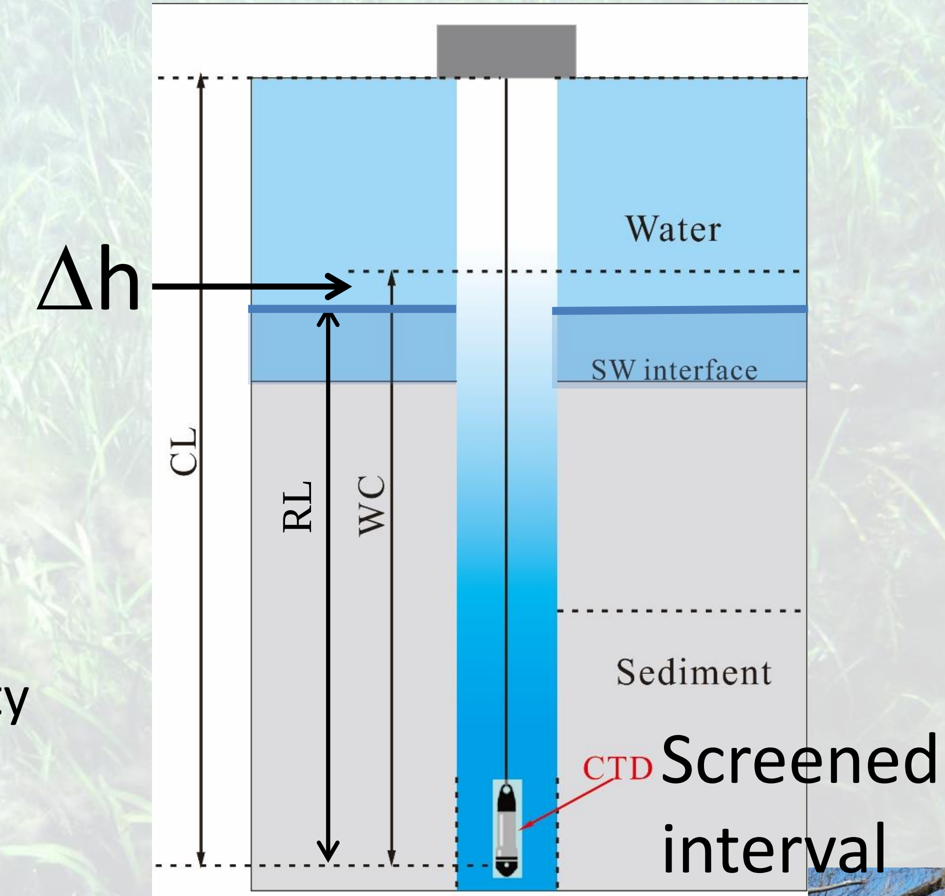
Benthic fluxes

- Red – "large" fluxes compared with spring solute discharge
- Really require understanding of ecosystem needs for each solute

Advective Fluxes:

Hydraulic conductivity (K), head gradients (Δh), and Darcy's Law

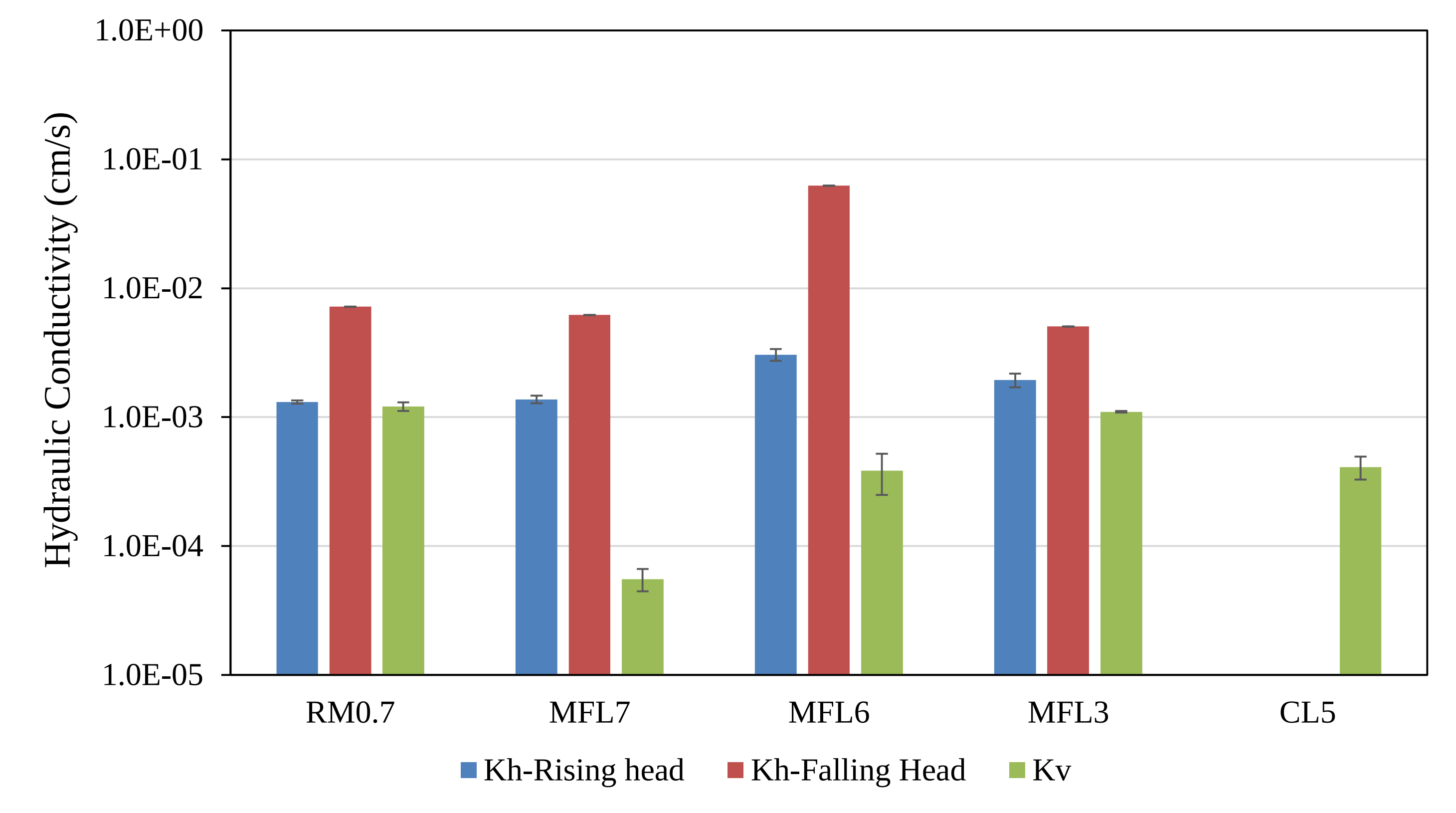
- CTD installed to compare river elevation and pore water head
- Use the same piezometers for measuring hydraulic conductivity
- Horizontal K
  - Screened PVC
  - Rising and falling head tests
- Vertical K
  - PVC open on bottom
  - Falling head tests



Two wells:

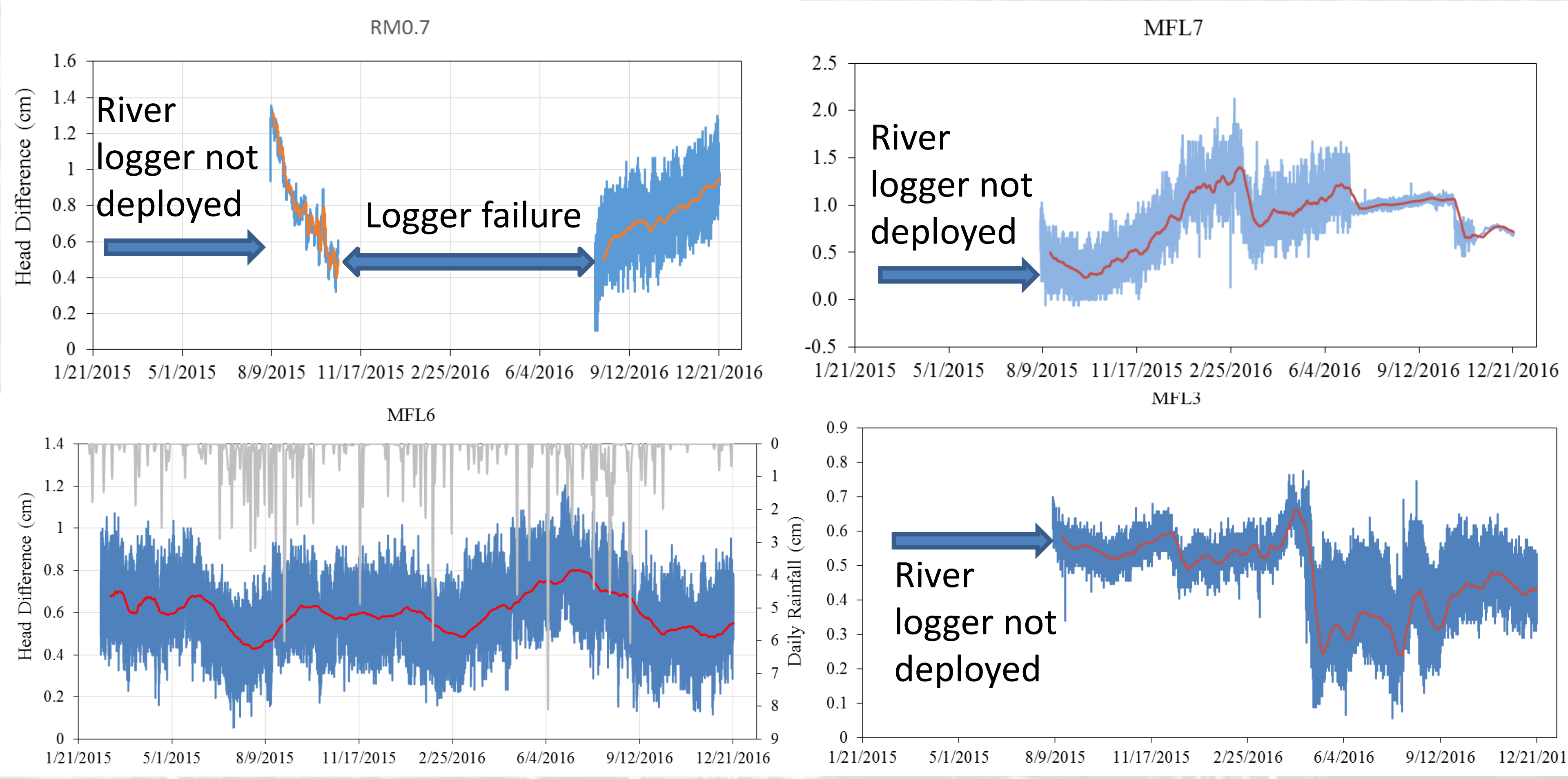
- Piezometer in sediments
- Stilling well in river

Hydraulic Conductivity



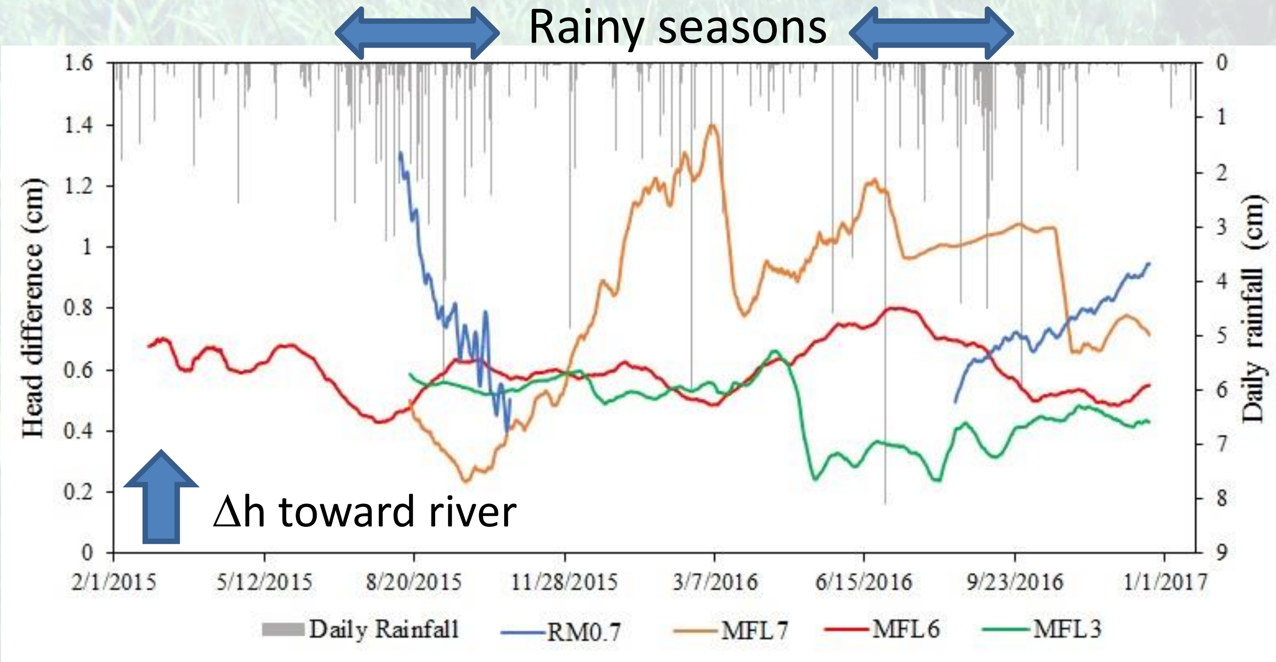
- Similar: Most within ~1 – 2 orders of magnitude
  - Falling head > Rising head
  - $K_h \geq K_v$
- High: clean sand to silty-sandy aquifers

Head Gradients

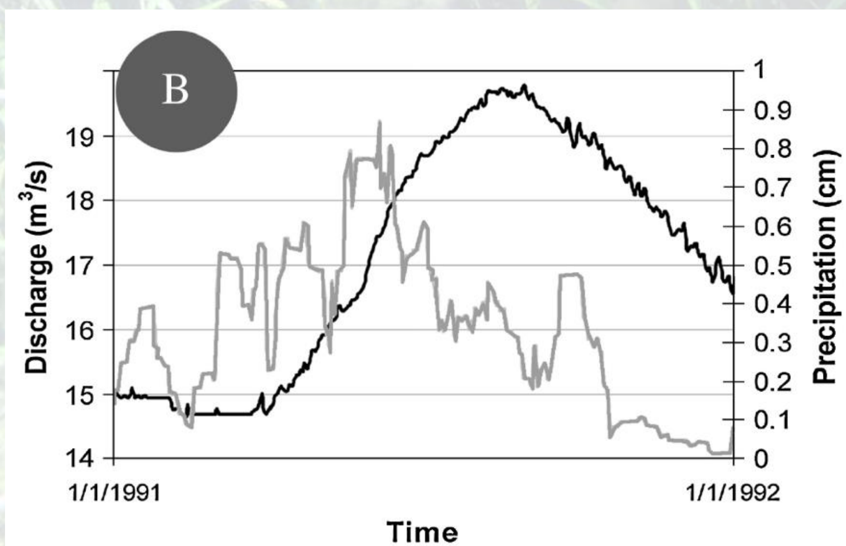


- Measurements:
  - 15 minute intervals (blue)
  - 5 – 10 day moving average (orange)
- Corrections:
  - Field measurements of Δh
  - Offset artifacts from downloading

Smoothed Head Gradients



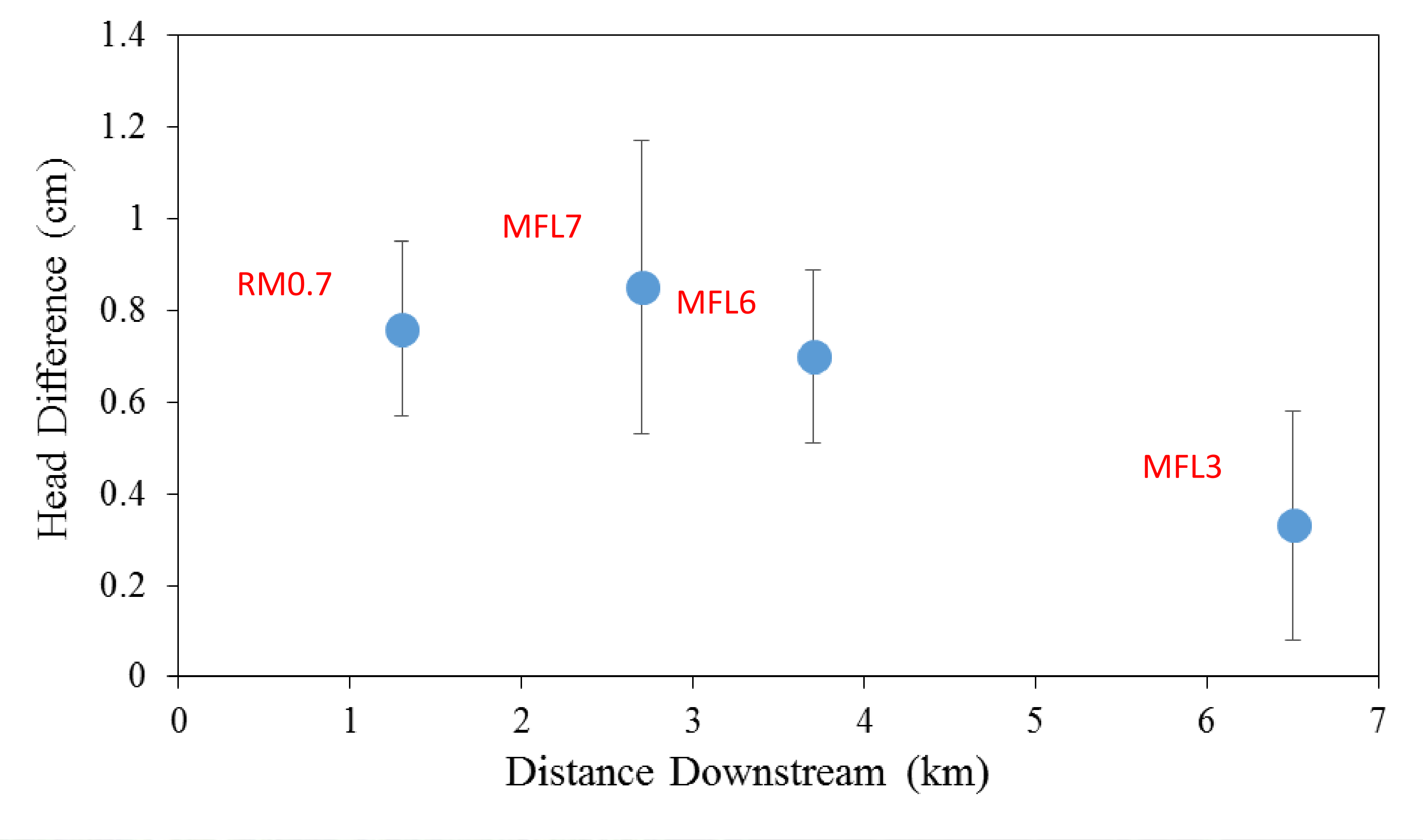
- Variable Δh
- No clear relationship with rainfall
- Possible lag?



(Florea et al., 2006)

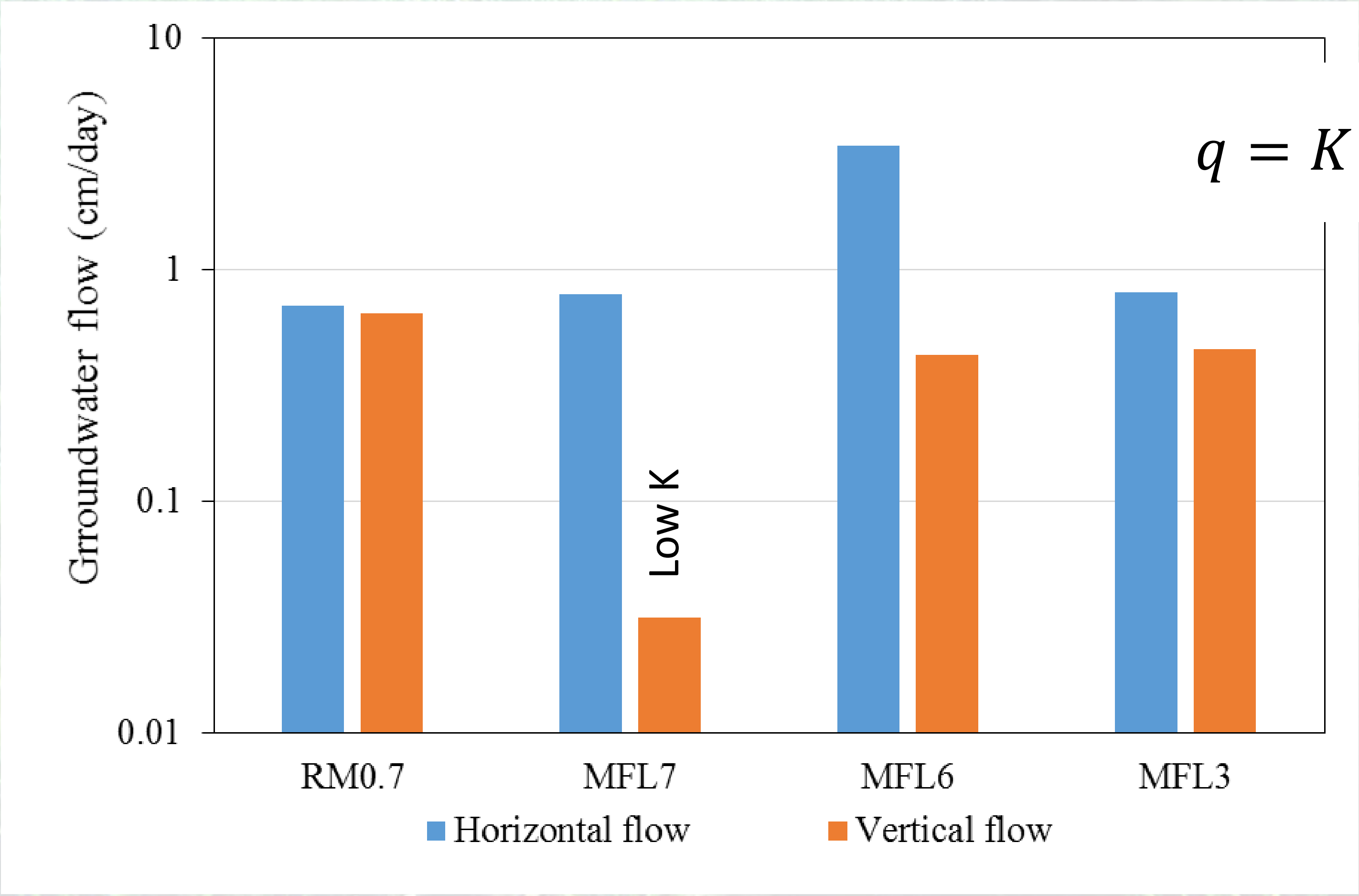
- No rapid precipitation response
  - Possible ~ 6 month lag

Downstream variation in Δh



- Downstream decrease in Δh?
- Missing data from RM0.7
  - During high Δh at MFL7

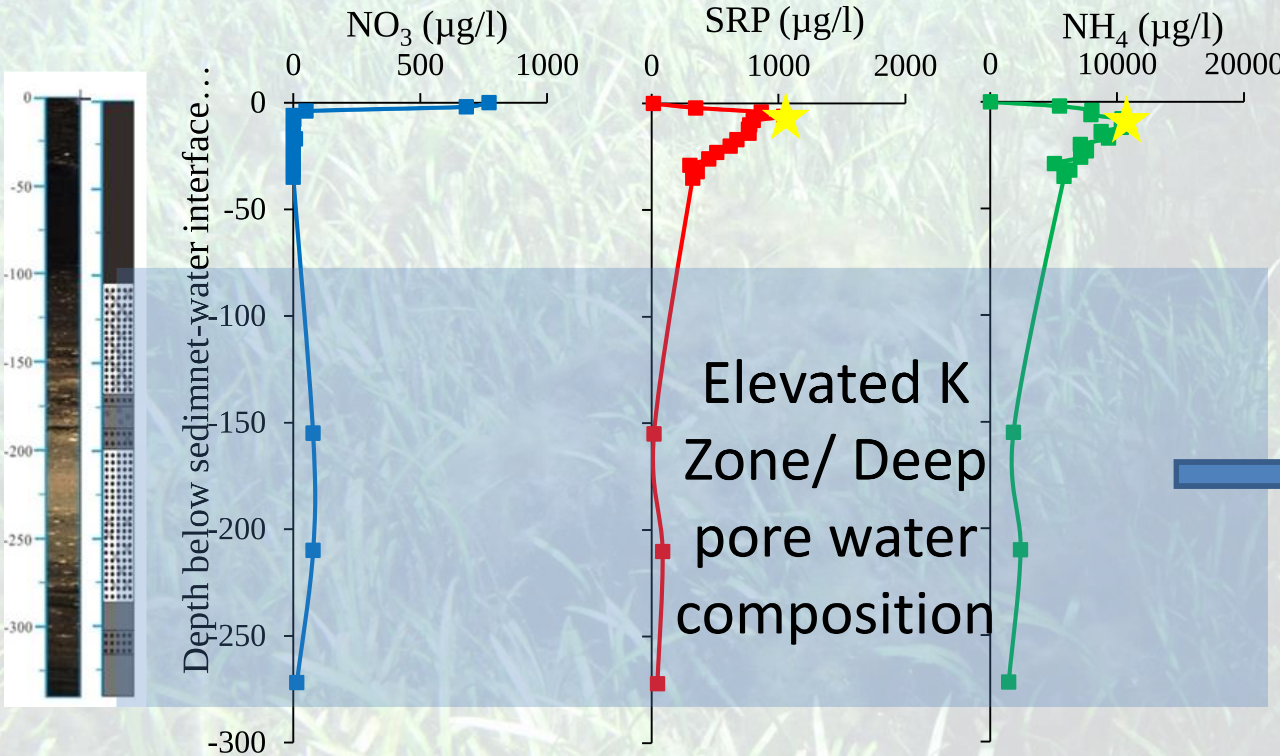
Specific discharge



$$q = K * \left(\frac{dh}{dl}\right)$$

- K_h for rising head only; similar to falling head
- K_v from in situ falling head

Solute Fluxes = q * [X]

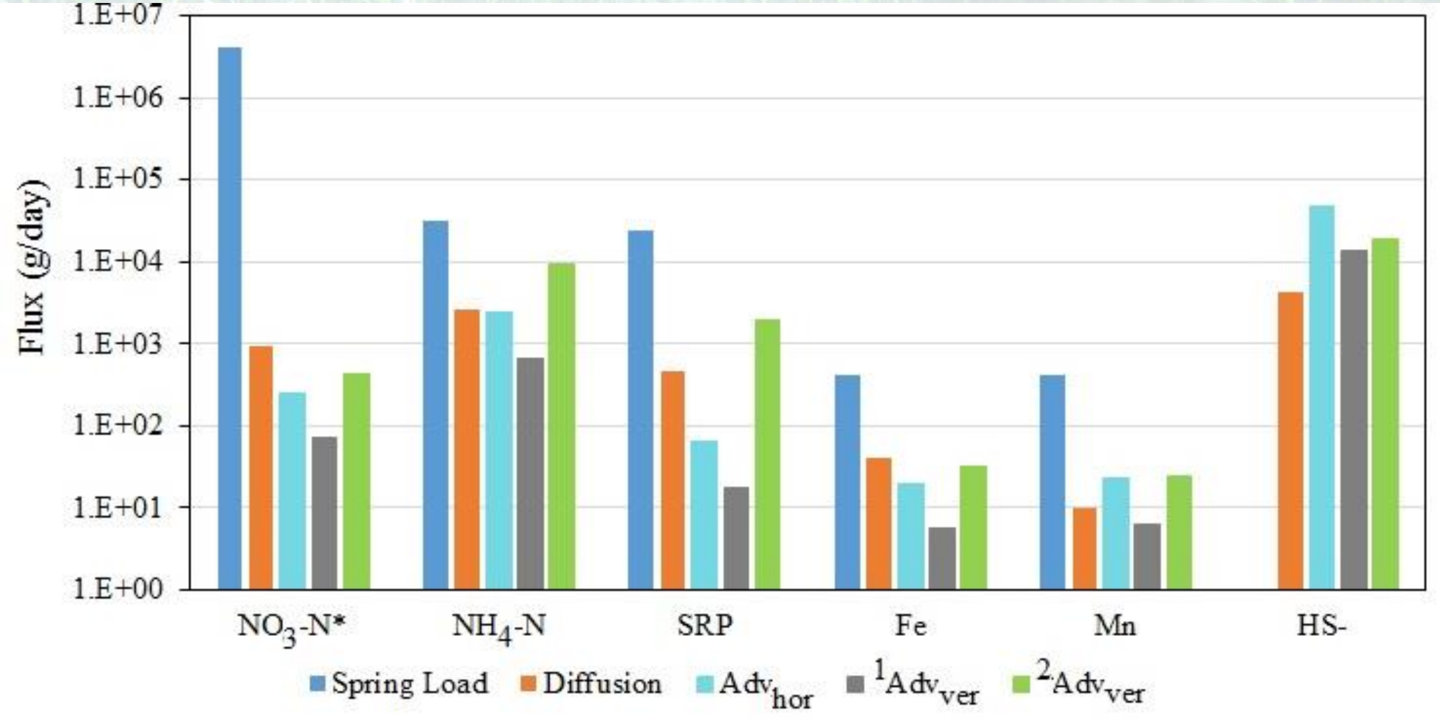


Vertical flux = flow (from K_v)
* maximum concentration
OR
* deep pore water concentration

Horizontal flux = flow (falling head K_h) * deep pore water concentration

Silver River End-member Flux Estimates				
Spring	**Diffusion**	Advection		
		Horizontal	Vertical	
			Deep pore water	**Max concentration shallow pore water**

Solute Fluxes



Solute	Spring (kg/day)	Diffusive flux (kg/day)	% of spring load	Adv_{hor} (kg/day)	% of spring load	[1]Adv_{ver} (kg/day)	% of spring load	[2]Adv_{ver} (kg/day)	% of spring load
NO3-N	4087	-0.95	0.02	0.25	0.01	0.07	0.00	0.43	0.01
NH4-N	30.94	2.58	8.35	2.44	7.88	0.68	2.19	9.30	30.06
SRP	24	0.46	1.9	0.06	0.27	0.02	0.07	1.90	7.92
Fe	0.41	0.04	9.89	0.02	4.90	0.01	1.36	0.03	7.65
Mn	0.41	0.01	2.43	0.02	5.53	0.01	1.54	0.02	5.99
HS-	0	4.38	100	48.56	100	13.53	100	18.45	100

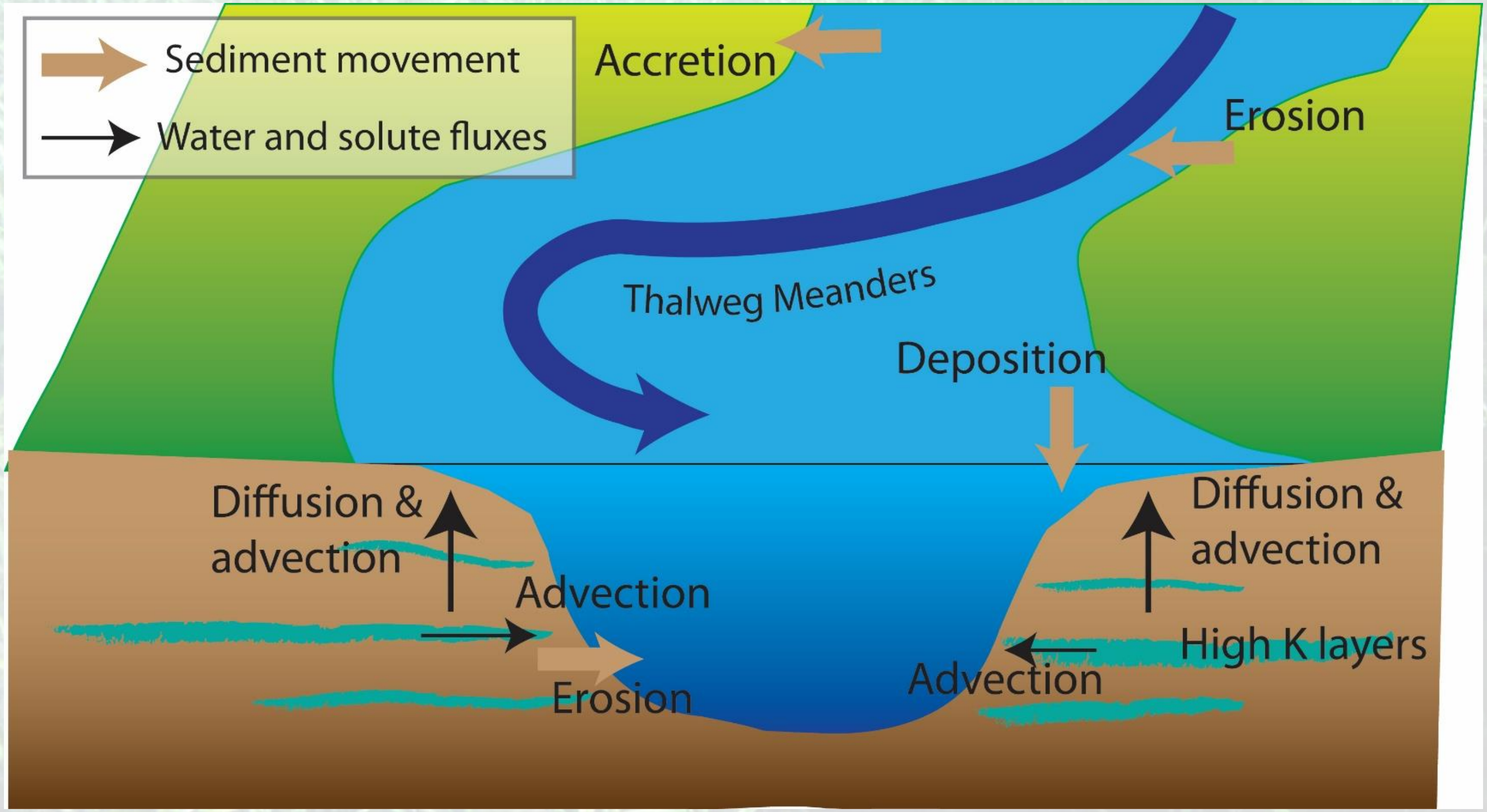
[1]Max Conc. [2]Deep pore water

Summary

- Shallow pore water compositions highly variable
  - Predictable reactions
  - Generates range of potential fluxes
- Advective and diffusive fluxes about same order of magnitude
- Benthic fluxes may be 10 to 50% of total spring load, depending on solute
- Order relative to spring fluxes:
  - NH_4-N > SRP ~ Fe ~ Mn
  - Sole H_2S source


Questions?
Discussion?

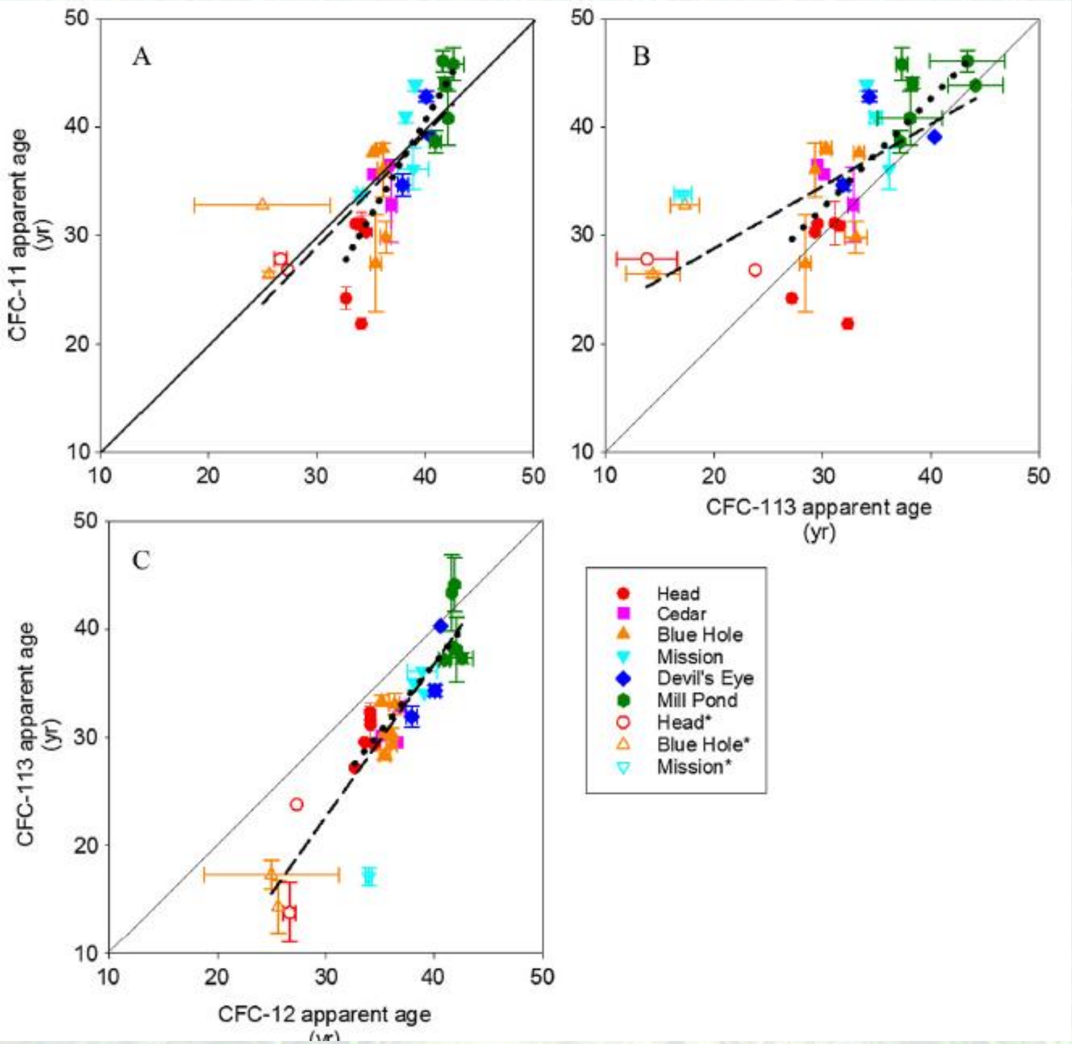
Crude Conceptual Diagram



1. Vertical diffusion from sediments (done)
2. Lateral and vertical advection (magnitudes TBD)
3. Sediment erosion and deposition down stream meanders

Some New (Pertinent) Results?

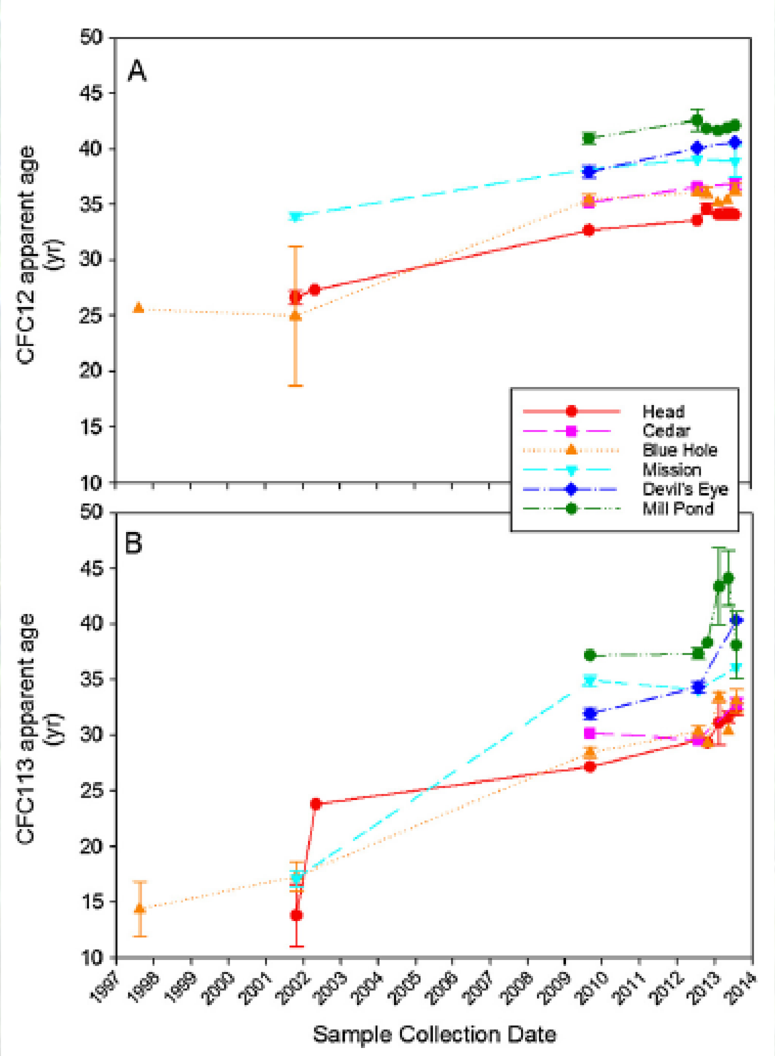
(Ichetucknee River)



- CFC age dates
  - CFC11
  - CFC12
  - CFC113
- More or less coherent

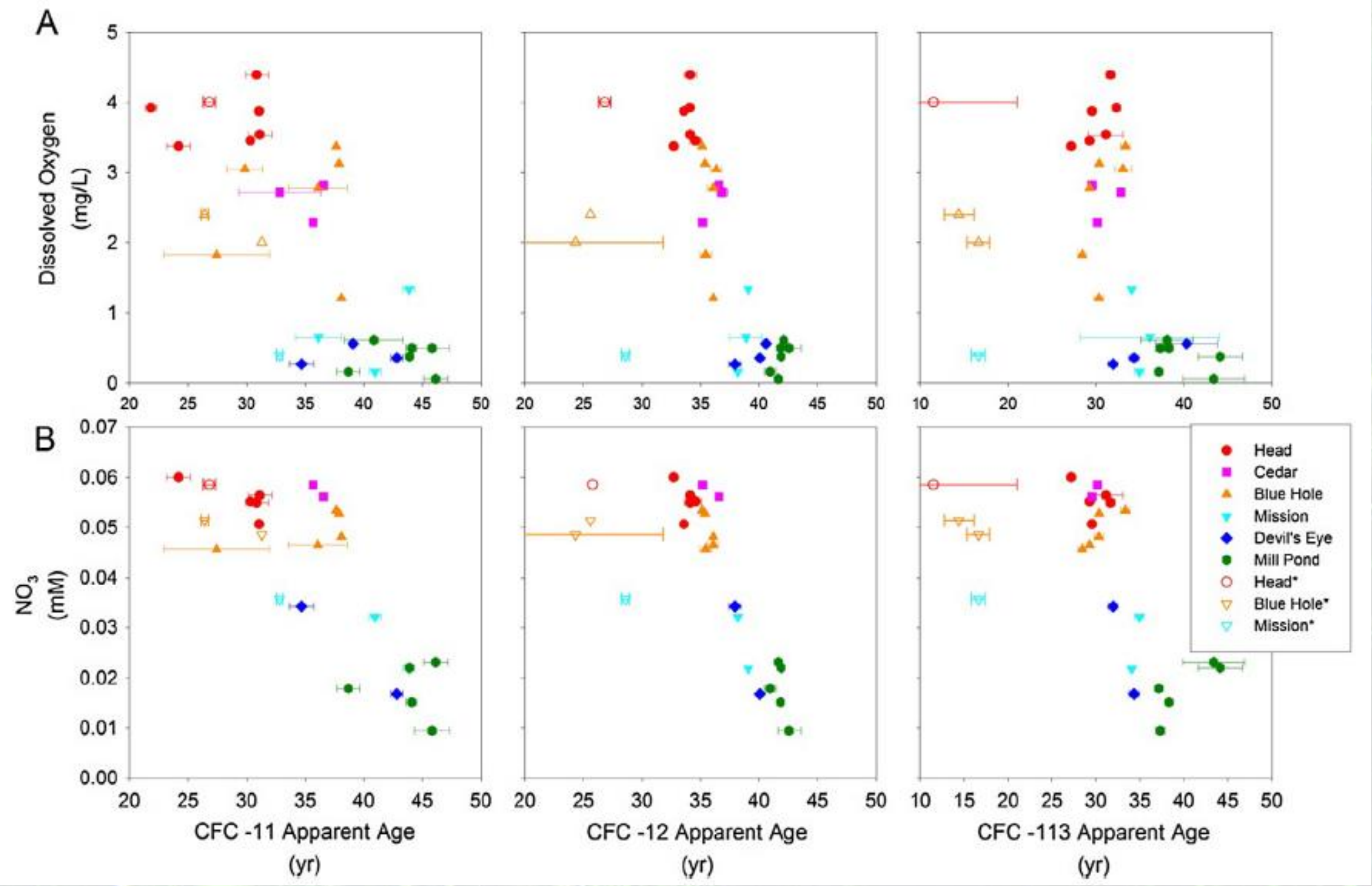
Martin et al., 2016, J Hydro

Water Age vs Sampling time



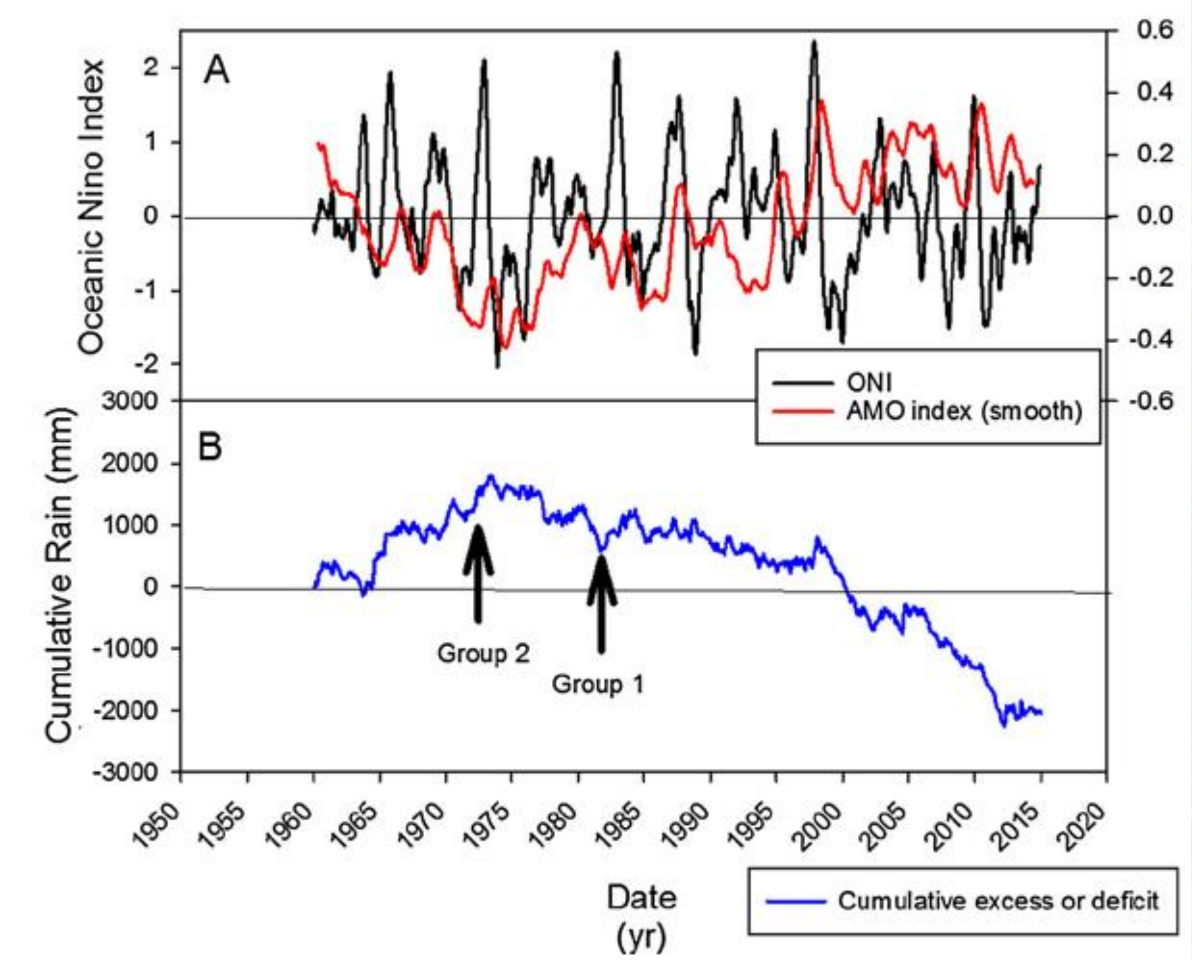
- ~17 yr record
- Water age increase with time
  - Increase ~0.3 to 0.7 yr/yr
- Why?
  - Increasingly older water = longer/deep flow paths

Age vs Solutes – Inverse relationships

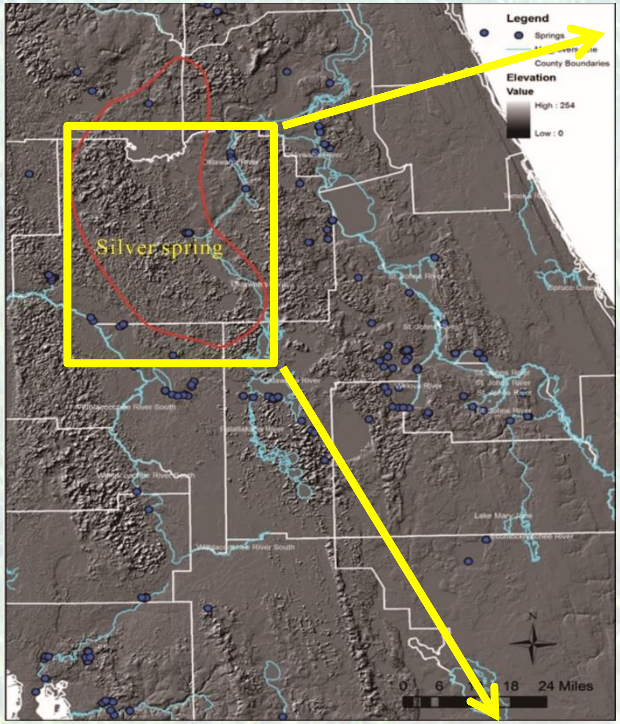


- Older with lower DO and less NO_3
  - more reducing?

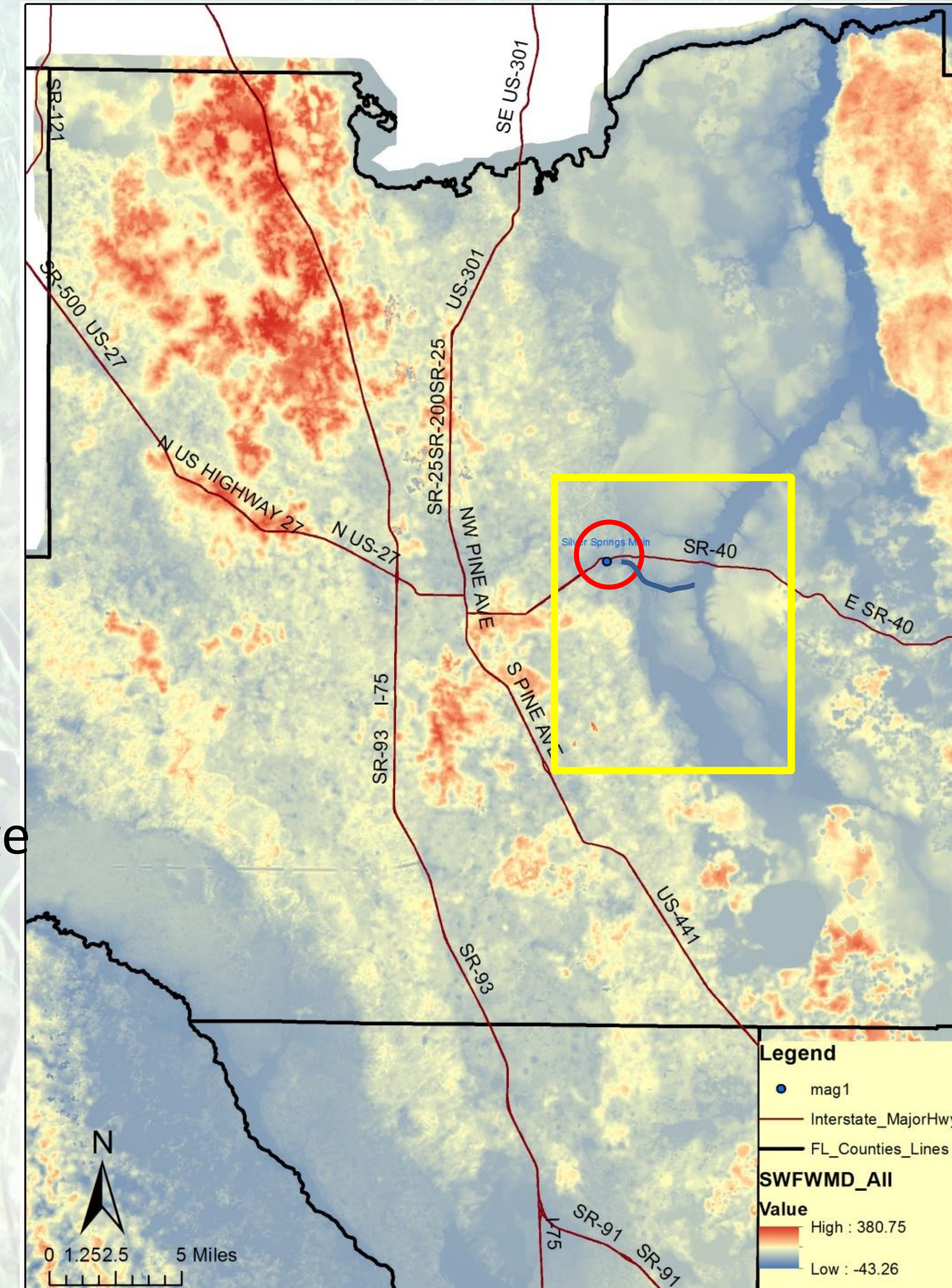
Rainfall vs El Niño and AMO



- Excess rain during El Niño in AMO cool phase
- Rain deficit during AMO warm phase



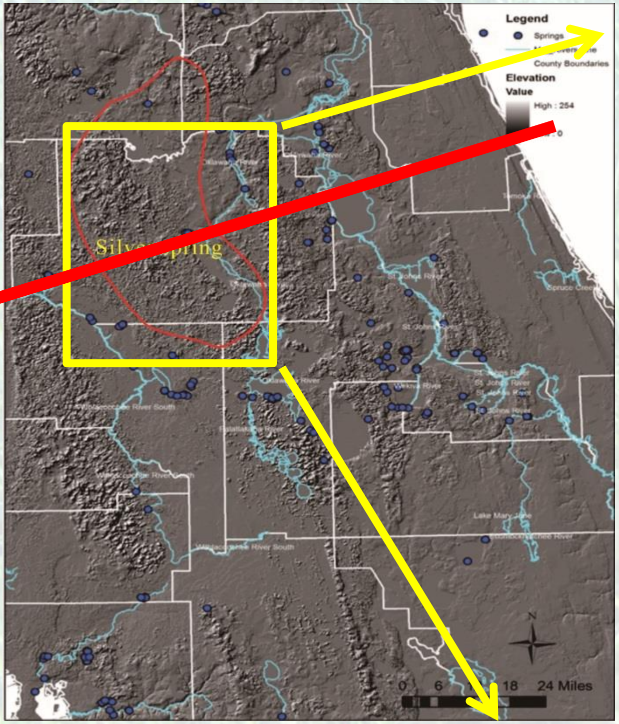
Regional DEM



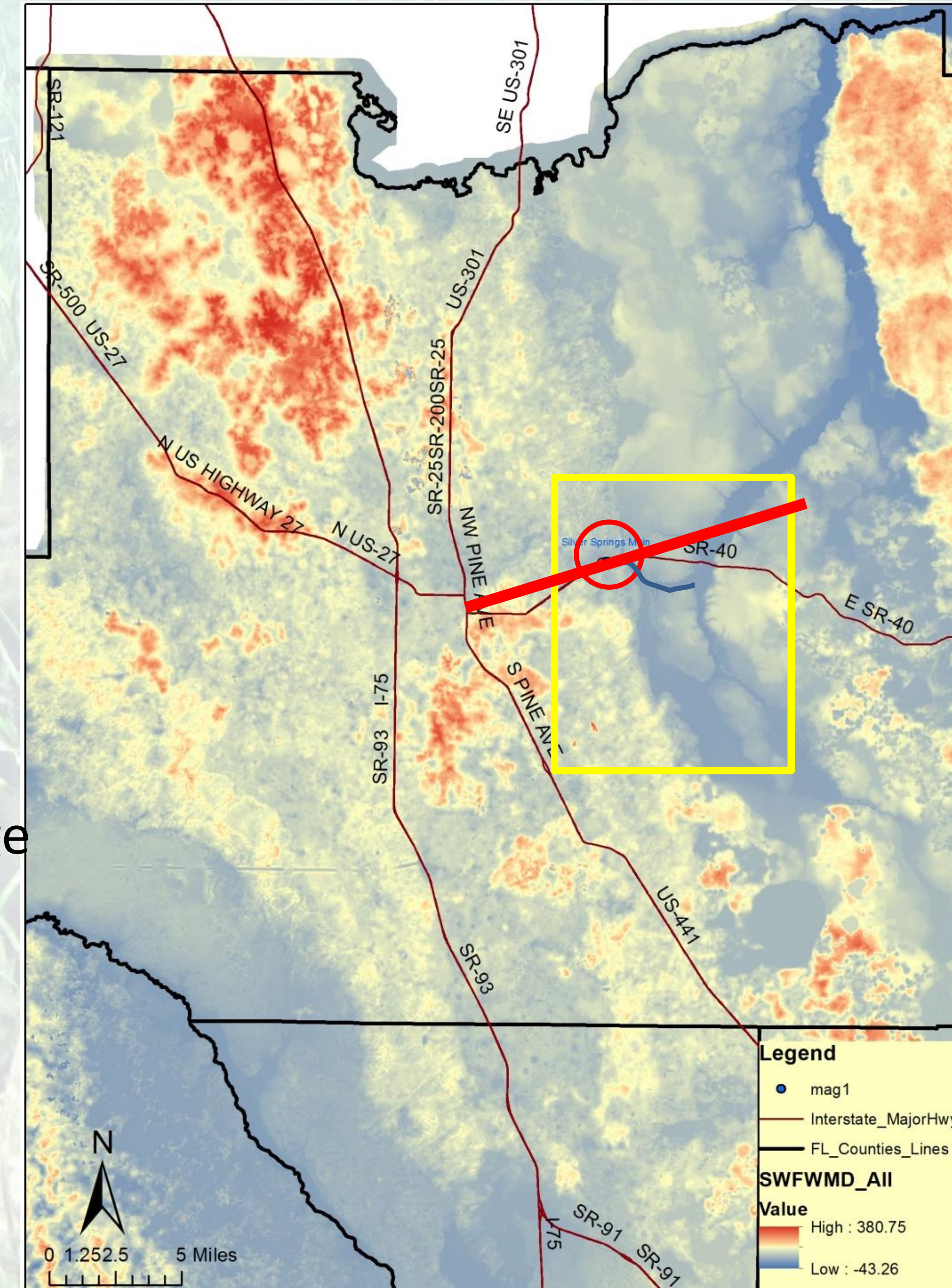
LIDAR Image

- Importance
  - Distribution of lakes and wetlands
  - Distribution and composition of highlands

Images thanks to Harley Means, FGS



Regional DEM

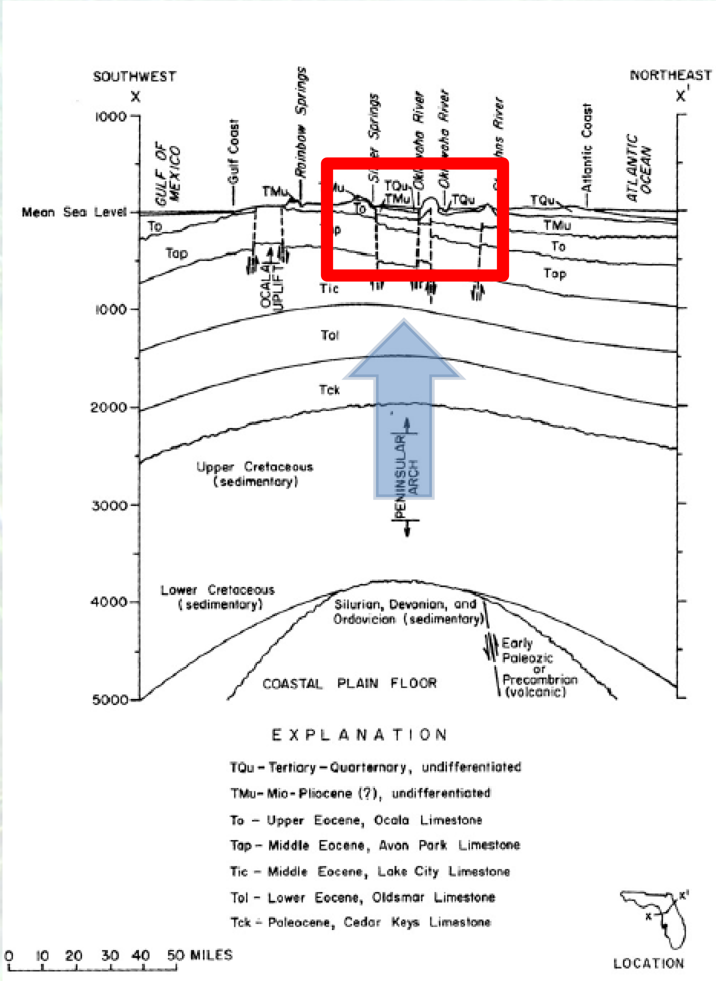


LIDAR Image

- Cross sections
  - Show stratigraphy

Images thanks to Harley Means, FGS

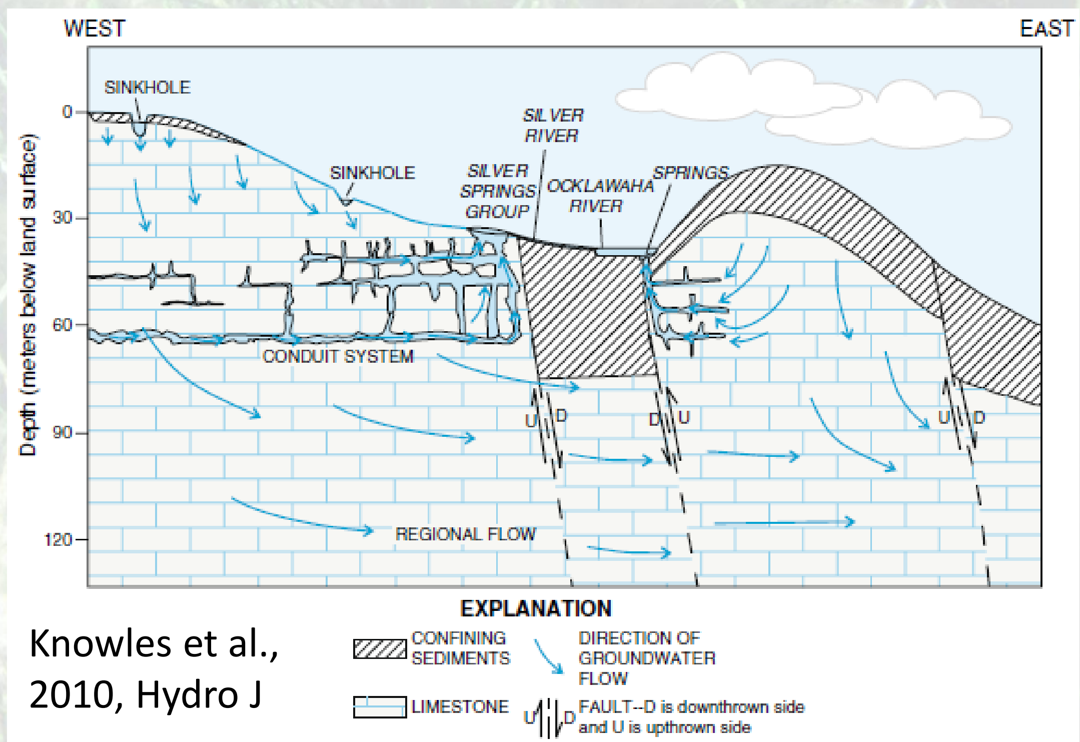
Faulkner 1973, USGS WRI 1-73



Cross Sections

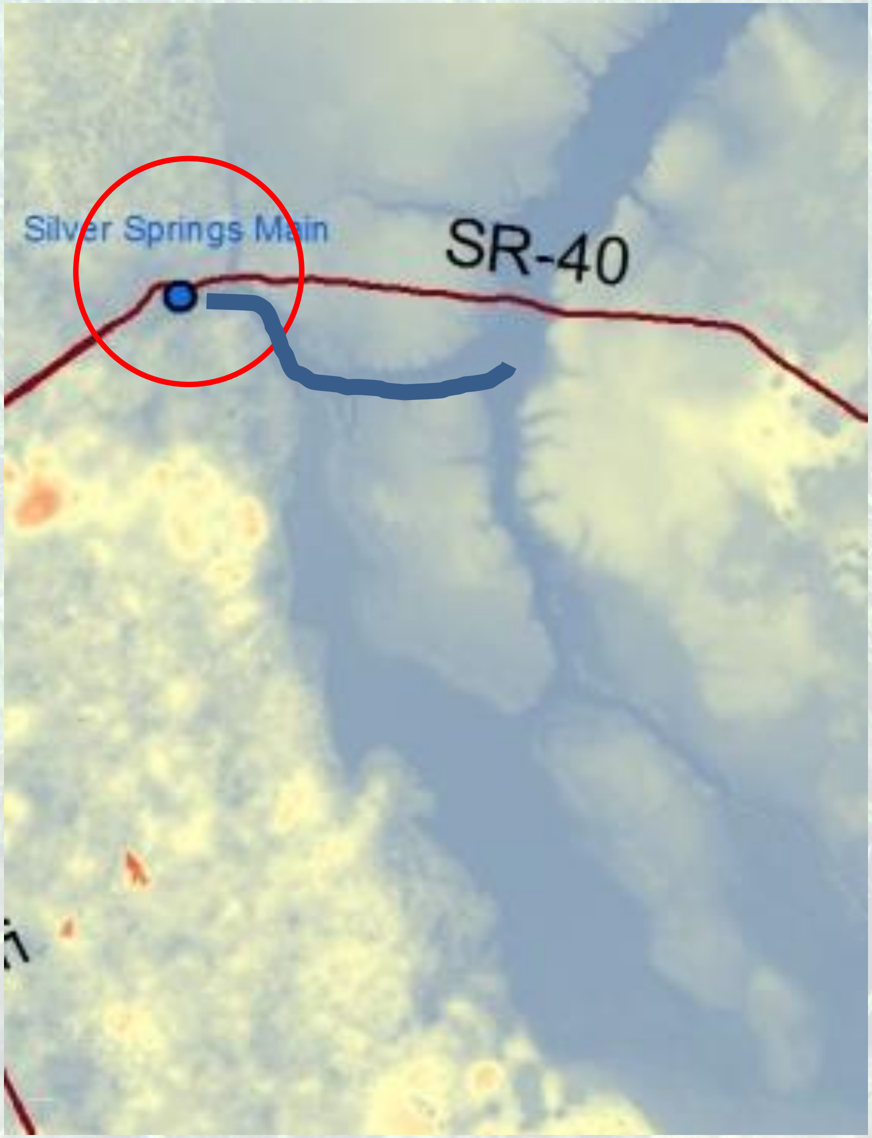
- Regional uplift causes
  - Exposure of Ocala Group rocks (Floridan aquifer) west of Silver spring
  - Blocking eastward flow creates springs
  - Silver River flows across confining unit

- Regional uplift of Peninsular Arch



Knowles et al., 2010, Hydro J

Expanded LIDAR

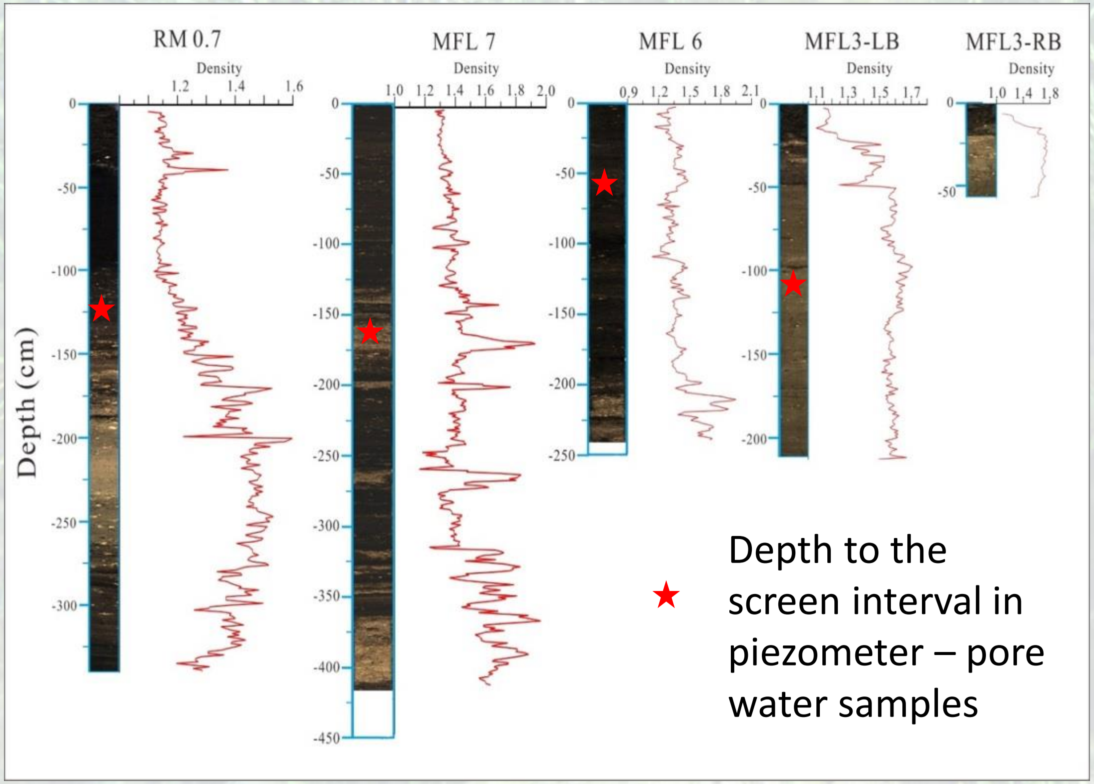


- Upland outcrops
  - Floridan aquifer
  - Silver River flows across confining sediments
- Sediment may limit flow to Silver River from Floridan
  - Possibly large fluxes of solutes from reactions in sediments
- Sediments compositions
  - Deposited in quiescent setting?
  - Lake bed?
- Drainage to river from surrounding wetlands?

Sedimentary Material

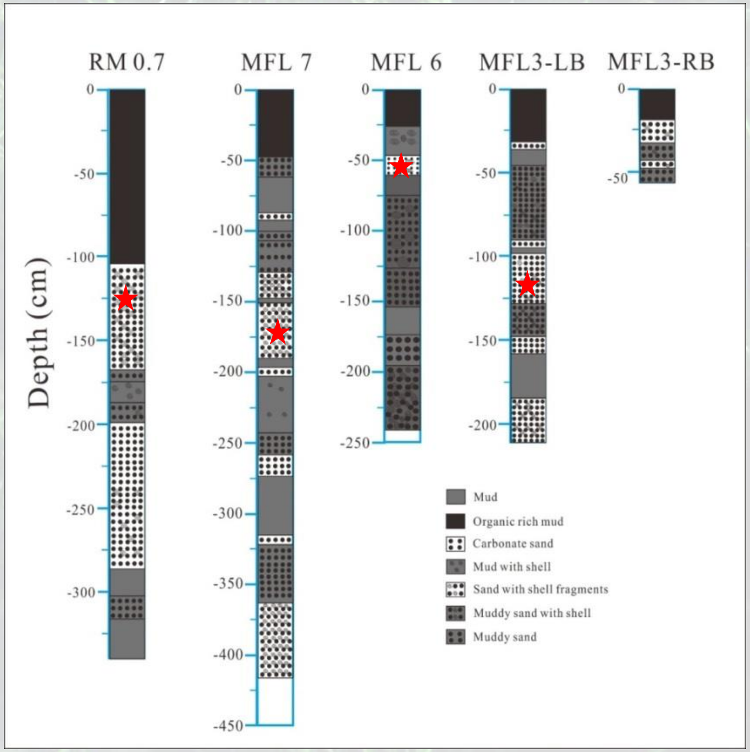
- Sediments consist of interbedded organic C-rich layers and shell-hash layers
- Lower portion higher carbonate content, lower OC contents

Upstream → Downstream



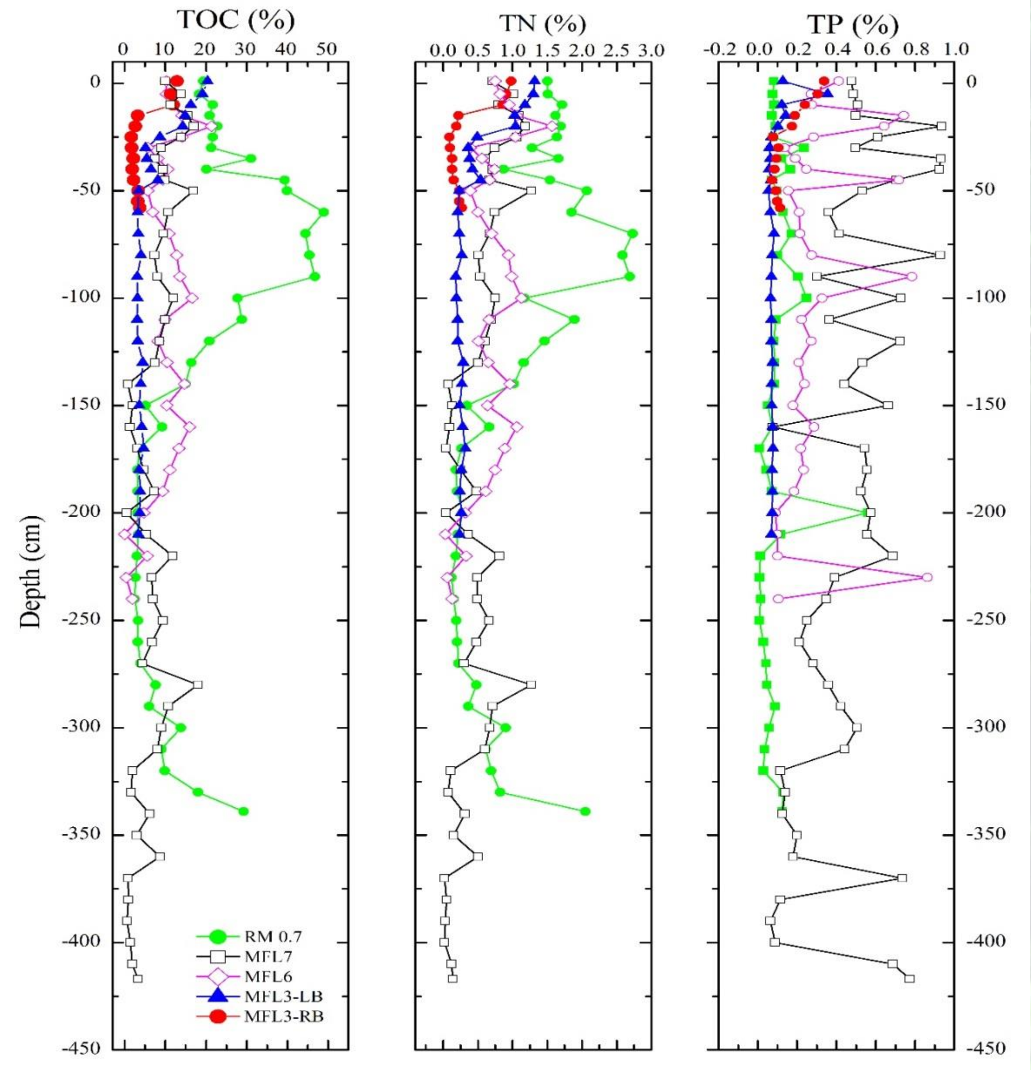
Core log images & gamma density

Upstream → Downstream



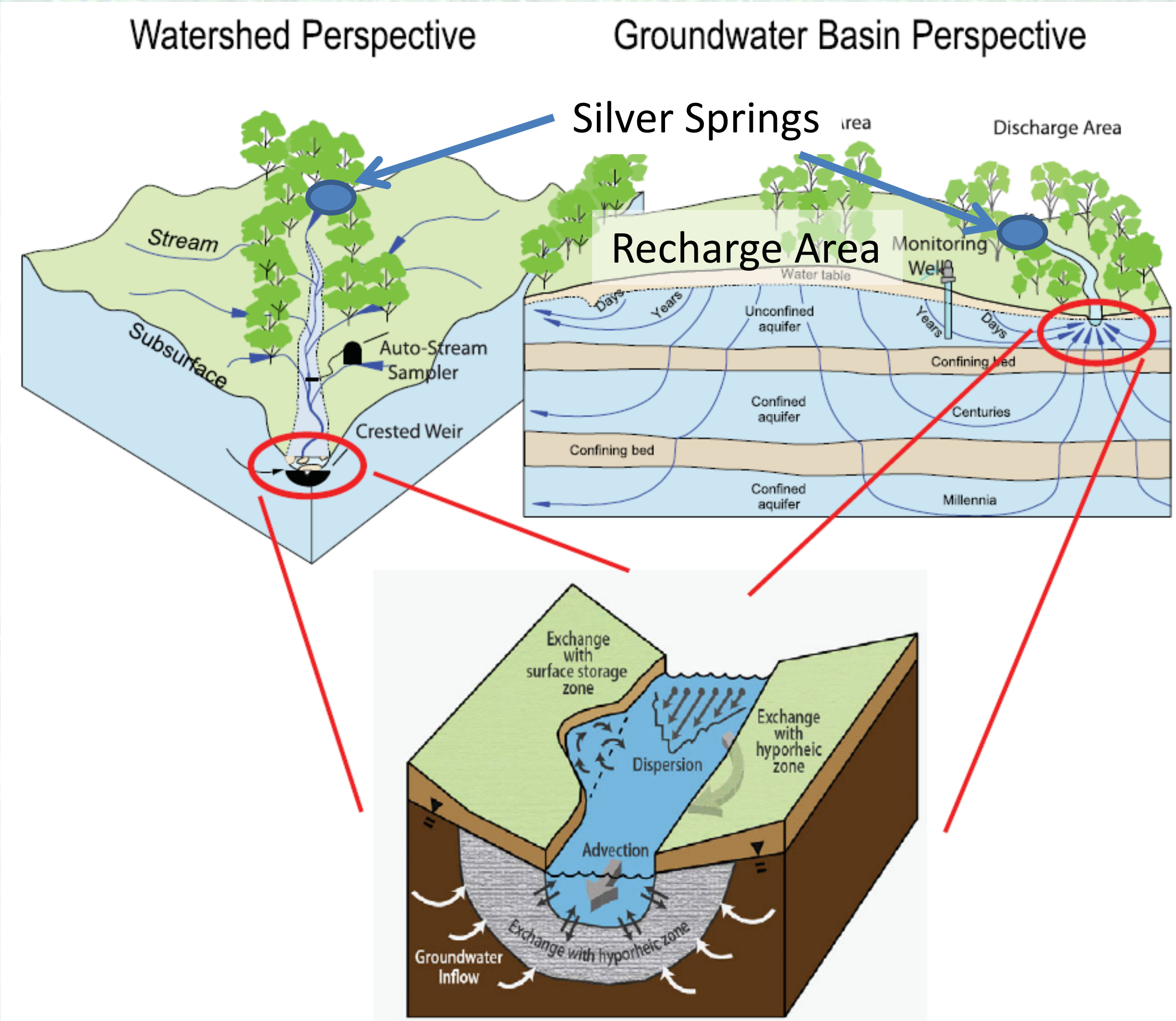
Stratigraphic Descriptions

Sediment Composition: OC, TN, TP



- OC in cores vary:
  - Nearly 50% OC upstream shallow depths
  - Decrease to ~5 to 20% downstream
- TN contents vary similarly to OC
- C/N ratios ~ constant
- C/P and P/N ratios variable
- See also Mitra's poster
  - discussion of possible OC sources
  - $\delta^{13}C$, $\delta^{15}N$, C/N ratios

River Corridor Science



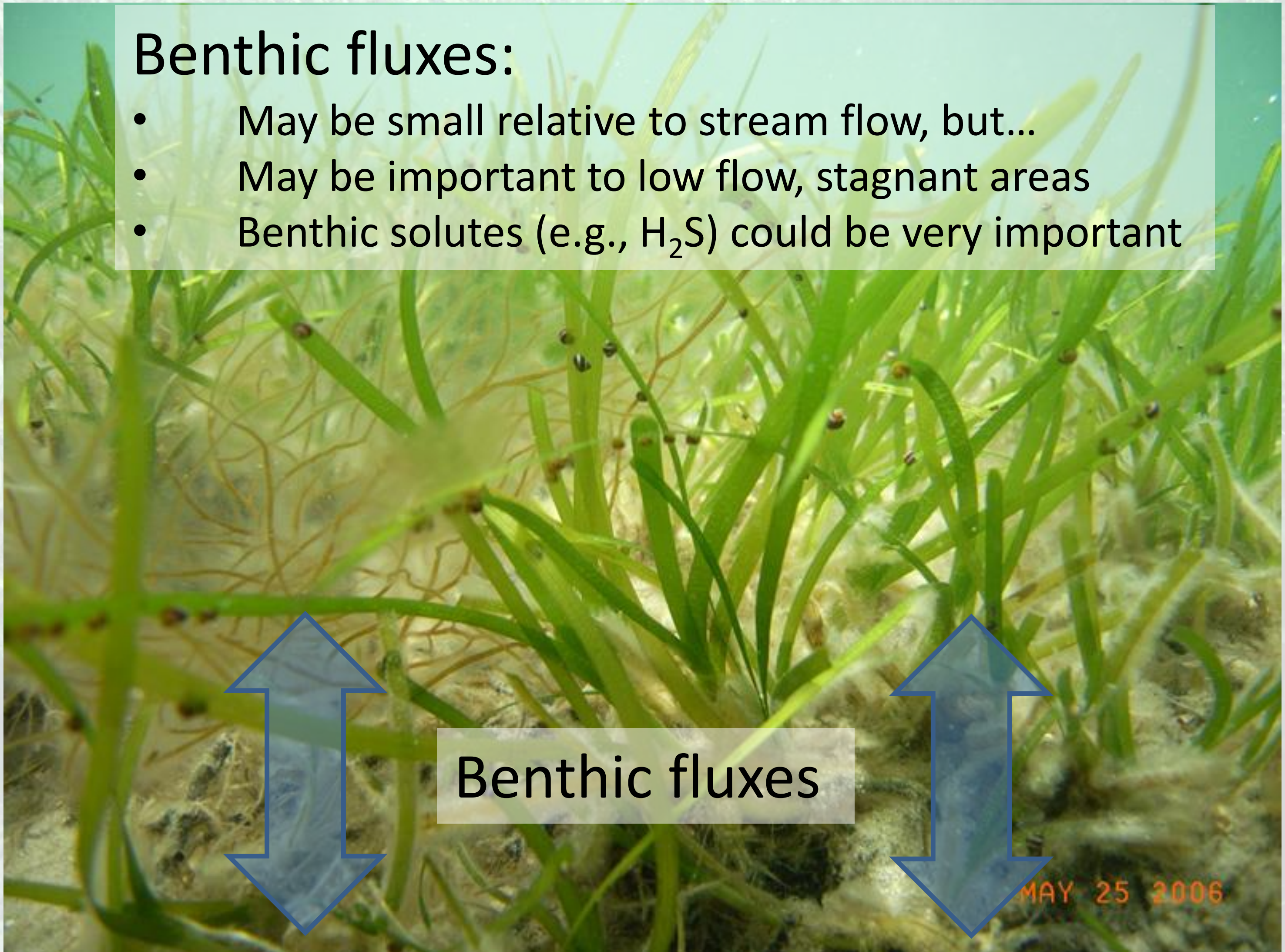
- Watershed perspective:
  - Overland flow
- Groundwater basin perspective:
  - Groundwater source – spring vent; benthic sediment
- Combined:
  - controls river corridor ecosystems
  - Our interest in Silver River (and other spring runs)

Harvey and Gooseff, 2015, WRR

SAV – Benthic flux relationship

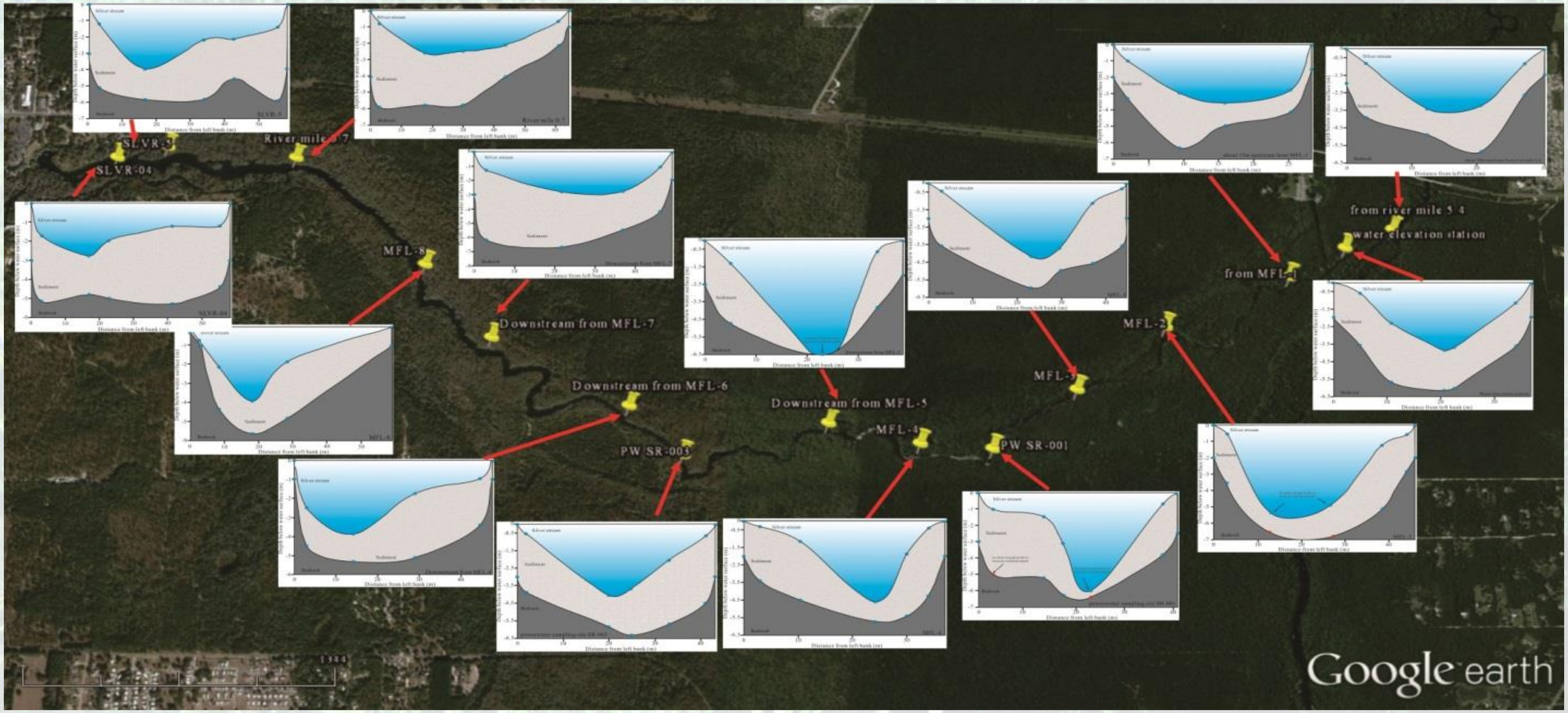
Benthic fluxes:

- May be small relative to stream flow, but…
- May be important to low flow, stagnant areas
- Benthic solutes (e.g., H_2S) could be very important



Benthic Sediment Distribution

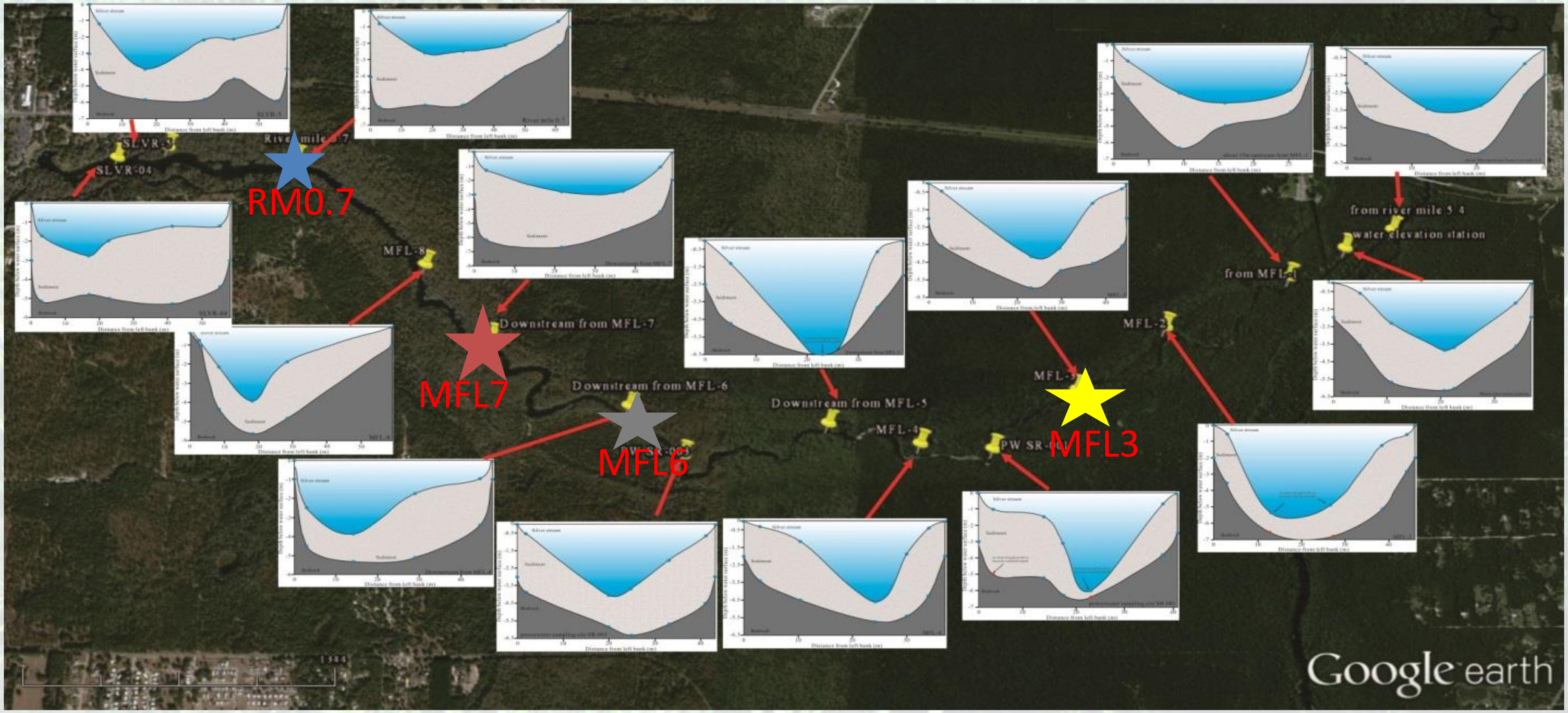
Upstream → Downstream



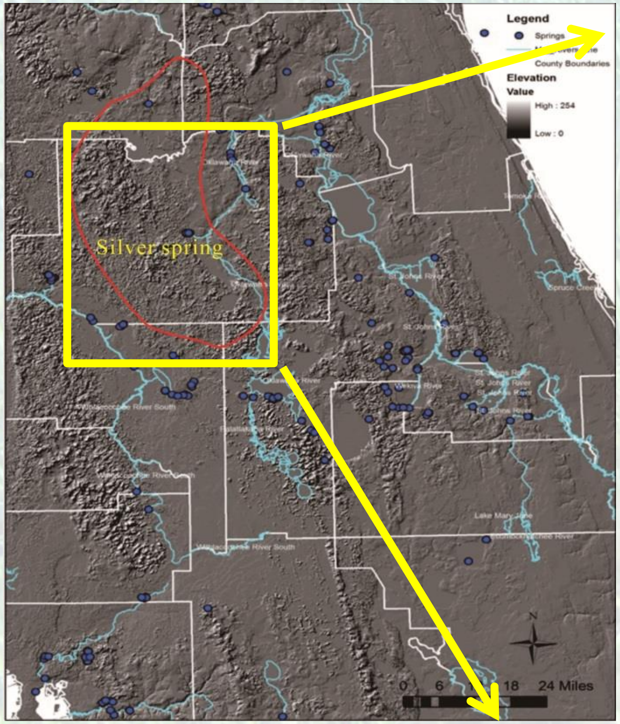
- 14 transects
- Thickness 1 to > 6 m
- Sediment distributed along entire river

Benthic Sediment Distribution

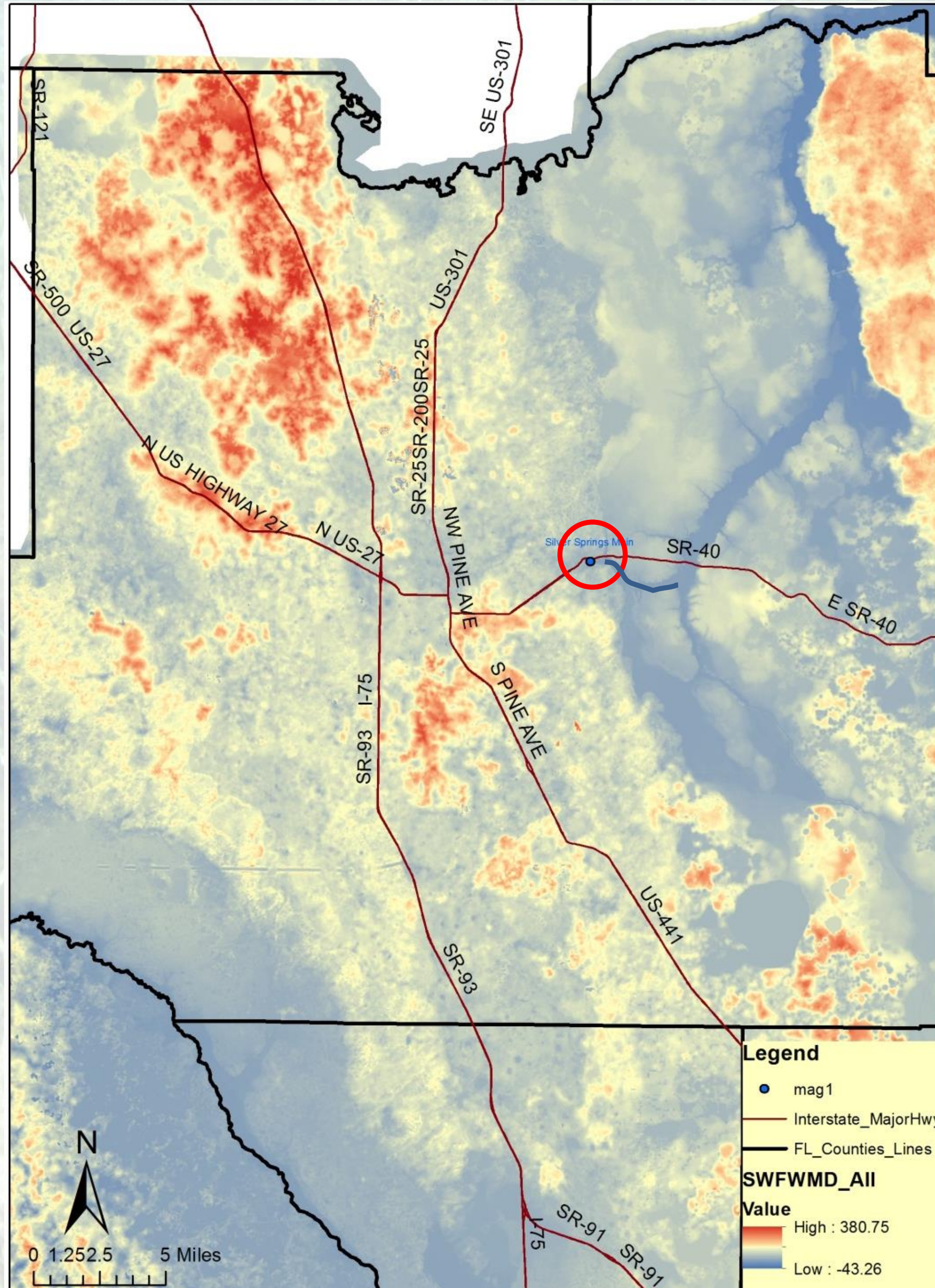
Upstream → Downstream



- Focus on four transects:
  - Coring: sediment composition
  - In situ hydrologic parameters: K, dH/dz
  - Pore water collection; solute analysis
  - Sediment age dating



Regional DEM



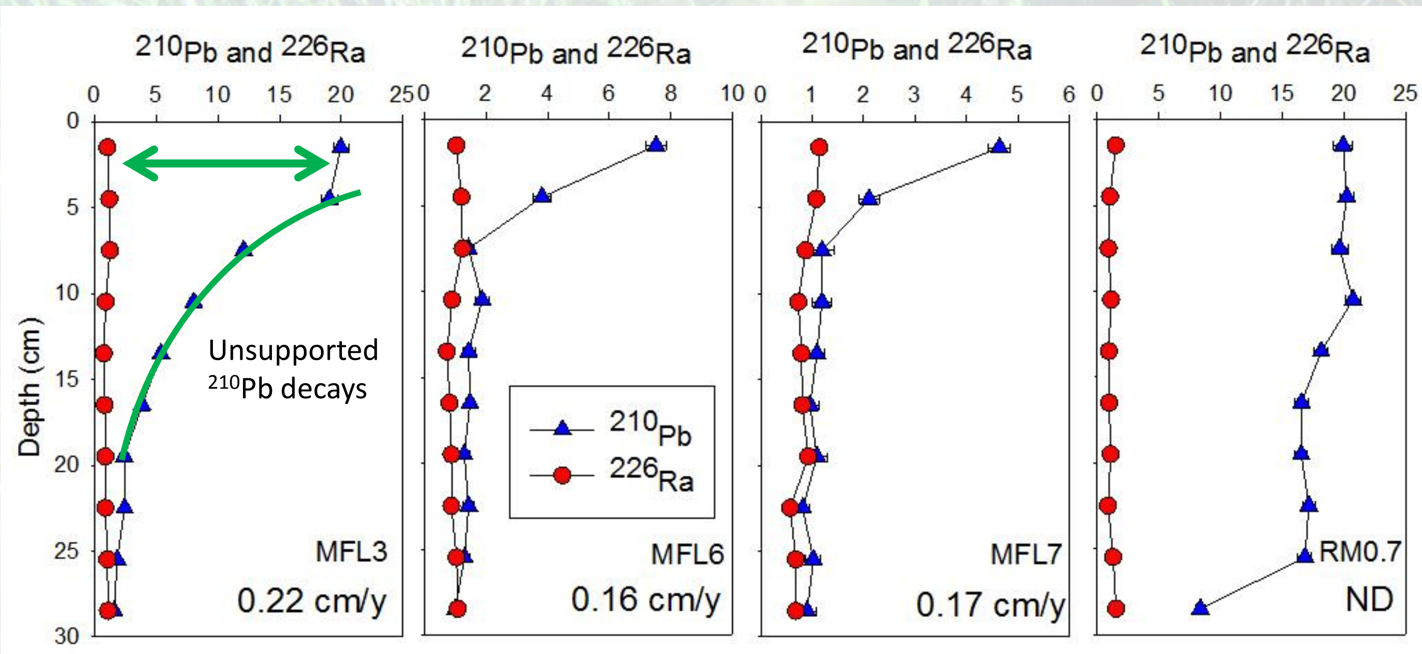
LIDAR Image

- Importance
  - Distribution of lakes and wetlands
  - Distribution and composition of highlands
  - Sediment age would be good test of hypothesis

Images thanks to Harley Means, FGS

Sedimentation Rates

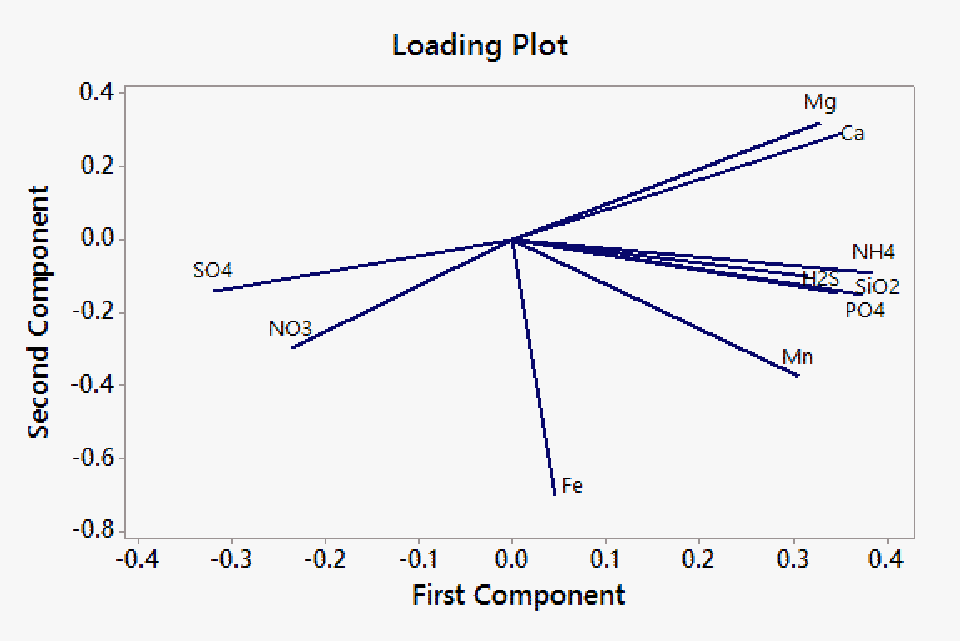
- Fairly consistent sedimentation rates except RM0.7
  - RM0.7 suggests rapid sedimentation
  - Rapid sedimentation (young sediment) suggest river also eroding

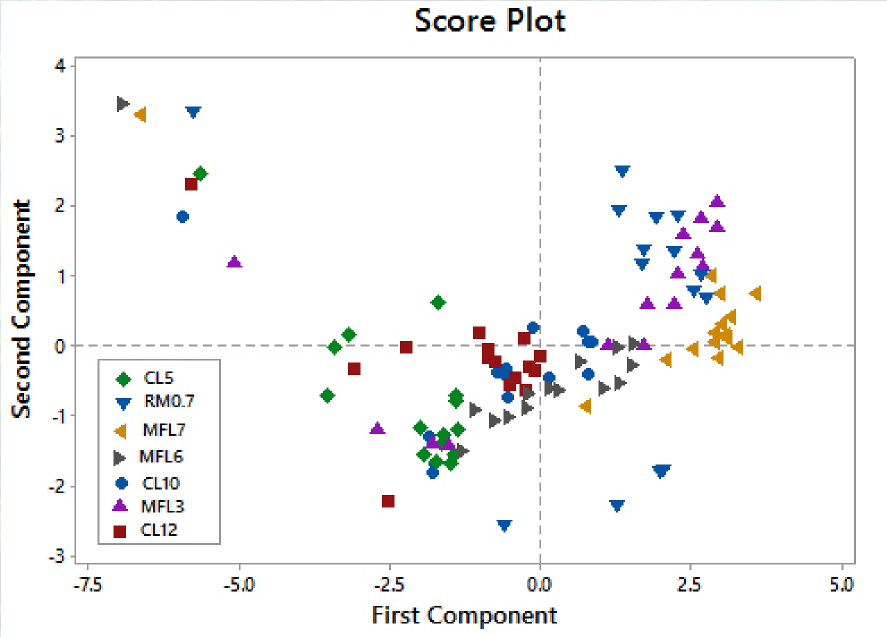


- All γ counting
- Provide ^{226}Ra activities
- Slow and difficult

$$^{226}\mathrm{Ra} \xrightarrow{1699\ \mathrm{yr}} \mathrm{X} \rightarrow {}^{210}\mathrm{Pb} \xrightarrow{22\ \mathrm{yr}} {}^{206}\mathrm{Pb}$$

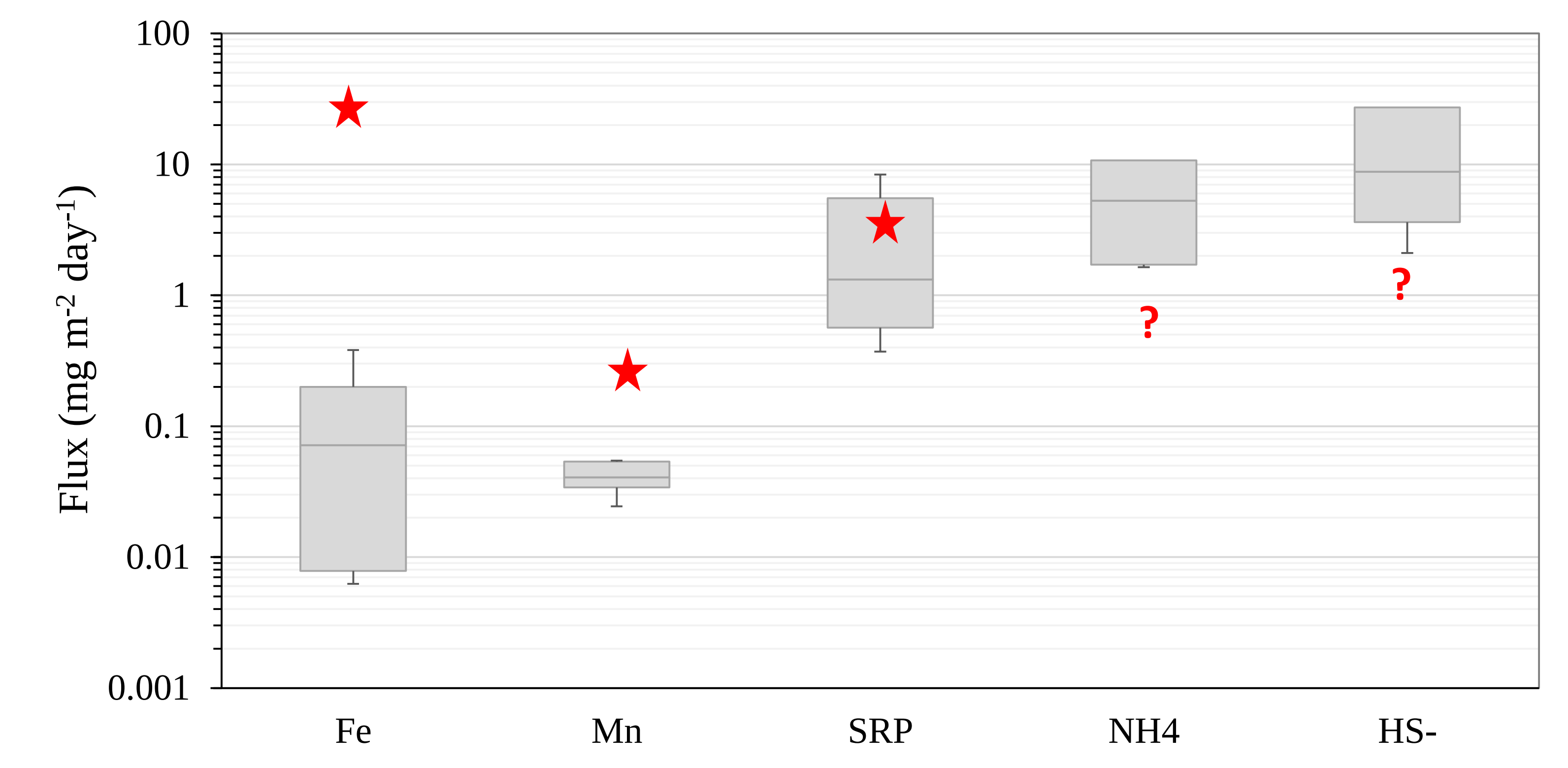
Porewater Chemistry – PCA





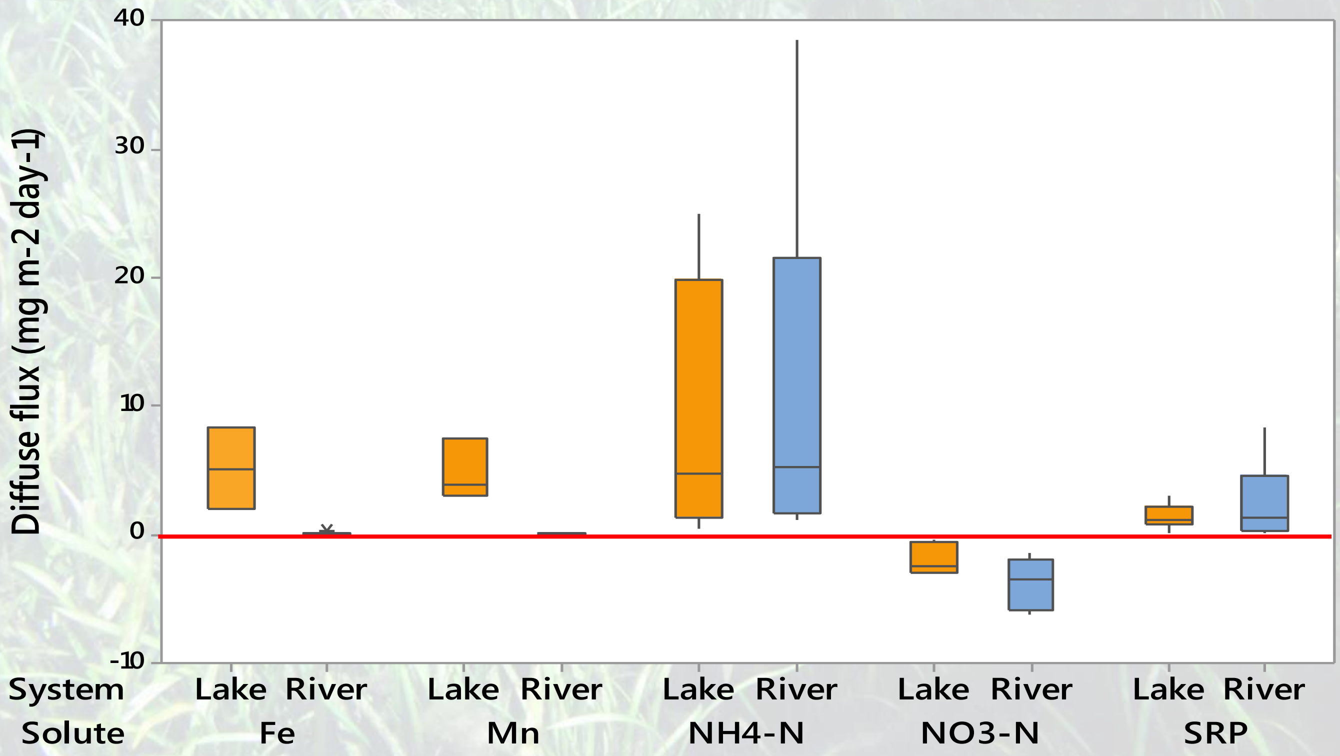
- Redox sensitive solutes and nutrients controlled by 1st component.
- No inverse correlation between oxidized and reduced species → other controlling factors than OC.
- Fe may be controlled by complex set of processes.

Compared with Ichetucknee fluxes



- Stars represent estimates for Ichetucknee River (Kurz et al., 2015; FW Science)
- Fe and Mn lower (sediment composition?)
- P similar

Silver River vs Lakes



Lake data: *Reddy et al;. 1996 (Lake Apopka: NH_4-N, SRP); Moore et al., 1997 (Lake Okeechobee: SRP); Small et al., 2014 (Lake Huron, Lake Erie: All solutes); Urban et al., 1997 (Lake Sempach, Swizerland: All solutes); Chowdury and Bakri, 2006 (Australian Lakes: NO_3-N, NH_4-N, SRP)*