Thinking inside the box

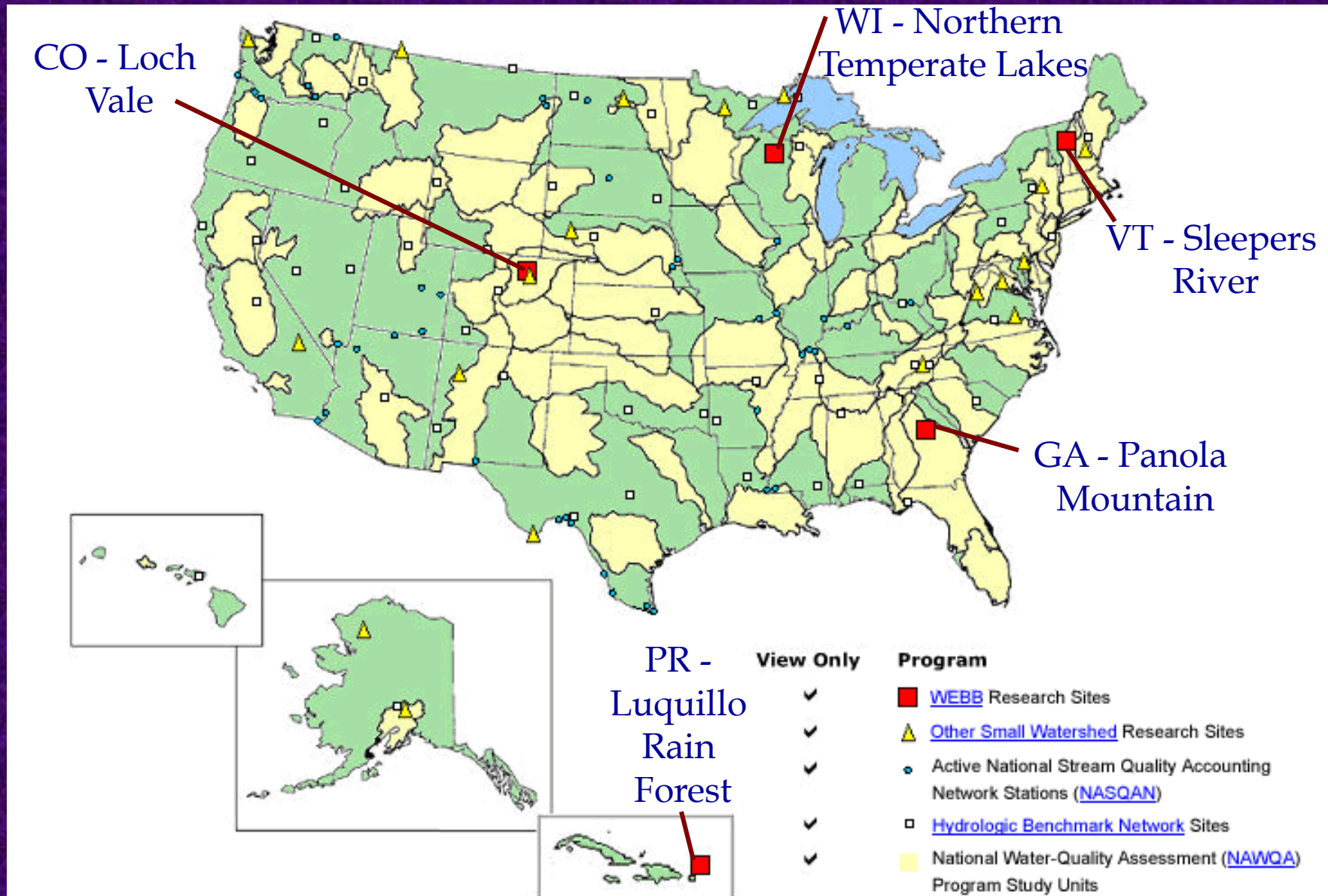
The small watershed approach to biogeochemical research

Jamie Shanley
USGS, Montpelier, VT

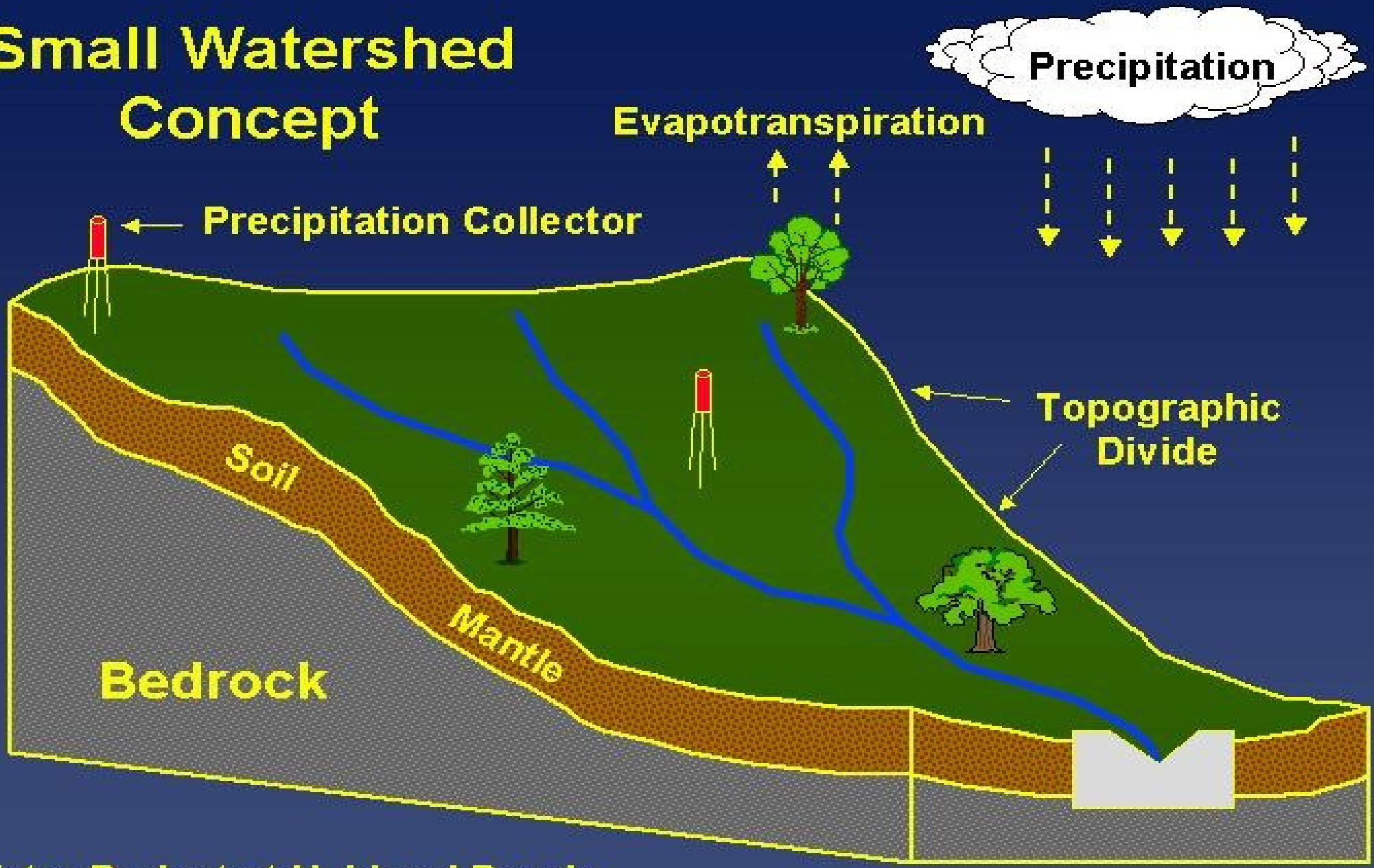
Outline

- Small Watershed Approach
  - Definition
  - History
  - Example applications
  - Example results
- Case studies
  - Sulfur -- isotopic approach
  - Mercury

USGS WEBB sites



Small Watershed Concept



Water Budget at Hubbard Brook:
Precipitation (100%) = Streamflow (60%) + Evapotranspiration (40%)

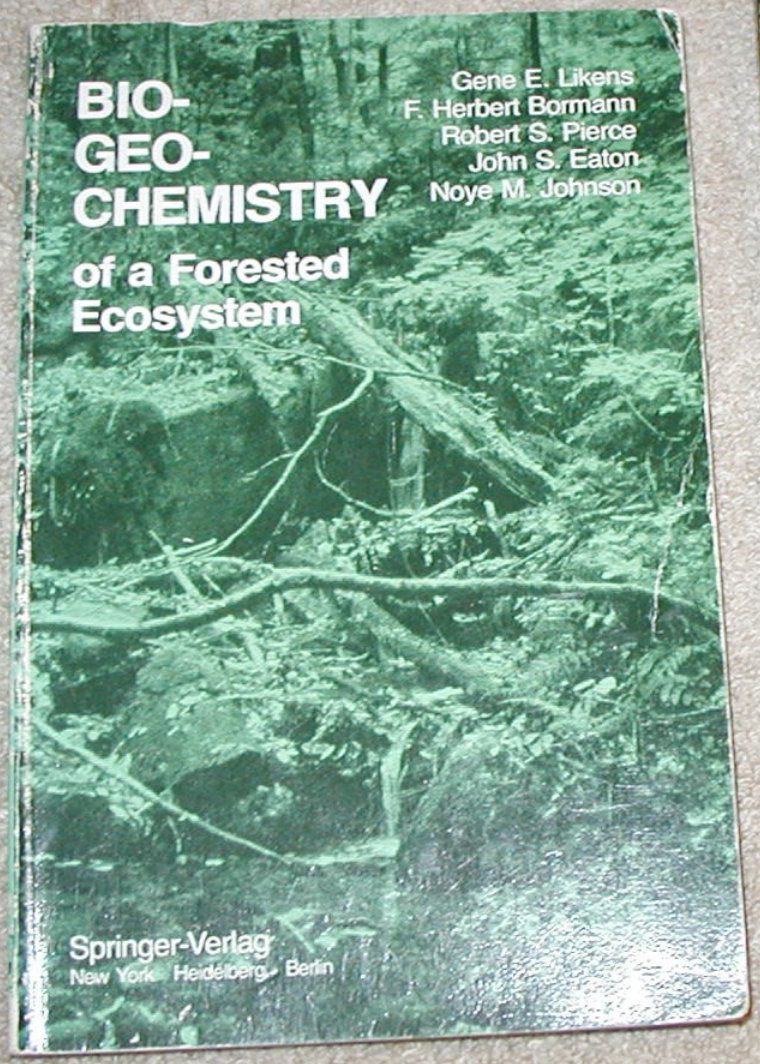
Elements of the Small Watershed Approach

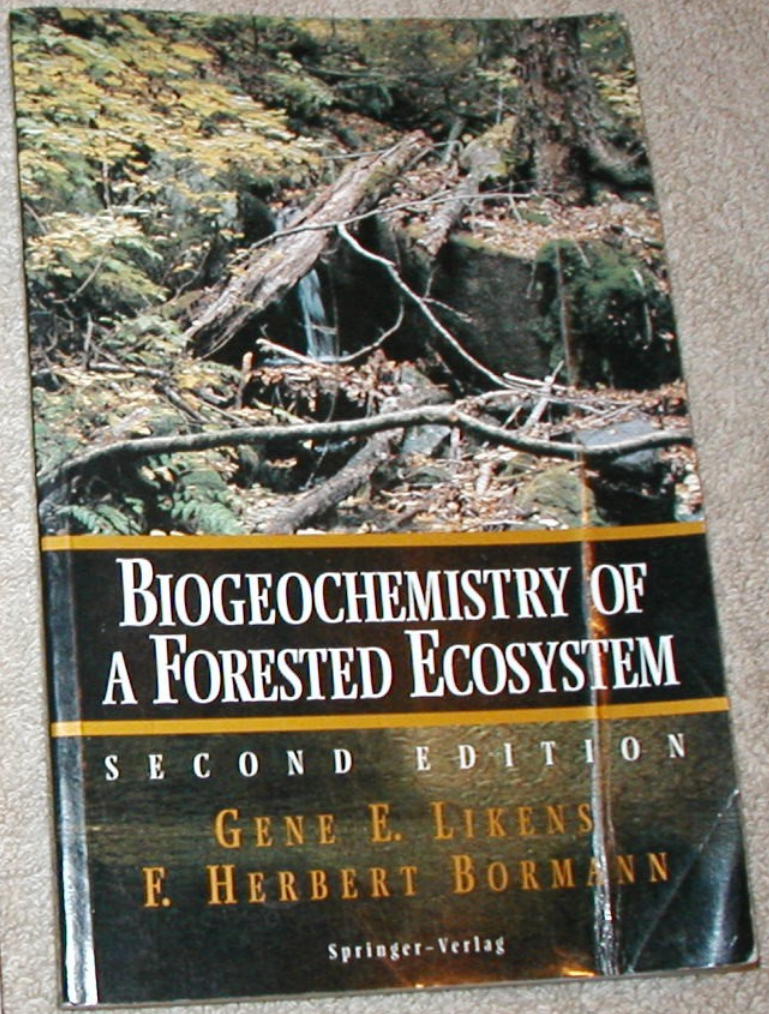
- Small , homogenous, representative
- Input / output budgets
- Internal measurements
- Event (high flow) sampling
- Hydrologic, chemical, and isotopic approaches
- Long-term: trend and pattern detection
- Paired watersheds / manipulations
- Real - time and proxy measurements
- Watershed intercomparisons
- Scaling up

History

- Forestry -- paired watersheds
    - Europe 1870s
    - Wagon Wheel Gap, CO, 1910-1928
    - Coweeta, NC, 1933-present
- Biogeochemistry
    - Hubbard Brook, NH, 1963-present
    - Acid rain era, 1980s
    - Climate change and other issues, 1990s - now
    - Intercomparisons

Streamgaging -- Who needs it?


BIO-
GEO-
CHEMISTRY
of a Forested
Ecosystem
Gene E. Likens
F. Herbert Bormann
Robert S. Pierce
John S. Eaton
Noye M. Johnson
Springer-Verlag
New York Heidelberg Berlin


BIOGEOCHEMISTRY OF
A FORESTED ECOSYSTEM
SECOND EDITION
GENE E. LIKENS
F. HERBERT BORMANN
Springer-Verlag

Inputs

Outputs

Wetfall-dryfall collector and rain gage

Internal measurements

Watershed manipulations

Silviculture treatments

Calcium addition

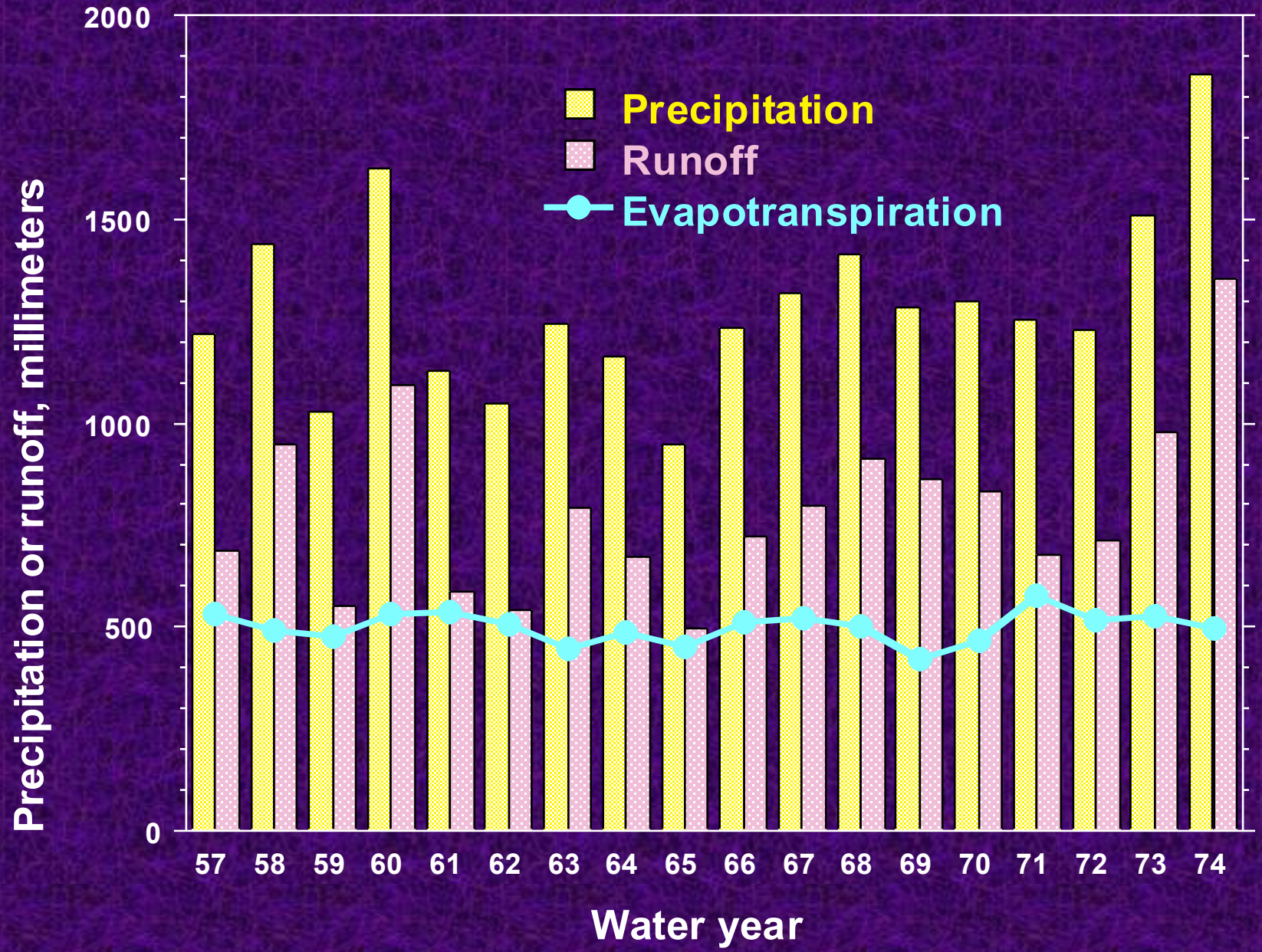
Sample archive

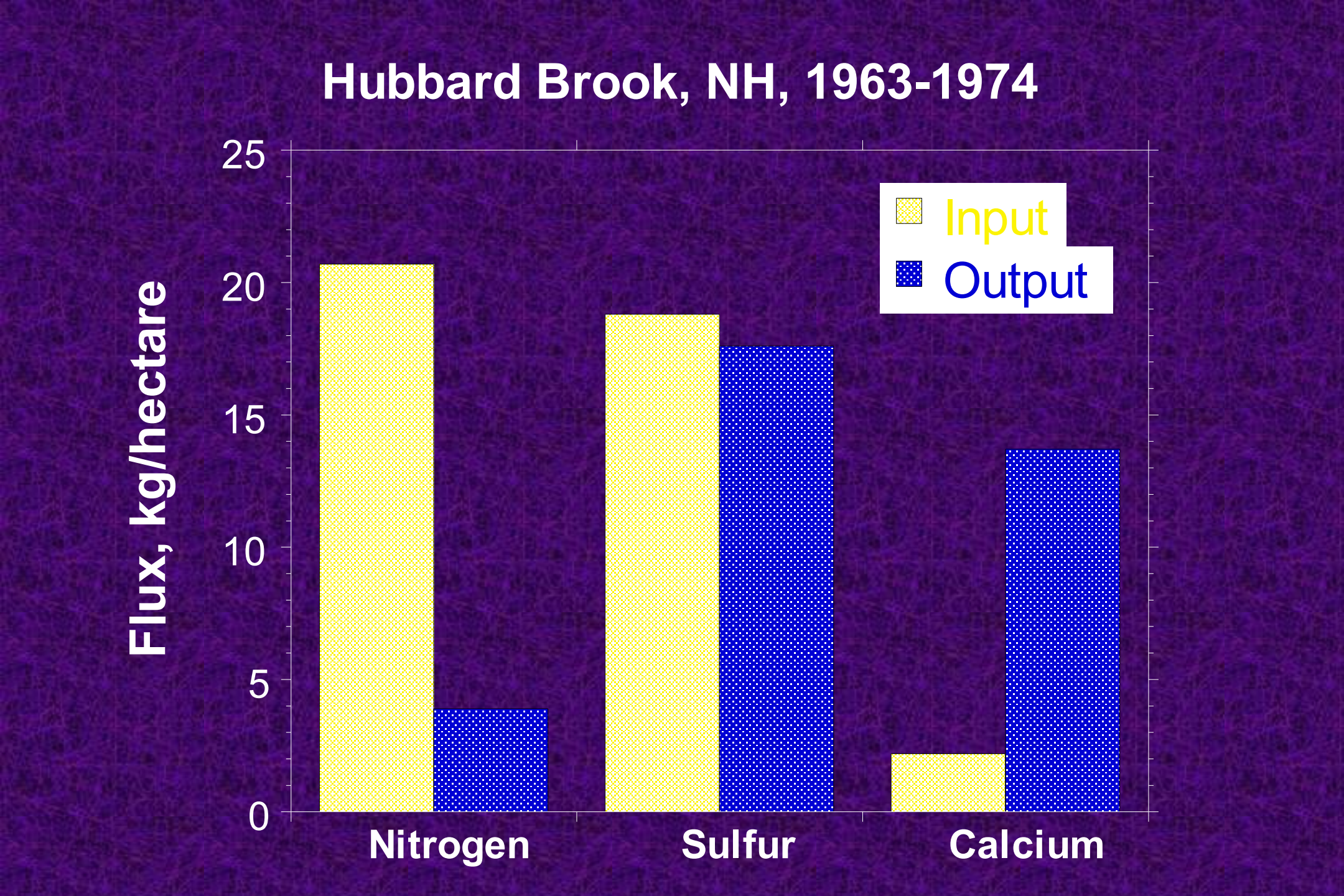
Disturbances

Human-induced

Natural

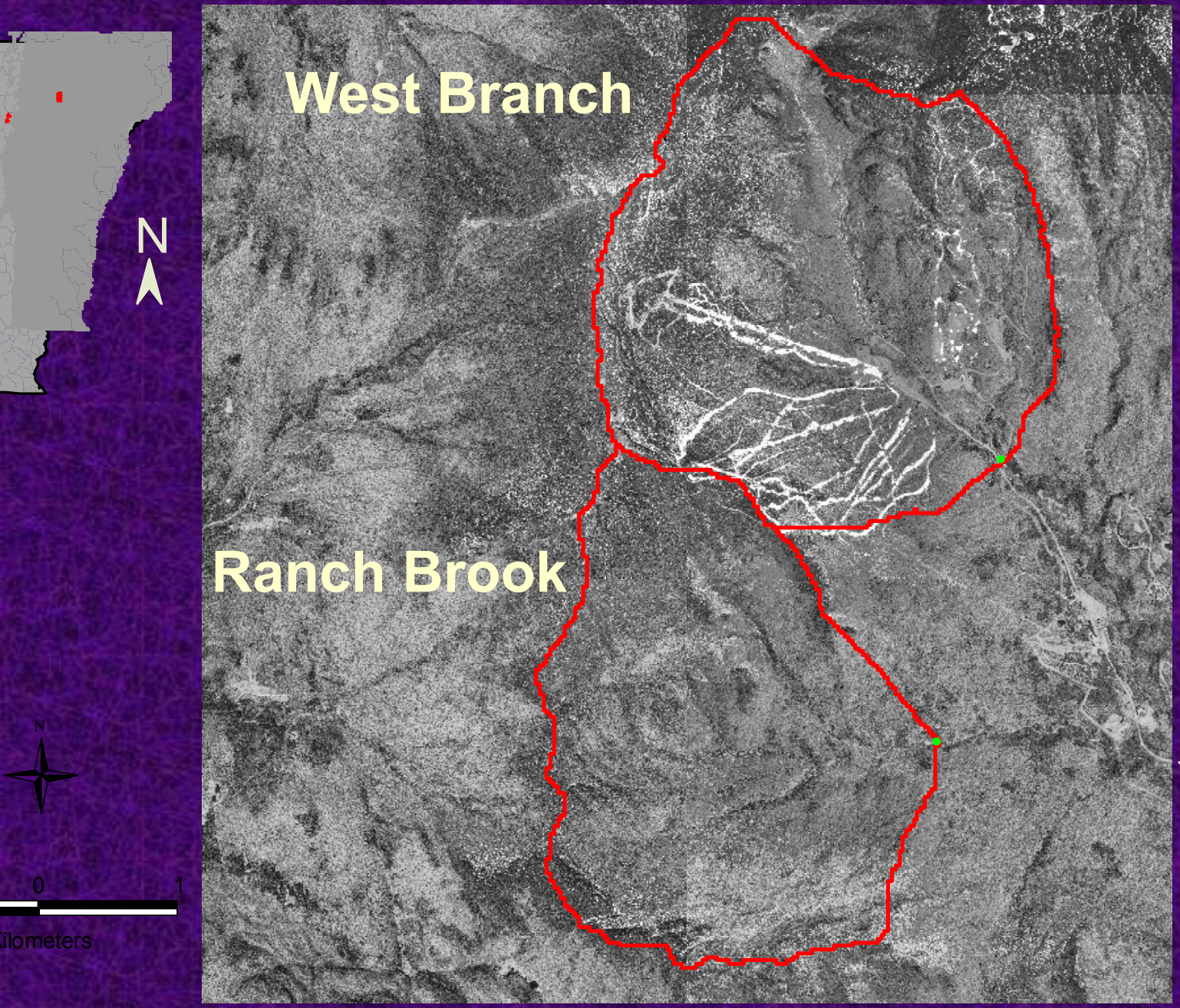
Water Balance at Hubbard Brook, NH




Hubbard Brook, NH, 1963-1974
Flux, kg/hectare
25
20
15
10
5
0
Input
Output
Nitrogen
Sulfur
Calcium

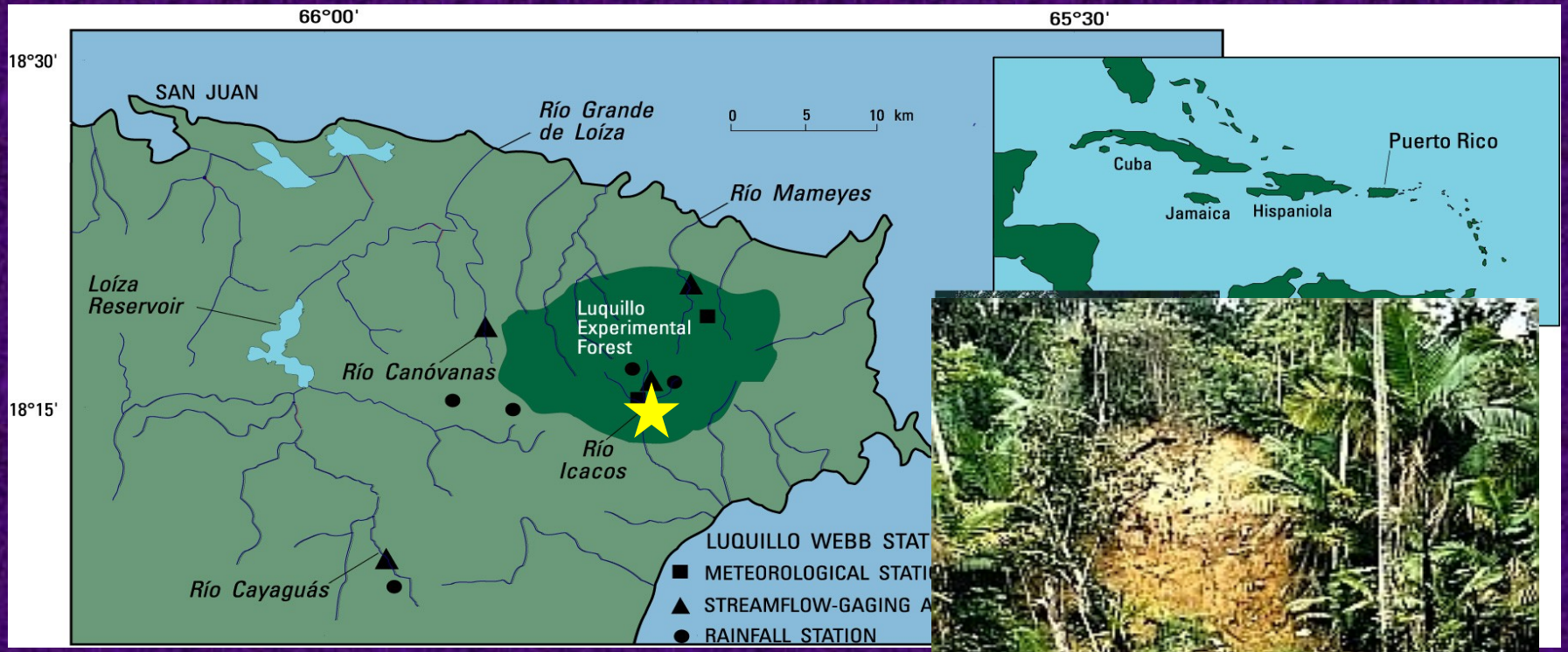
Applications of small watershed research

- Atmospheric deposition effects
  - Sulfate retention
  - Nitrogen saturation
  - Ca depletion (forest decline)
- Mercury cycling
- Agricultural
  - Phosphorous
  - Pesticides
- Disturbance
  - Forestry effects (water and solutes)
  - Urbanization effects



Paired Watershed Study

Rio Icacos, Luquillo LTER, PR

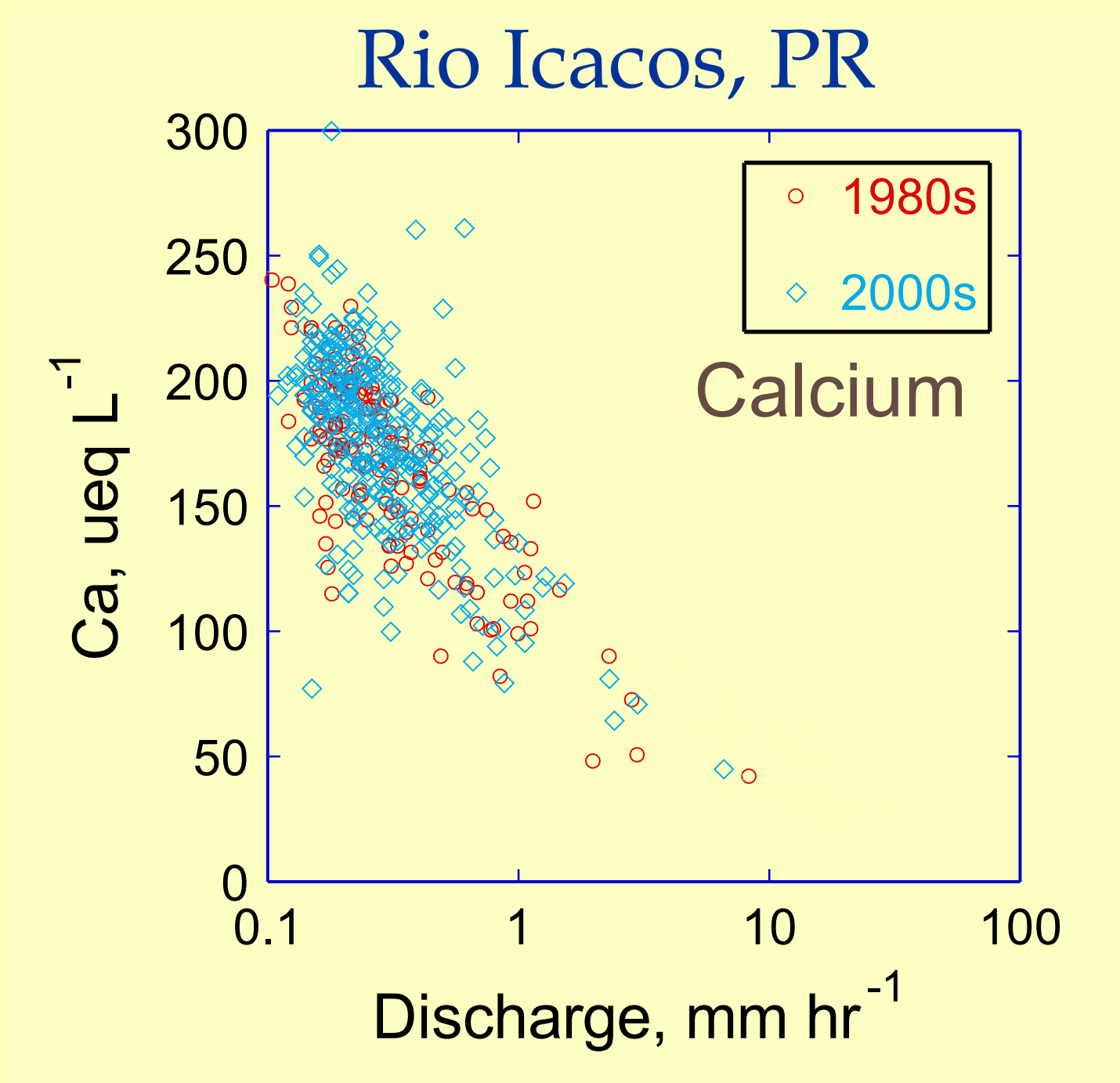


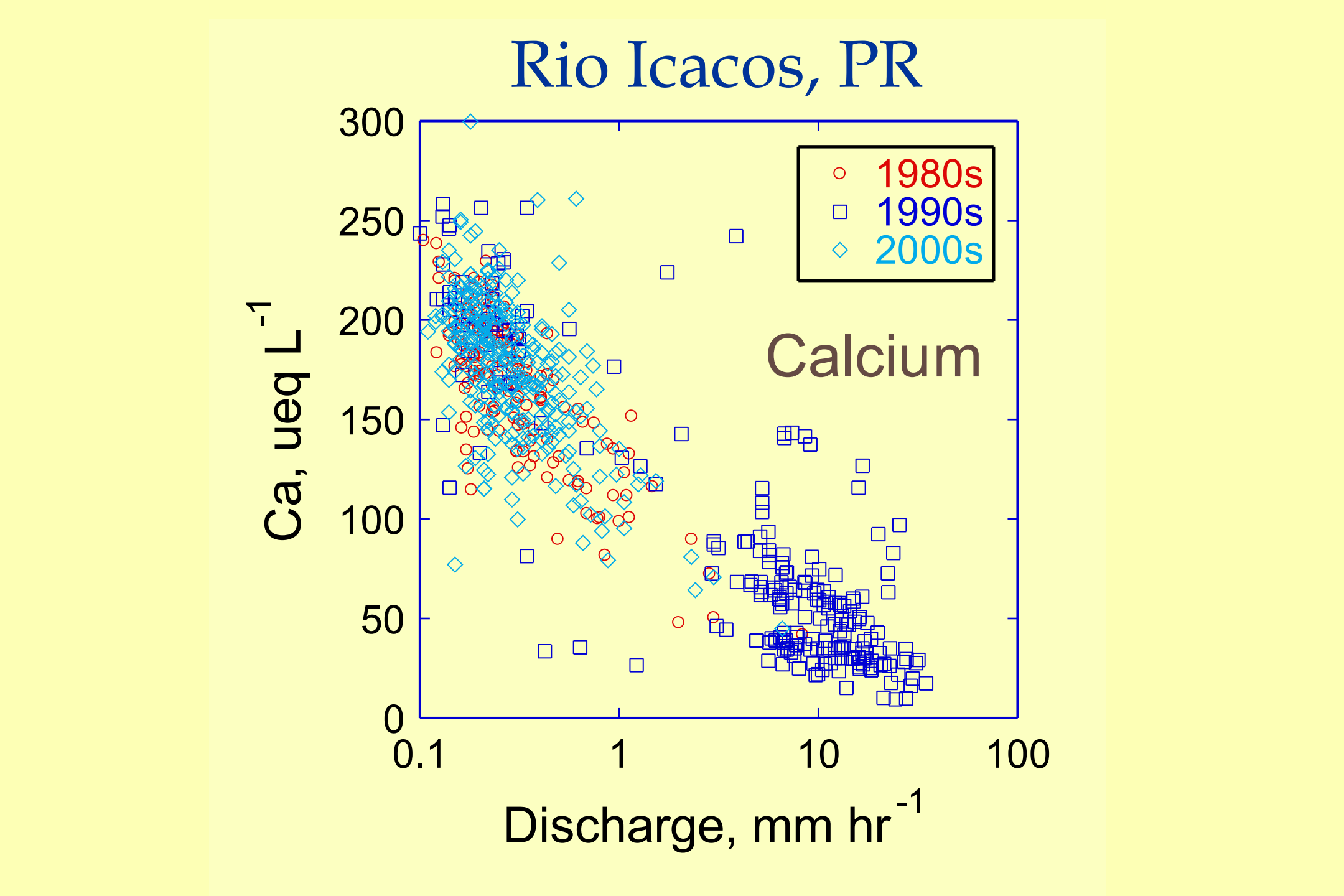
Three datasets

McDowell, 1983-86, weekly

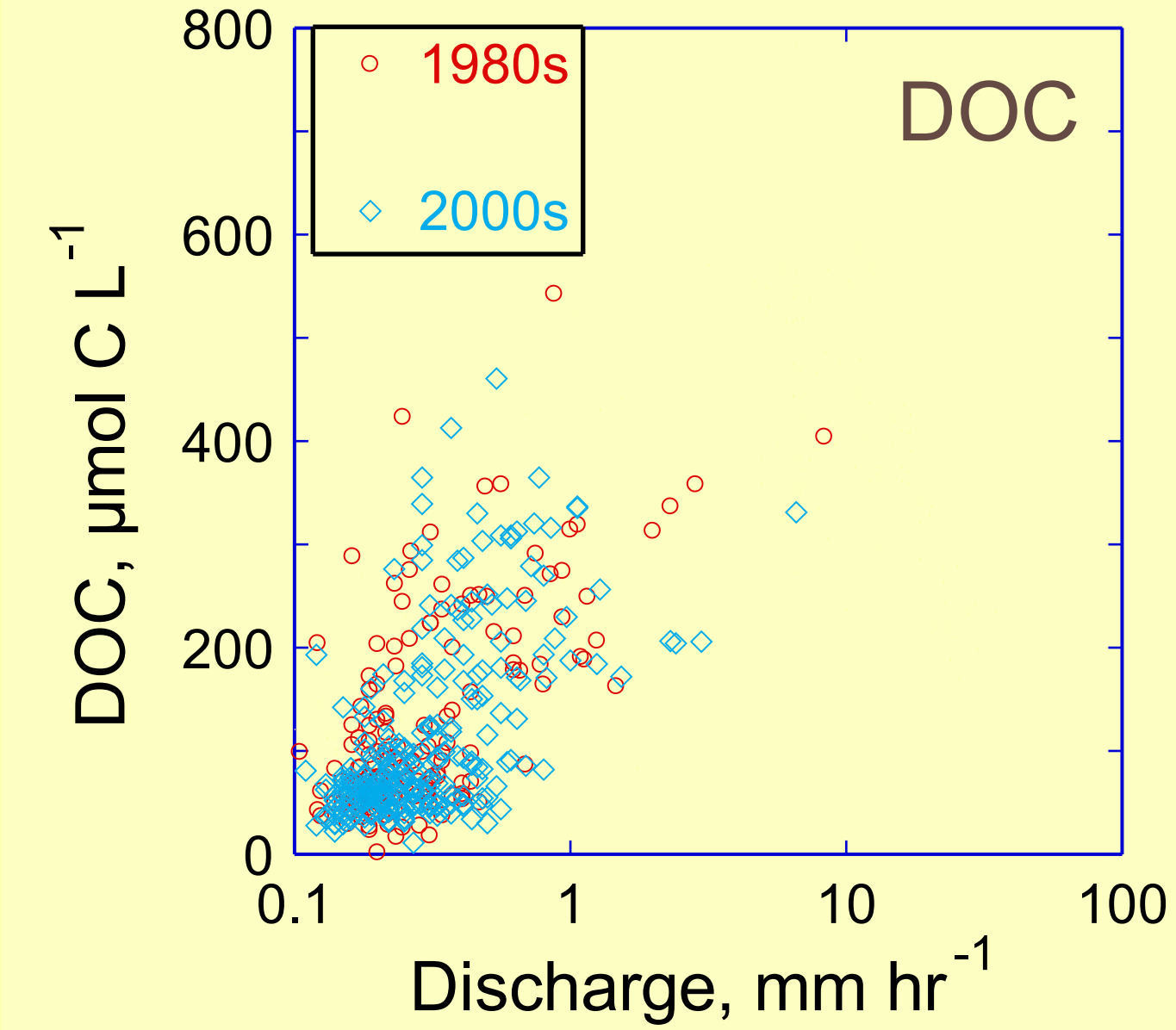
USGS, 1991-97, event

LTER, 2001-05, weekly

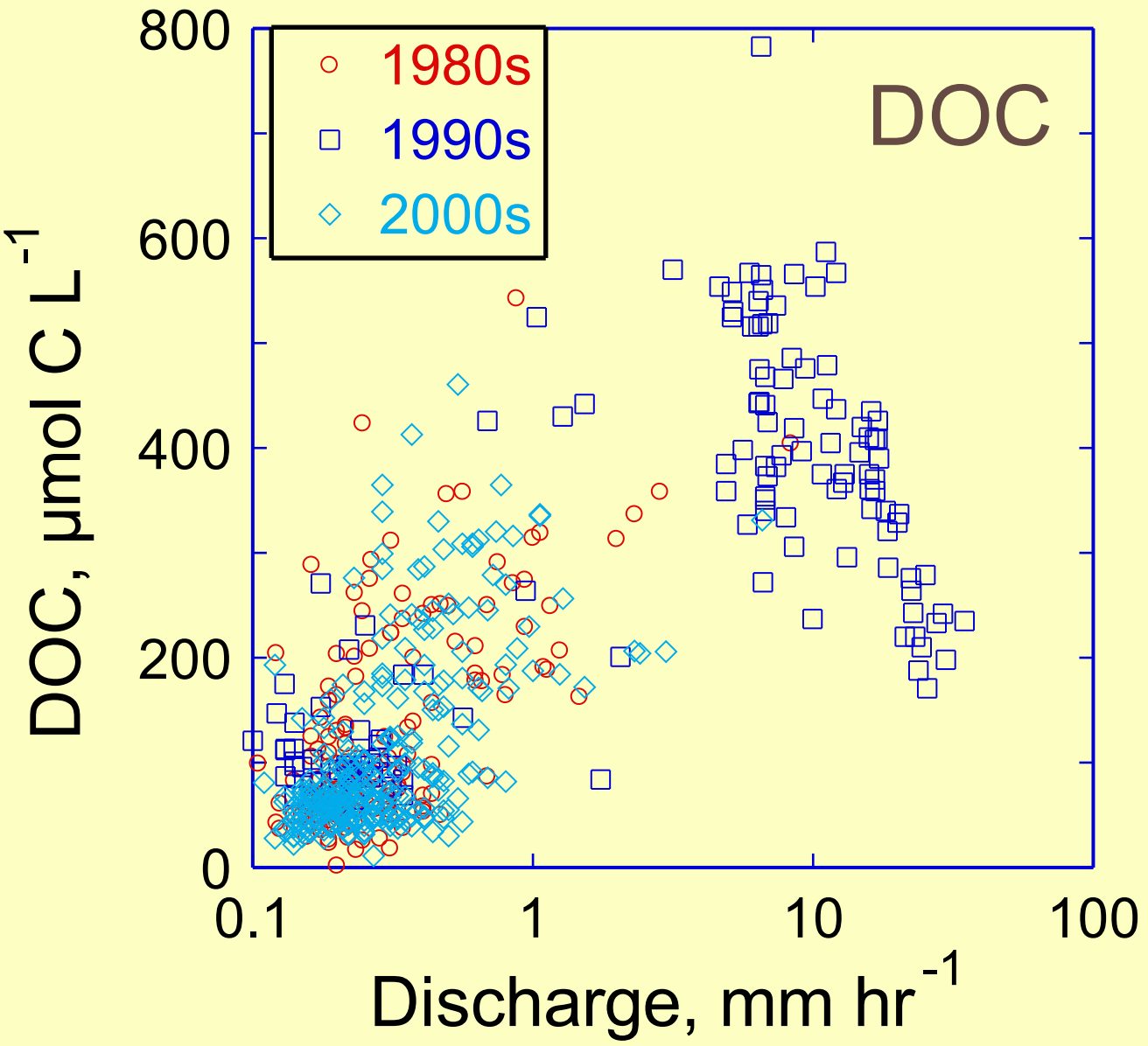

Rio Icacos, PR
1980s
2000s
Calcium
Ca, ueq L-1
Discharge, mm hr-1
300
250
200
150
100
50
0
0.1
1
10
100

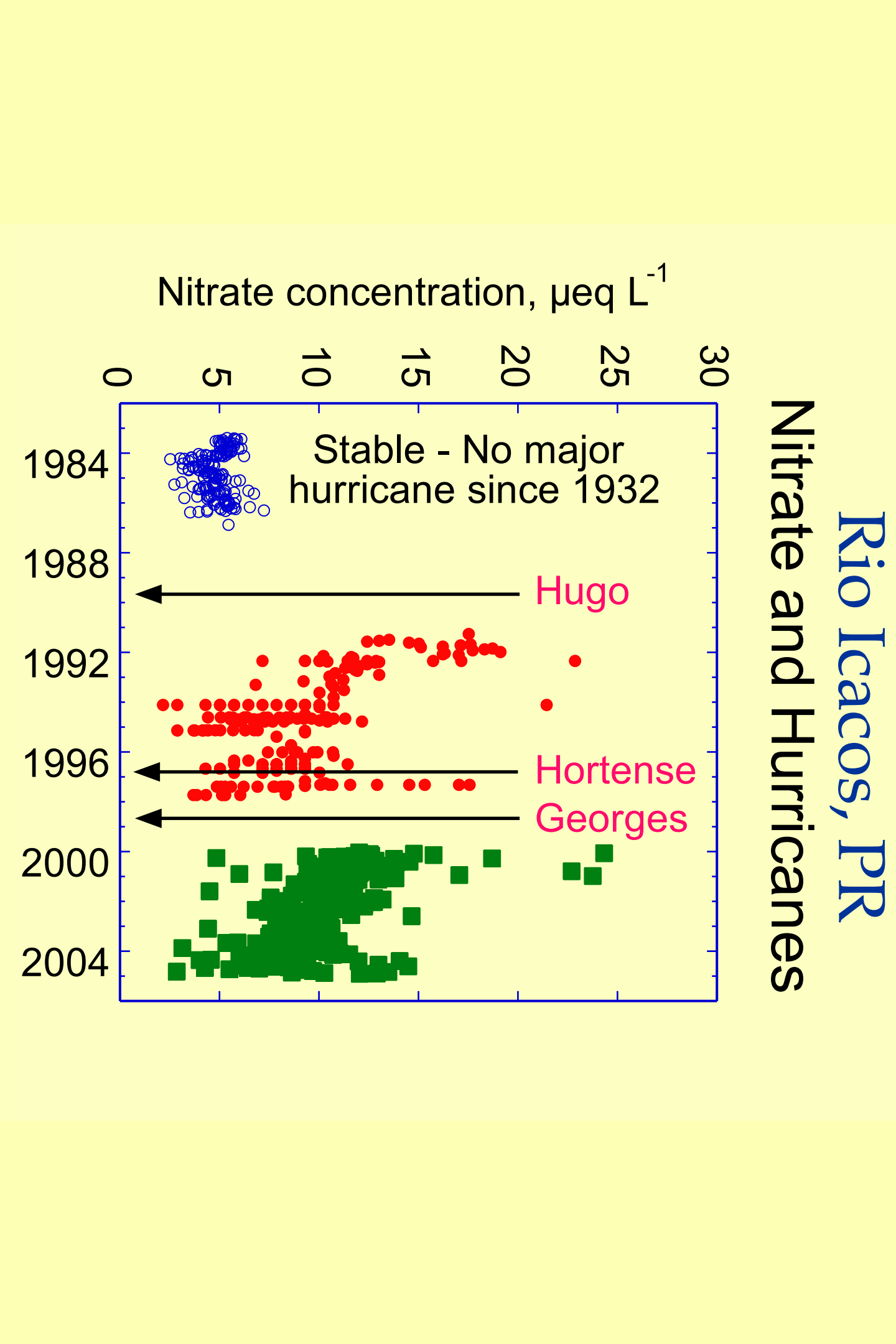

Rio Icacos, PR
300
250
200
150
100
50
0
0.1
1
10
100
Ca, ueq L-1
Discharge, mm hr-1
1980s
1990s
2000s
Calcium

Rio Icacos, PR



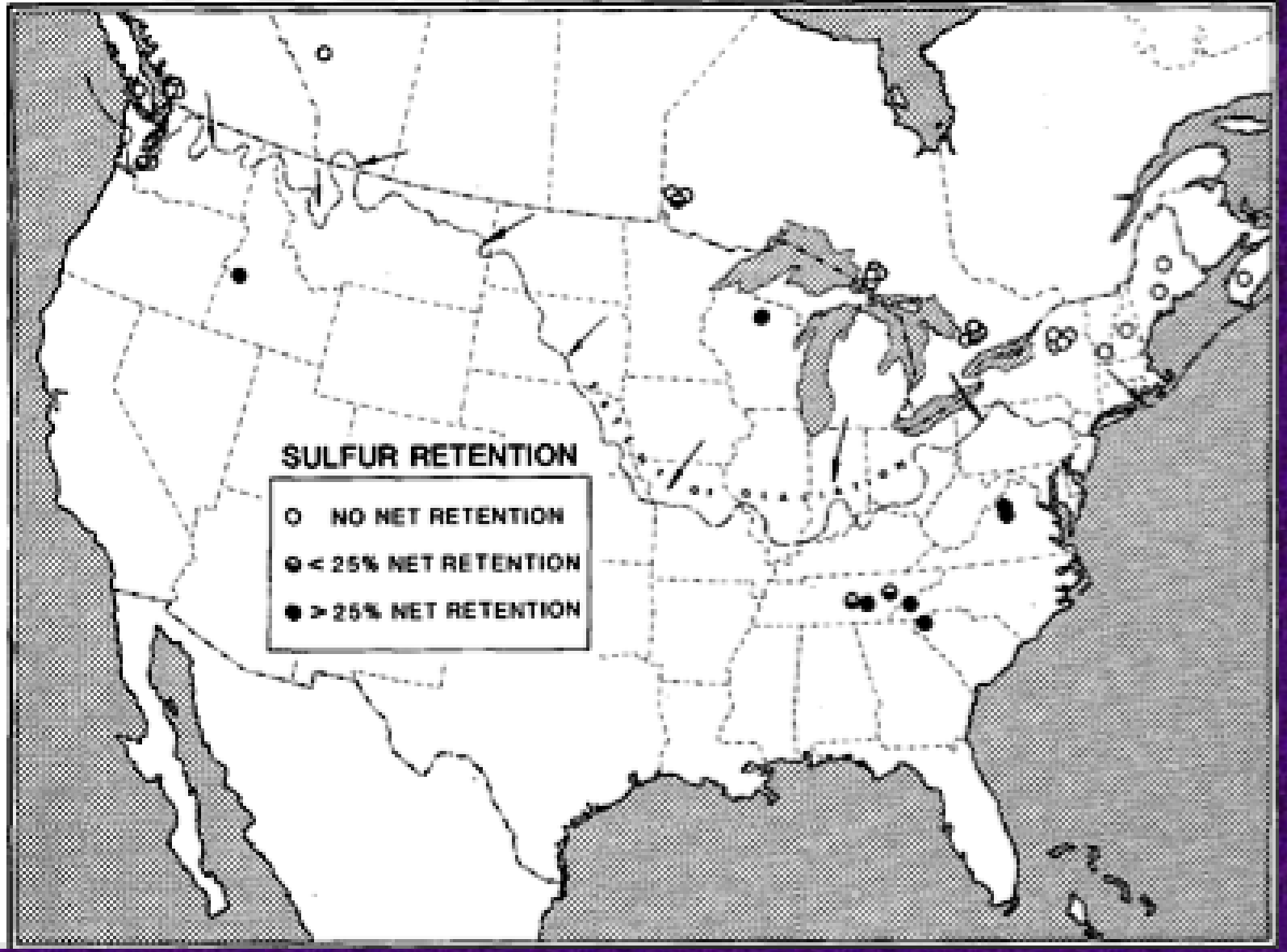
Rio Icacos, PR




Nitrate concentration, µeq L-1
0
5
10
15
20
25
30
1984
1988
1992
1996
2000
2004
Stable - No major hurricane since 1932
Hugo
Hortense
Georges
Nitrate and Hurricanes
Rio Icacos, PR

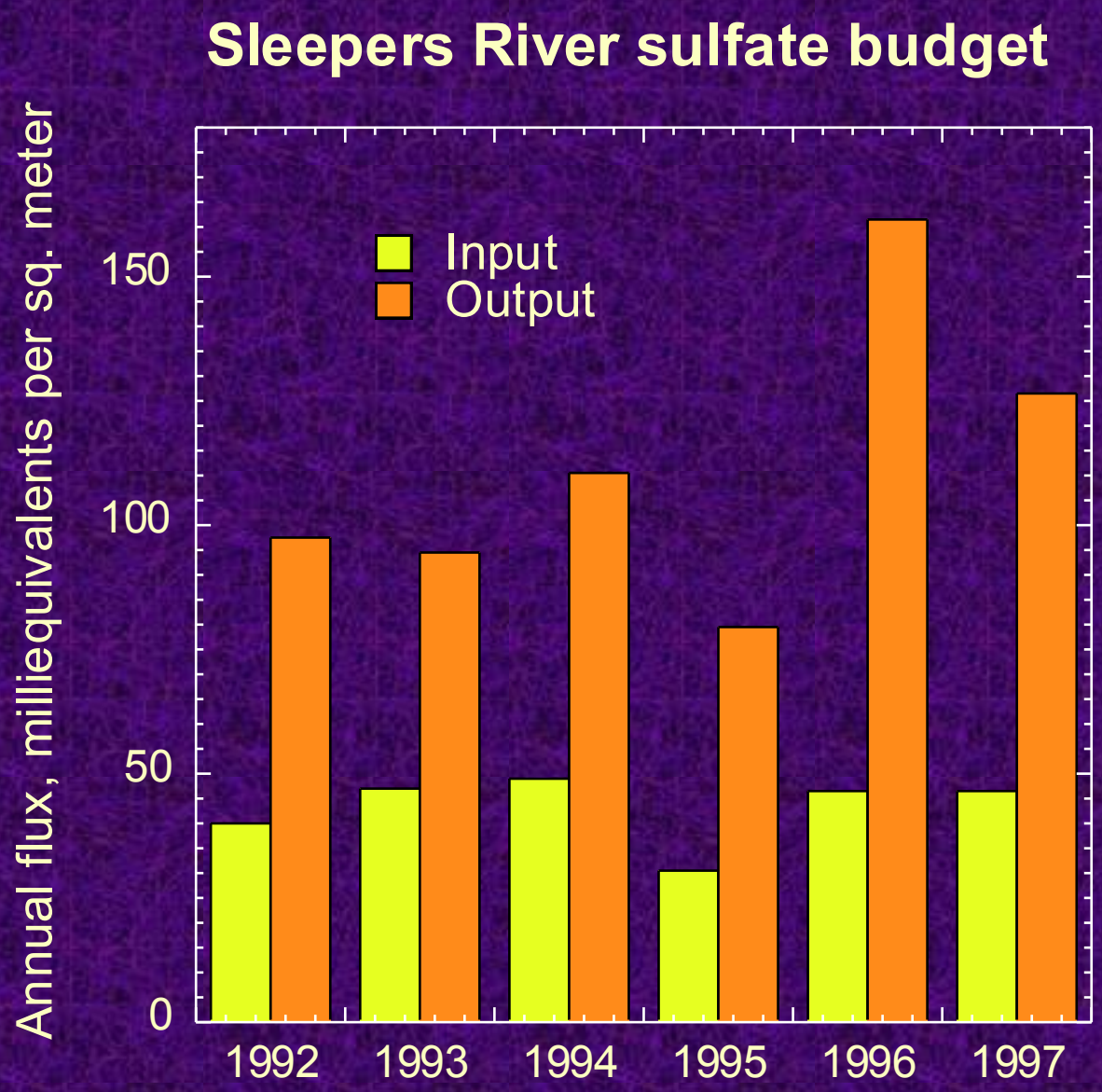
Watershed sulfur cycling studies

Jamie Shanley
USGS-VT
Bernhard Mayer
U. Calgary
Myron Mitchell
SUNY ESF
Bob Michel
USGS-CA
Scott Bailey
US Forest Service -NH
Carol Kendall
USGS-CA



Sulfur Retention

Rochelle et al., 1987


Sleepers River sulfate budget
Annual flux, milliequivalents per sq. meter
Input
Output
150
100
50
0
1992
1993
1994
1995
1996
1997

Questions

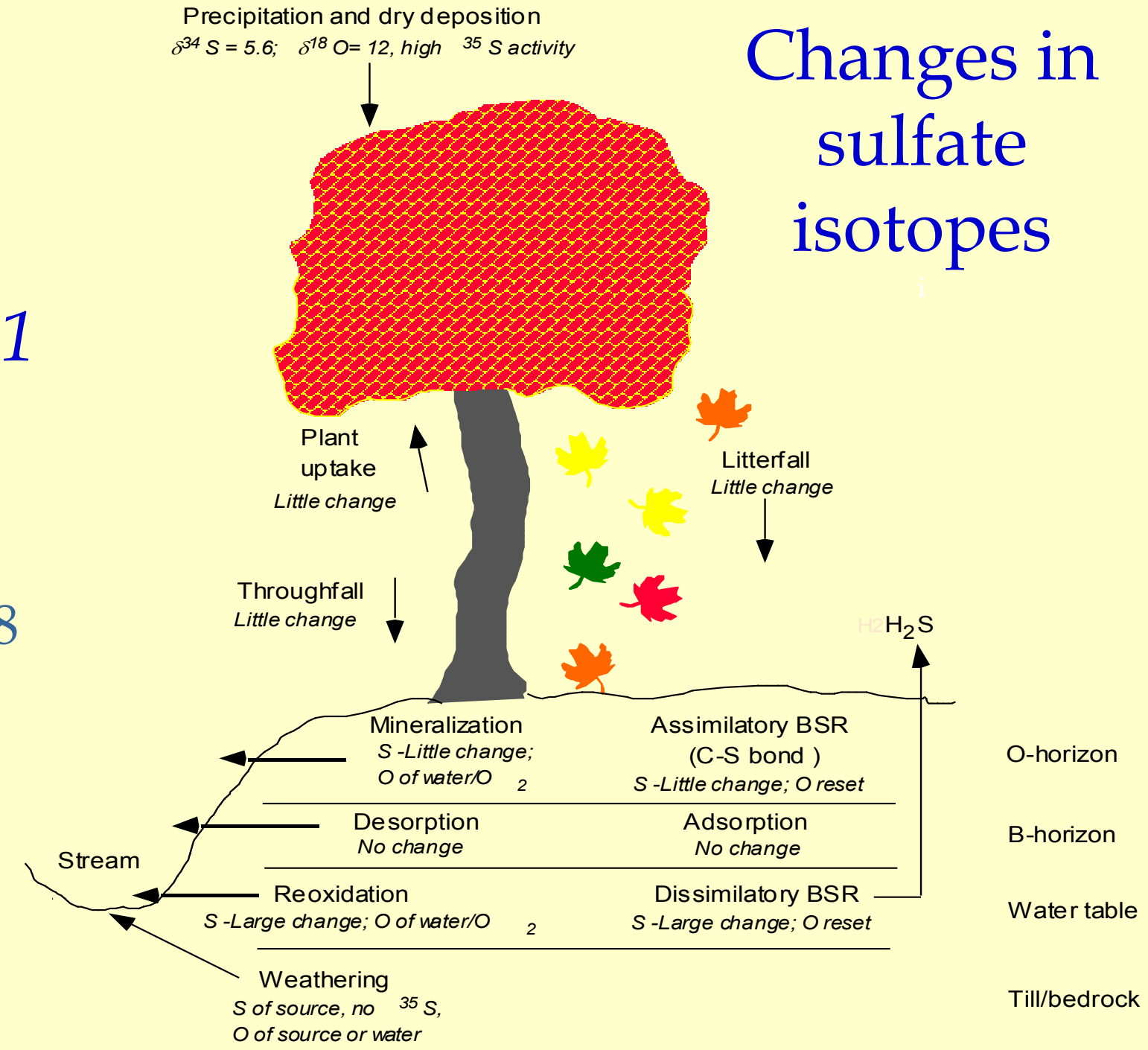
1. How much sulfate comes from weathering and how much from the atmosphere?
2. Does sulfate simply pass through the ecosystem or is it retained for a time?
3. Is sulfate reduction an important process?

Changes in sulfate isotopes

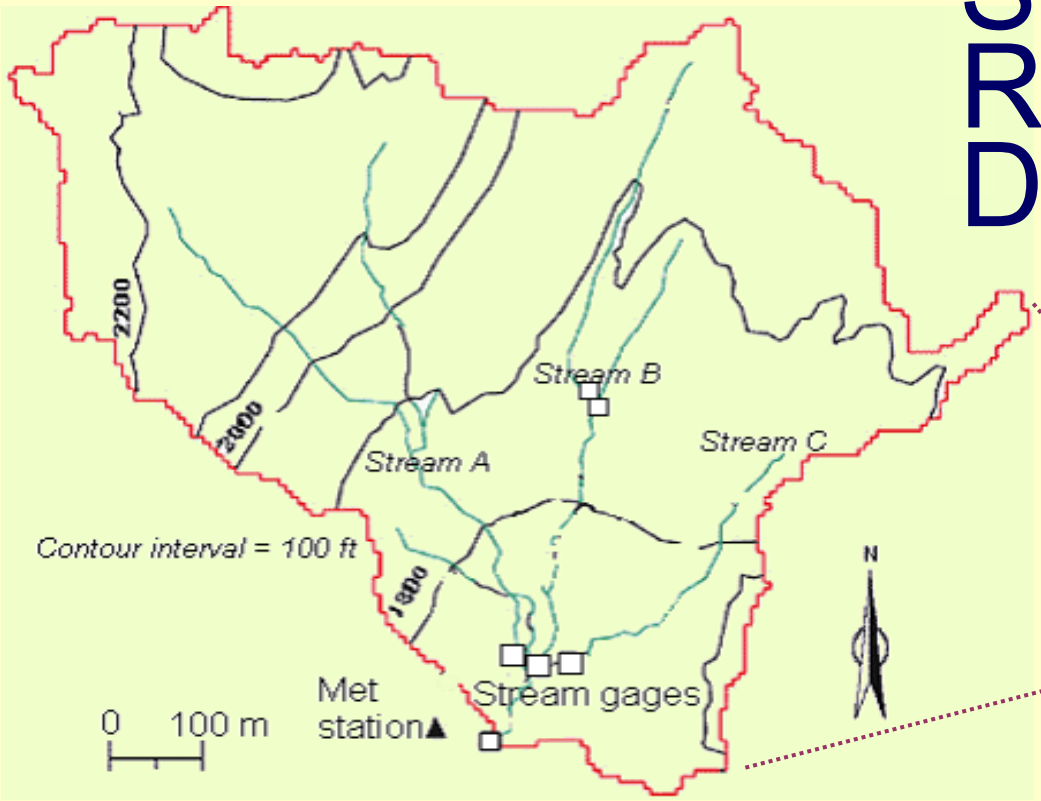
Isotopes 101

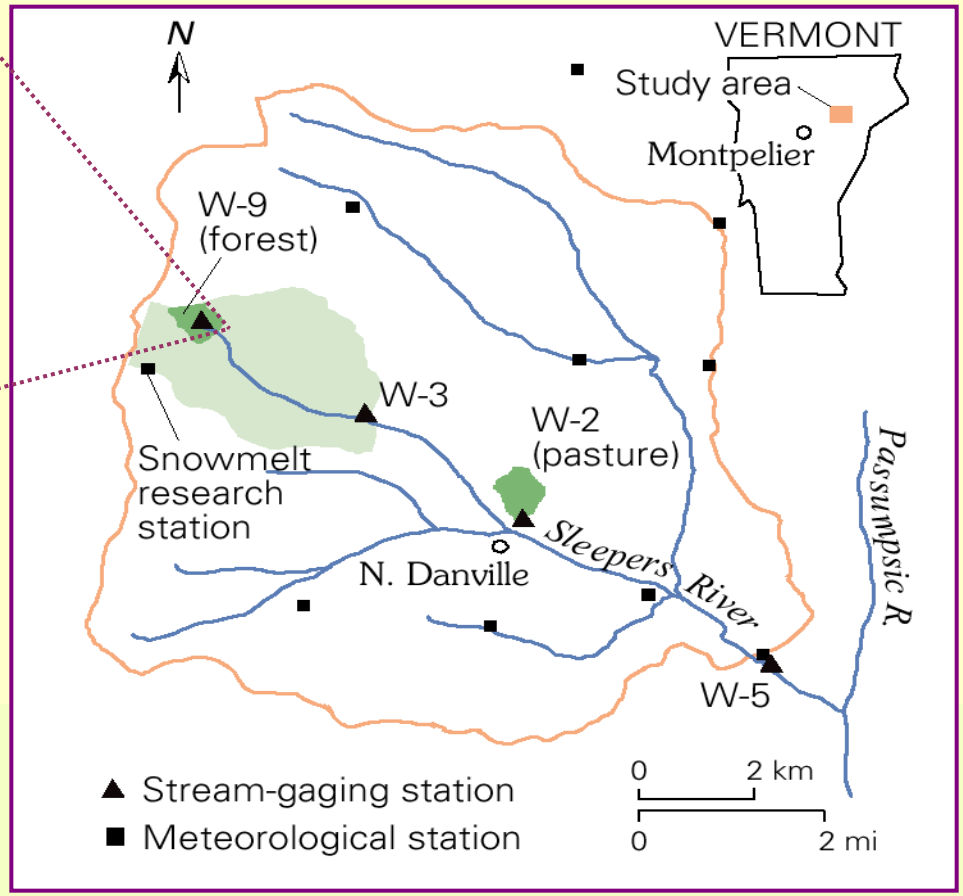
SO_4

32, 34 16,18



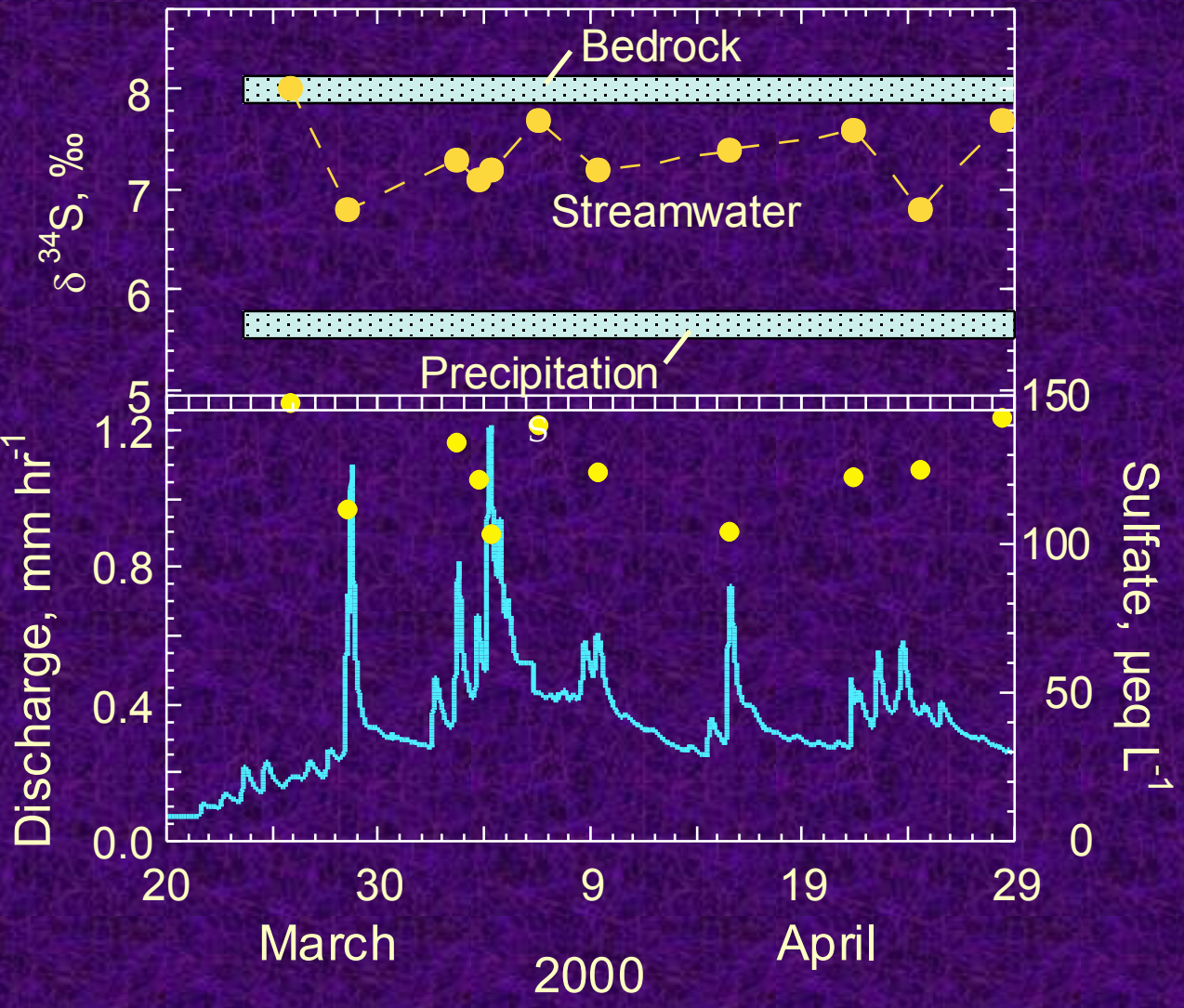
Sleepers River Research Watershed Danville, VT

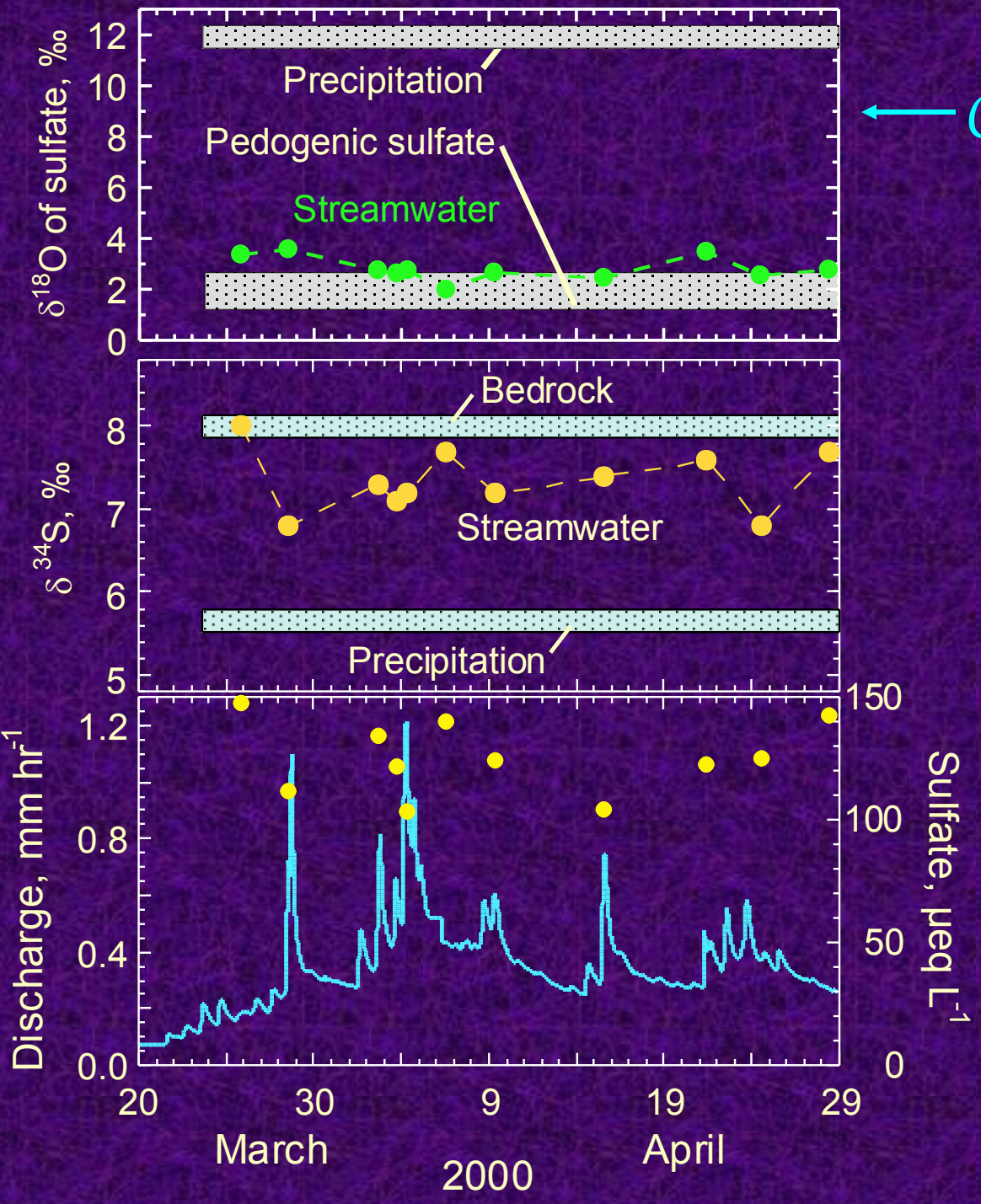




Sulfate isotope studies

Sleepers Stream B during snowmelt



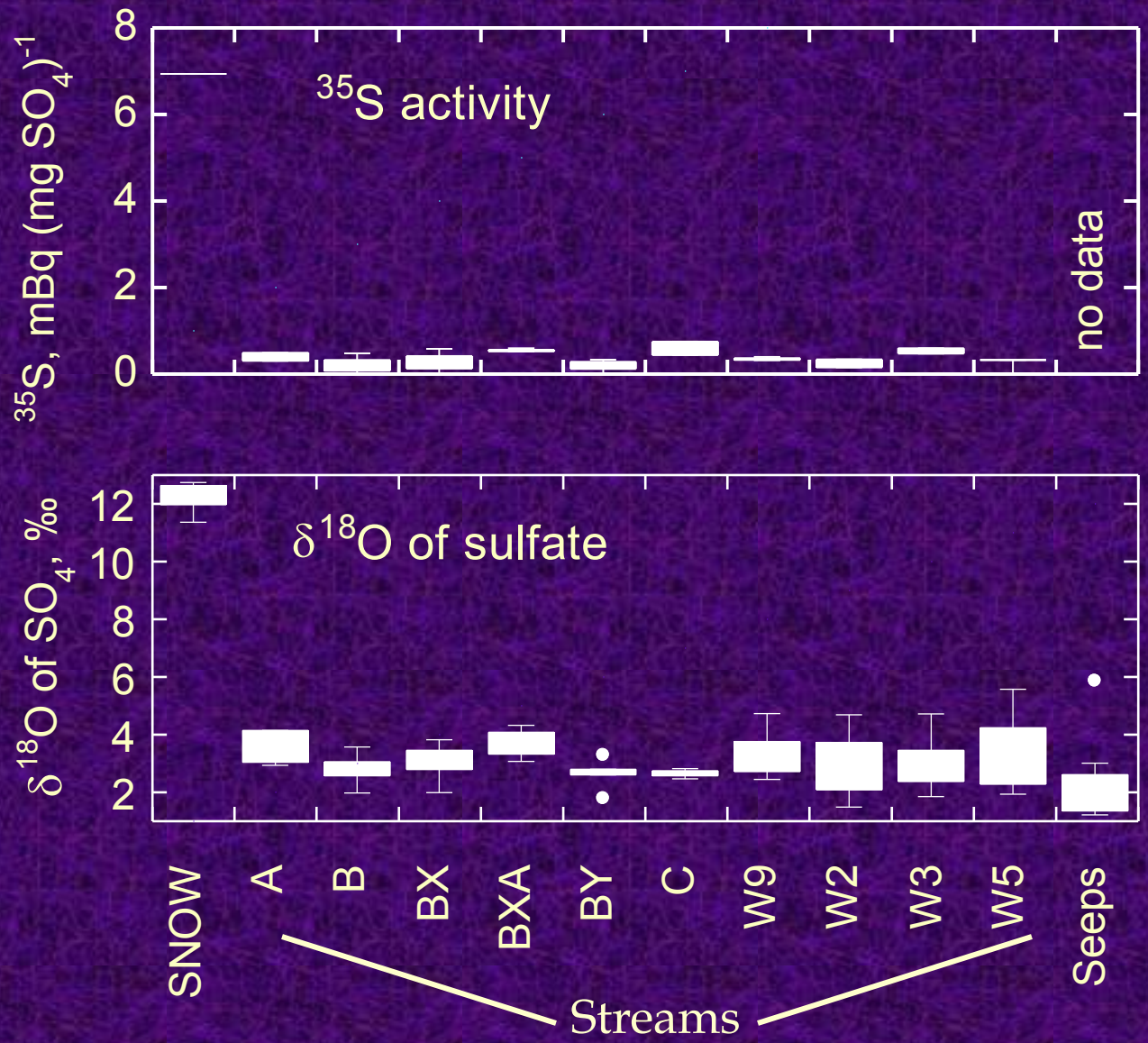


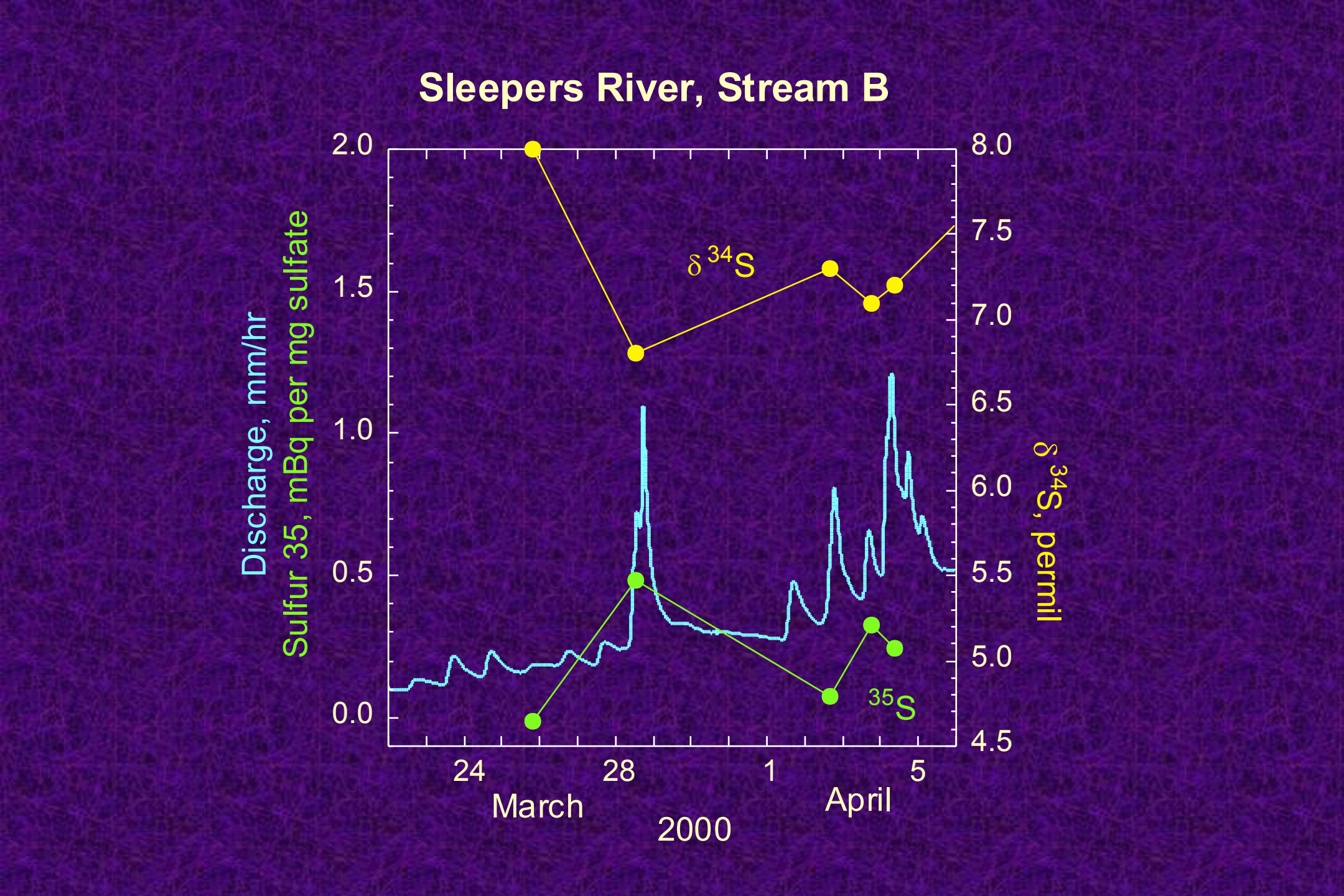
← *Oxygen isotopes of sulfate*

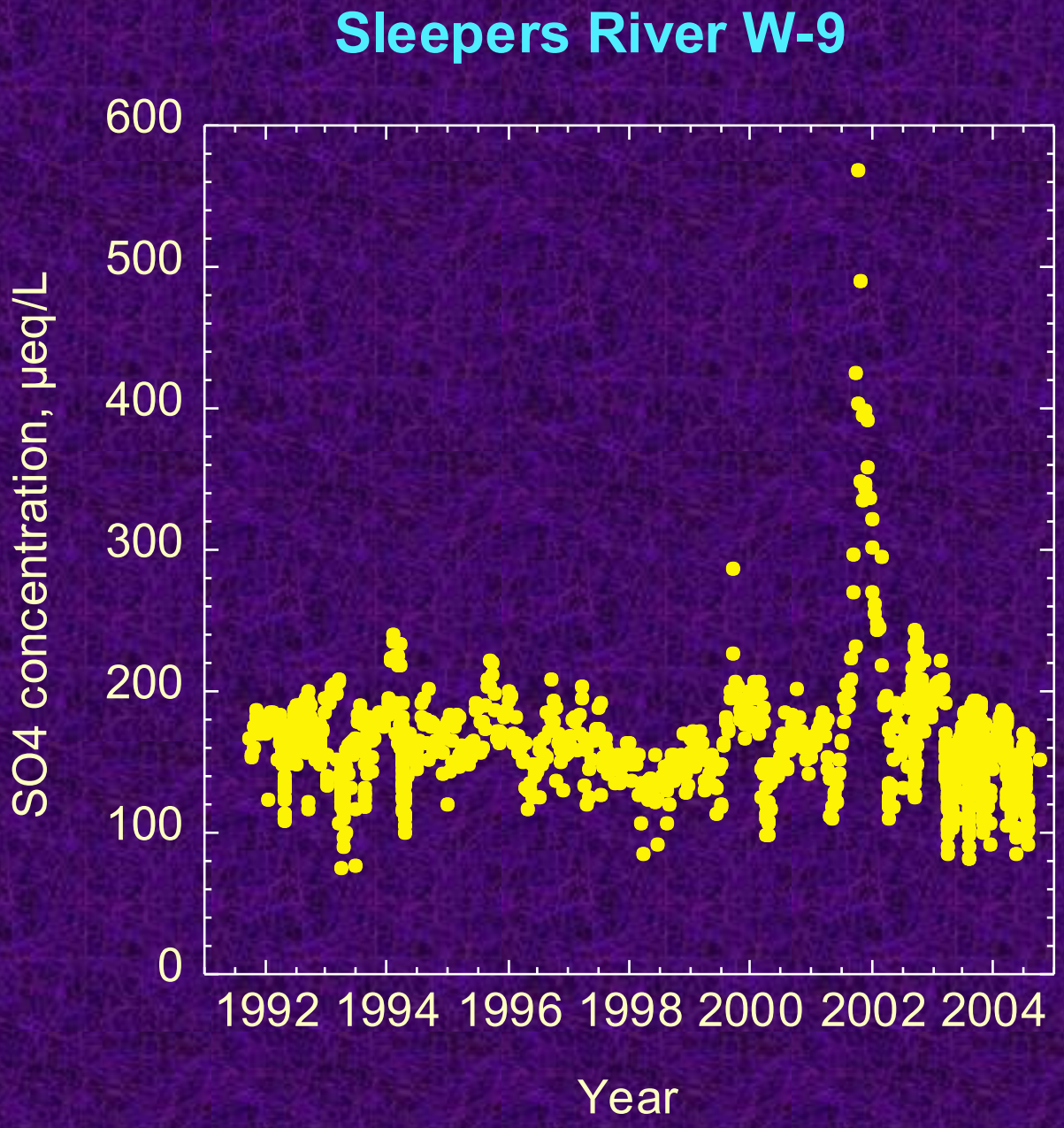
Sulfur 35

1. Cosmogenic, from spallation of Argon
2. Half life 87 days
3. Can be detected up to 1-2 years

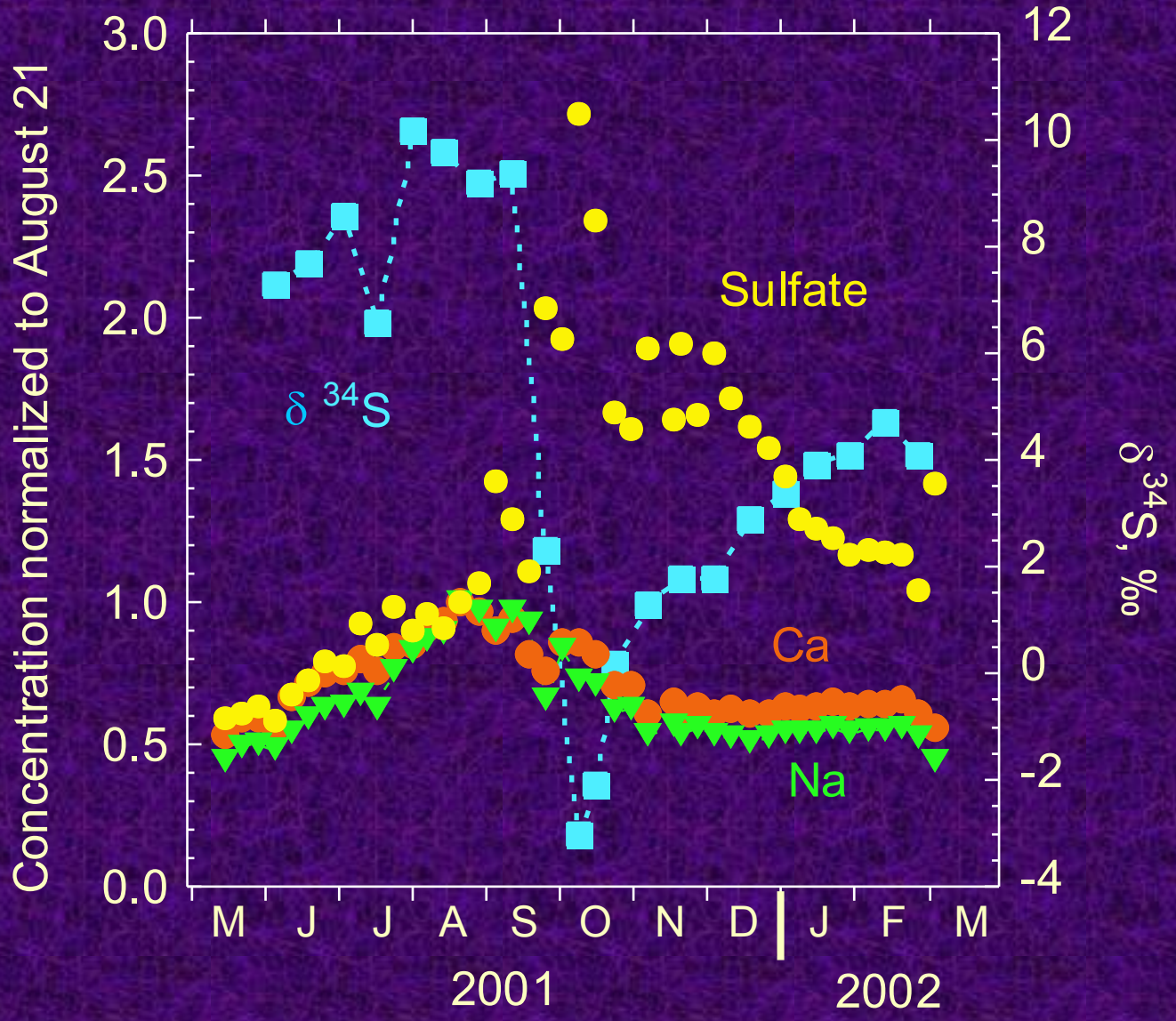
^{35}S and $\delta^{18}O$ in precipitation and streams




Sleepers River, Stream B
Discharge, mm/hr
Sulfur 35, mBq per mg sulfate
δ 34S, permil
2.0
1.5
1.0
0.5
0.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
δ 34S
35S
24
28
1
5
March
April
2000


Sleepers River W-9
600
500
400
300
200
100
0
SO4 concentration, µeq/L
1992 1994 1996 1998 2000 2002 2004
Year

Sulfate concentration and isotopic shifts

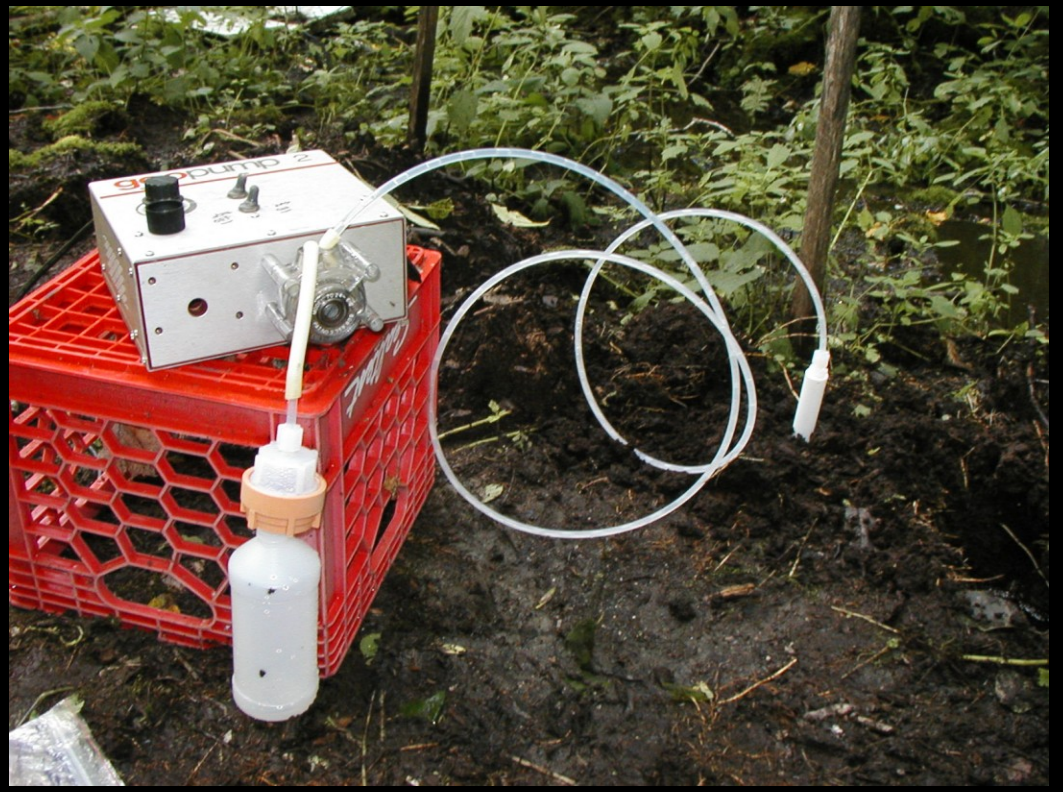


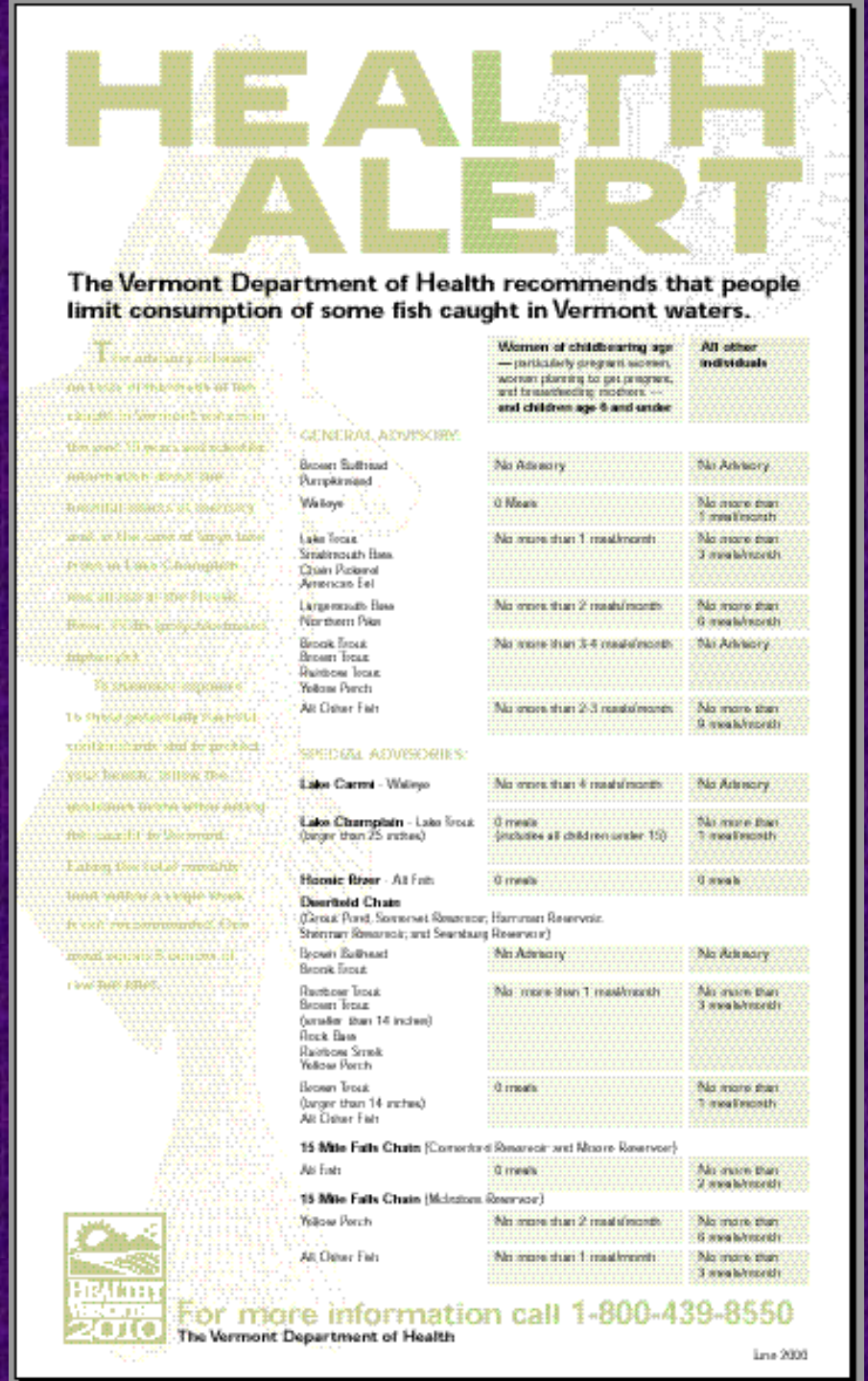
Conclusions:

Sulfate studies

1. Atmospheric sulfur contributes up to 50% to stream sulfate
2. But … nearly all atmospheric sulfate is transformed in the soil
3. Apparent S ages ~300 days => lots of old sulfate + a little bit of young sulfate
4. Reoxidation of secondary sulfide drives high stream sulfate after drought

Mercury





HEALTH ALERT

The Vermont Department of Health recommends that people limit consumption of some fish caught in Vermont waters.

	Women of childbearing age — particularly pregnant women, women planning to get pregnant, and breastfeeding mothers — and children age 6 and under	All other individuals
GENERAL ADVISORY		
Brown Bullhead Pumpkinseed	No Advisory	No Advisory
Walleye	0 Meals	No more than 1 meal/month
Lake Trout Smallmouth Bass Chain Pickerel American Eel	No more than 1 meal/month	No more than 3 meals/month
Largemouth Bass Northern Pike	No more than 2 meals/month	No more than 6 meals/month
Brook Trout Brown Trout Rainbow Trout Yellow Perch	No more than 3-4 meals/month	No Advisory
All Other Fish	No more than 2-3 meals/month	No more than 9 meals/month
SPECIAL ADVISORIES:		
Lake Carmi - Walleye	No more than 4 meals/month	No Advisory
Lake Champlain - Lake Trout (larger than 25 inches)	0 meals (includes all children under 15)	No more than 1 meal/month
Hazen Brook - All Fish	0 meals	0 meals
Deerfield Chain (Grout Pond, Somerset Reservoir, Harriman Reservoir, Sherman Reservoir, and Searsburg Reservoir)		
Brown Bullhead Brook Trout	No Advisory	No Advisory
Rainbow Trout Brown Trout (smaller than 14 inches) Rock Bass Rainbow Smelt Yellow Perch	No more than 1 meal/month	No more than 3 meals/month
Brown Trout (larger than 14 inches) All Other Fish	0 meals	No more than 1 meal/month
15 Mile Falls Chain (Connecticut Reservoir and Moore Reservoir)		
All Fish	0 meals	No more than 2 meals/month
15 Mile Falls Chain (Wallace Reservoir)		
Yellow Perch	No more than 2 meals/month	No more than 6 meals/month
All Other Fish	No more than 1 meal/month	No more than 3 meals/month

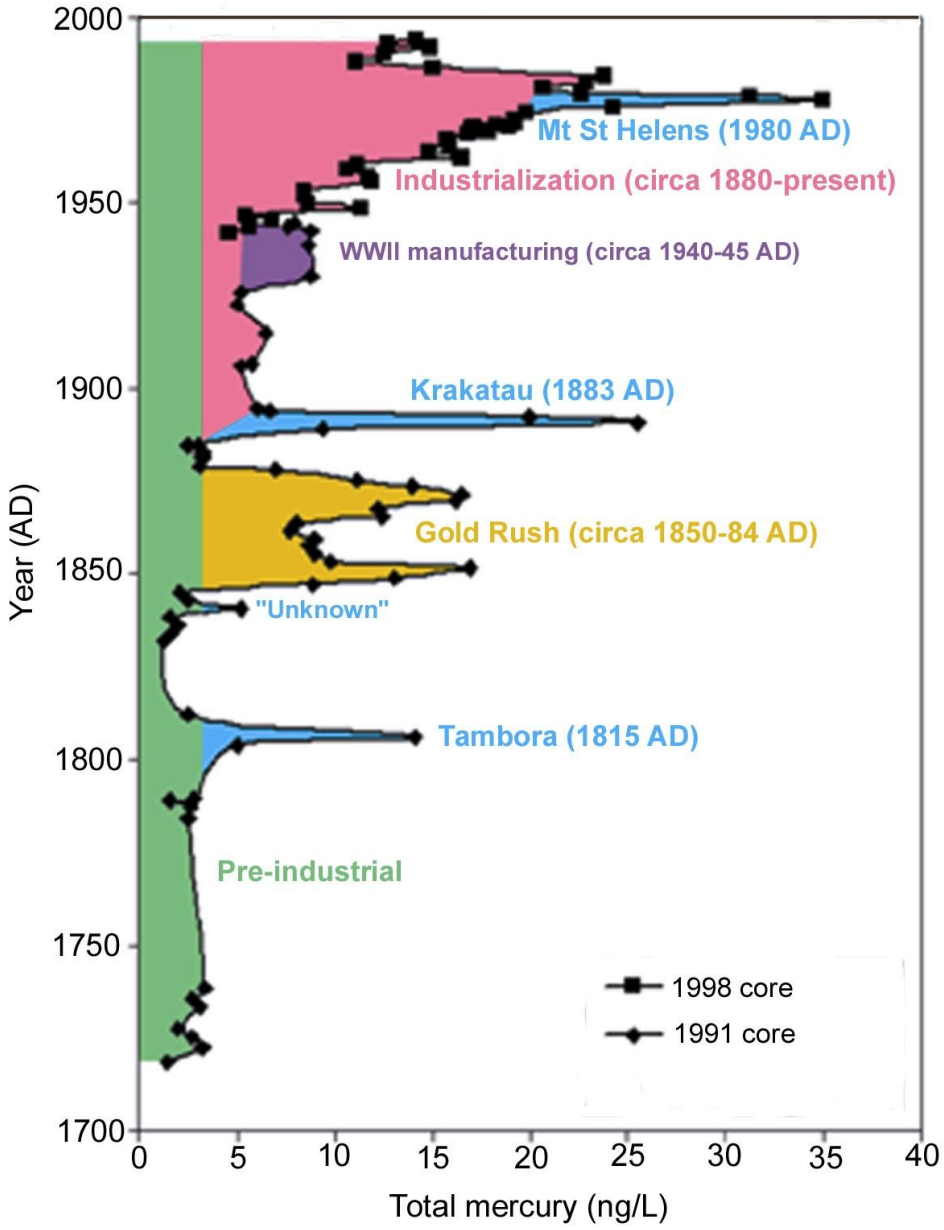
For more information call 1-800-439-8550

The Vermont Department of Health

June 2000

- Mercury damages the nervous system
- People acquire mercury from fish
- Children and pregnant women most at risk

Figure 2

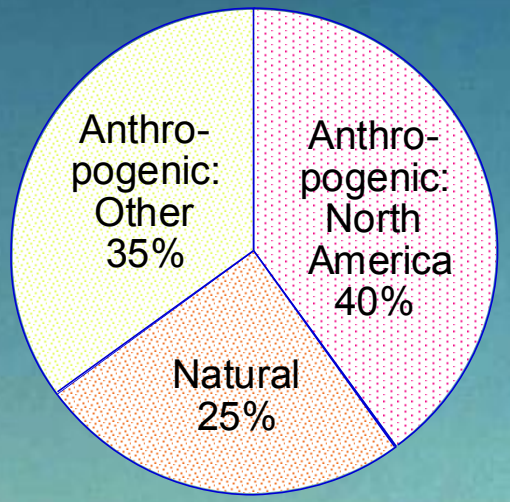


Mercury deposition preserved in ice

Fremont Glacier, Wyoming

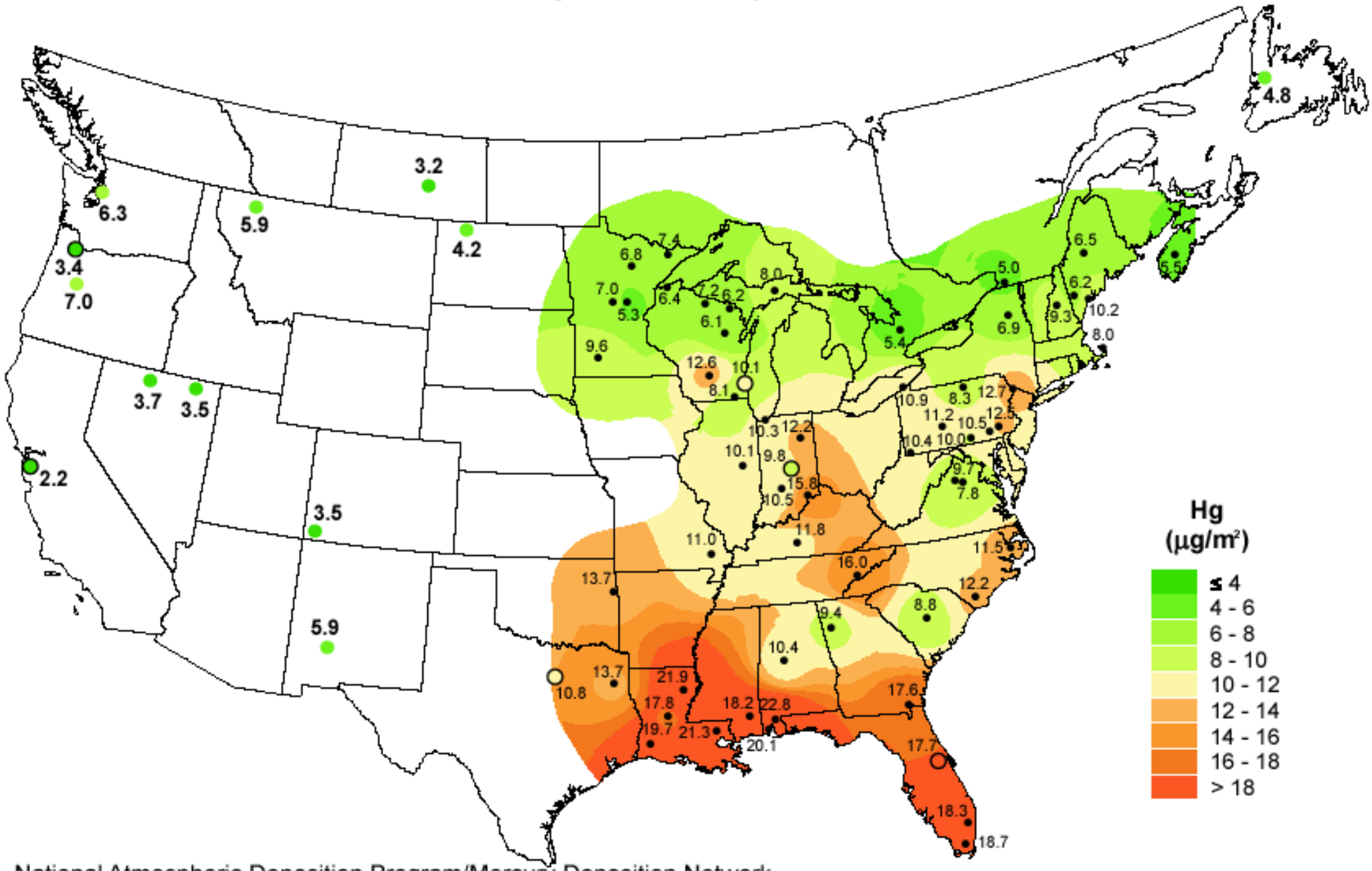
Schuster et al., 2002

Mercury sources



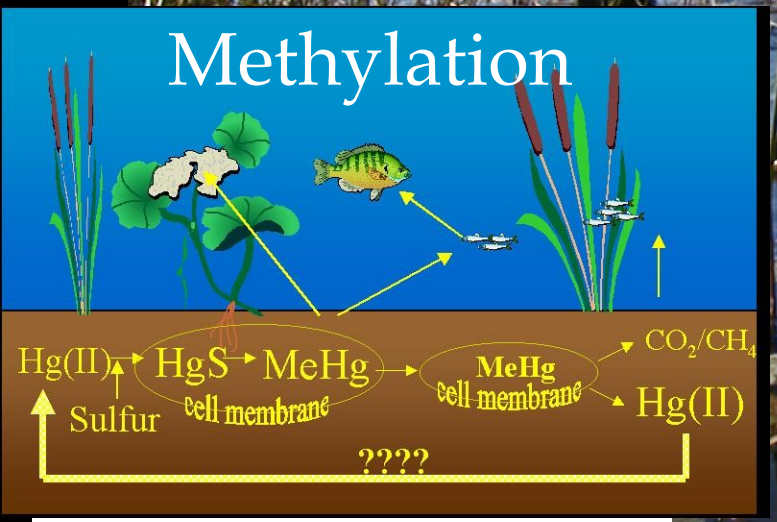
Seigneur et al., 2004

Total Mercury Wet Deposition, 2004



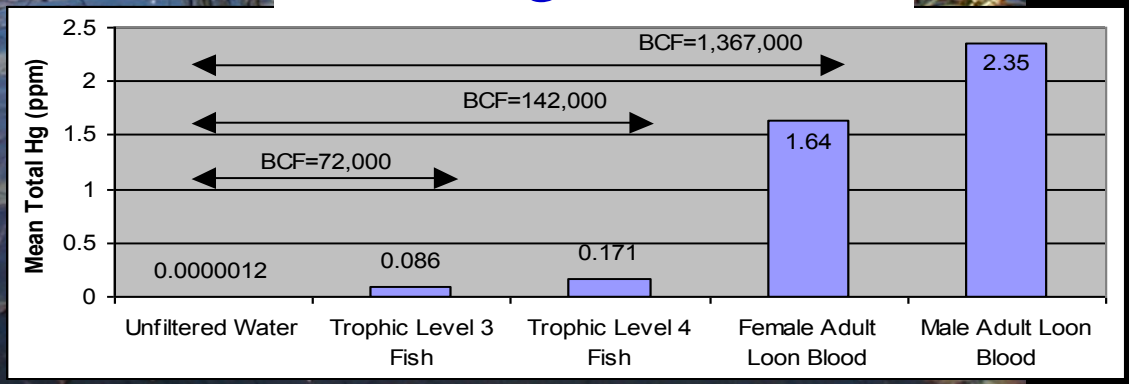
National Atmospheric Deposition Program/Mercury Deposition Network

Mercury in the Food Chain



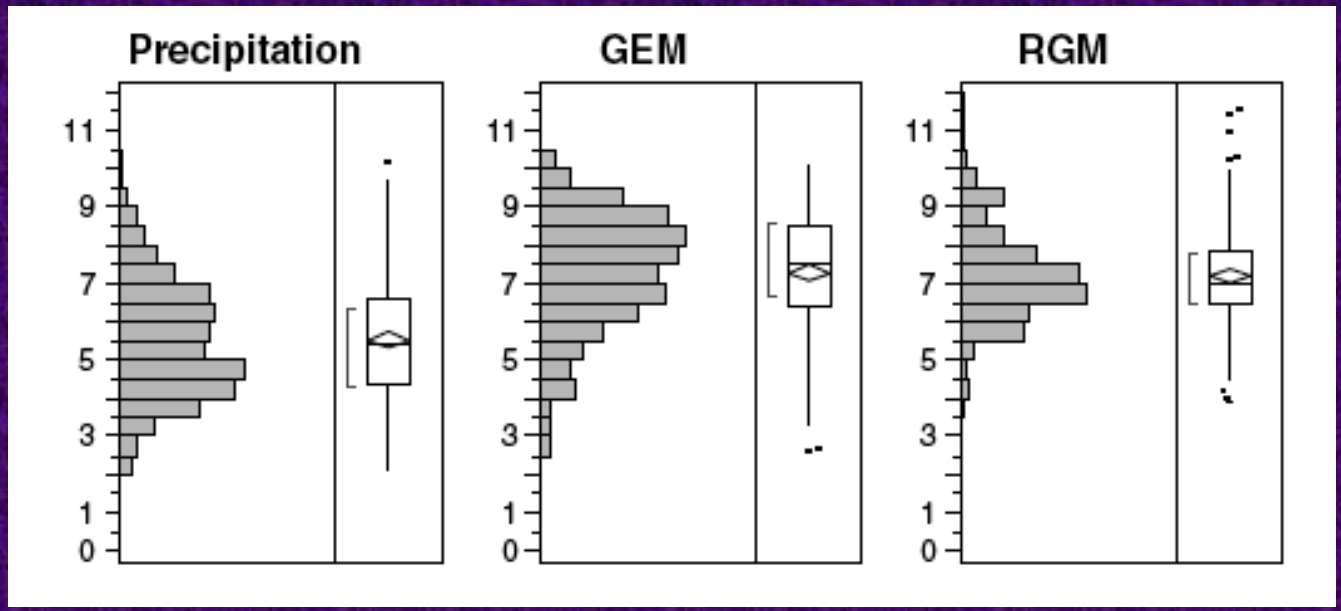
Hg+C+S

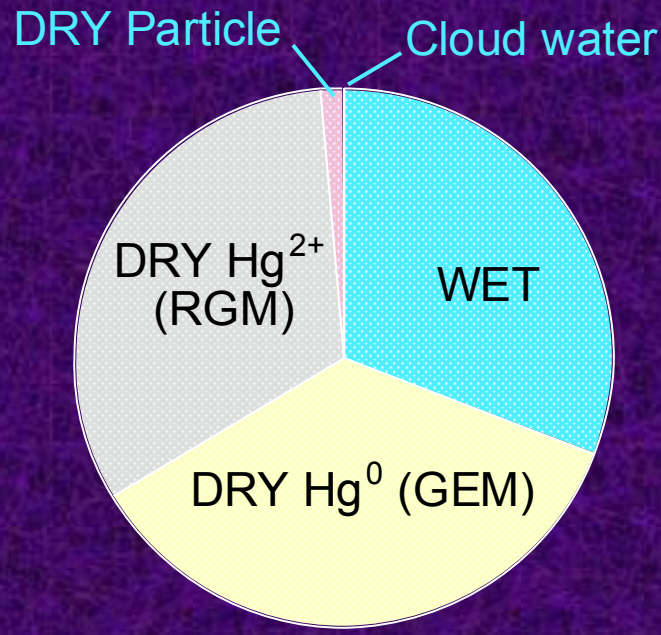
Biomagnification



Forms of Mercury Deposition, Vermont and New Hampshire

Wet *Dry*

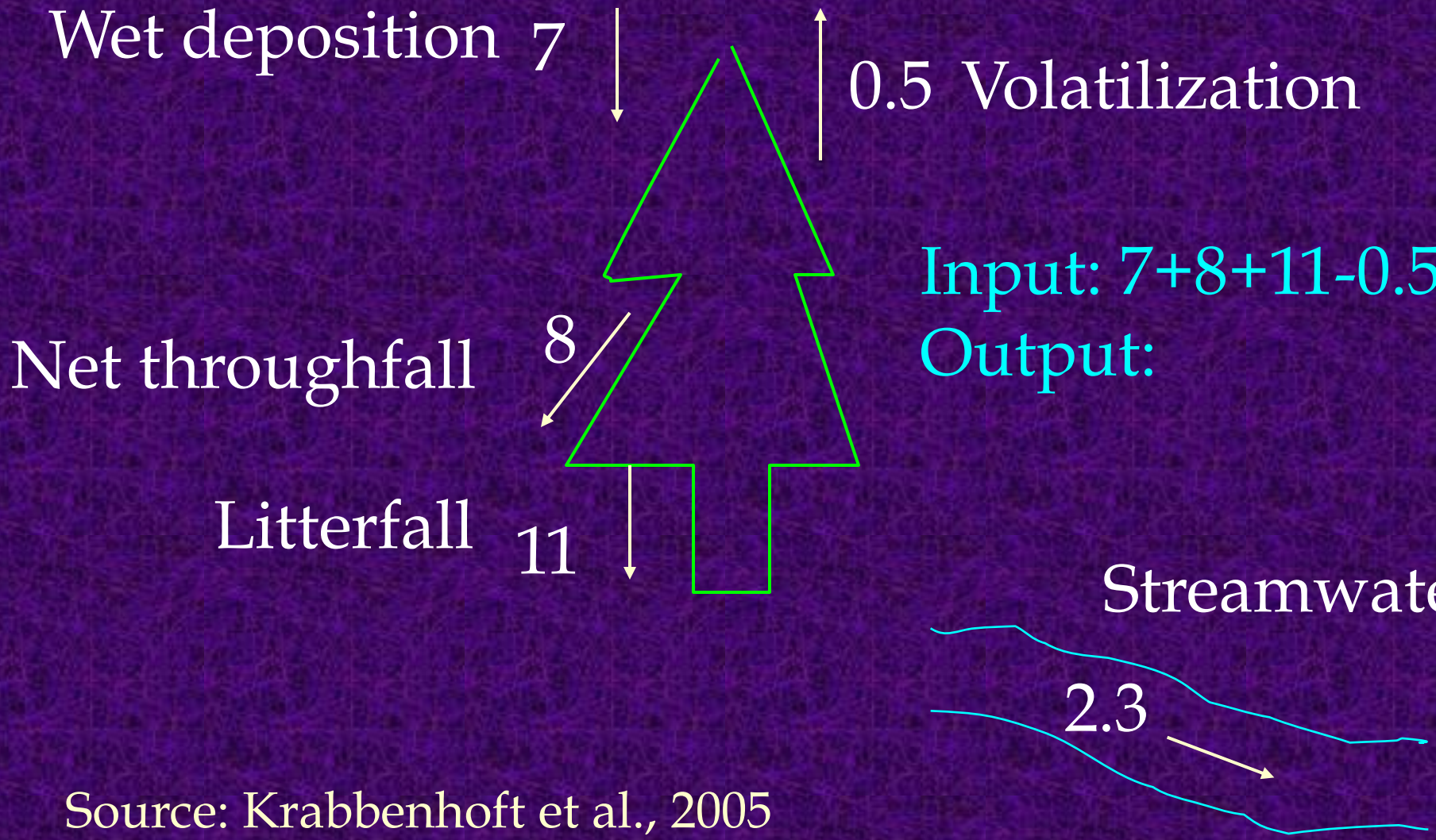




Source: Miller et al., 2005, Ecotoxicology 14, 53-70

Hg fluxes in an upland temperate forest

Hg fluxes in $\mu g/m^2/yr$



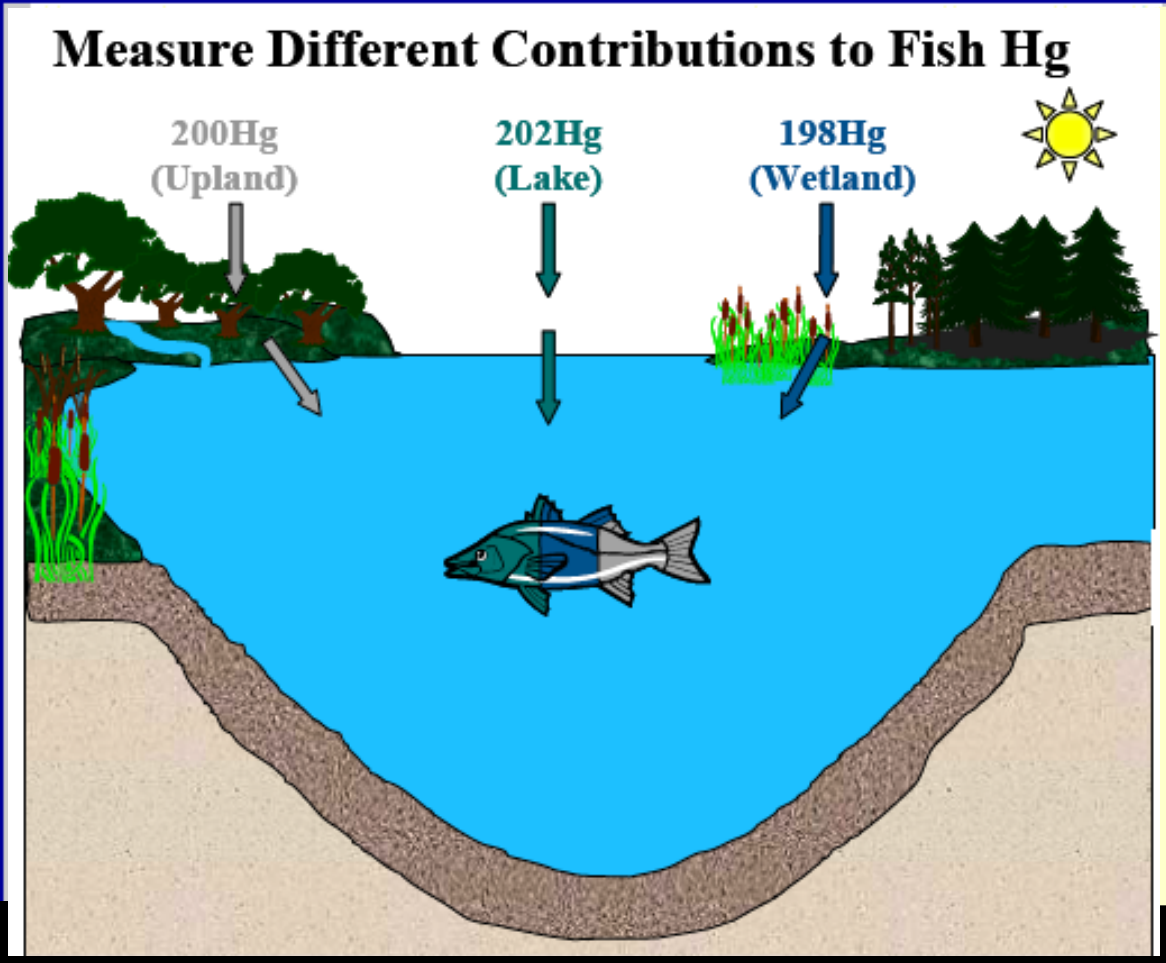
Input: 7+8+11-0.5=25.5

Output: 2.3

Source: Krabbenhoft et al., 2005

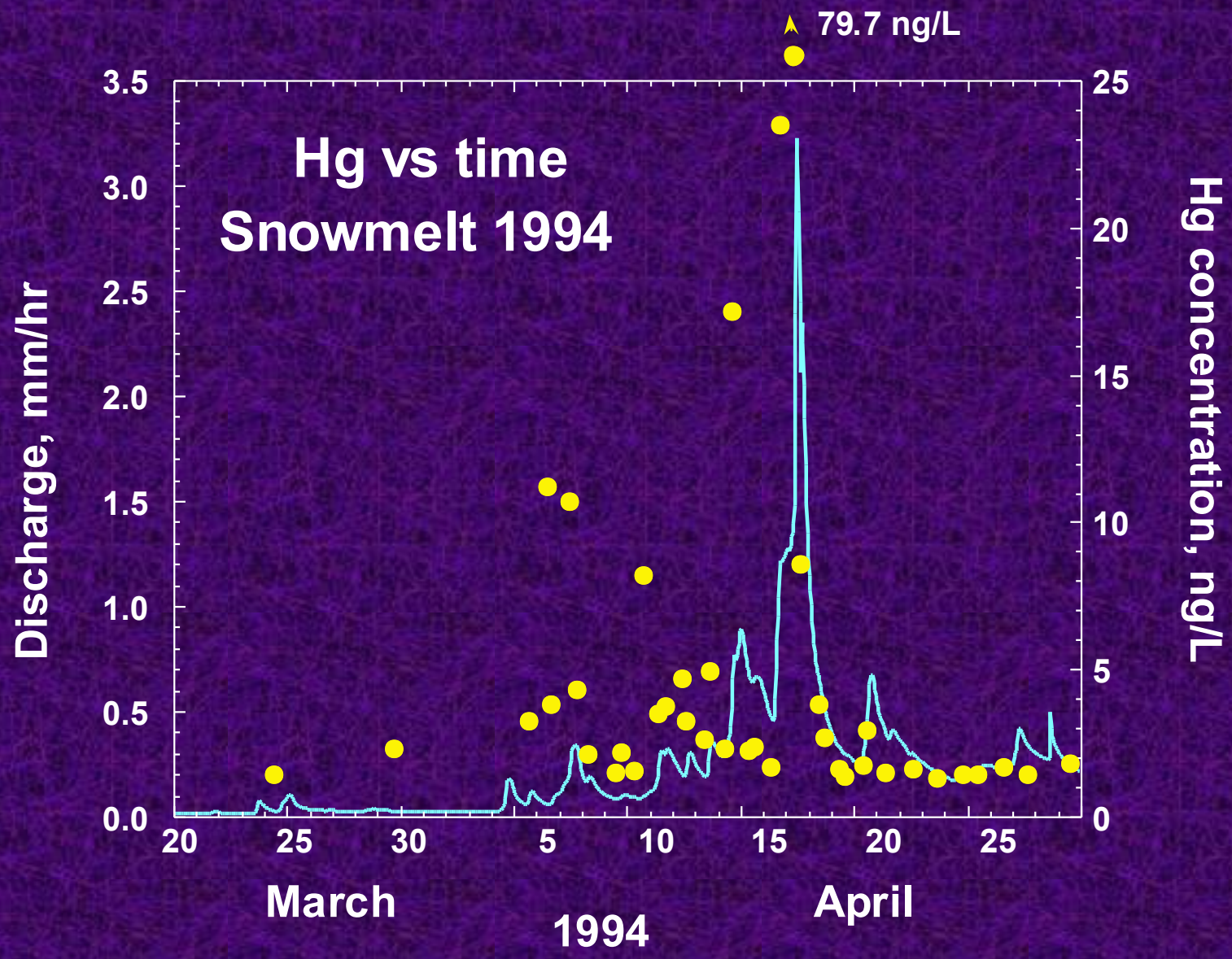
METAALICUS

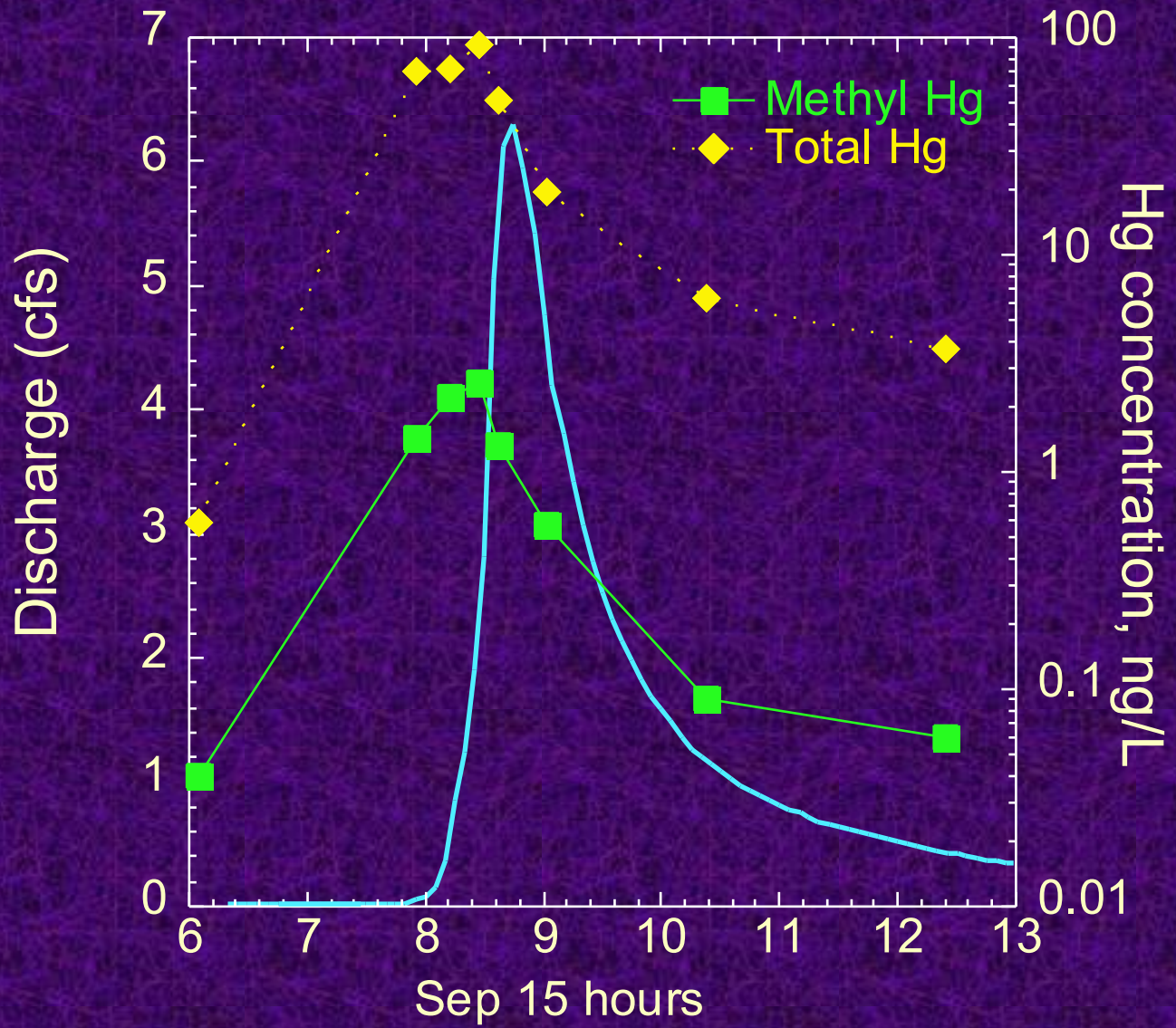
Mercury Experiment To Assess Atmospheric Loading In Canada and the United States

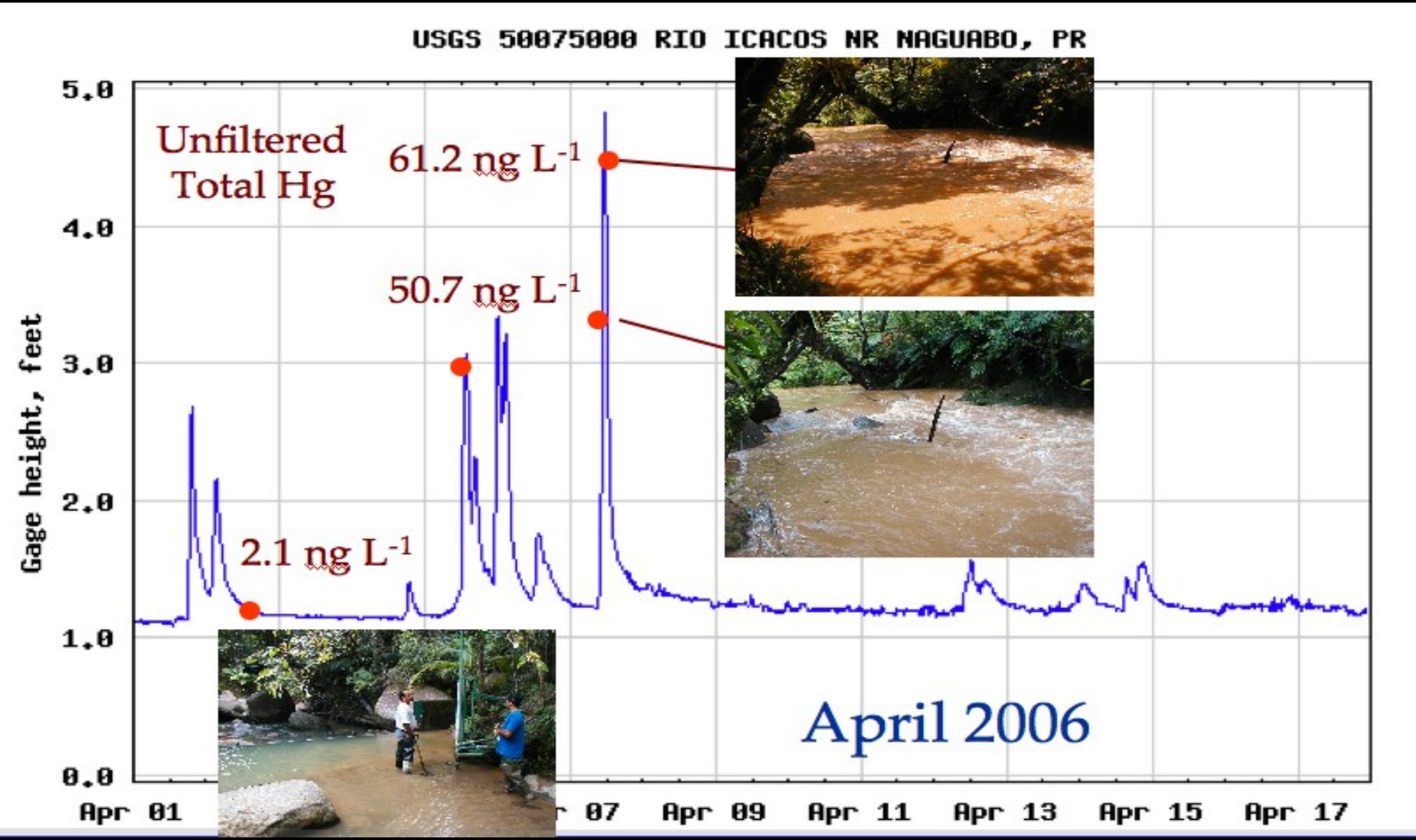


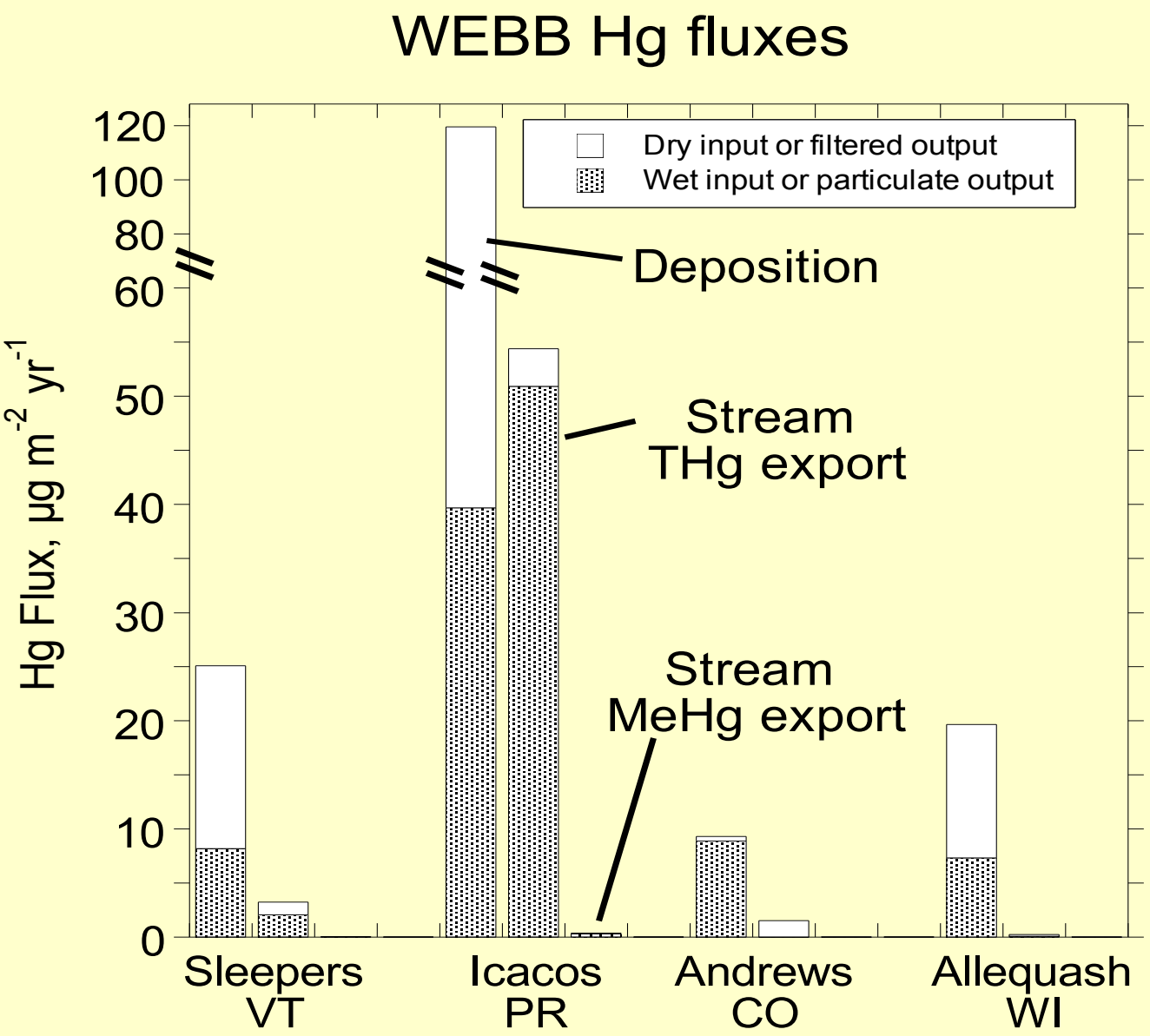
How does fish Hg respond to changes in Hg deposition?

Mercury Research, Nettle Brook

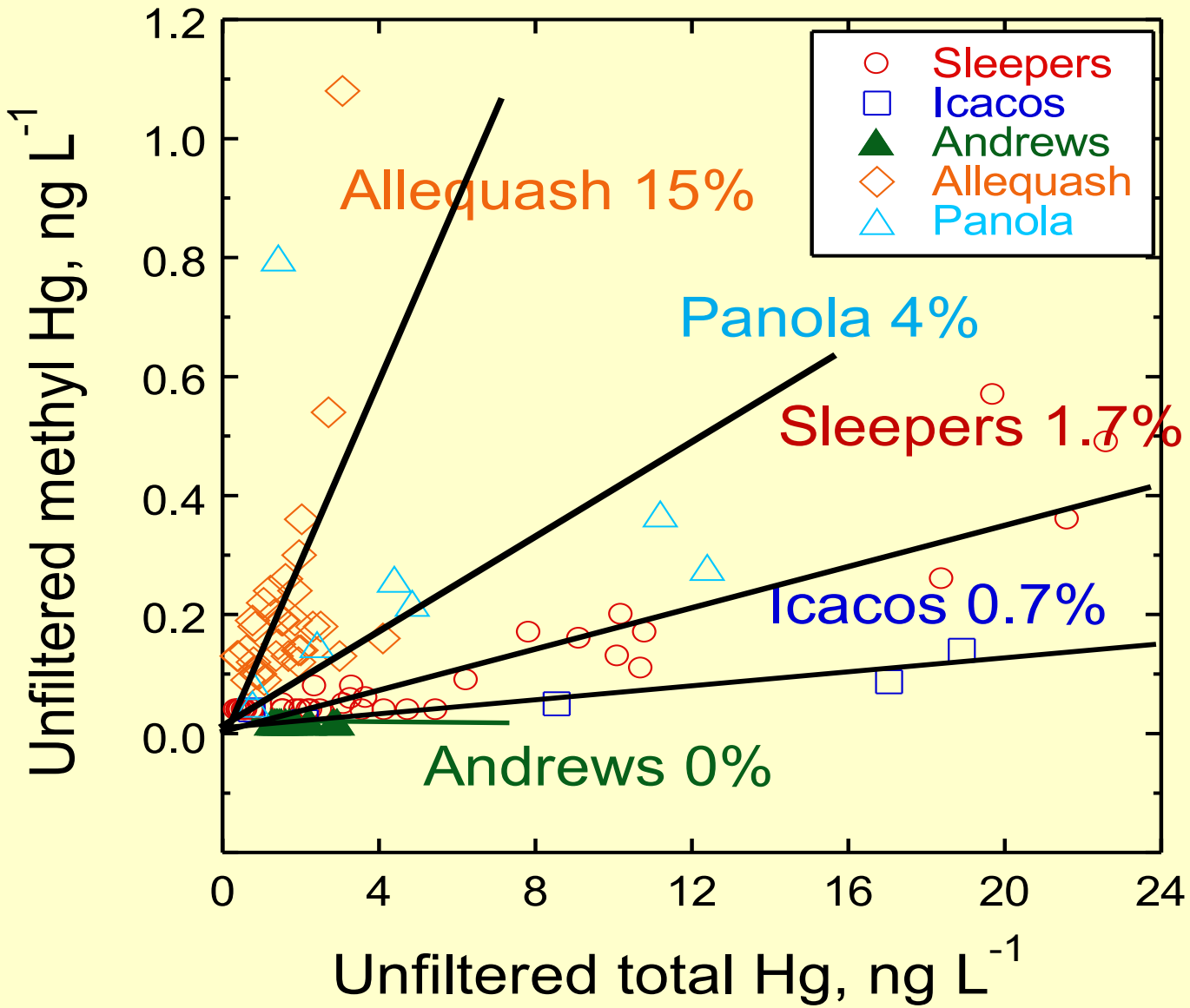



Sleepers R. W-9 rewetting event, 9/15/02
Methyl Hg
Total Hg
Discharge (cfs)
Hg concentration, ng/L
Sep 15 hours
0
1
2
3
4
5
6
7
0.01
0.1
1
10
100
6
7
8
9
10
11
12
13

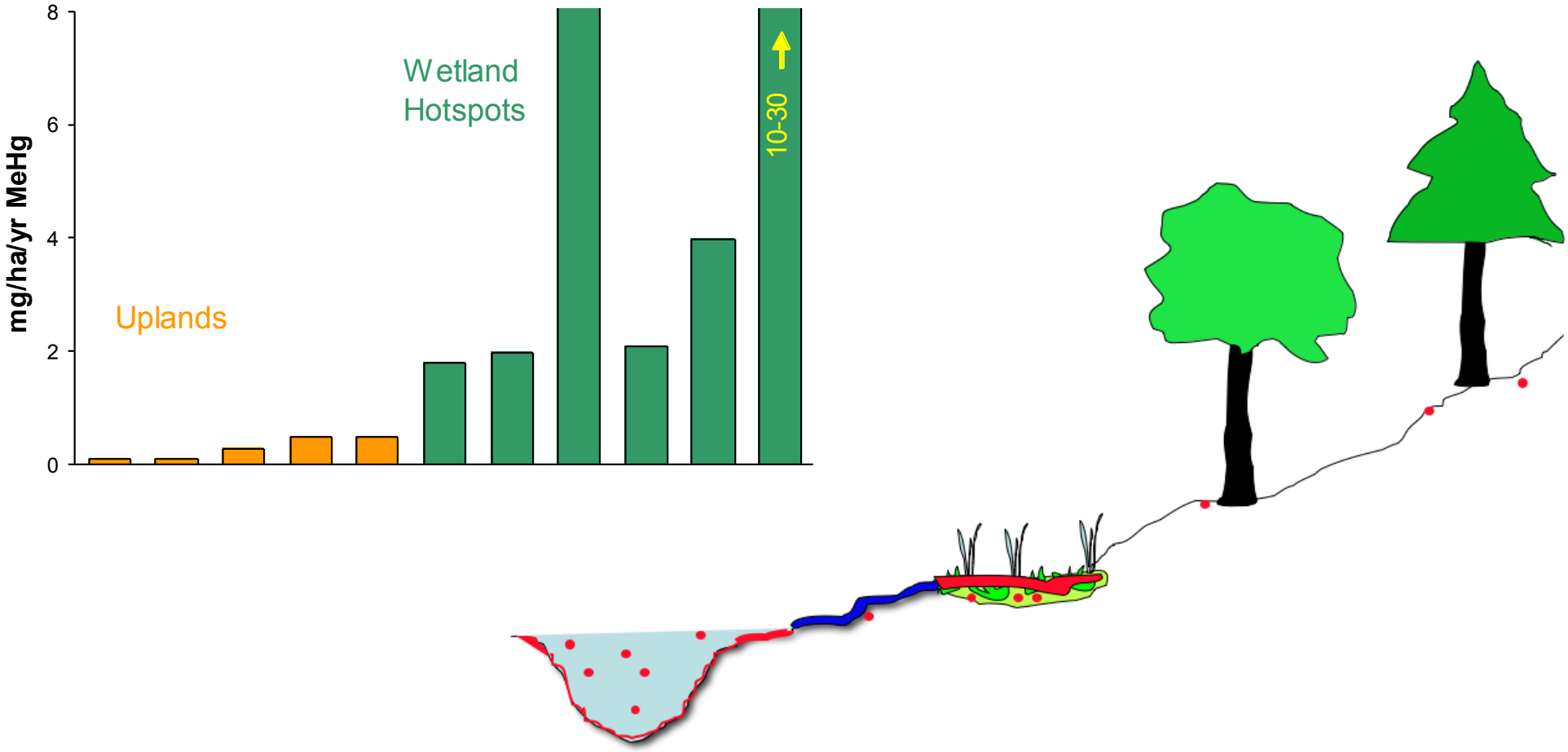

USGS 50075000 RIO ICACOS NR NAGUABO, PR
Unfiltered
Total Hg
61.2 ng L-1
50.7 ng L-1
2.1 ng L-1
Gage height, feet
5.0
4.0
3.0
2.0
1.0
0.0
Apr 01
07
Apr 09
Apr 11
Apr 13
Apr 15
Apr 17
April 2006


WEBB Hg fluxes
Dry input or filtered output
Wet input or particulate output
Deposition
Stream
THg export
Stream
MeHg export
Hg Flux, µg m-2 yr-1
120
100
80
60
50
40
30
20
10
0
Sleepers
VT
Icacos
PR
Andrews
CO
Allequash
WI

Percent methylated in streamwater



Methylmercury Hotspots

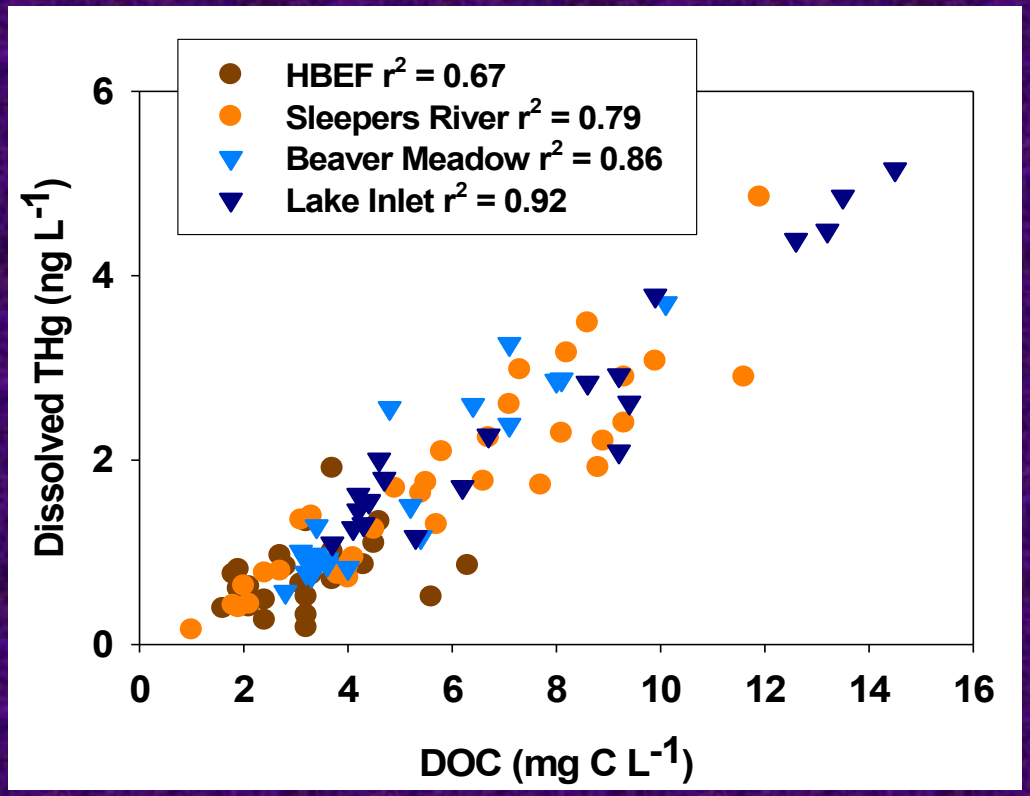


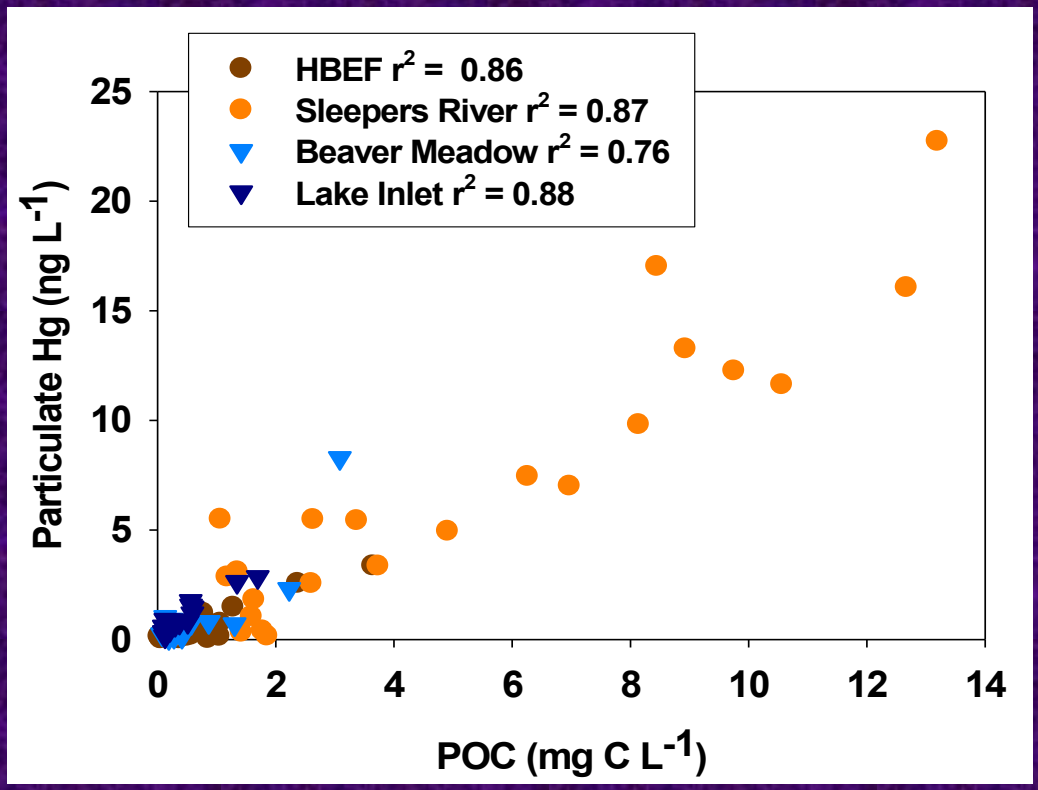
Mercury Mobility in Relation to DOC Quality across a Wetland Gradient

Jason Dittman[1], Jamie Shanley[2], Charles Driscoll[1], George Aiken[3], Ann Chalmers[2], Janet Towse[4]

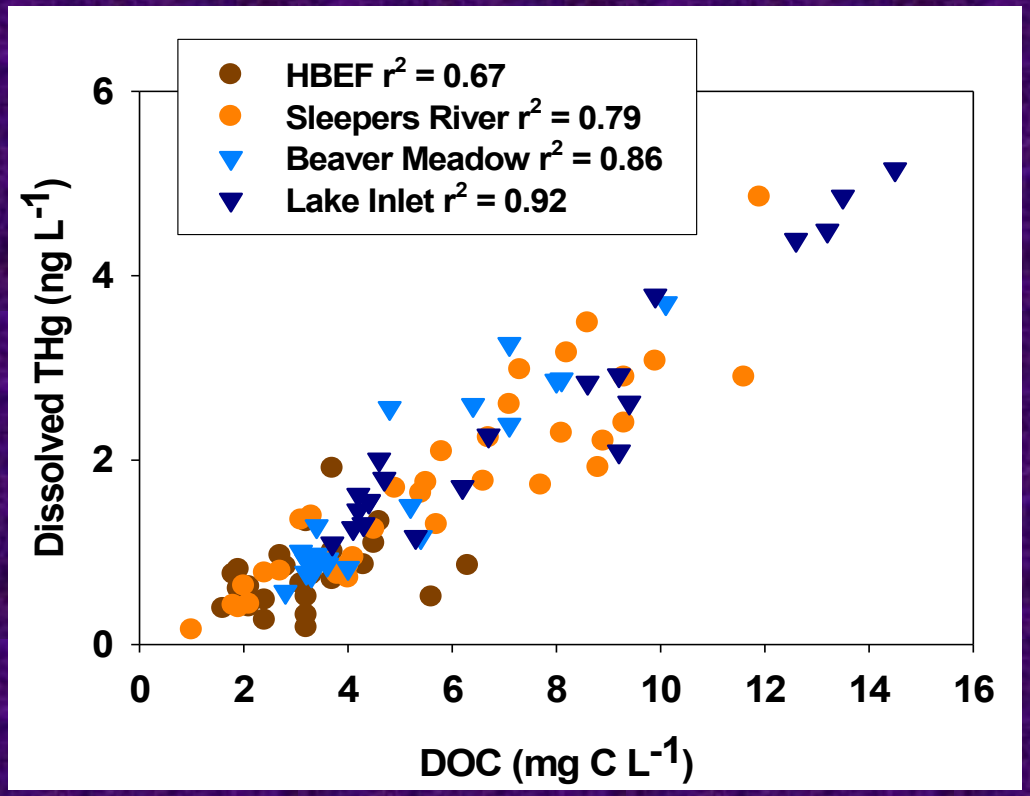
[1]Syracuse University; [2]U.S. Geological Survey, Montpelier, Vermont; [3]U.S. Geological Survey, Boulder, Colorado; [4]Plymouth State University

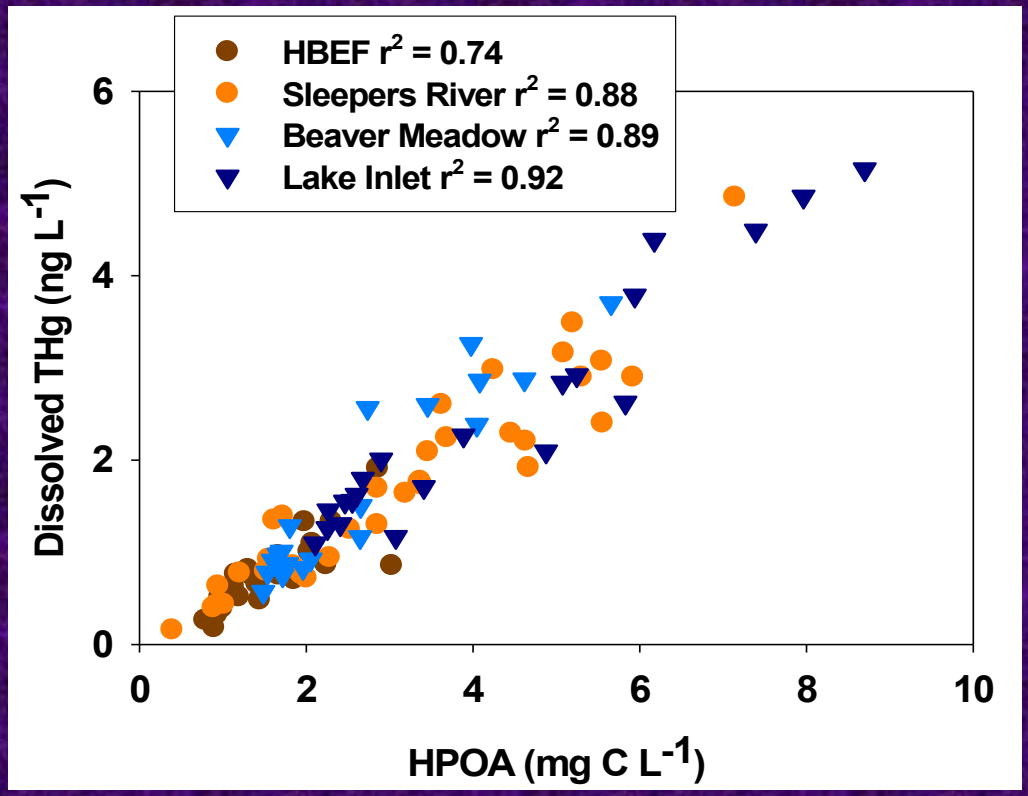
Dissolved Hg vs. DOC
Particulate Hg vs. POC



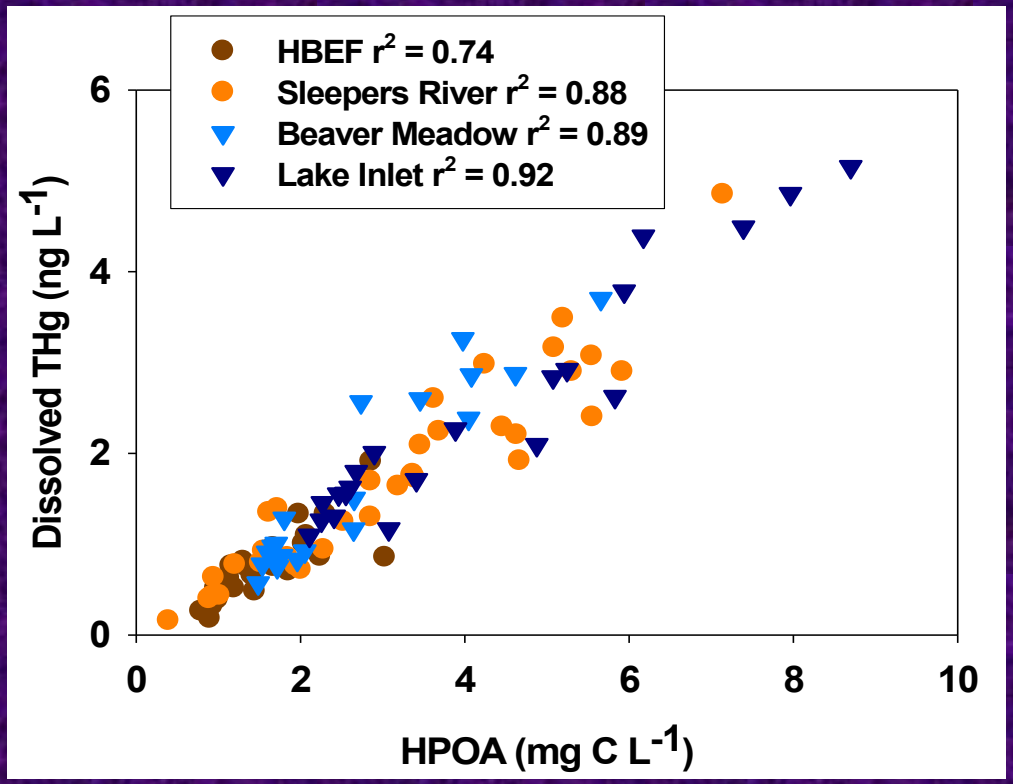


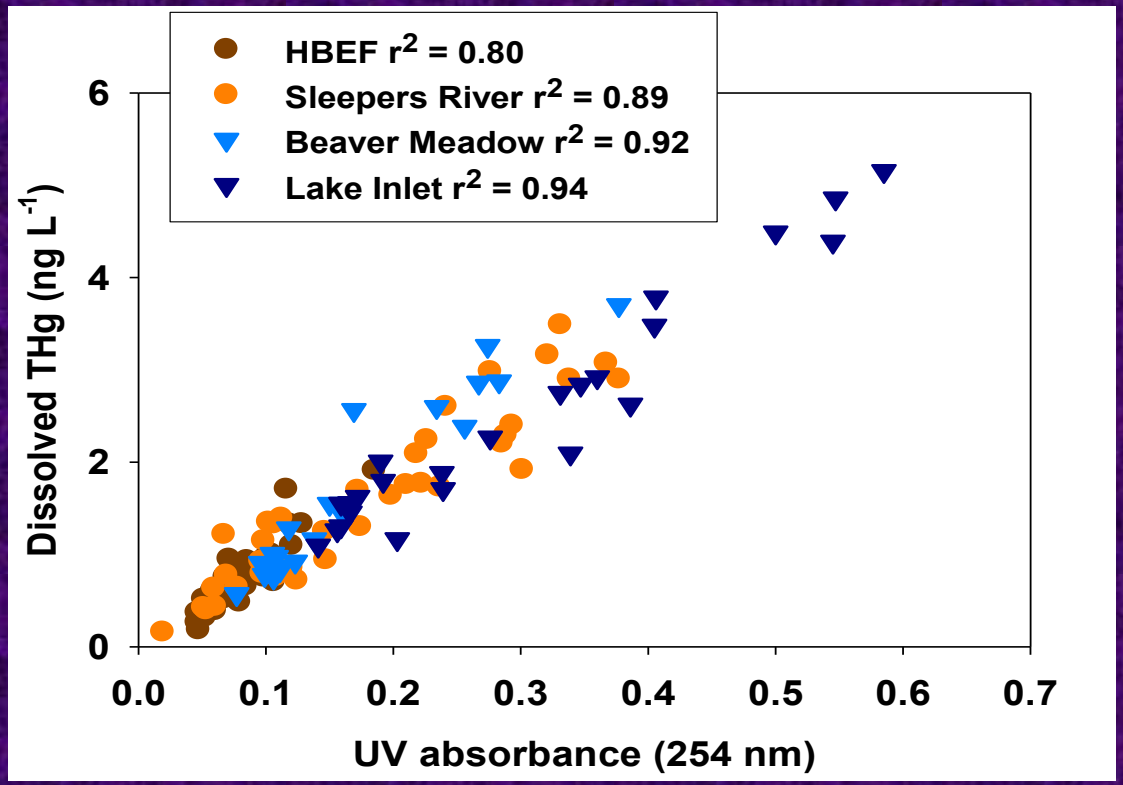
Total Hg vs. DOC
Total Hg vs. HPOA





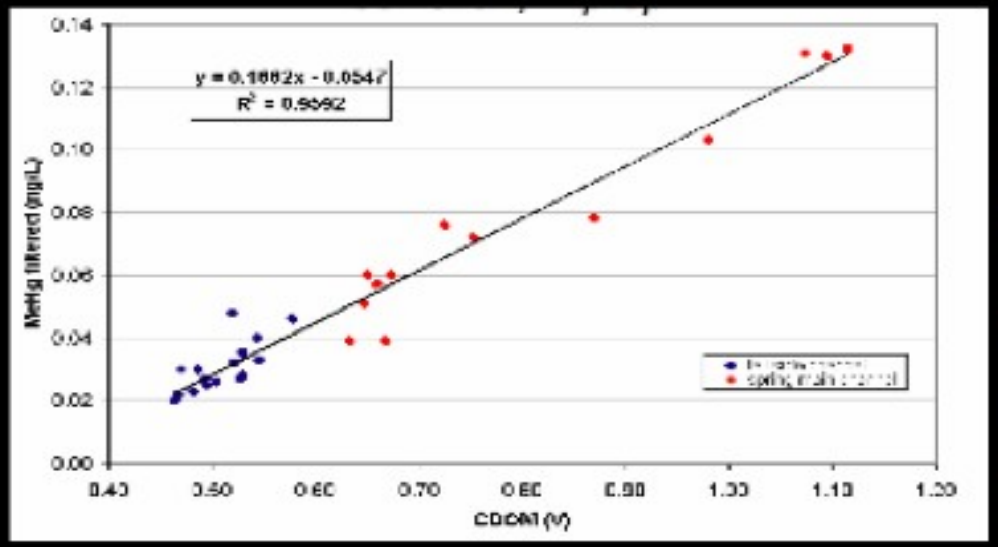
Total Hg vs. HPOA
Total Hg vs. absorbance





In situ proxy measurements

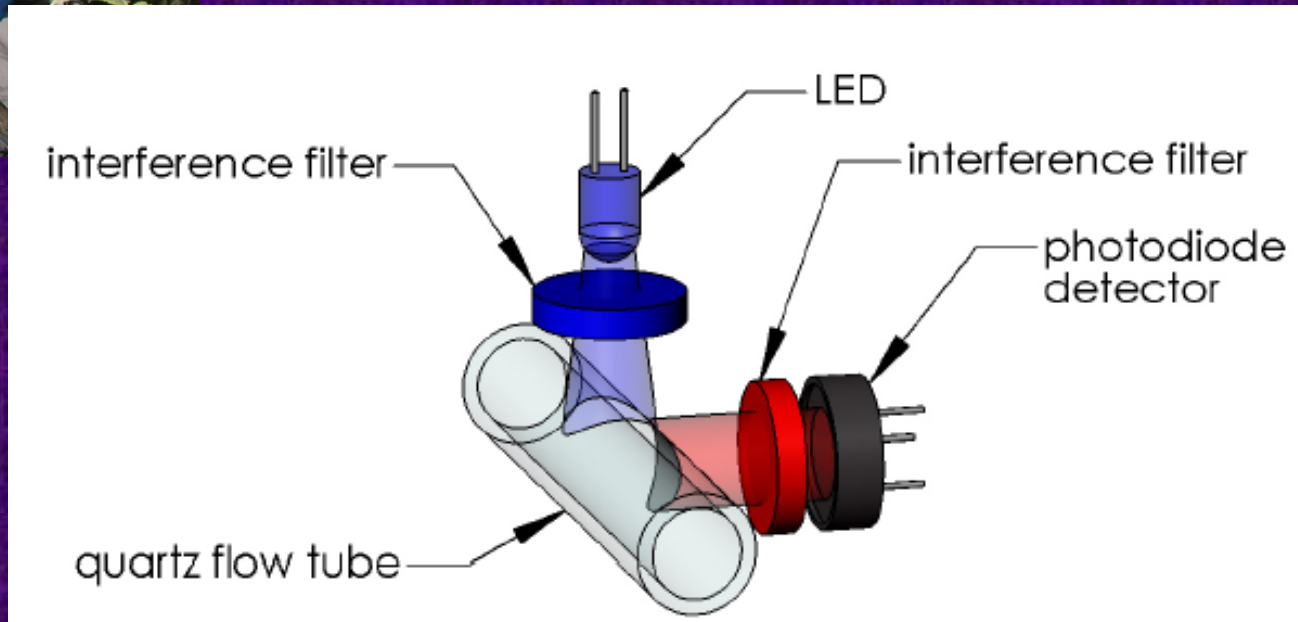
MeHg vs. cDOM



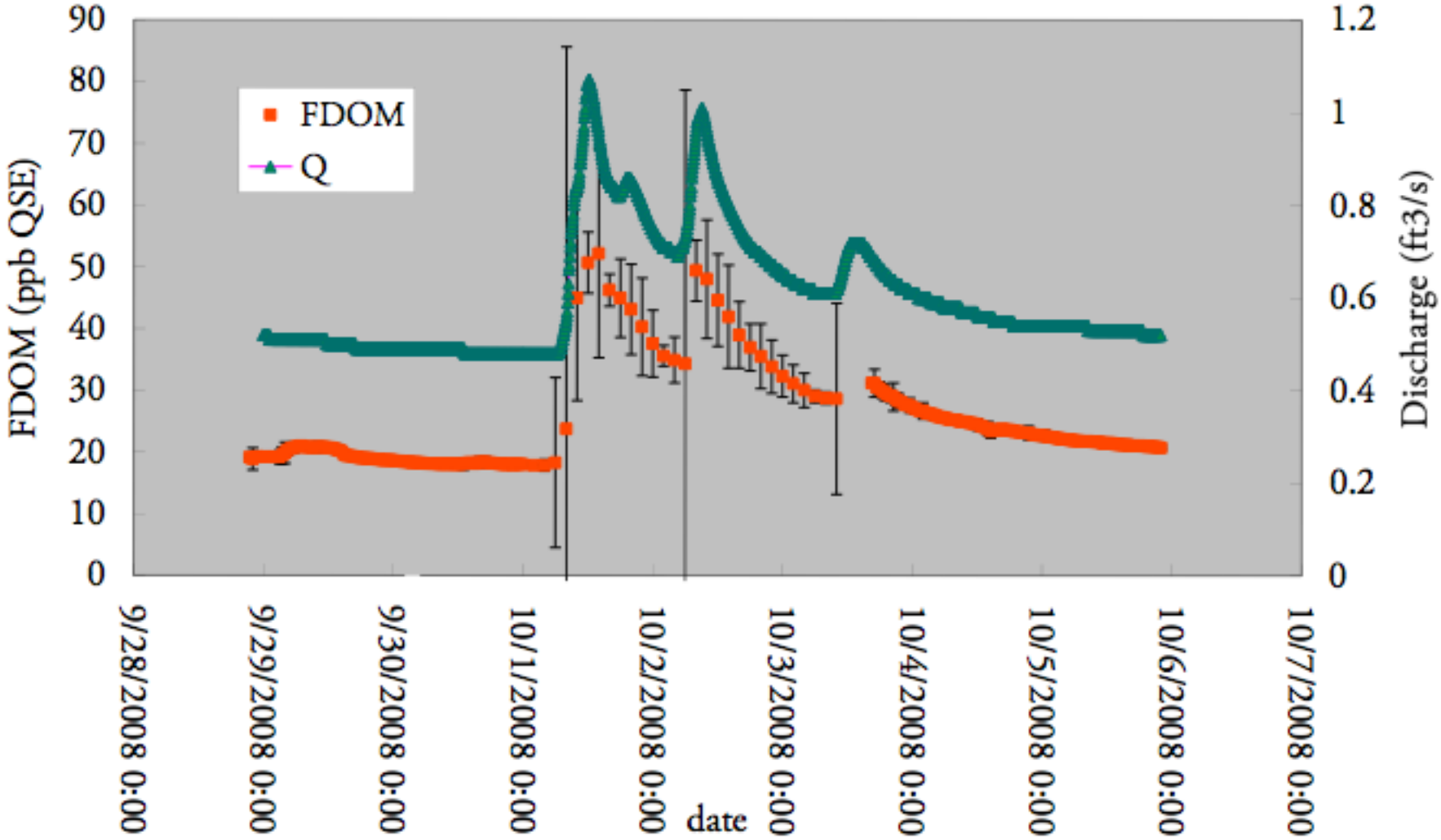
Logging Fluorometers

Installation at Hubbard Brook

Fluorescence



cDOM during 2008 leaf fall at Sleepers R.



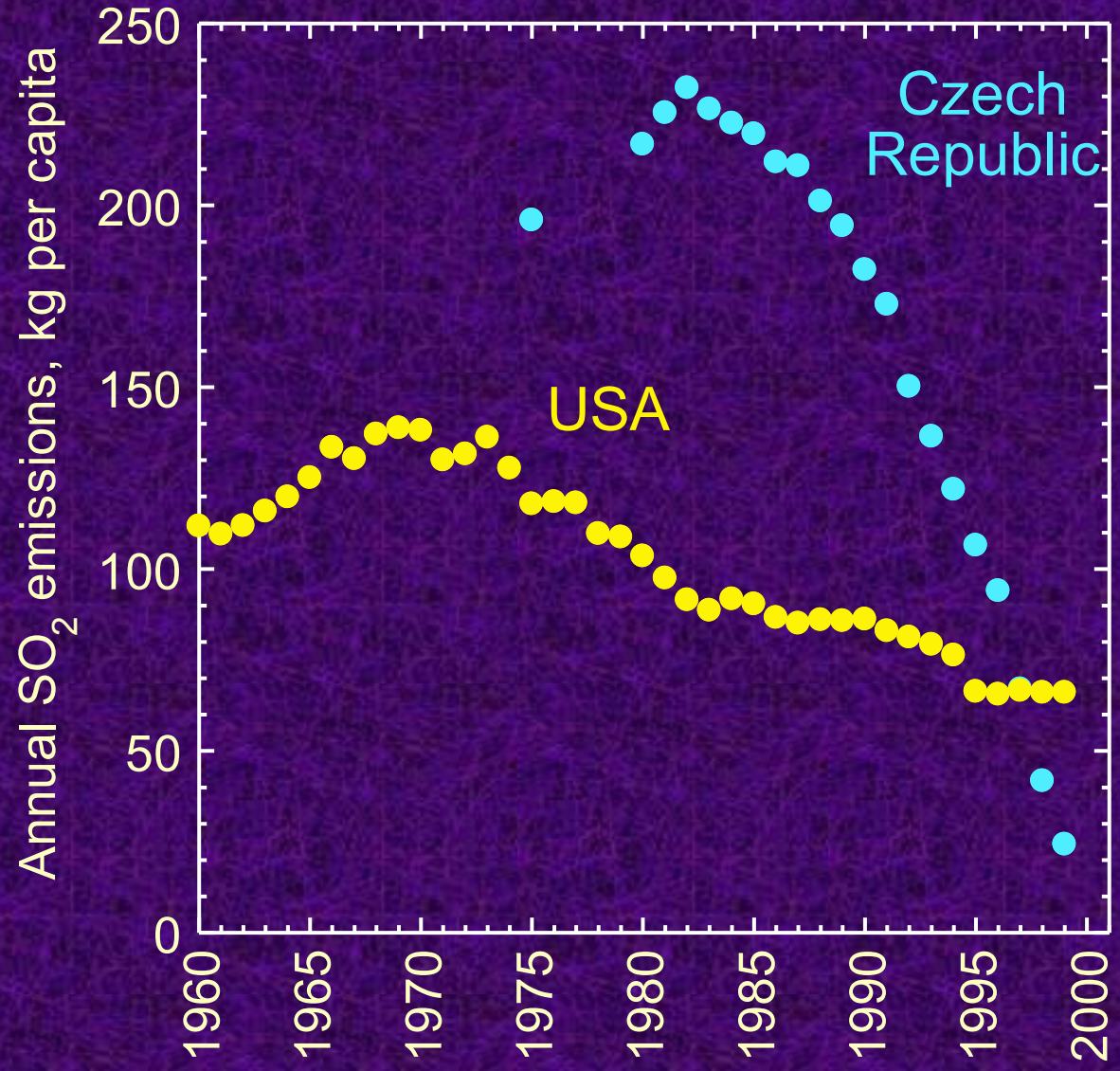
Conclusions: *Mercury studies*

- Humans exposed to Hg through fish consumption
- Hg pollution global: remote areas susceptible
- Dry deposition typically more important than wet
- Only ~10% of Hg reaches aquatic system
- Only ~10% of this Hg transforms to toxic methyl-Hg
- Hg, C, and S: Biogeochemical axis of evil
- Landscape characteristics trump deposition (hot spots)
- Hg transport with OM, at high flow (hot moments)
- DOC *quality* matters
- Legacy Hg may “leak out” for decades, centuries

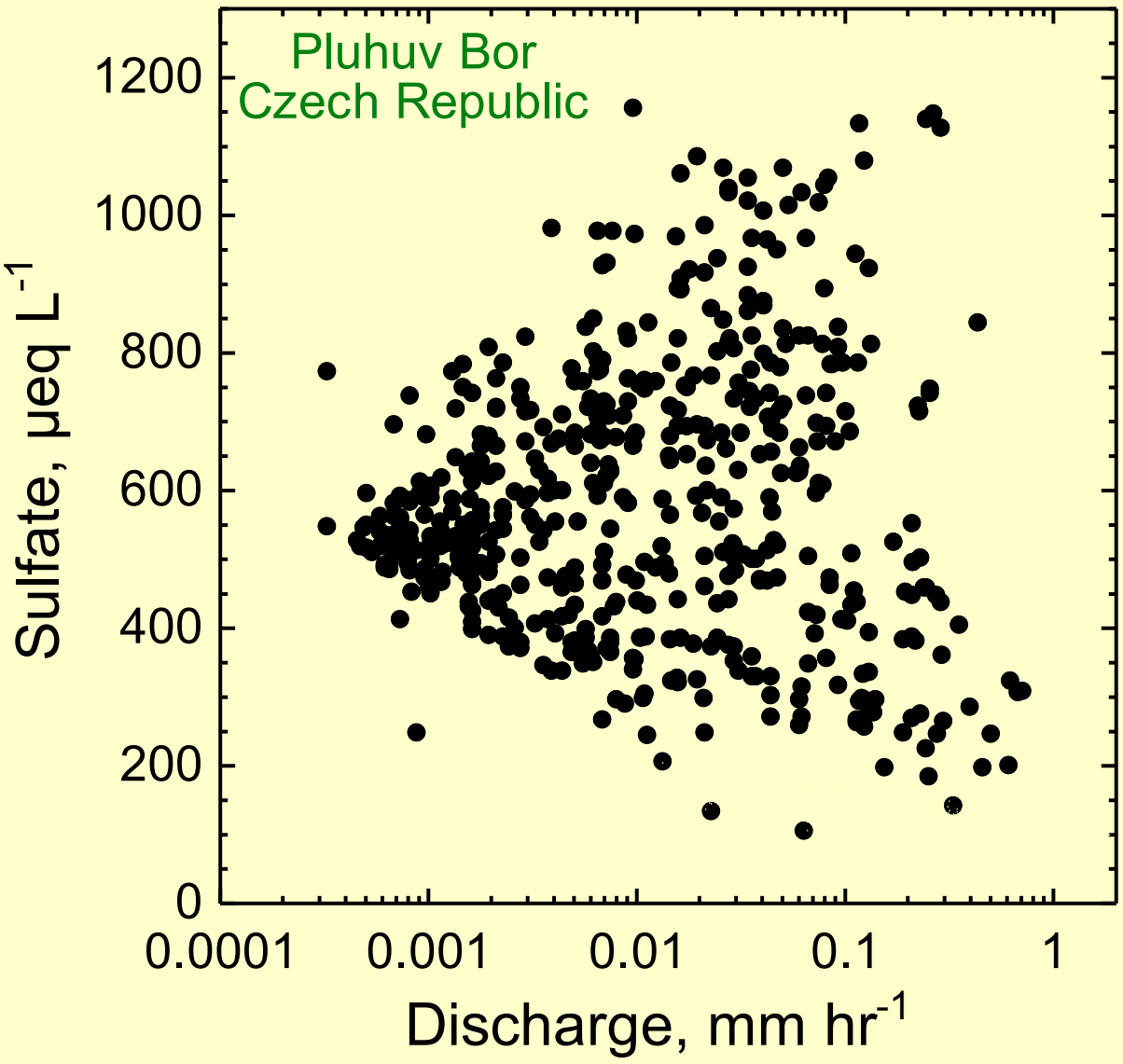
Concepts

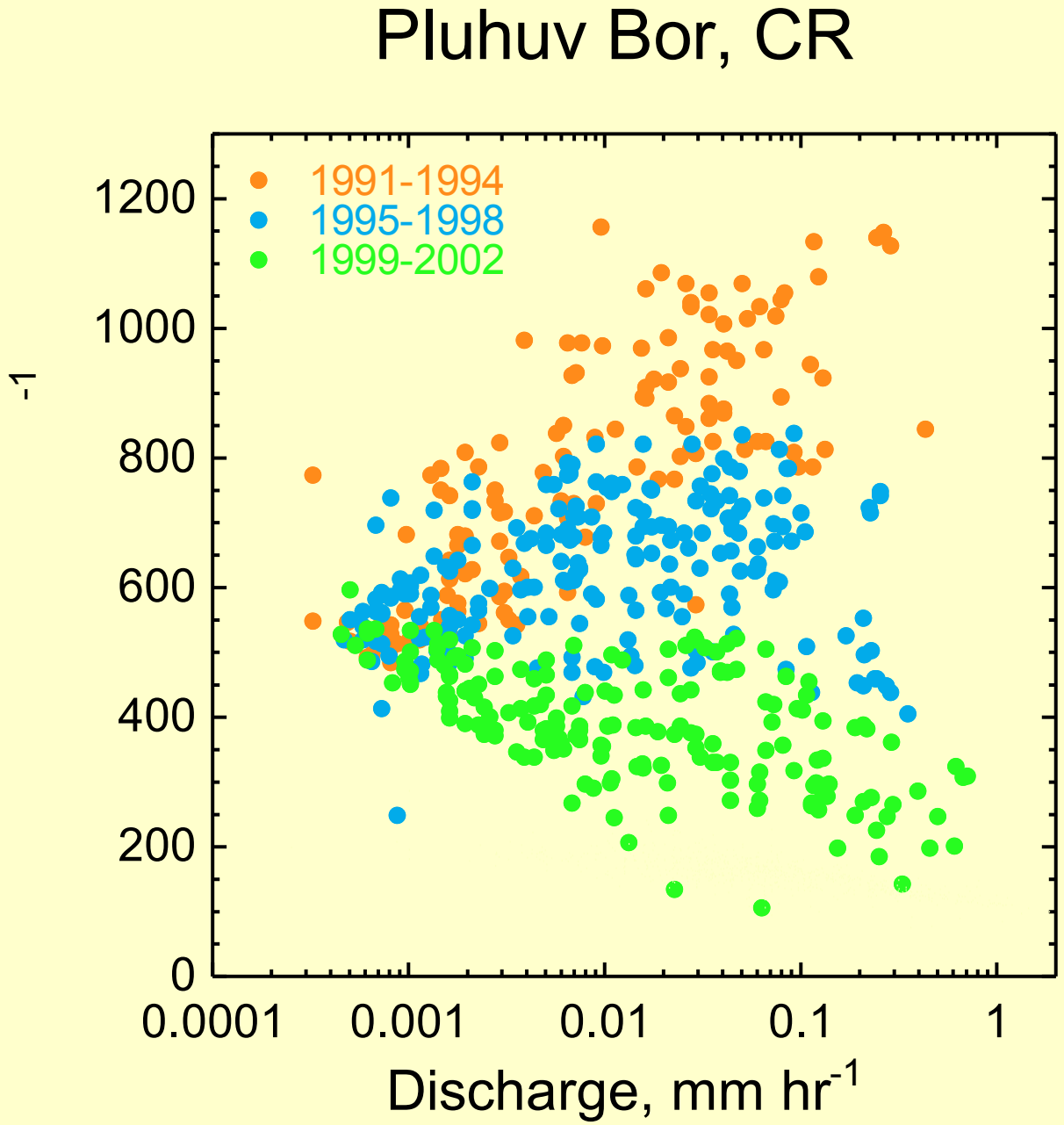
- The small watershed approach is an enduring method for environmental study
- Study of simple landscape unit helps isolate processes
- Long-term watershed studies are valuable benchmarks, barometers of change
- Watershed comparisons reinforce findings and/or lead to new inferences
- Findings and applications often serendipitous

SO_2 emission reductions

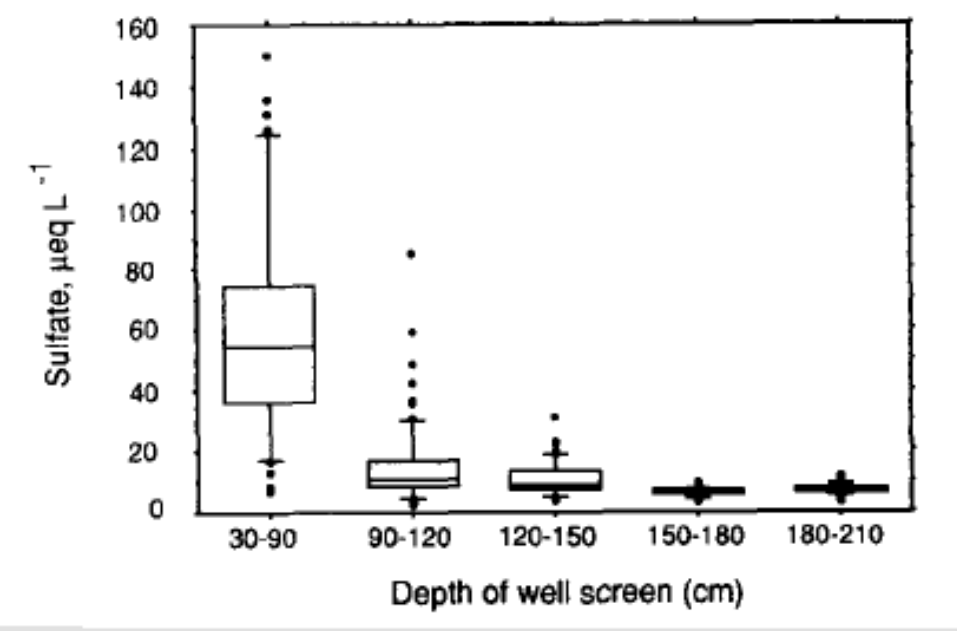


Black Triangle?

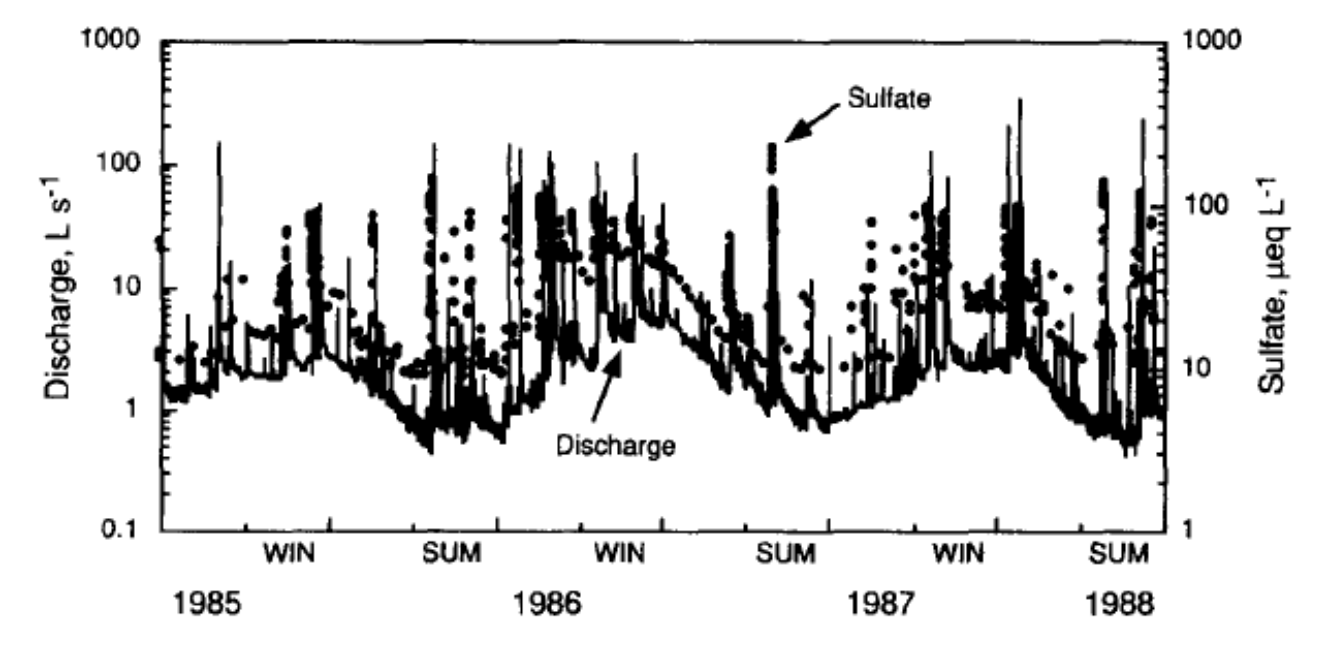



Pluhuv Bor, CR
1991-1994
1995-1998
1999-2002
1200
1000
800
600
400
200
0
-1
0.0001
0.001
0.01
0.1
1
Discharge, mm hr-1

Panola Mountain, Georgia



Sulfate decreases with depth in groundwater



Sulfate is low at base flow and increases with flow

Overall, net sulfate retention due to adsorption in soil