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Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

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Some Major Climatic Effects in Northeastern U.S.A.

- Summer
  - Higher temperatures
  - More droughts
  - More extreme events
- Winter
  - Warmer temperatures
  - Shorter period of snowpack
  - More rain on snow events

Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

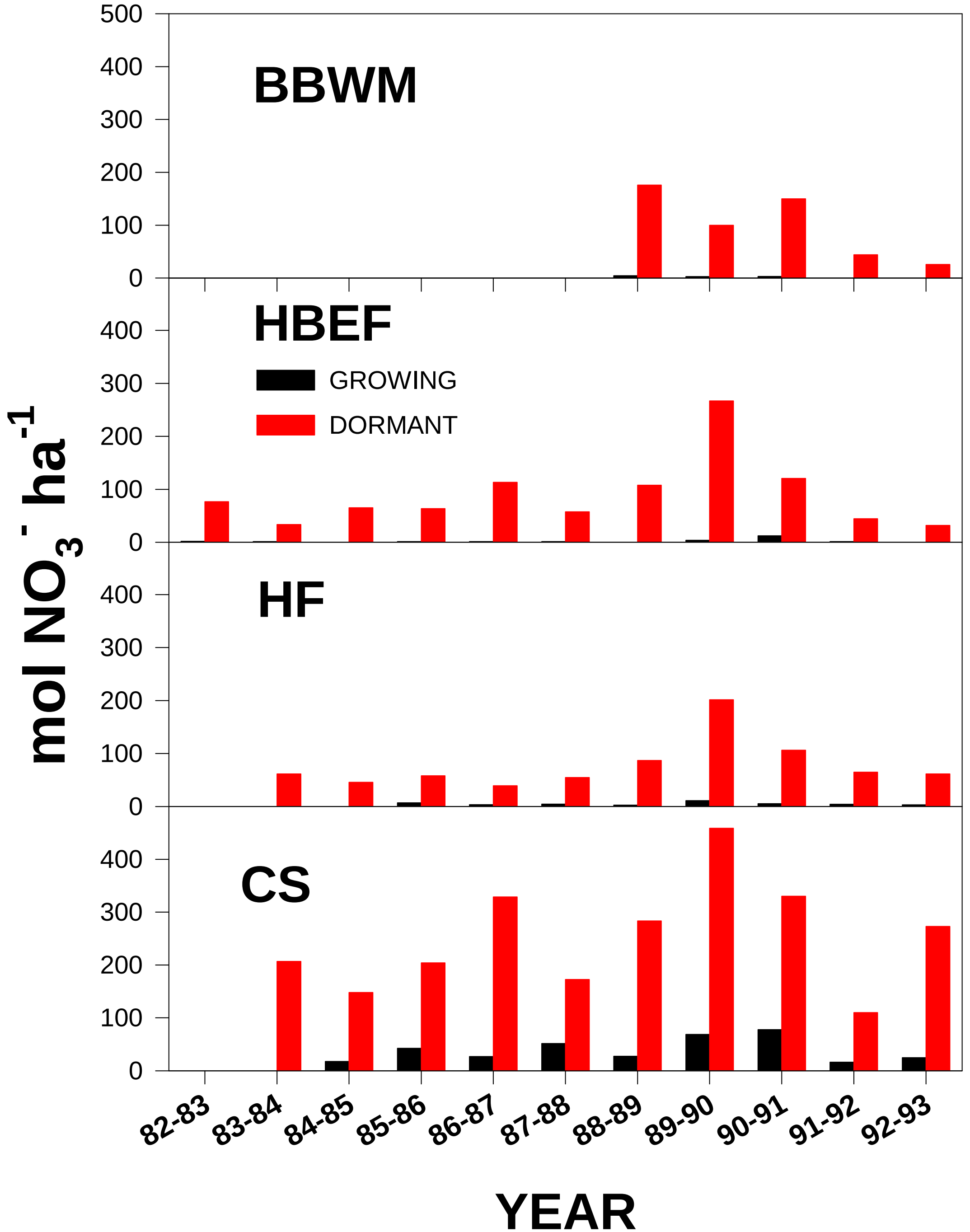
- Nitrogen (nitrate)--Winter
- Sulfur (sulfate)--Summer
- Mercury--Summer

Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

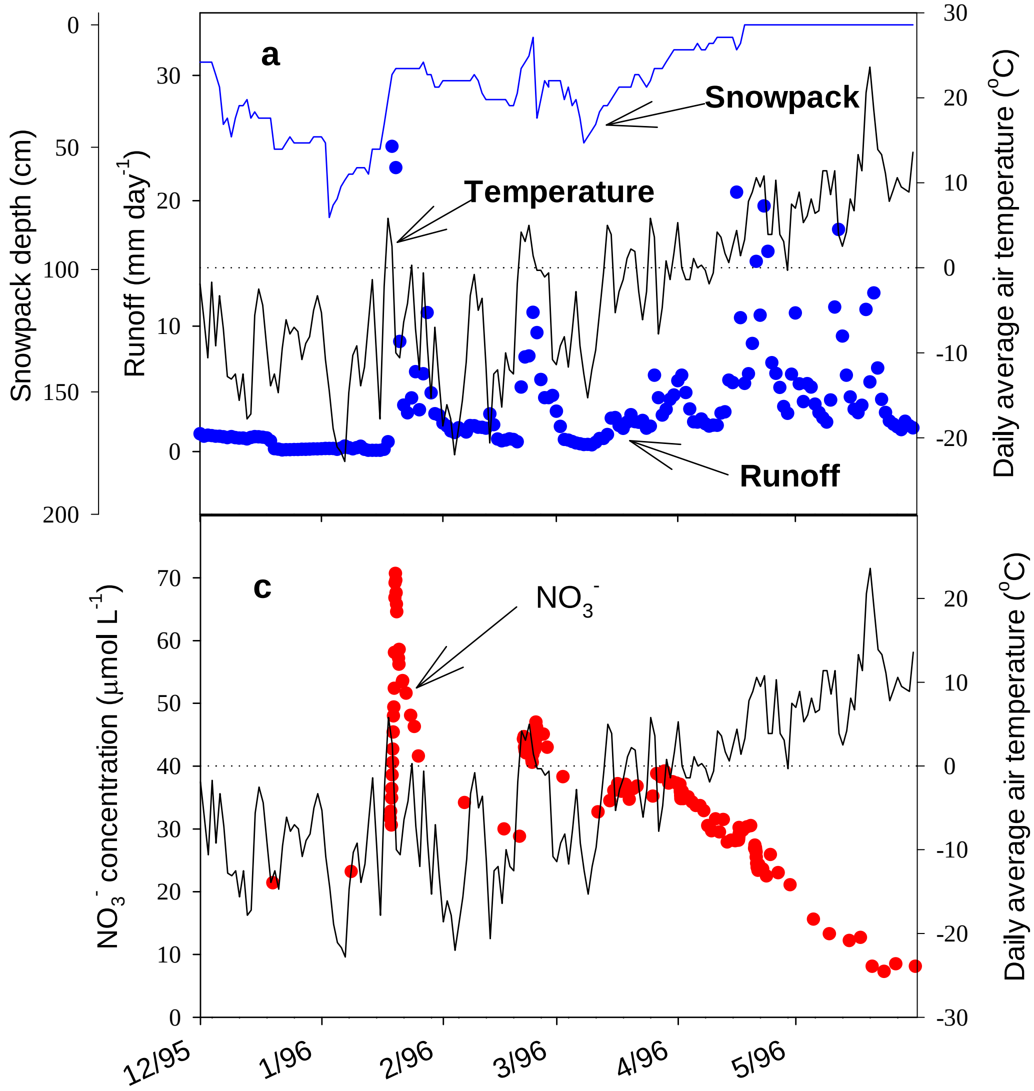
- Nitrogen (NO_3^-)
  - Importance of nitrate to chronic and episodic acidification
  - Explanation for long-term (interannual) changes in NO_3^- concentrations in watersheds still not complete
  - Nitrogen important limiting nutrient
  - Understanding of winter processes in affecting NO_3^- dynamics incomplete

For snow dominated watersheds >87% NO_3^- lost during dormant season:

High discharge & microbial generation of nitrate dominates



Mitchell, M.J., C.T. Driscoll, P. Murdoch, G.E. Likens, J.S. Kahl and L. Pardo. 1996a. [Climatic control of nitrate loss from forested watersheds in the northeast United States.] Environmental Science and Technology 30: 2609-2612.

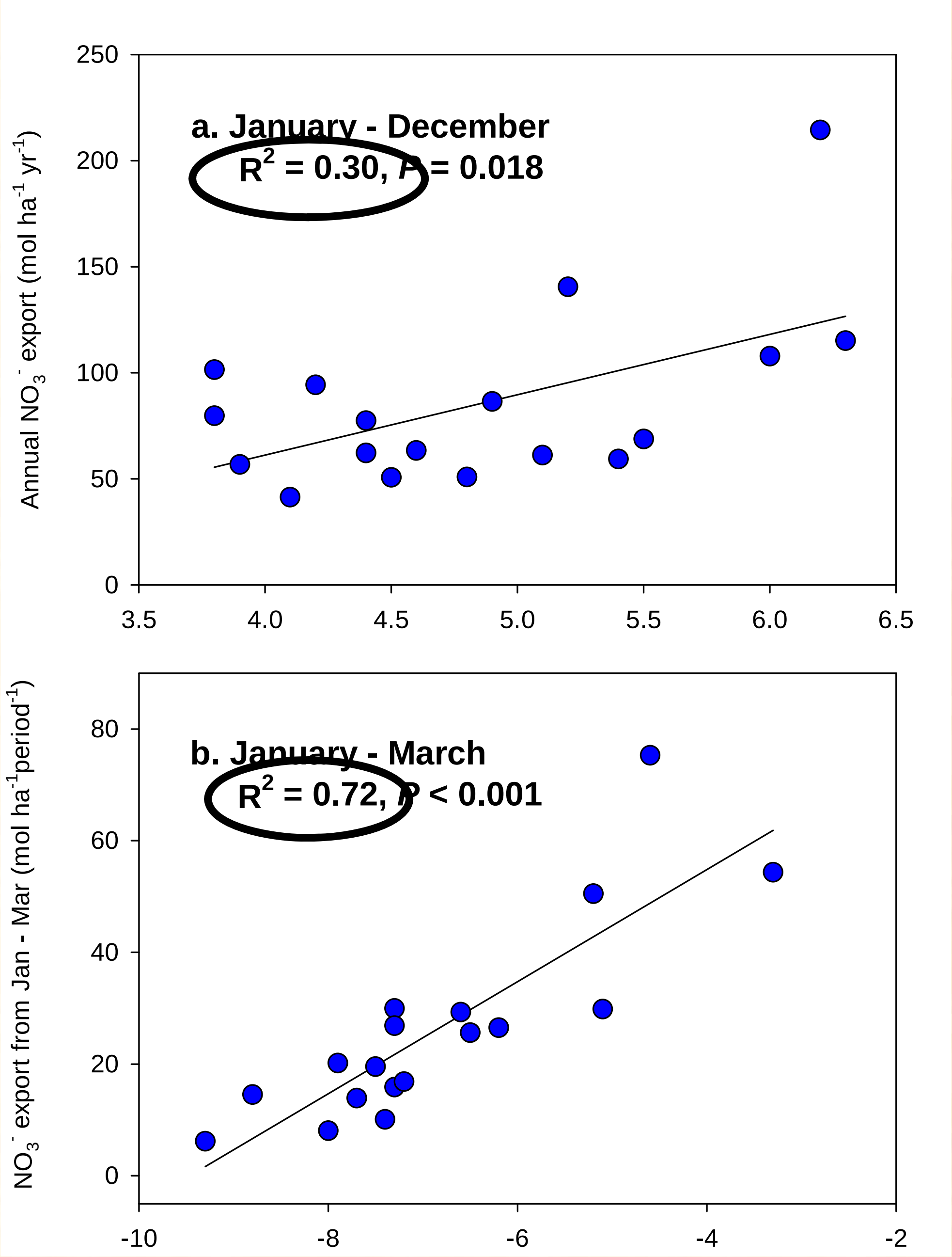


Responses of snowpack depths, runoff amounts, and nitrate concentrations in drainage water from the Archer Creek catchment to temperature changes from December 1995 to May 1996. Adirondack Mountains, New York State)

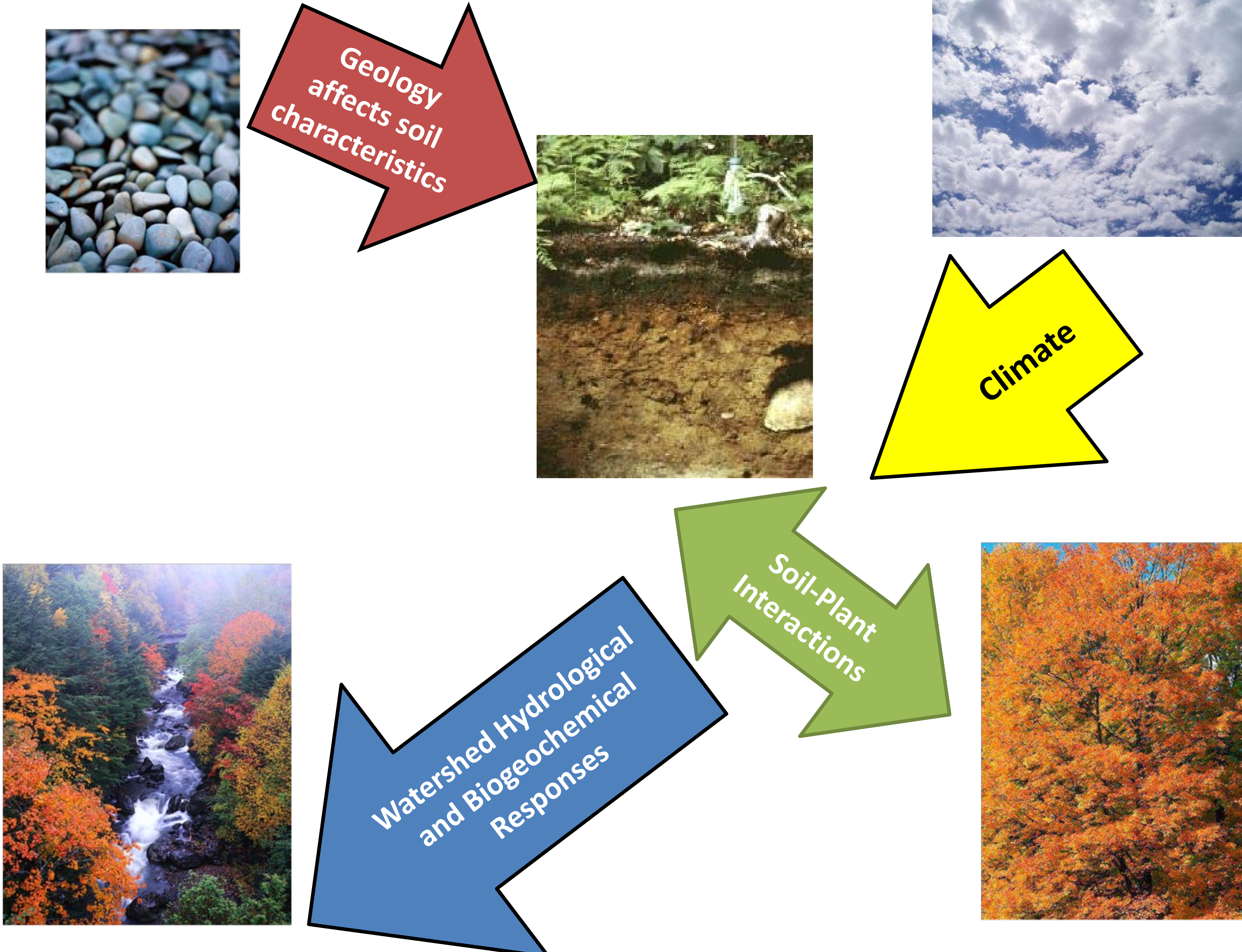
Park, J., M.J. Mitchell, P.J. McHale, S.F. Christopher and T.P. Myers. 2003. [Interactive effects of changing climate and atmospheric deposition on N and S biogeochemistry in a forested watershed of the Adirondack Mountains, New York State.]() Global Change Biology 9: 1602-1619.

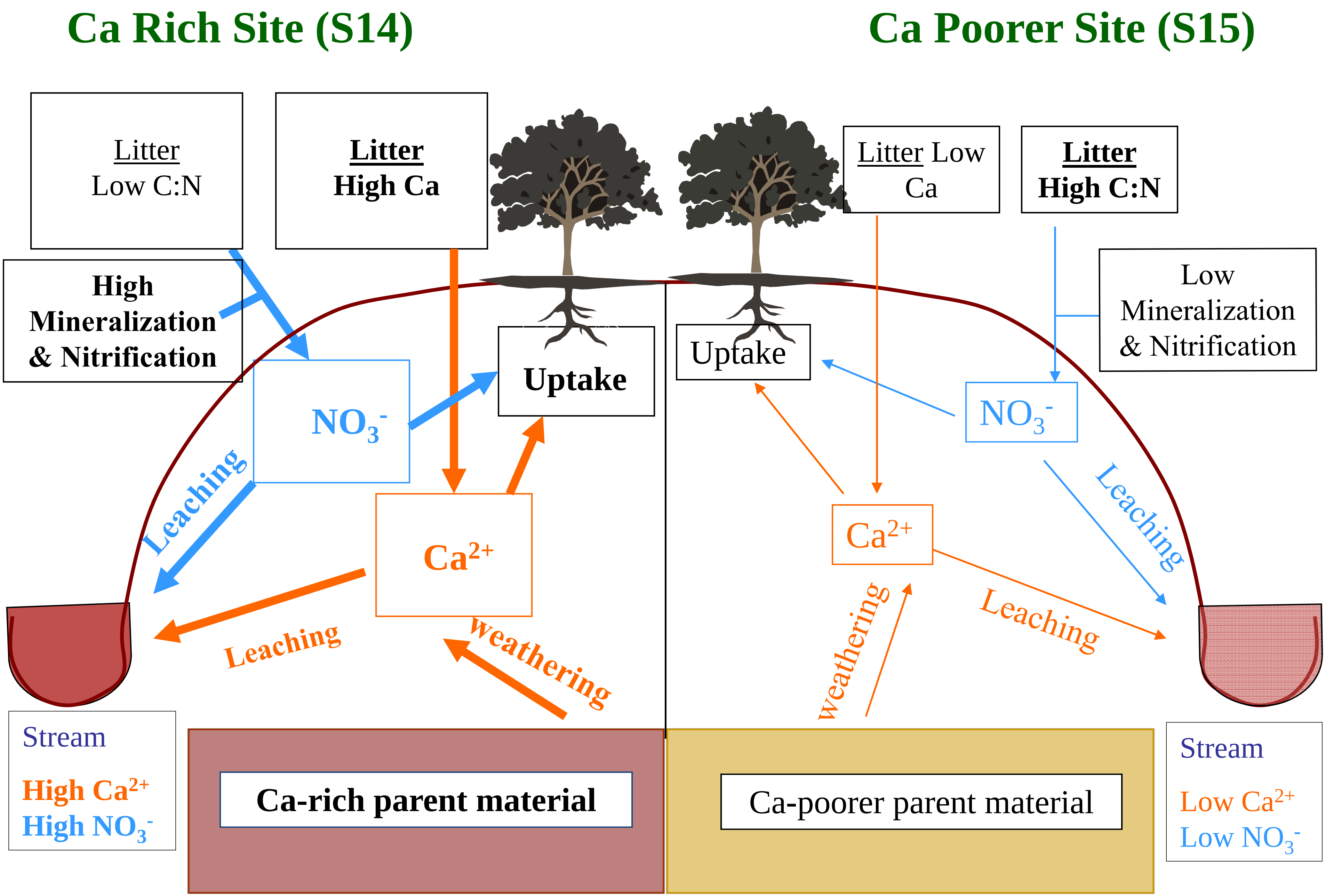
Relationships between average air temperatures and NO_3^- export in Arbutus Lake outlet for either the entire year or the months preceding spring snowmelt from 1984 to 2001. **Winter air temperature major driver of NO_3^- export.** Our current research is trying to evaluate what is causing this relationship.

Is this a linear relationship or is there some tipping point?



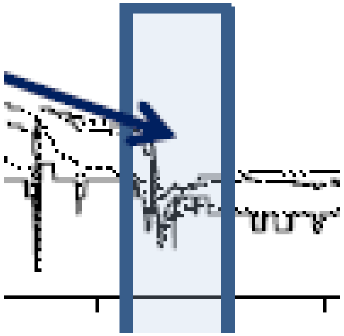
Average daily air temperature °C


Geology affects soil characteristics
Climate
Soil-Plant Interactions
Watershed Hydrological and Biogeochemical Responses

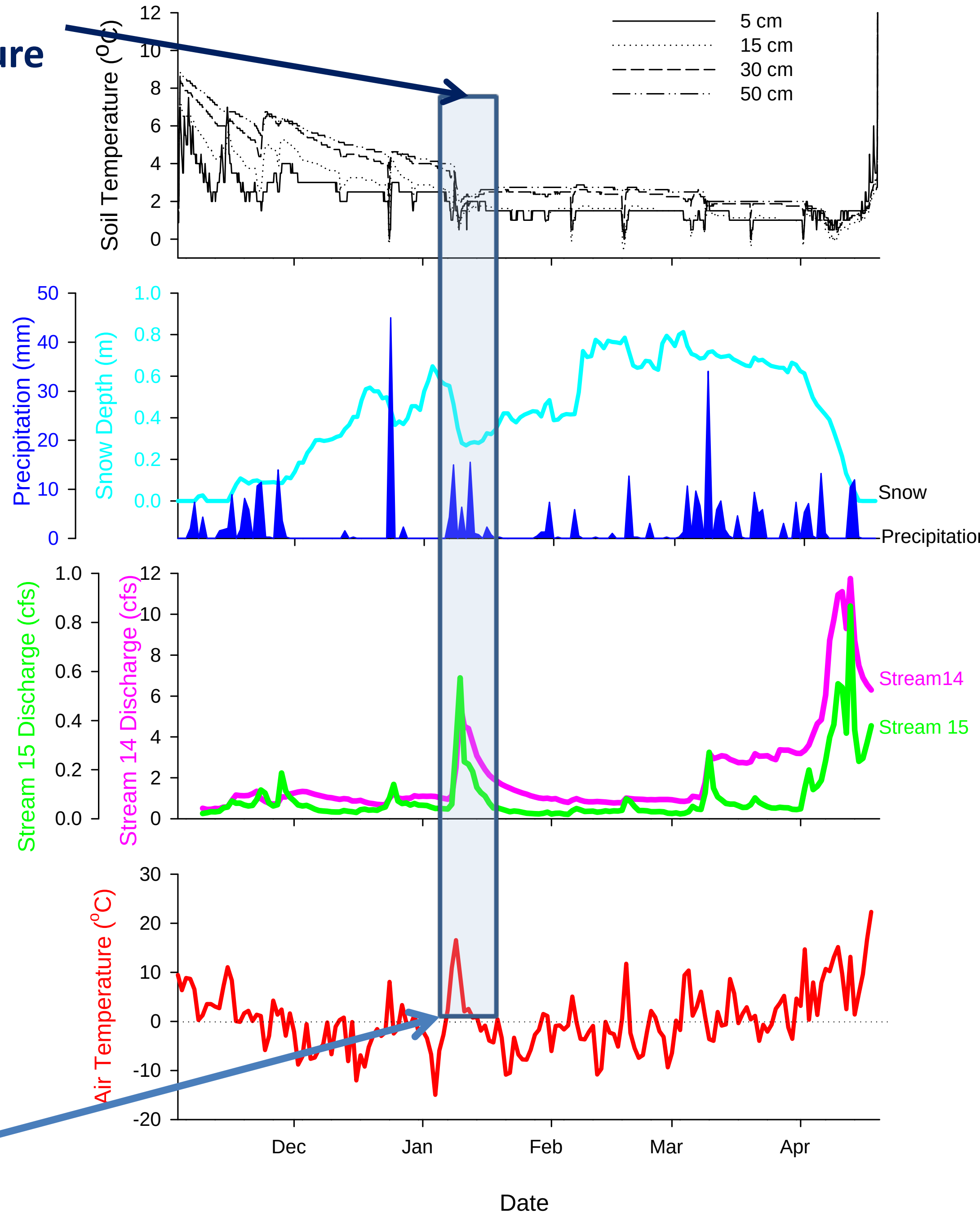


Geology affects vegetation→ influence on N dynamics

Christopher, S.F., B.D. Page, J.L. Campbell and M.J. Mitchell. 2006. Contrasting biogeochemistry in two adjacent catchments: The contributions of soil Ca and forest vegetation in affecting spatial and temporal patterns of NO3- in surface waters. Global Change Biology 12: 364-381.



Note changes in soil temperature

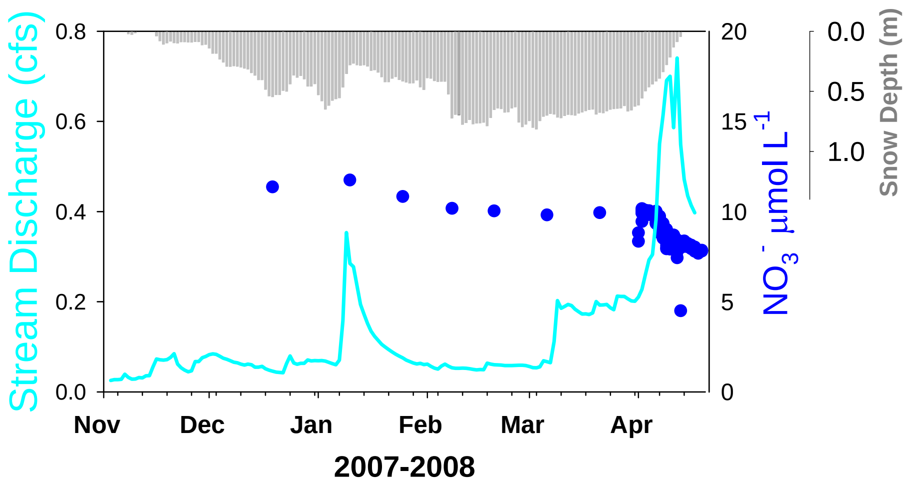


Winter Meteorology and Hydrology at Two small headwater catchments (S14 and S15) in the Adirondack Mountains of New York

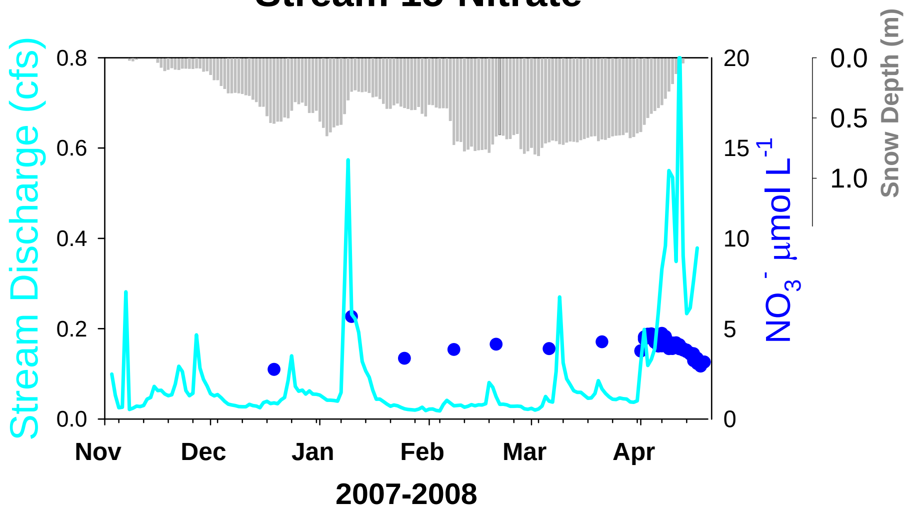
Lisa Kurian, M.S. Thesis SUNY-ESF (2009) Unpublished data

Rain on snow event

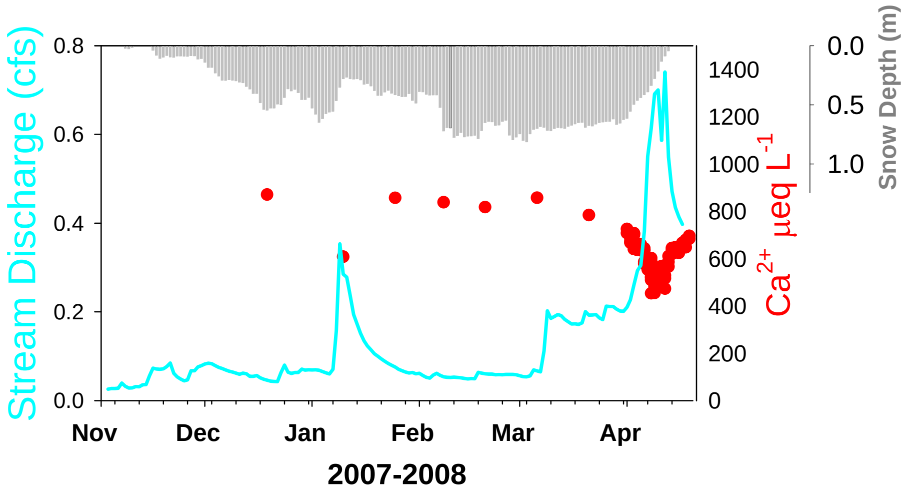
Stream 14-Nitrate



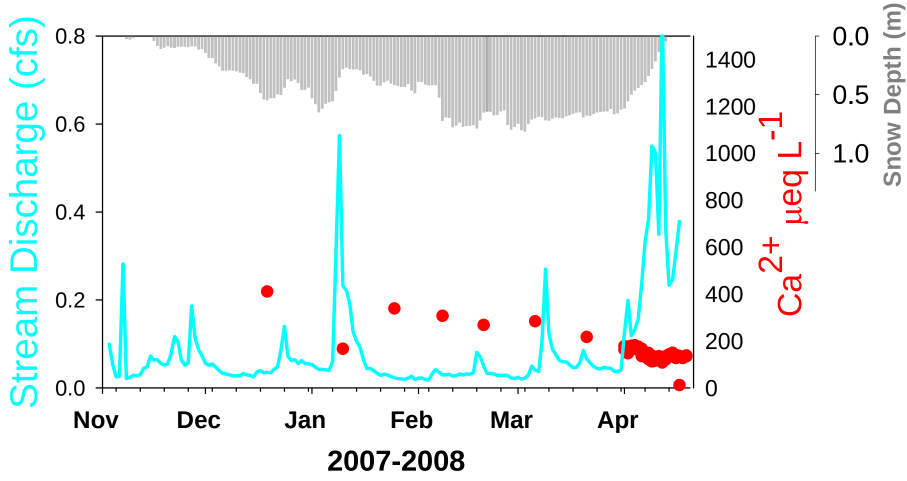
Stream 15-Nitrate



Stream 14-Calcium



Stream 15-Calcium



Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

- Sulfur
  - Importance of sulfur in watersheds linked to chronic and episodic acidification
  - Sulfur emissions and SO_4^{2-} concentrations in surface waters decreasing in the northeastern U.S.
  - Watershed drying and wetting has a major impact on sulfur oxidation and reduction processes (summer events)

Sulfur Reduction/Oxidation

- Dissimilatory Reduction: Sulfate to sulfide (consumes acidity, stored/immobilized as FeS_2 and organic sulfides)

- Oxidation: sulfide to sulfate (mobilization, generates acidity)

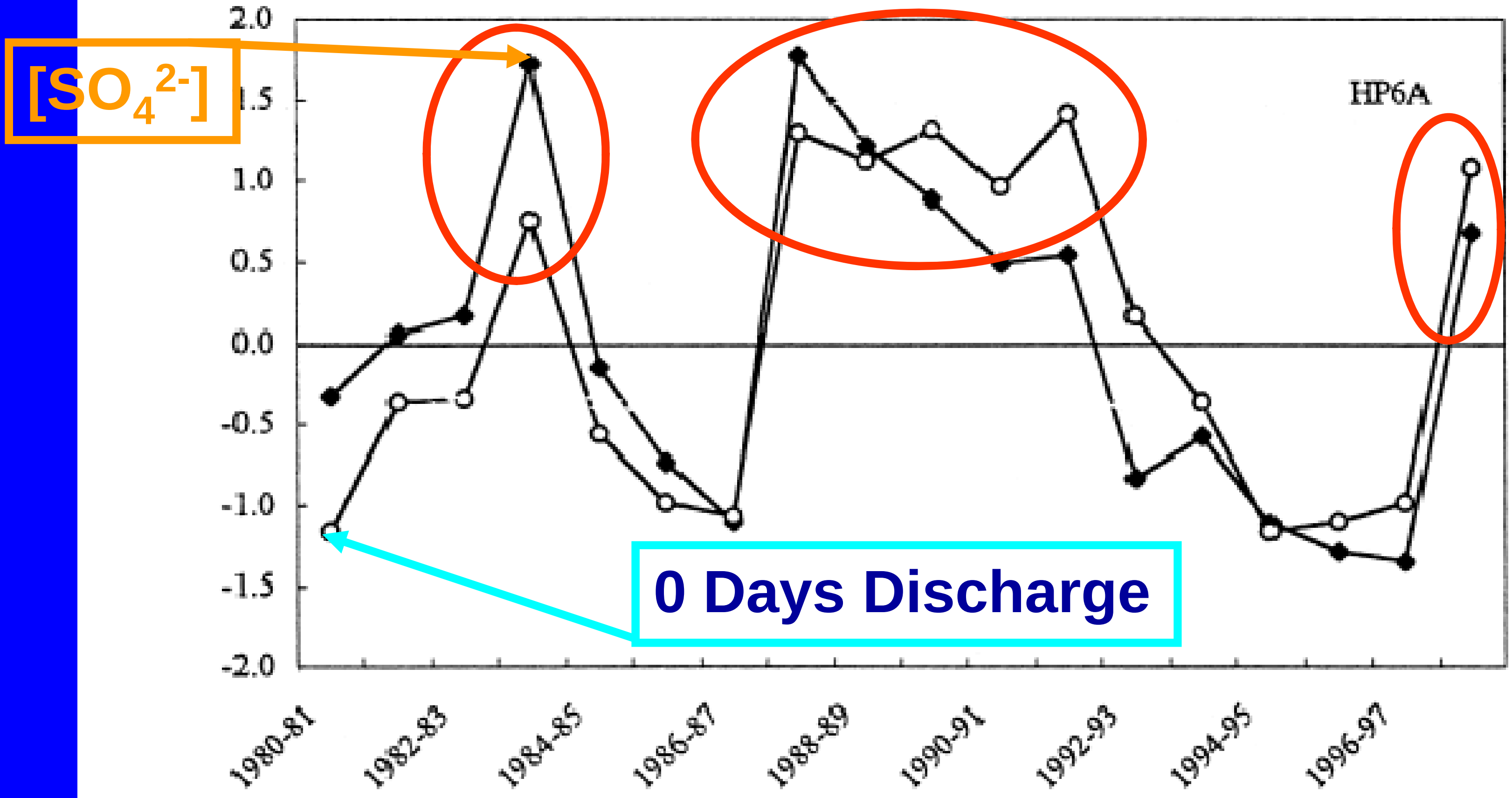
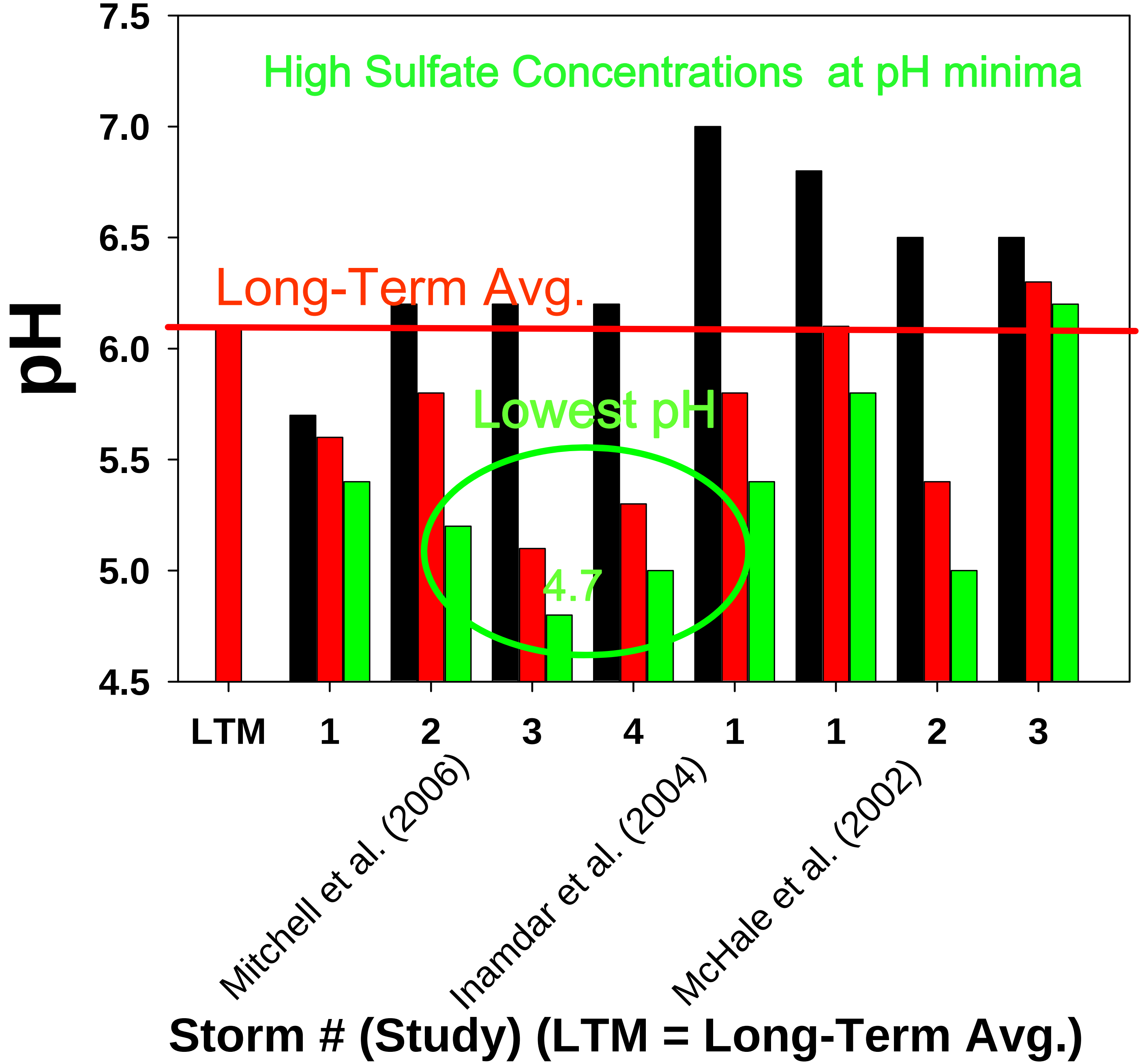
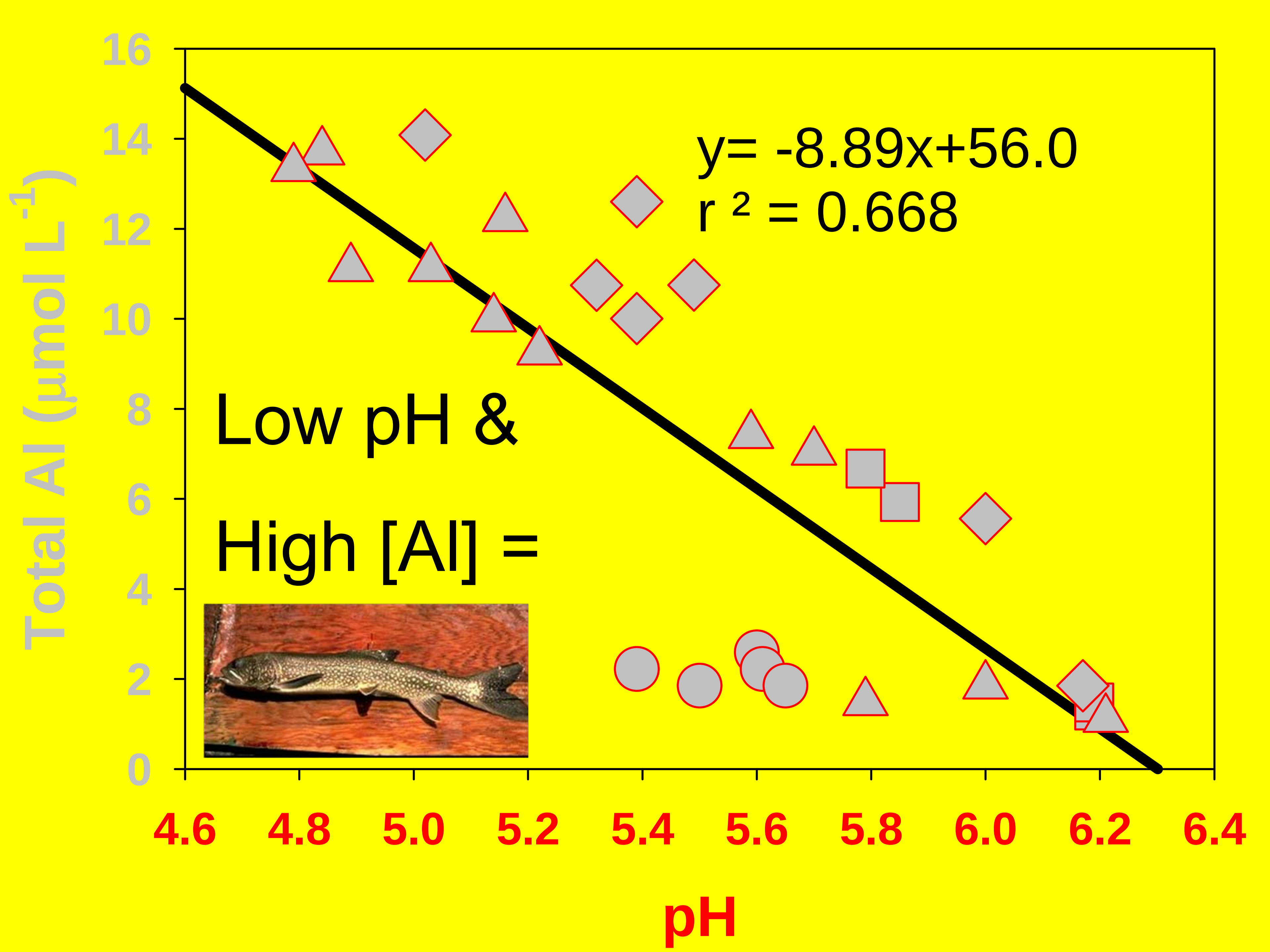


Figure 9. Z-scores of mean annual sulphate concentration (closed diamonds), and number of days with zero-discharge (open circles) for PC1 ($r = 0.87$, $p < 0.05$) and HP6-A ($r = 0.85$, $p < 0.05$).

Drier conditions result in higher SO_4^{2-} concentrations in Ontario, Canada (Eimers and Dillon, 2002) (Harp Lake). Are droughts a type of tipping point?

Late Summer/Fall Storms at Archer Creek

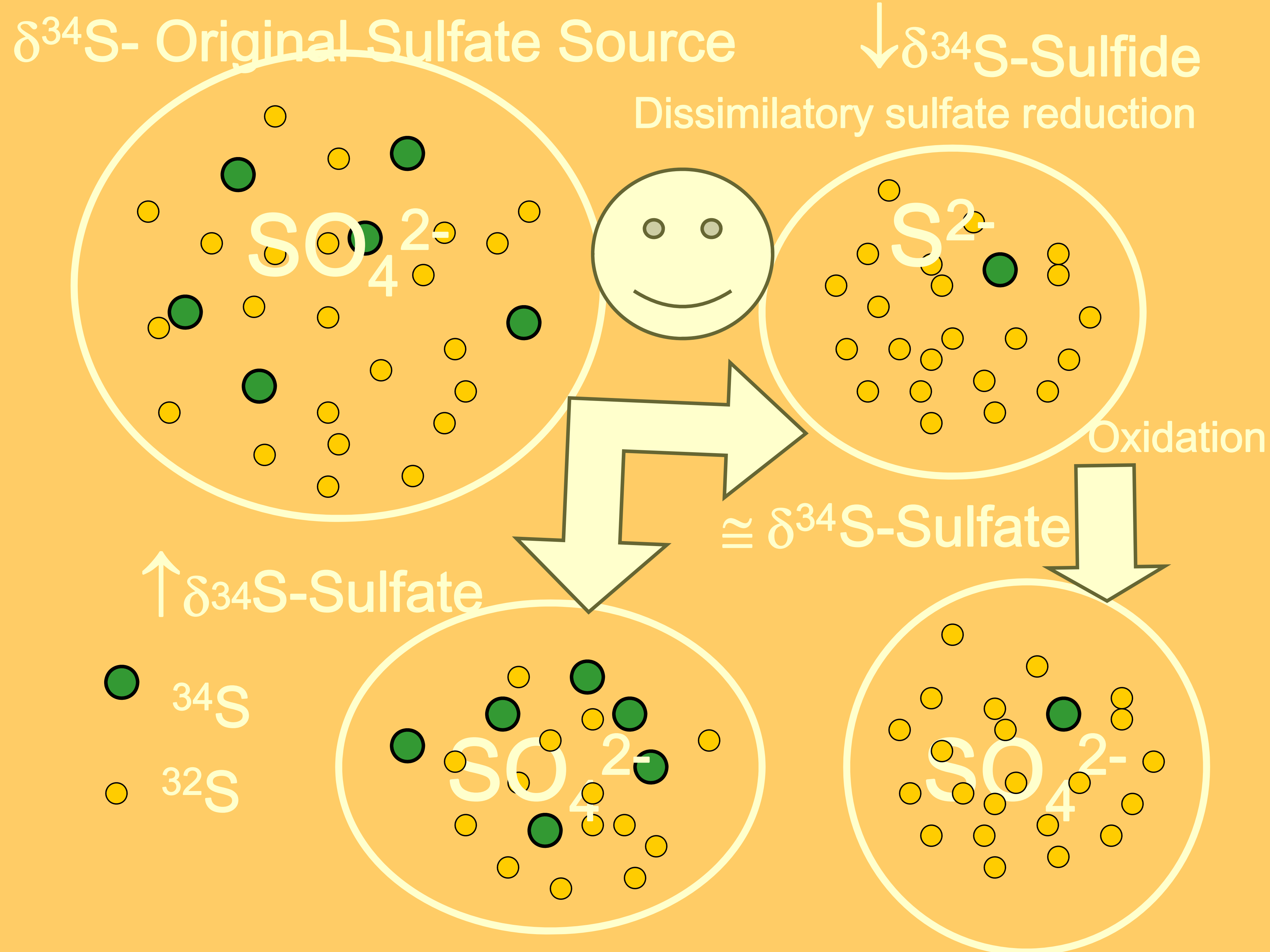




y= -8.89x+56.0
r ² = 0.668
Low pH &
High [Al] =
Total Al (µmol L-1)
0
2
4
6
8
10
12
14
16
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
pH

Sulfur isotopic composition of ecosystem components

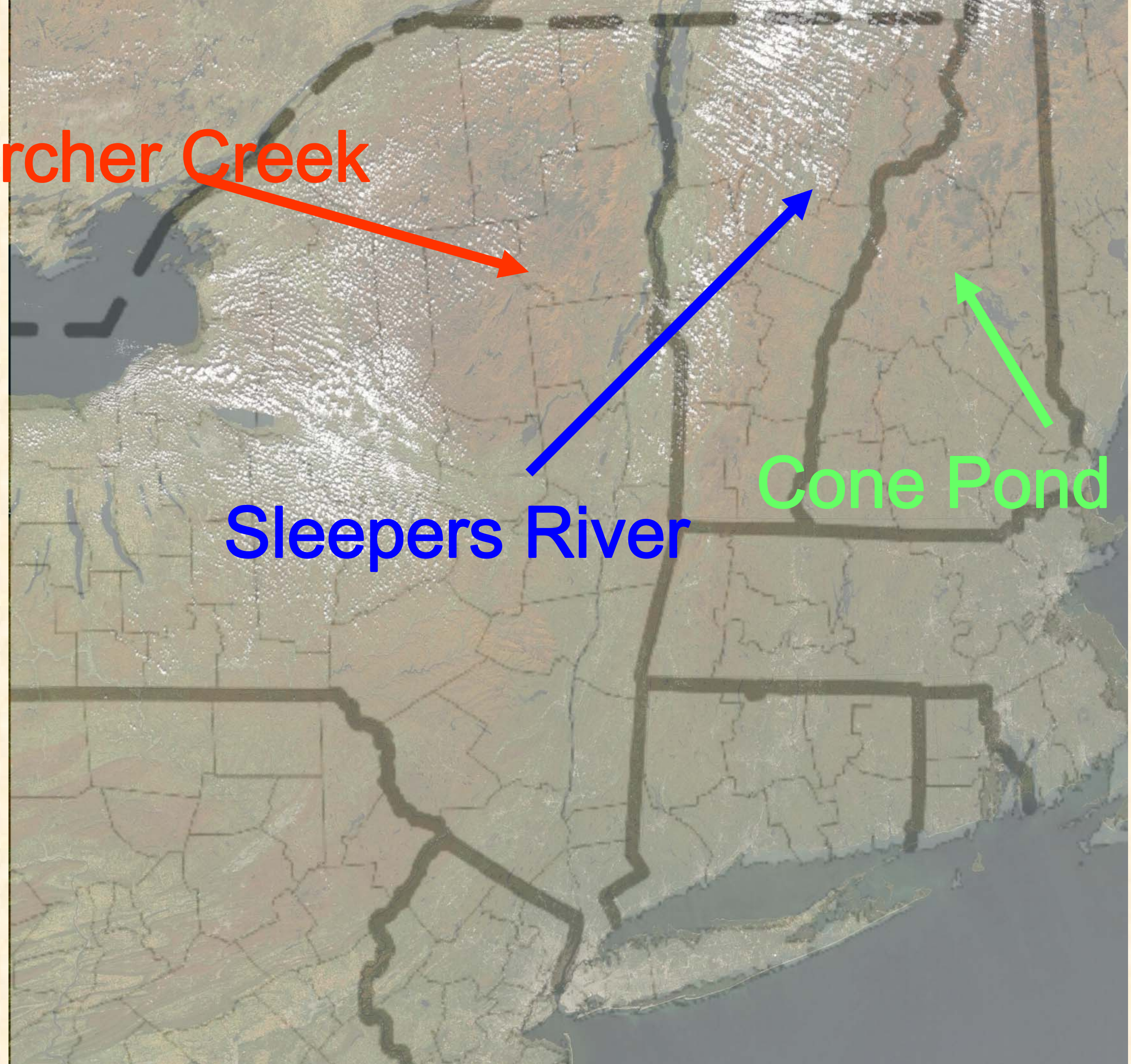
- Stable isotope of an element defined by the number of neutrons in the nucleus which can vary
- Isotopic composition Controlled by two factors
  - isotopic composition of sources (in combination with mixing ratios)
  - isotopic discrimination during sulfur transformations.
  - Most important-- dissimilatory sulfate reduction ($2H^+ + SO_4^{2-} + 4H_2 \rightarrow H_2S + 4H_2O$)


δ34S- Original Sulfate Source
↓δ34S-Sulfide
Dissimilatory sulfate reduction
SO42-
S2-
Oxidation
≅ δ34S-Sulfate
↑δ34S-Sulfate
SO42-
SO42-
34S
32S

How do the relationships between $\delta^{34}S$ values and $[SO_4^{2-}]$ compare among watersheds?

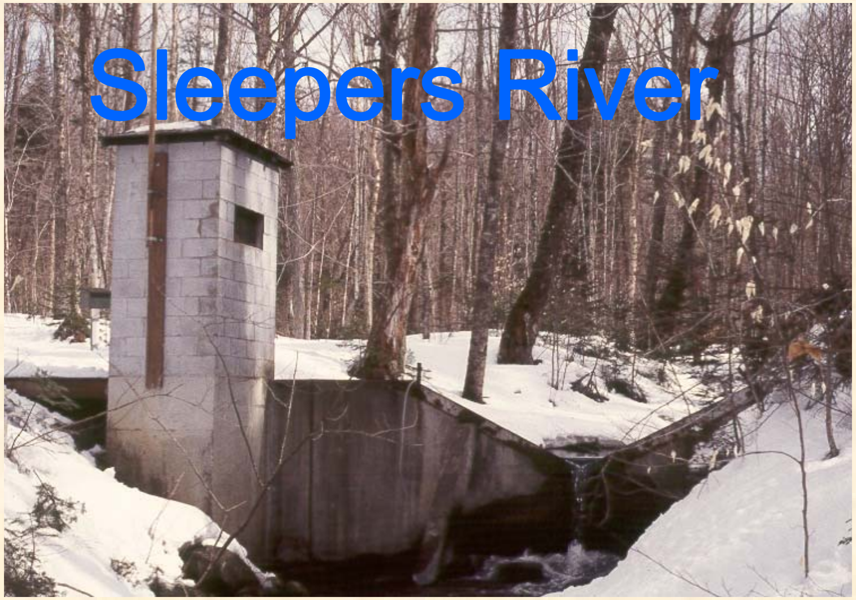
Example of three watersheds in 2002

Mitchell, M.J., S.W. Bailey, J.B. Shanley and B. Mayer. 2008. Evaluating storm events for three watersheds in the northeastern United States: a combined hydrological, chemical and isotopic approach. Hydrological Processes 22:4023-4034.



Archer Creek
Sleepers River
Cone Pond


Archer Creek

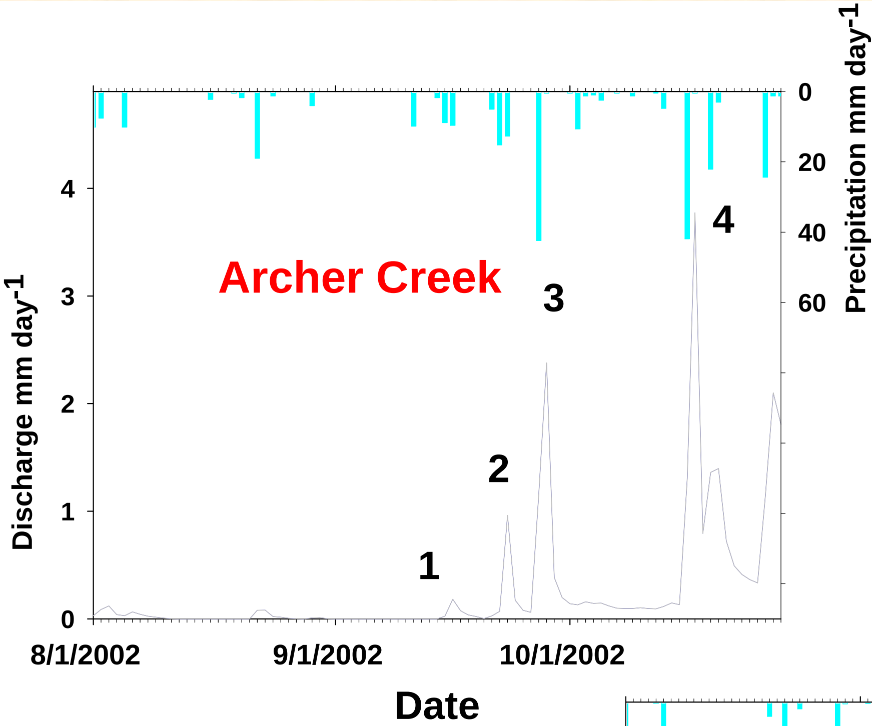

Sleepers River

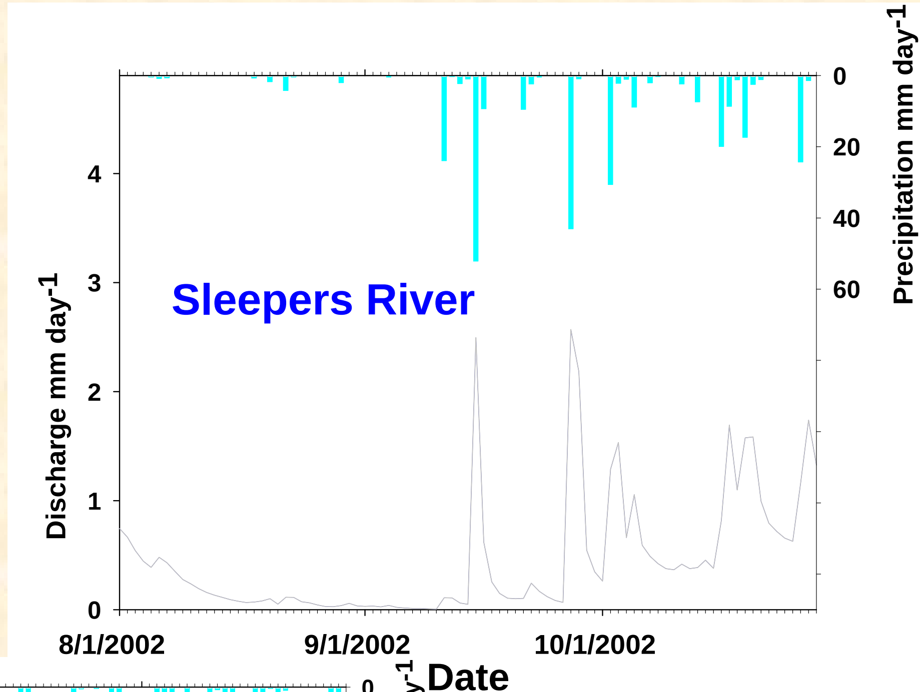

Cone Pond

Watershed Attributes

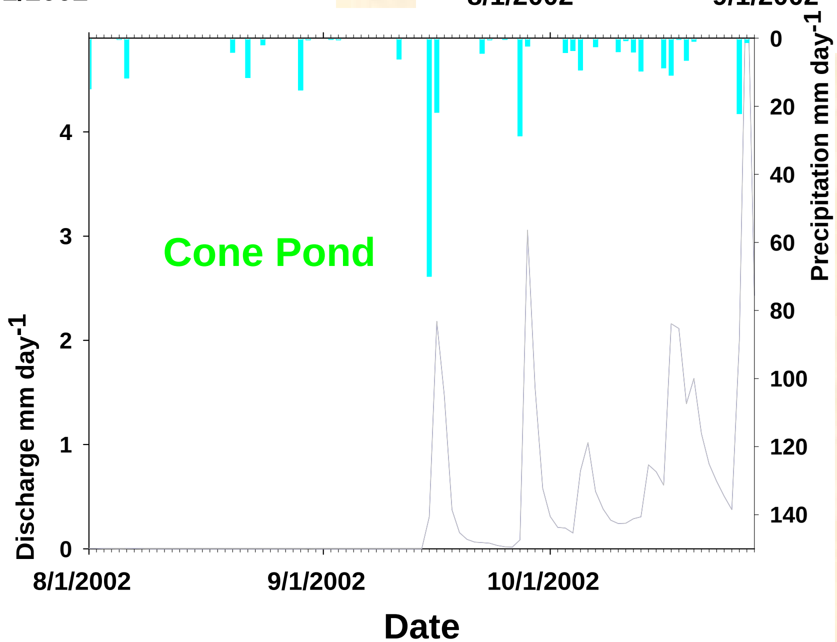
Watershed	Archer Creek	Sleepers River	Cone Pond
Location	Adirondack Mts, NY	NE Vermont	White Mts, NH
Landuse History/ Vegetation	Second Growth Hardwood	Second Growth Hardwood	First Growth Conifer (some hardwoods); fire in early 1800's)
Atm. Dep. (03-04) kg/yr	SO_4 (13) NO_3 (12)	SO_4 (14) NO_3 (12)	SO_4 (14) NO_3 (12)
Size (ha)	135	(W-9) 49	53
Geology	Granitic gneiss bedrock influenced by Grenville Formation (Ca, Mg) [Inter. base status]	Calcareous granulite interbedded with sulfidic micaceous phyllites & biotite schists [High base status]	Sillimanite-grade metapelites [Low base status]

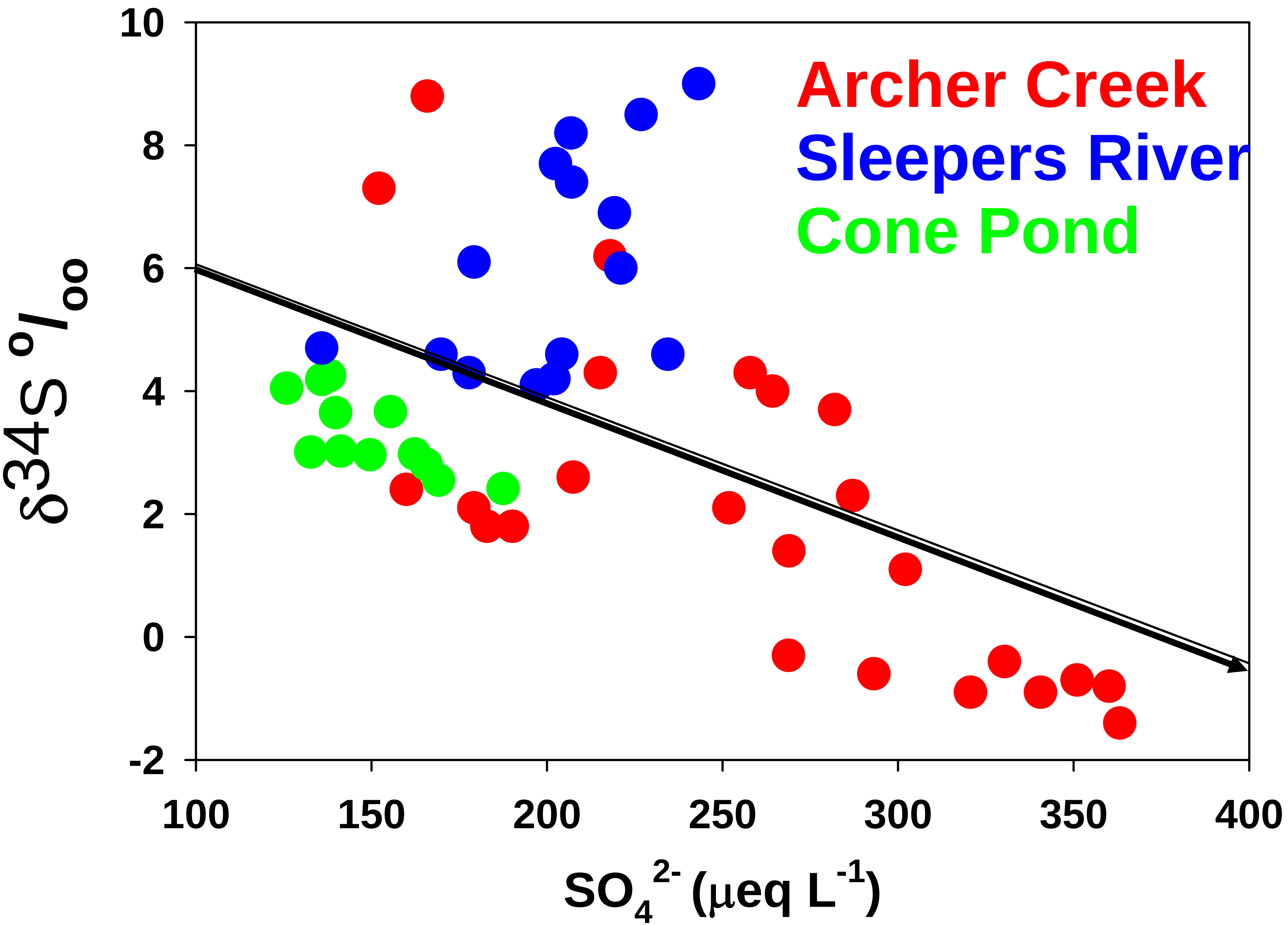
Hydrology in Late Summer/Early Fall 2002



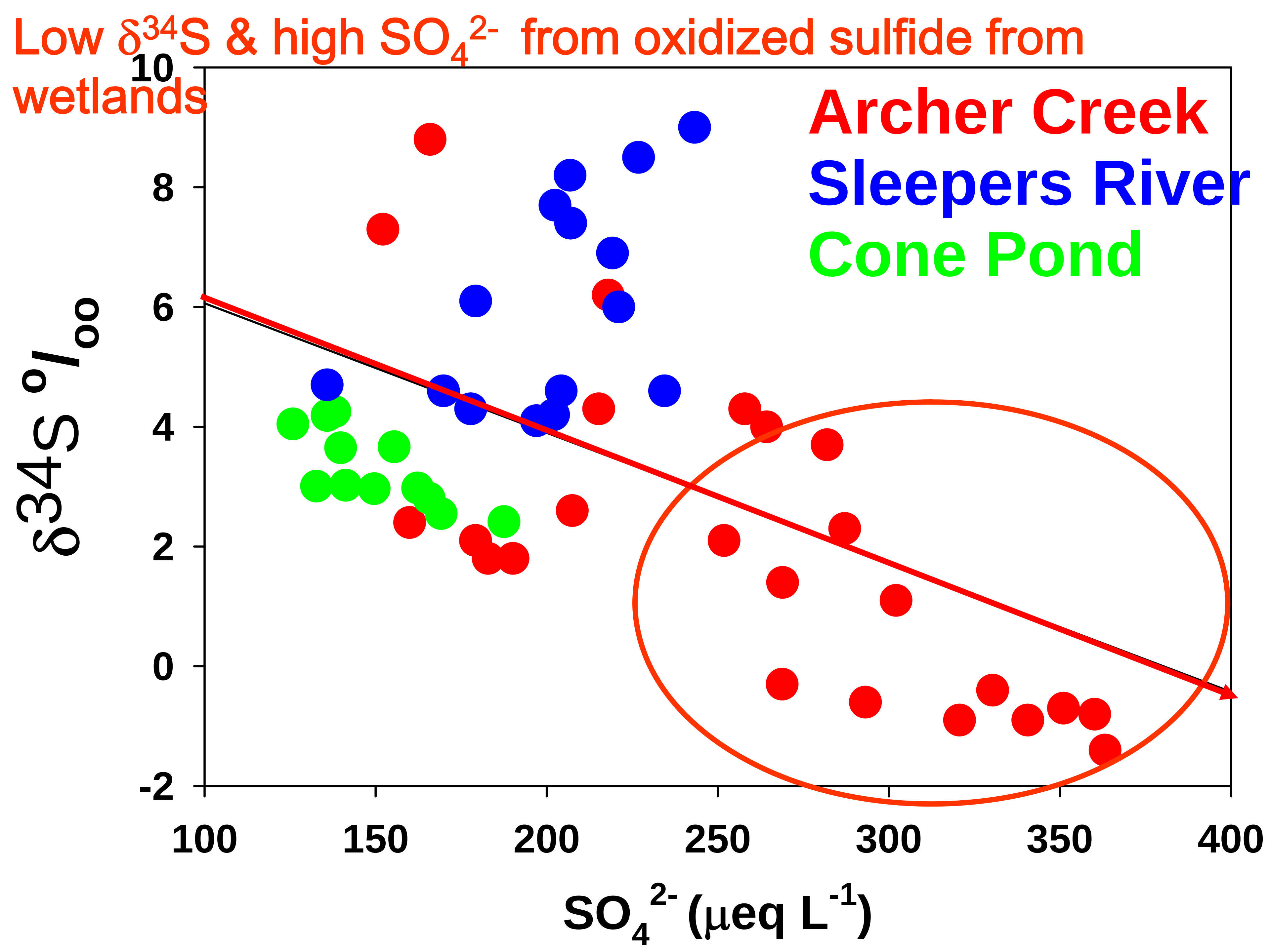


Biogeochemical responses vary substantially among watersheds: effect of landscape on climate response

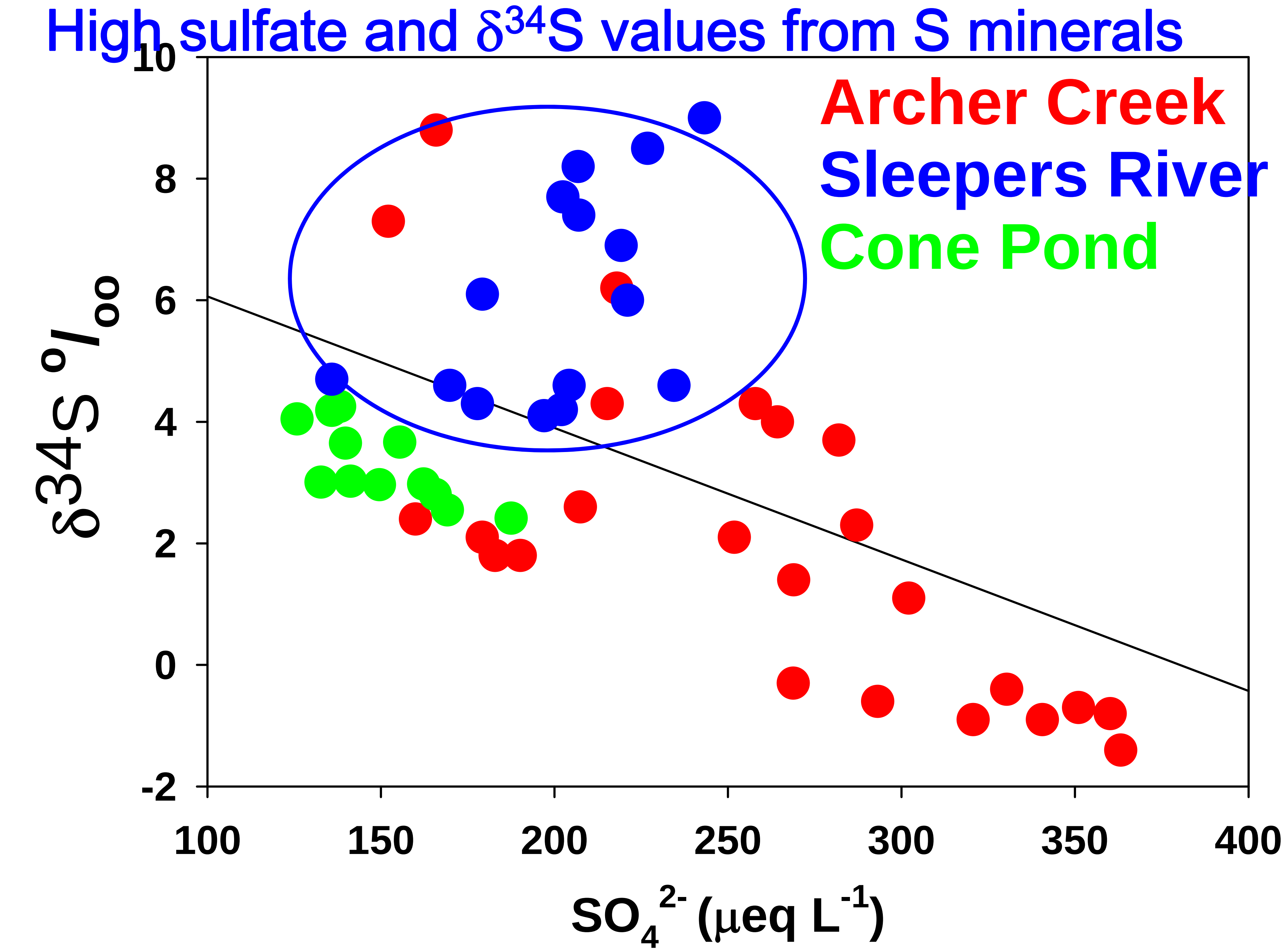




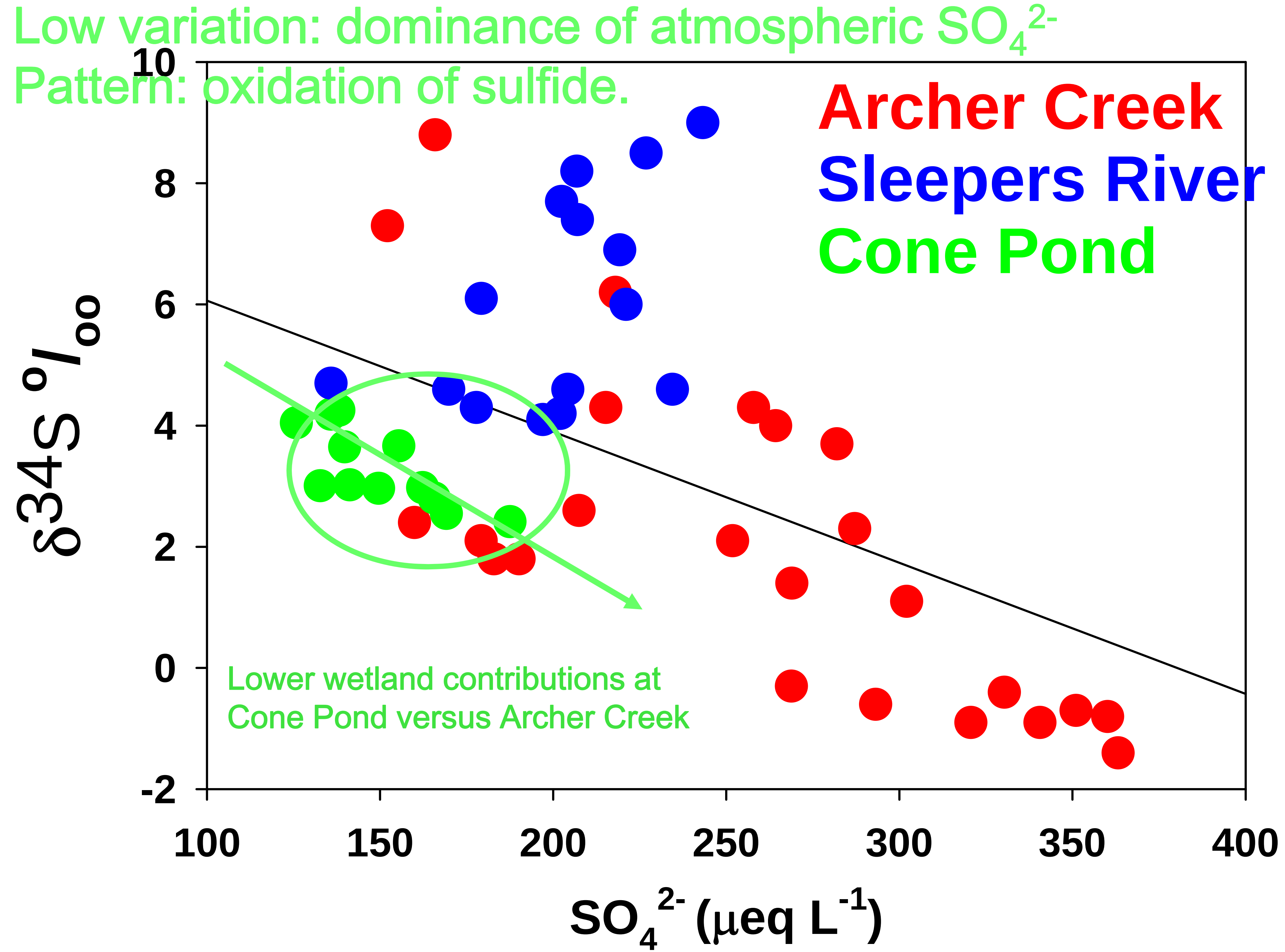
Archer Creek
Sleepers River
Cone Pond
δ34S ‰
SO4 2- (μeq L-1)
10
8
6
4
2
0
-2
100
150
200
250
300
350
400

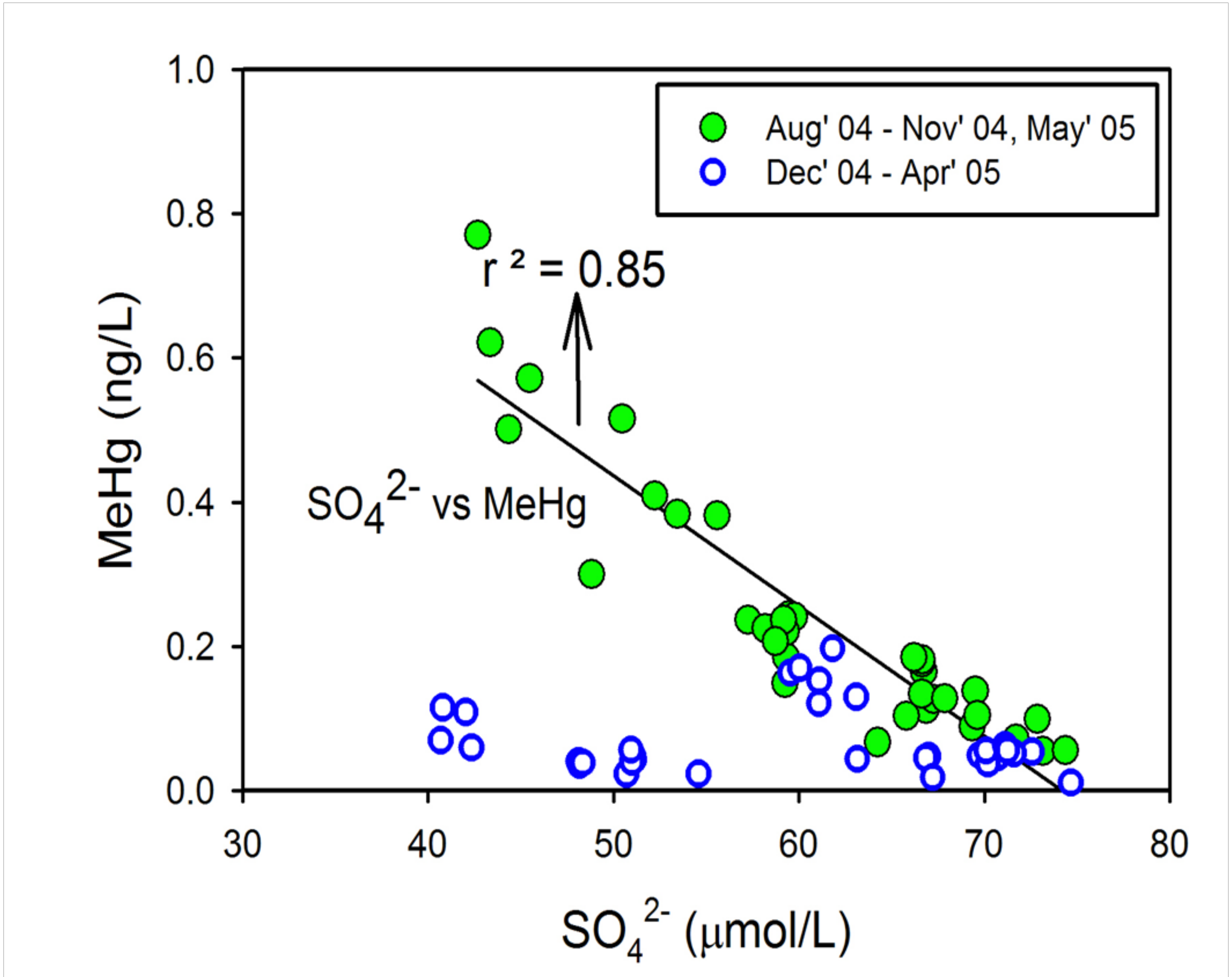


Low δ34S & high SO4 2- from oxidized sulfide from wetlands
Archer Creek
Sleepers River
Cone Pond
δ34S ‰
SO4 2- (μeq L-1)
10
8
6
4
2
0
-2
100
150
200
250
300
350
400

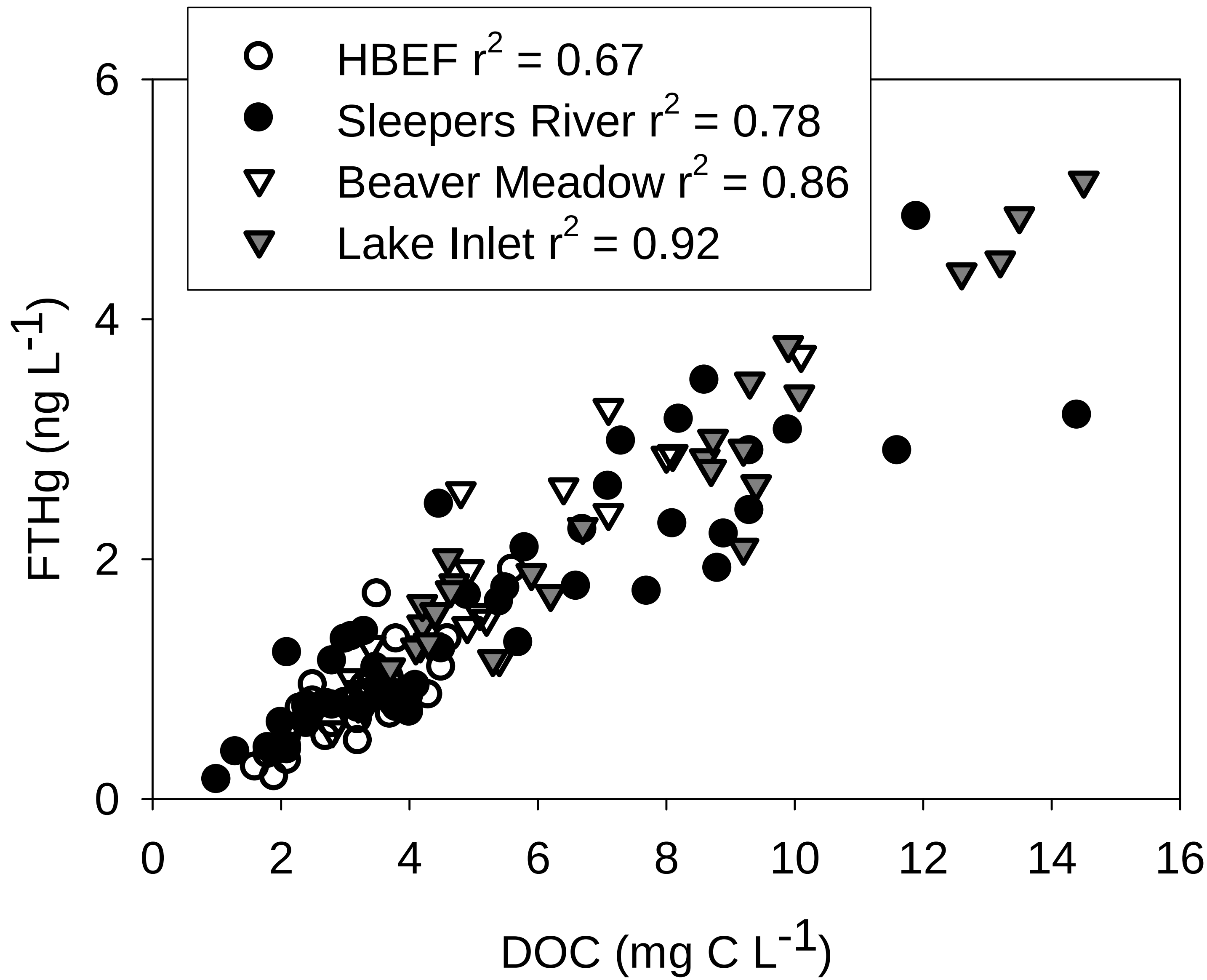


High sulfate and δ34S values from S minerals
Archer Creek
Sleepers River
Cone Pond
10
8
6
4
2
0
-2
100
150
200
250
300
350
400
δ34S ‰
SO4 2- (μeq L-1)

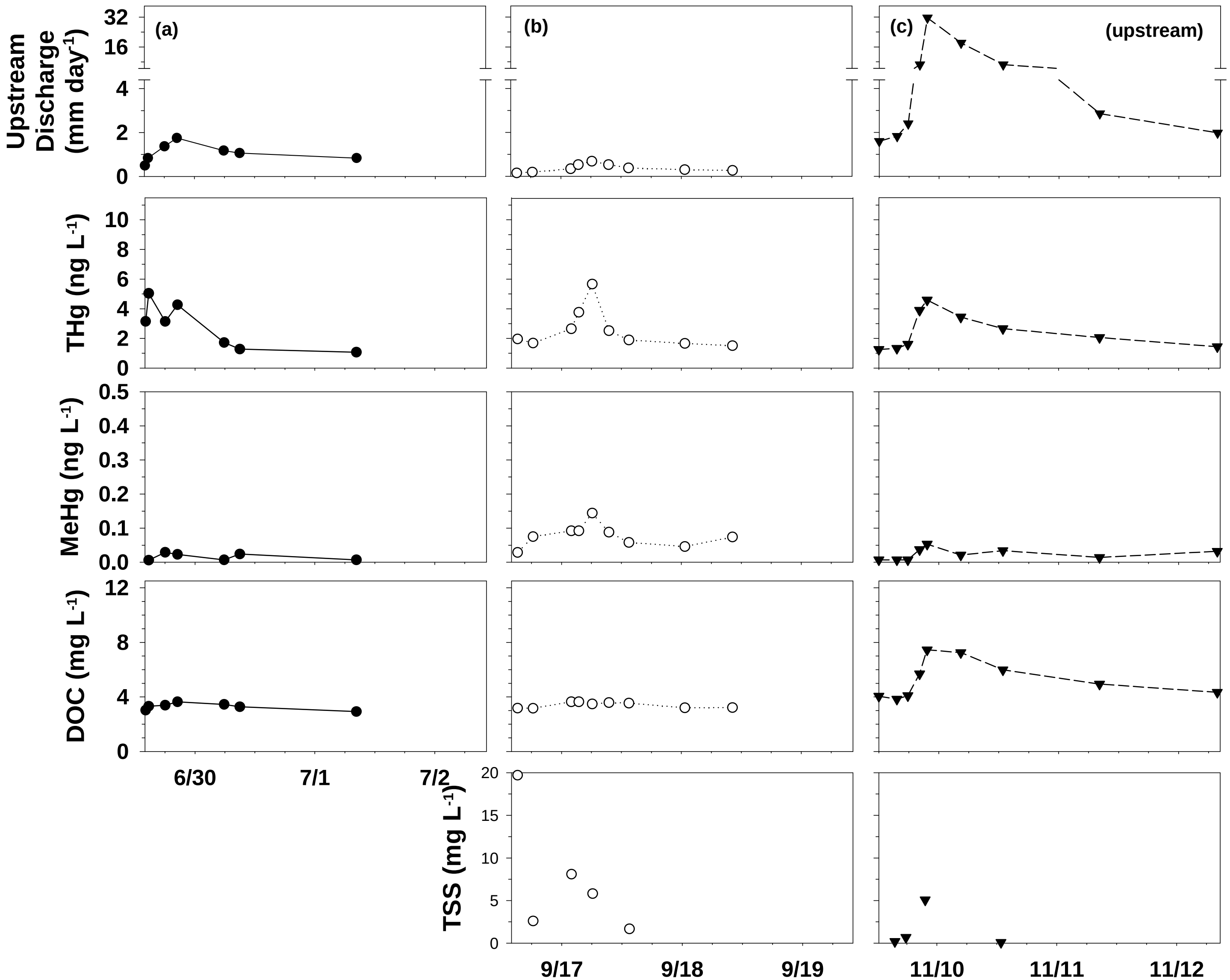

Low variation: dominance of atmospheric SO_4^{2-}
Pattern: oxidation of sulfide.
Archer Creek
Sleepers River
Cone Pond
Lower wetland contributions at
Cone Pond versus Archer Creek
$\delta^{34}S$ ‰
SO_4^{2-} ($\mu eq\ L^{-1}$)
10
8
6
4
2
0
-2
100
150
200
250
300
350
400



Derived from: Selvendiran, P., C.T. Driscoll, M.R. Montesdeoca, H-D Choi and T. M. Holsen. 2009. Mercury dynamics and transport in two Adirondack lakes. Limnology and Oceanography 54:413-427



Dittman, J.D., J.B. Shanley, C.T. Driscoll, G.R. Aiken, A.T. Chalmers, and J.E. Towse (2009), Ultraviolet absorbance as a proxy for total dissolved mercury in streams. *Environ. Pollut.,* 157, 953-1956 doi:10.1016/j.envpol.2009.01.031



Bushey, J.T., C.T. Driscoll, M.J. Mitchell, P. Selvendiran, and M.R. Montesdeoca. 2008a. [Mercury transport in response to storm events from a northern forest landscape.](#) Hydrological Processes DOI:10.1002/hyp.7091:14 pp.

Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

- What we know
  - Events show marked responses to watershed biogeochemistry of NO_3^- ,SO_4^{2-} , THg and MeHg)
  - It is clear that these solute responses vary as a function of changing atmospheric inputs (N, S, Hg) and climatic conditions of watersheds (temperature, wetting, snow pack, etc.)

Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

- What we do not know
  - The overall importance of these events in affecting overall watershed response over the long-term with respect to climate change.
  - Whether extreme, infrequent events will have a disproportionate effect on watershed responses compared to more gradual changes.

Climatic Impacts on Watershed Biogeochemistry: Nitrogen, Sulfur, and Mercury Dynamics

- What we do not know (Continued)
  - The consequences of these changes in the overall context of other changes including the effects of atmospheric deposition and biotic changes including invasive species and species composition.
  - Will these extreme biogeochemical responses also affect biotic responses?