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Title: Concentration-Discharge Relations in Rivers: Importance of a Watershed Perspective

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Concentration-Discharge Relations in Rivers: Importance of a Watershed Perspective

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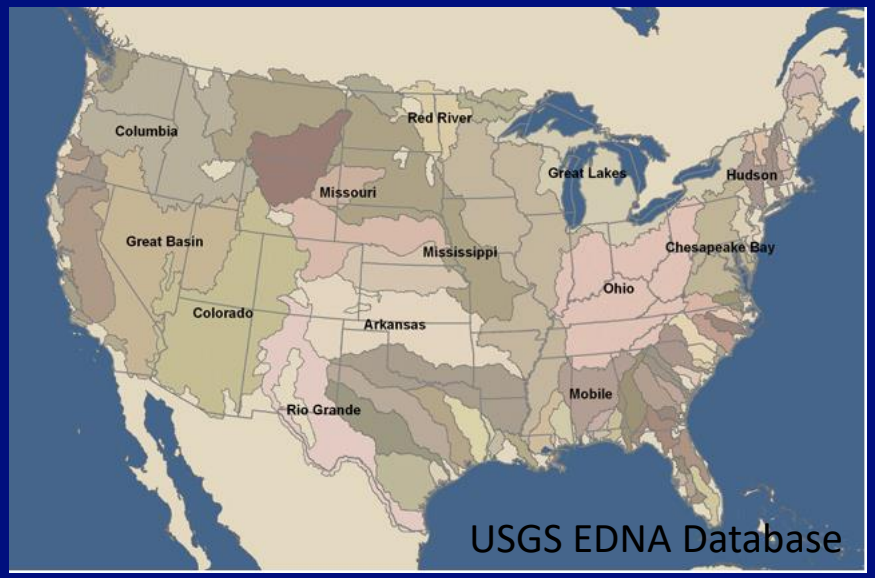
What are concentration-discharge (C/Q) relations?

- C/Q behaviors describe how concentrations of dissolved geochemical (or biogeochemical) species respond to changes in stream flow (i.e., discharge)

- C/Q relations can vary between different types of solutes (e.g., nutrients, contaminants, other biogeochemical species)

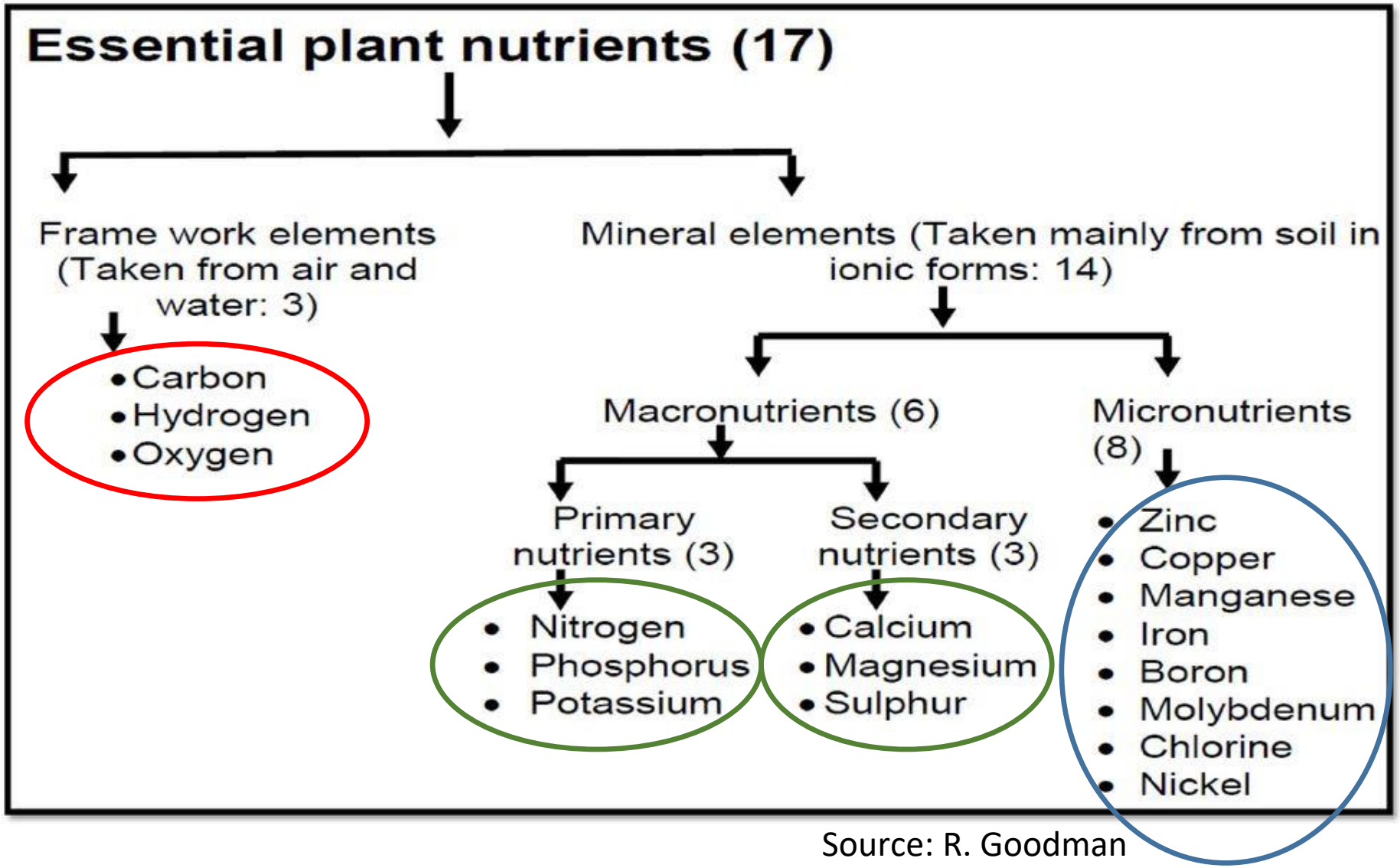
Why do we care about C/Q?

- C/Q relations are important because they:
  - affect how solutes are transferred from tributaries to higher order streams within a watershed
  - control exports from watersheds and basins to coastal marine zones or terminal lakes
  - important consequences for ecosystem function



USGS EDNA Database

Essential plant nutrients



Source: R. Goodman

Favorite River Scenario

- Think about your favorite river or stream
  - Pick one in a temperate climate!

Photos: O. Newman

What happens to concentrations when discharge increases?

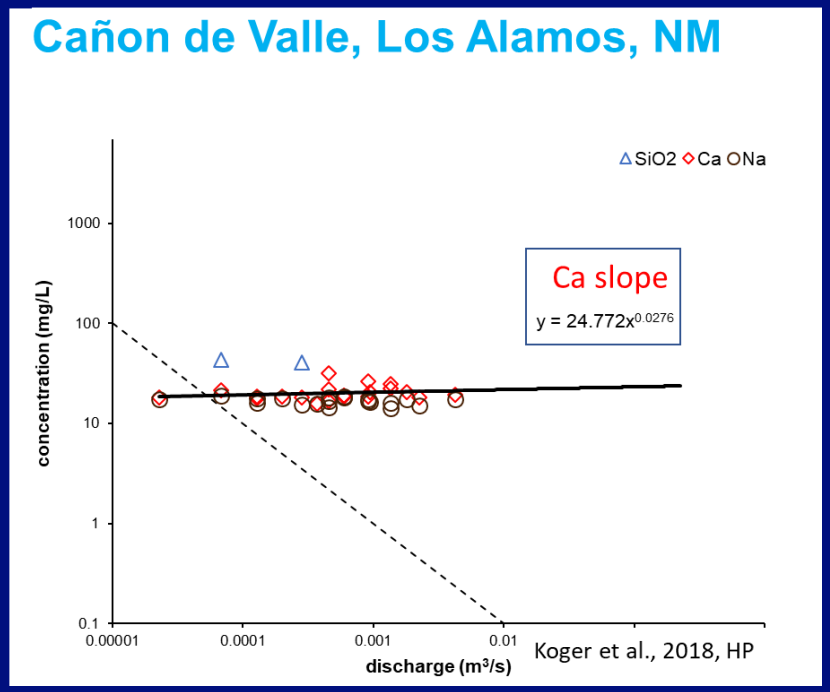
- Think about geogenic solutes such as Ca, Mg, Si

Concentrations can do 3 main things as discharge increases

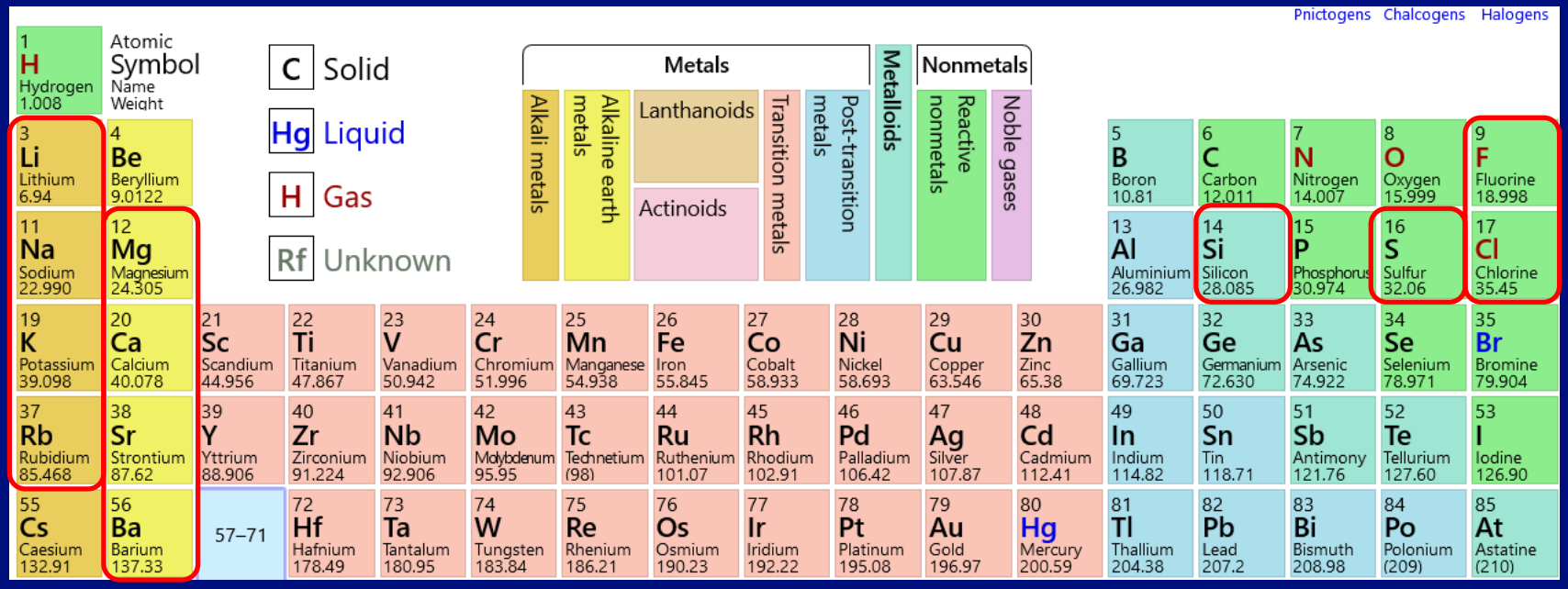
- Concentrations can increase (Flushing) ↑
- Concentrations can stay the same —
- Concentrations can decrease (Dilution) ↓

In temperate rivers, concentrations of geogenic solutes tend to stay the same with increasing discharge

- Known as <u>chemostatic</u> behavior
- Flushing and dilution are types of <u>chemodynamic</u> behavior



Chemostatic geogenic solutes include most of the major ions in natural waters



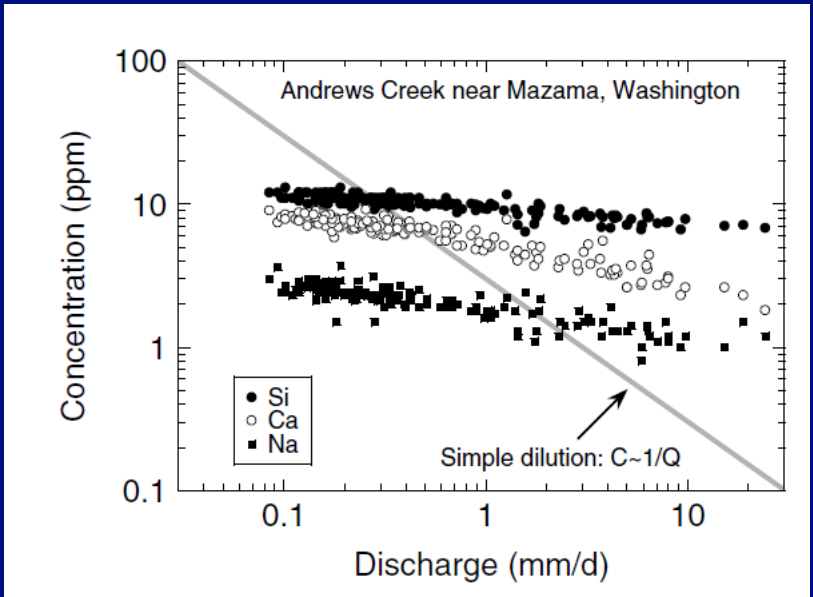
- Will focus on non-redox sensitive geogenic solutes (circled in red).
- Redox sensitive solutes (geogenic or not) more frequently behave chemodynamically

C/Q Power Law Equation

$$C = aQ^b$$

- C is concentration, a is a constant, Q is discharge, and b is the slope of the log concentration versus log discharge relation.

- Obtain slopes using linear regression and "b" is the main way of categorizing C/Q behaviors
  - Positive slopes indicate flushing
  - Slopes close to zero indicate chemostatic behavior
  - Negative slopes indicate dilution



Godsey et al., 2009 HP

How well supported is geogenic chemostasis in temperate rivers?

- Godsey et al., 2009 HP – 59 US rivers were found to be chemostatic for geogenic solutes

- Godsey et al., 2019 HP, 2,186 catchments show geogenic chemostasis on an interannual basis

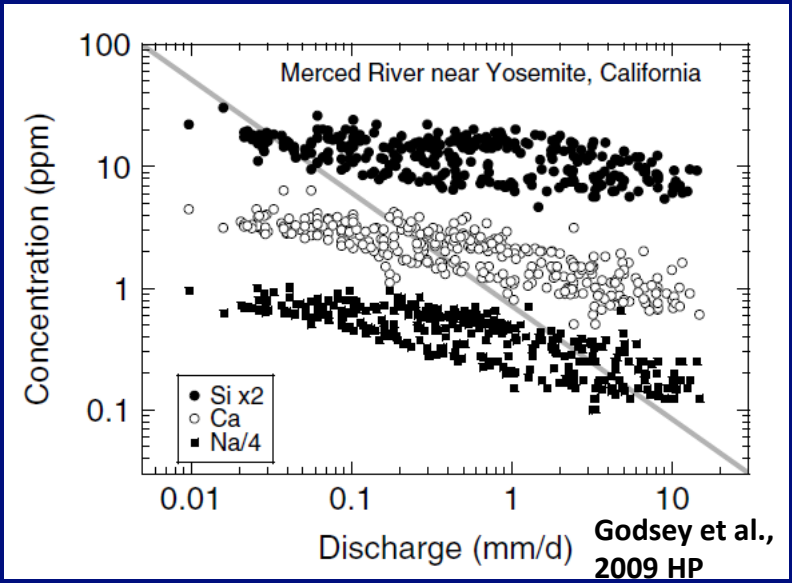
- Cartwright et al., 2019; Cartwright, 2020; Koger et al., 2018; Musolff et al. 2015; Thompson et al., 2011 and several others have demonstrated chemostasis.

How can this be?

I don't see how this can work.

This is crazy!

What the $#*&%!



Godsey et al., 2009 HP

Gnomes ensure chemostasis?

Are we using a bad assumption????

Where does the water in a river really come from??

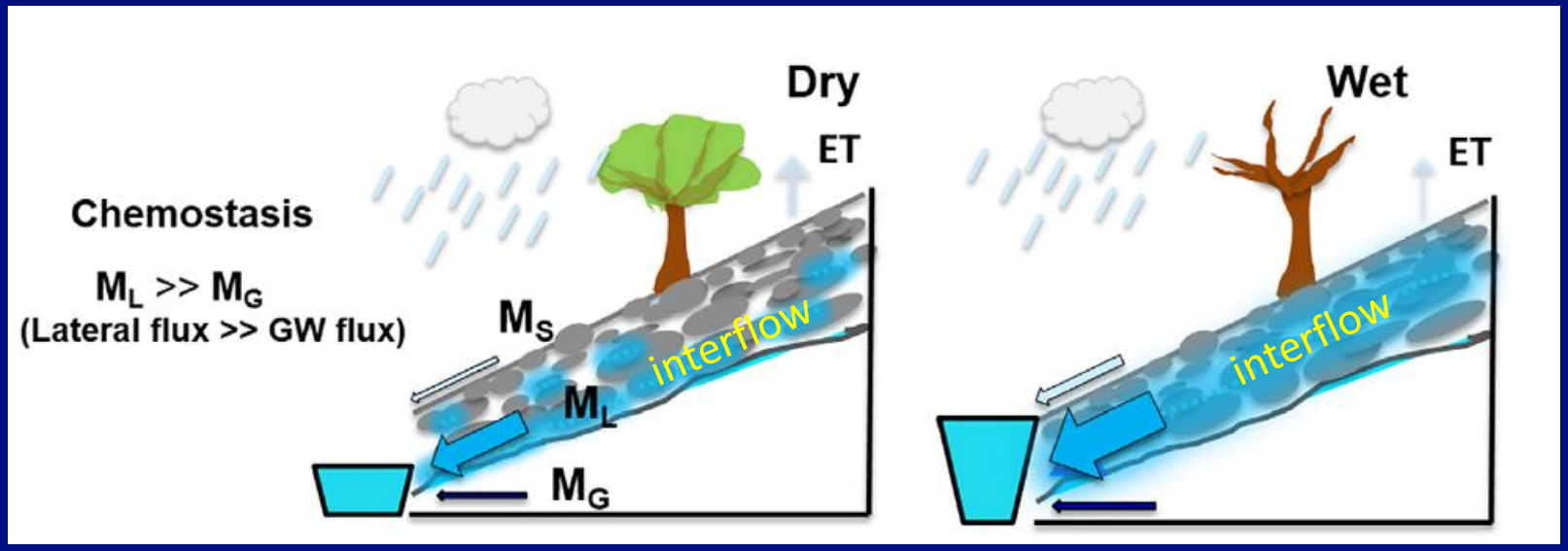
- **A lot of the water in a stream, often most of the water, is old- or pre-event water, even during high flows.**
  - **Demonstrated many times using stable isotopes and geochemical tracers (e.g., Sklash & Farvolden, 1979 JOH; McDonnell, 1980 WRR; Pearce et al., 1996 WRR; and many others).**

- **Old water/groundwater contributions makes the watershed scale an important aspect of chemostasis because of the long timescales of subsurface flow**
  - **Even zero order watersheds can have hydrologic residence times of 10s to 1000s of years**
  - **Obviates concern about slow dissolution kinetics**
  - **Groundwater & interflow help buffer dilution effects from rainfall or snowmelt (i.e., new water).**

    (e.g., Clow & Mast, 2010 Chemgel; Maher, 2011 EPSL; Siebert et al., 09 HESS)

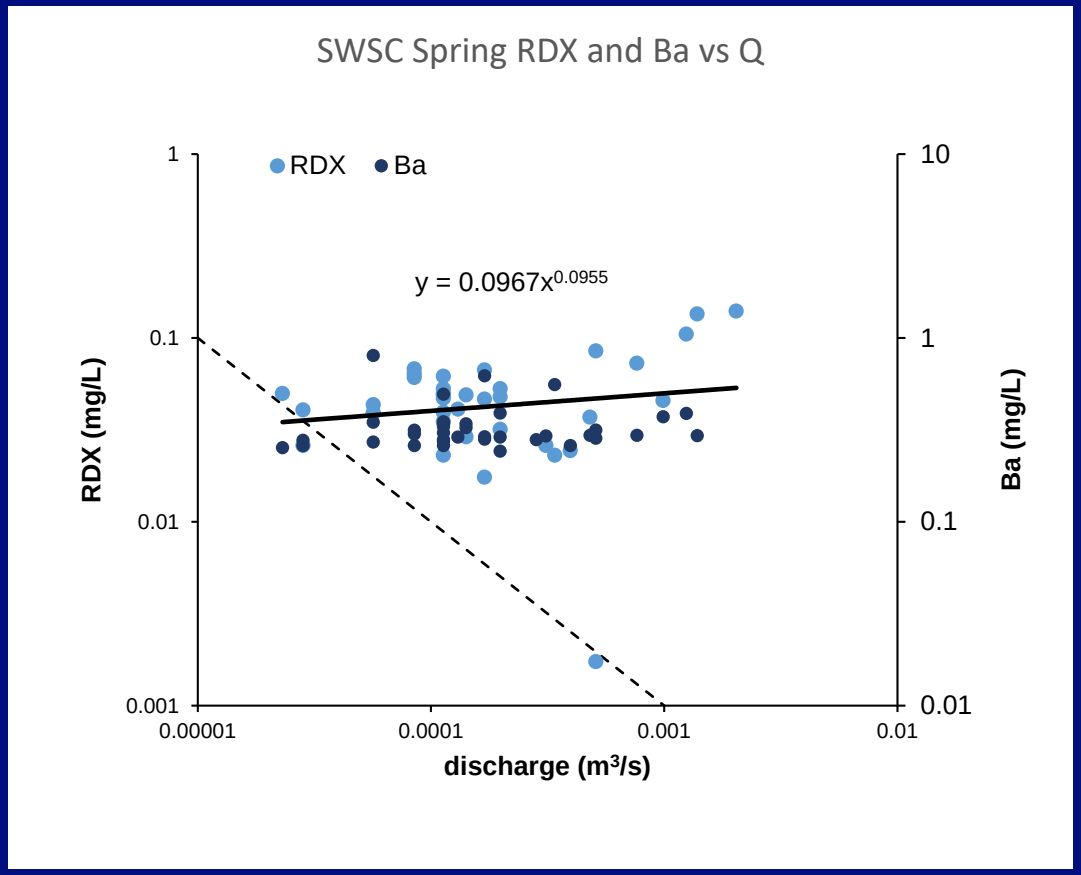
- **Isolated subsurface water stores can also contribute high concentration water during high flows as hydrologic connectivity increases**

  (e.g., Cartwright et al., 2020 HP; Cartwright, 2020 AppGeo; Li et al., 2017 WRR; Musolff et al., 2015 AdvWatRes)



Li et al., 2017 WRR

Can Contaminants behave chemostatically?



- **RDX and Ba contamination in springs and stream, Los Alamos NM**

Koger et al., 2018, HP

- **Chemostatic nitrate behavior has been observed in agricultural areas**

  (Basu et al. 2010, GRL; Musloff et al., 2015 Adv wat res; Thompson et al., 2011, WRR)

- **Nitrate residence times can be multi-decadal or longer indicating long periods of high concentrations after mitigation/remediation actions are taken.**

  (e.g., Howden et al., 2011 WRR; Kaown et al., 2018 Hydrogeol J.; MacDonald et al. 2003 Hydrogeol J.; Vautier et al., 2021 STOTEN; Wang et al., 2016, STOTEN; Wild et al., 2018, WRR; and many more)

Review of Midwestern agricultural catchments; Basu et al., 2011, WRR

- **Phosphorus transport was episodic at smaller spatial scales, but chemostatic at larger scales.**

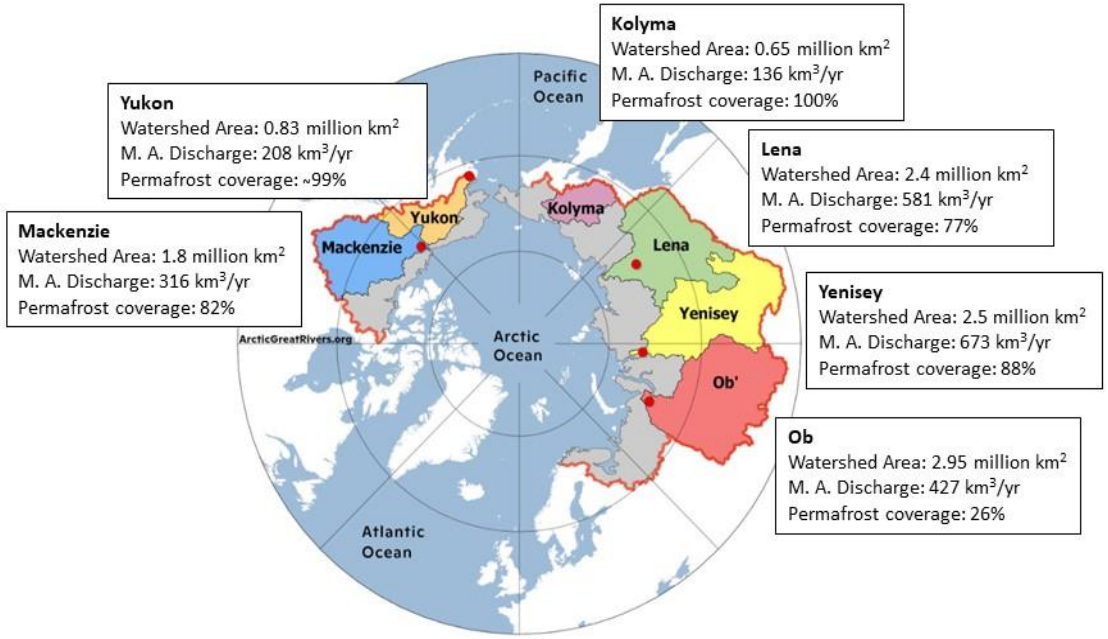
- **“Chemostatic response dominates in transport-limited catchments that have internal sources of the solute to buffer the periodicity in episodic inputs”**

- **Episodic response (e.g., pesticides) dominates in source-limited catchments.**

Where do we find exceptions to the chemostatic dogma?

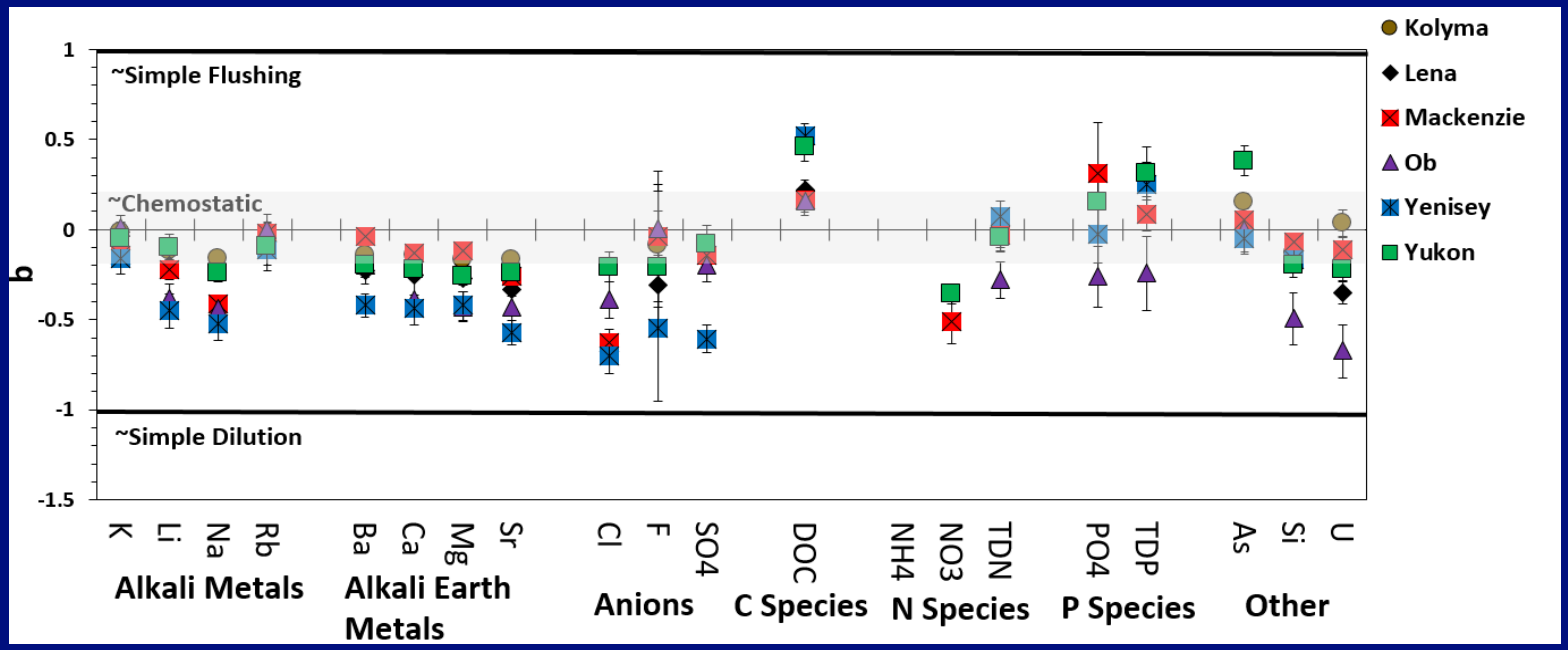
- Tropics – Luquillo Puerto Rico, ultrafast weathering; Shanley et al., 2011 WRR
- Arctic?
  - Because flow path lengths/residence times are important for chemostasis, Arctic rivers may be very different than than temperate.
  - Permafrost and frozen ground, or other cryo-characteristics affect deep flow & subsurface storage.

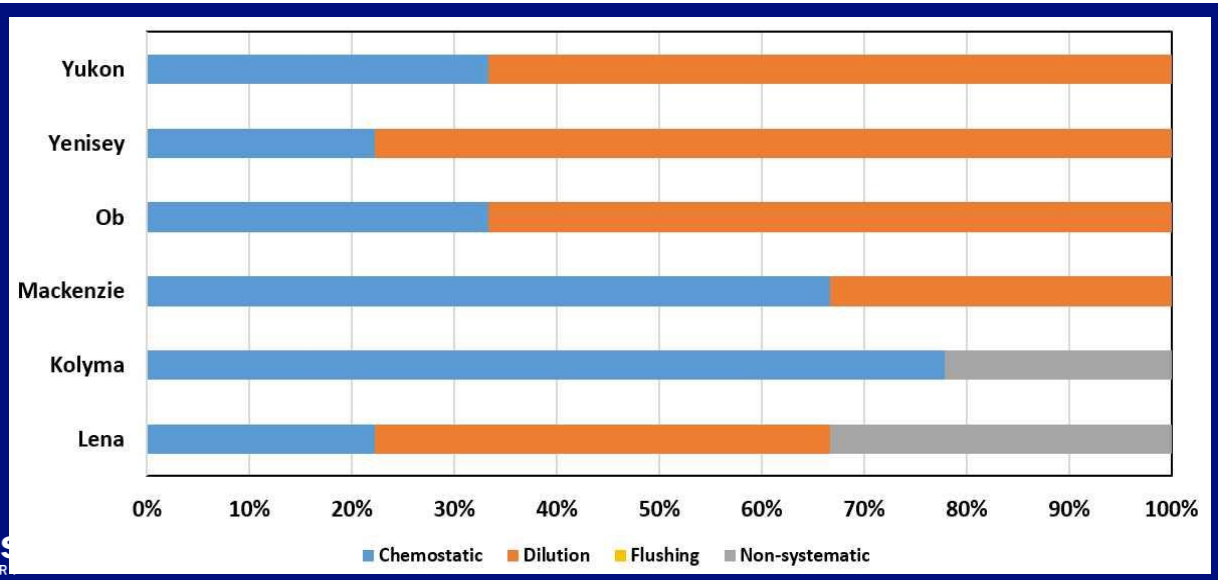
We examined C/Q relations from the 6 largest Arctic river basins (using the ArcticGRO database)



Newman et al., in prep.

Results show much more evidence for chemodynamic behavior especially dilution in these Arctic rivers



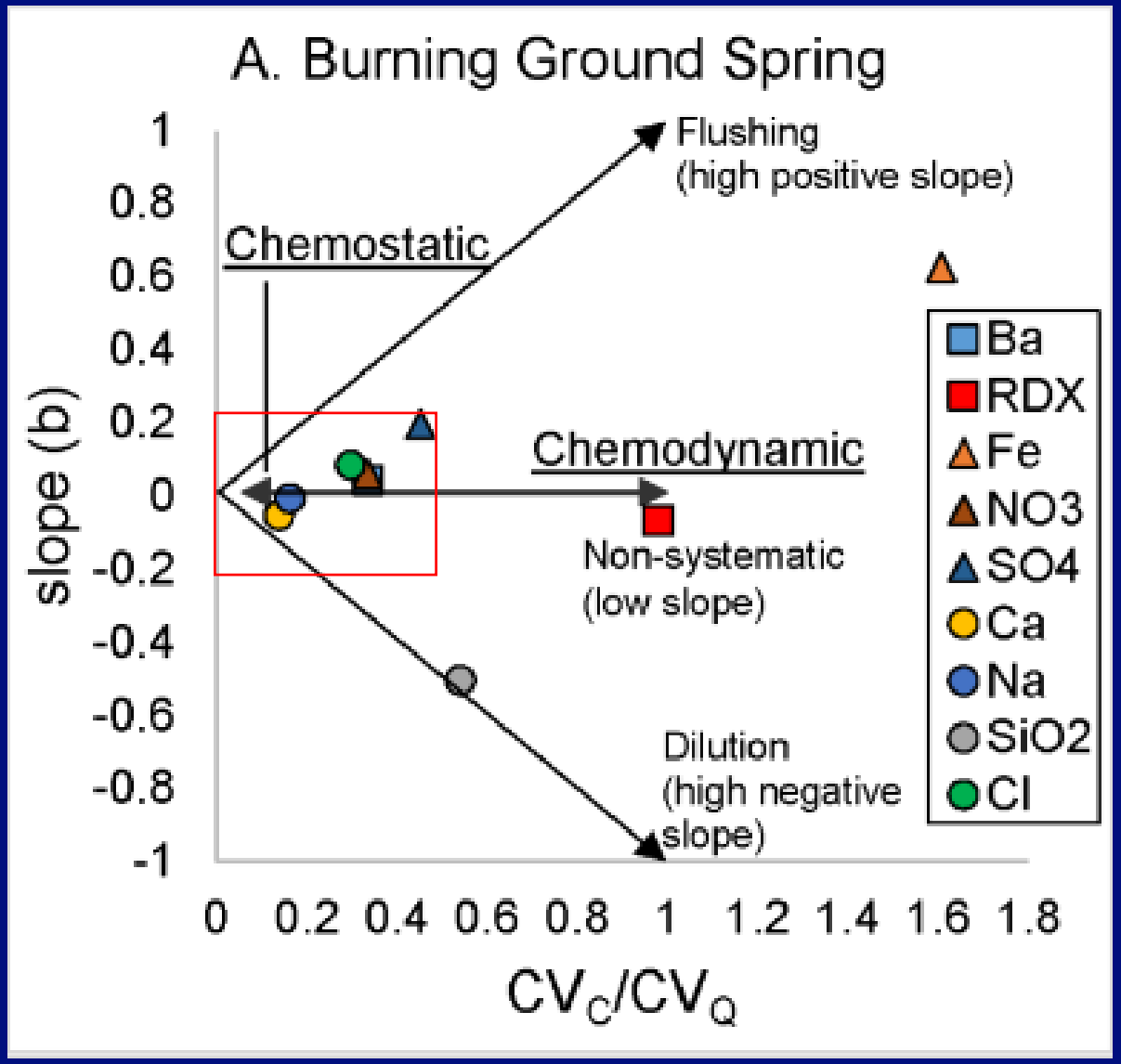


Summary

- **Chemostasis rules for geogenic solutes in temperate rivers**
  - **maybe not so much in Tropics and Arctic**
- **Redox sensitive species (SO_4 is an exception) are more chemodynamic**
  - **High contaminant loads can lead to chemostasis (e.g., nitrate)**
- **Important to consider the watershed scale where subsurface contributions to the stream are critical**
  - **Thus, mixing is a key factor for development of chemostatic conditions.**
  - **Changes in watershed hydrologic connectivity can also matter**

Acknowledgements

Los Alamos Environmental Program, Next Generation Ecosystem-Arctic project (DOE OBER)


A. Burning Ground Spring
Flushing
(high positive slope)
Chemostatic
Chemodynamic
Non-systematic
(low slope)
Dilution
(high negative
slope)
Ba
RDX
Fe
NO3
SO4
Ca
Na
SiO2
Cl
slope (b)
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
CVC/CVQ