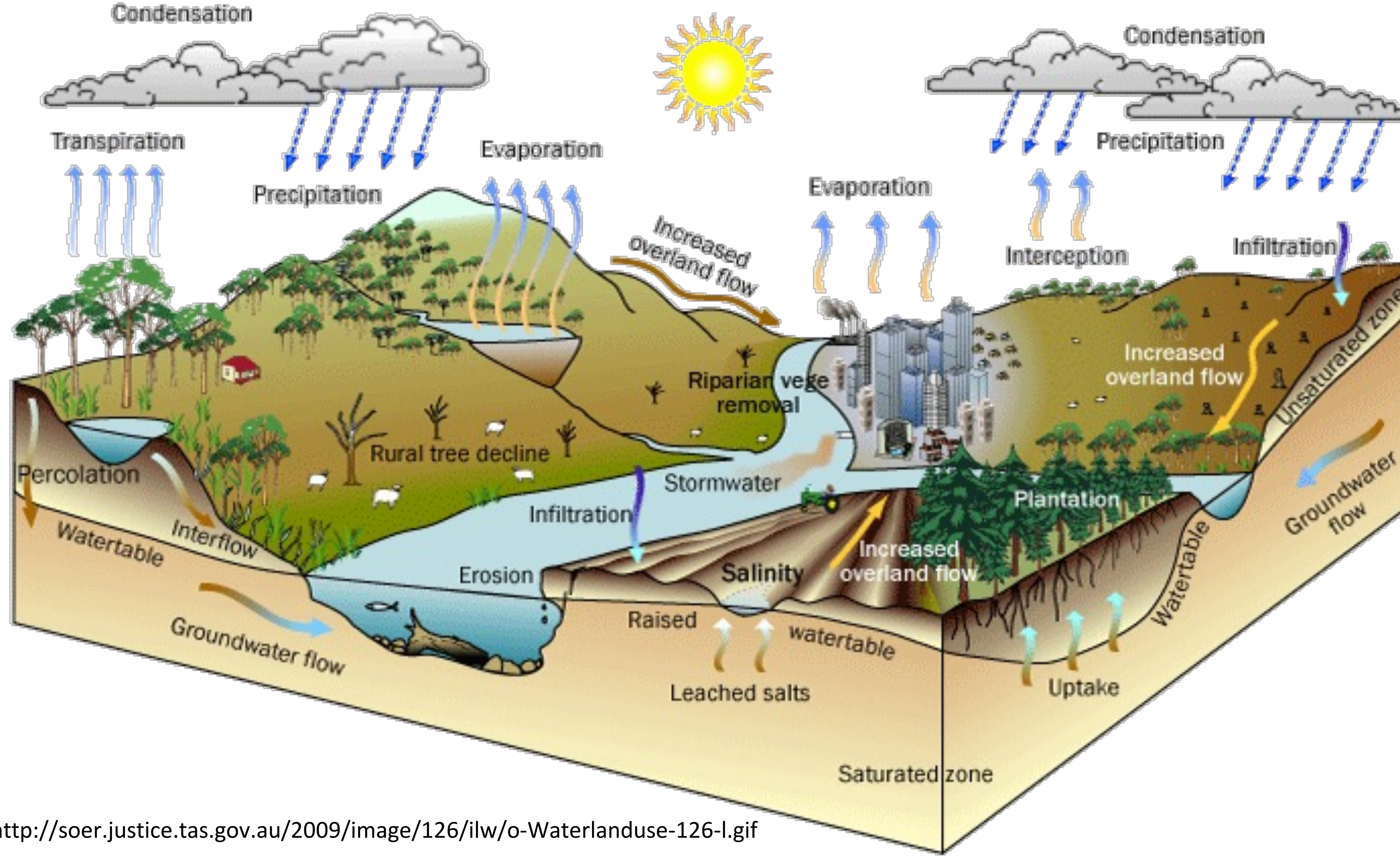
Catchment Hydrogeochemistry

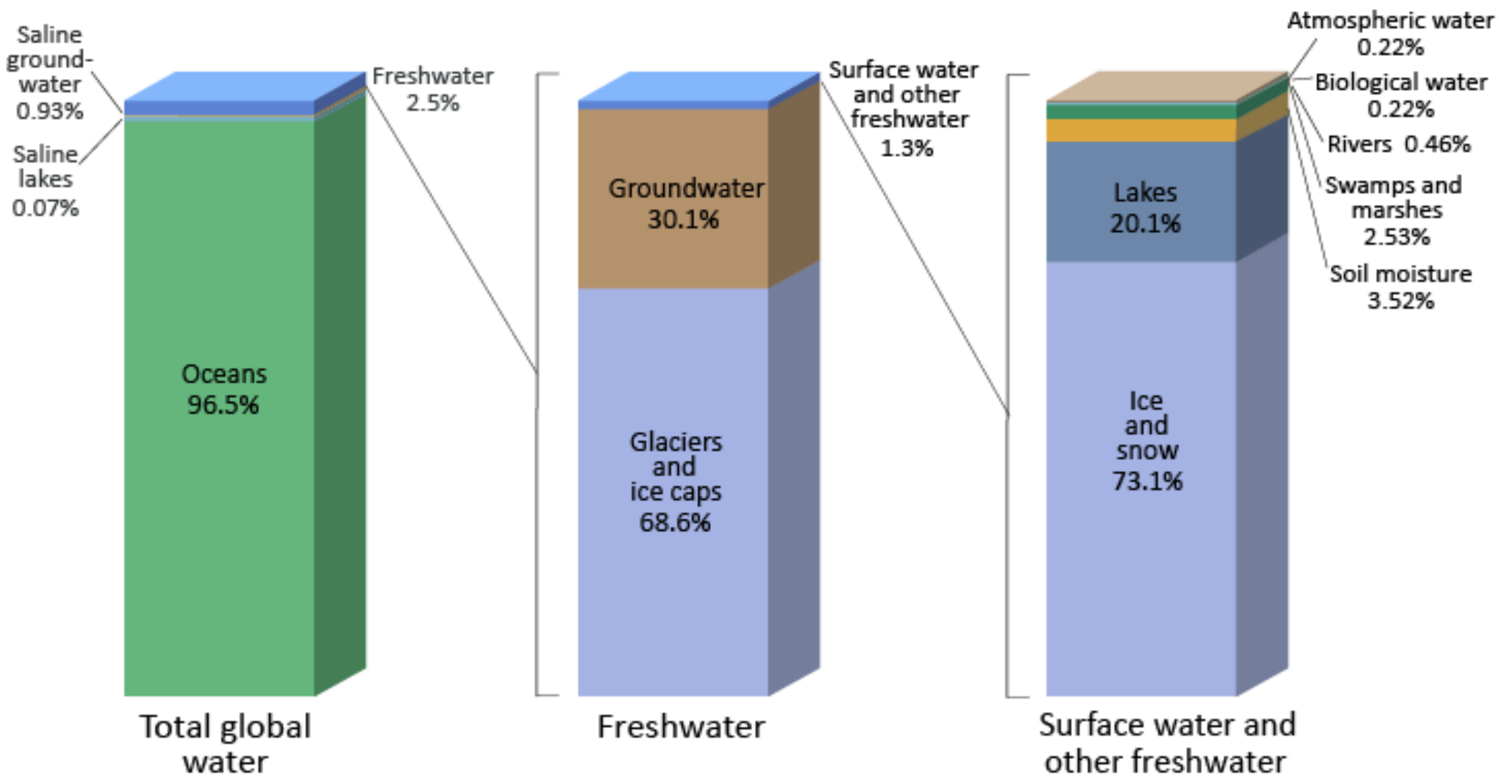
Streams integrate complex biogeochemical processes that occur within a catchment



Source: http://soer.justice.tas.gov.au/2009/image/126/ilw/o-Waterlanduse-126-l.gif

Chemistry of major water reservoirs

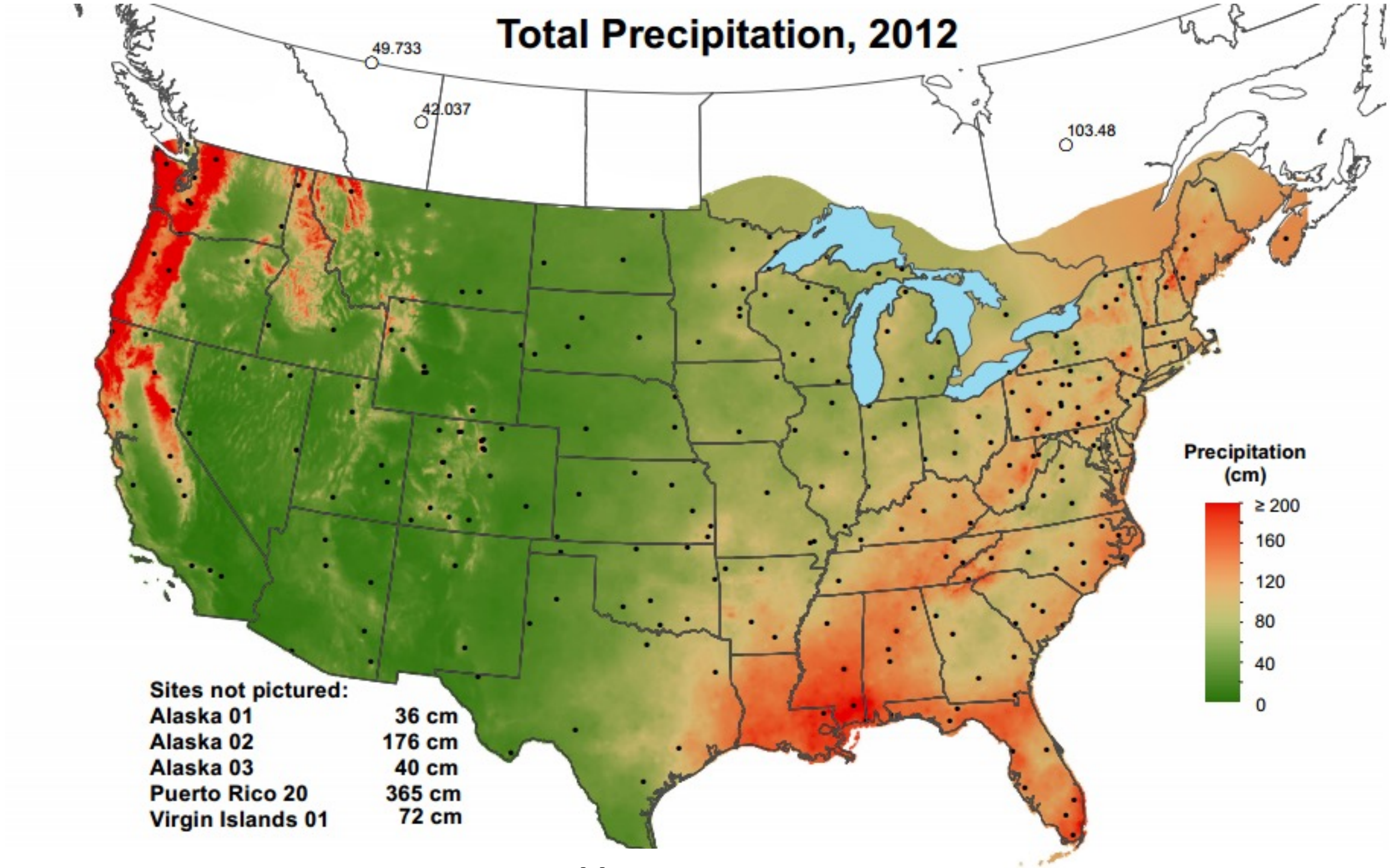
- Rainwater
- Groundwater
- Streams and rivers, lakes
- Oceans



Source: Igor Shiklomanov's chapter "World fresh water resources" in Peter H. Gleick (editor), 1993, Water in Crisis: A Guide to the World's Fresh Water Resources.

Precipitation is dilute (low solute concentrations)

- ***Major source of Cl^-, SO_4^{2-}, NO_3^- and NH_4^+ to surface waters***



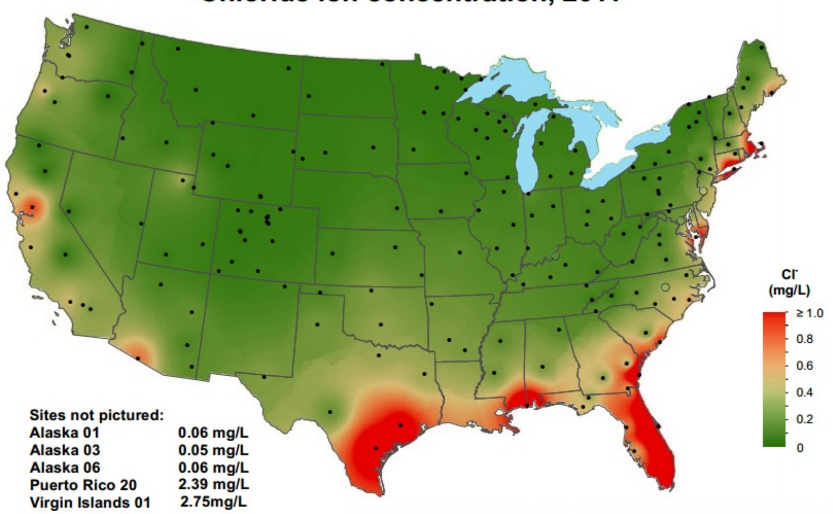
Maps and data available from https://nadp.slh.wisc.edu

Meteoric water refers to water derived from the atmosphere in recent geologic times

Precipitation chemistry varies by location due to differences in dominant inputs

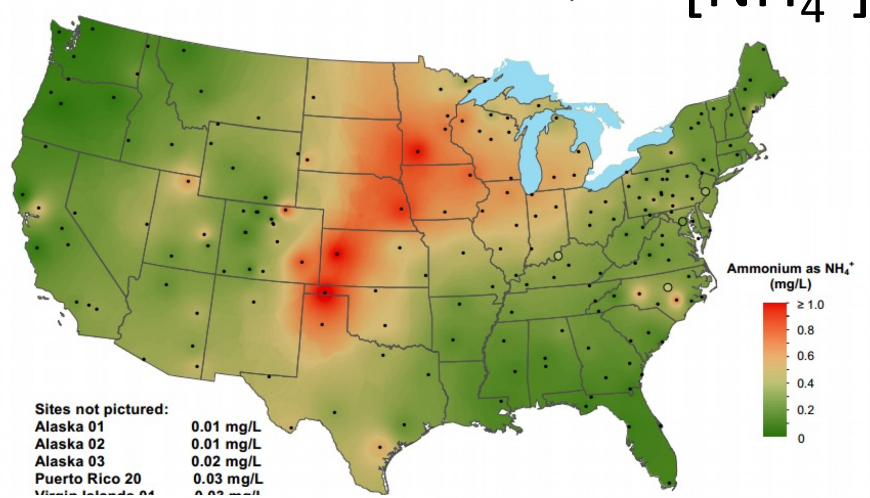
[Cl^-]

Chloride ion concentration, 2011



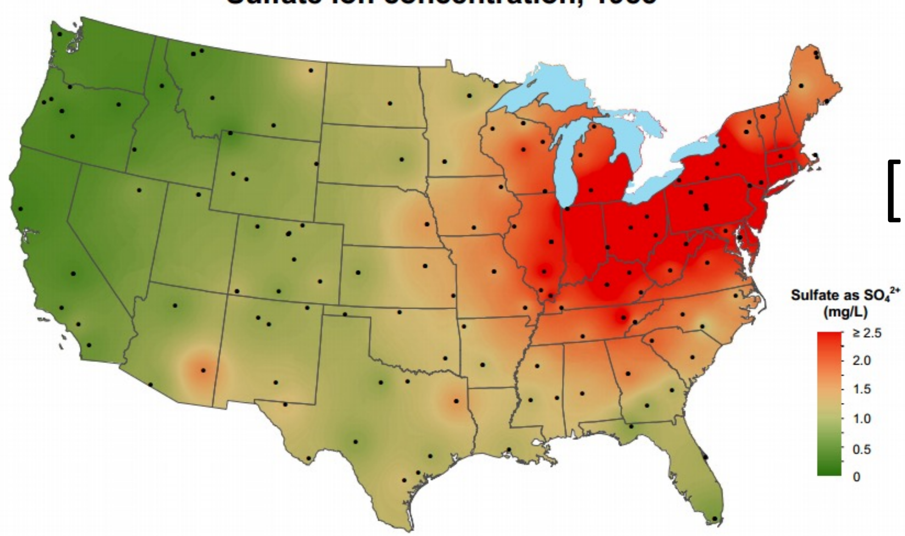
Ammonium ion concentration, 2012

[NH_4^+]



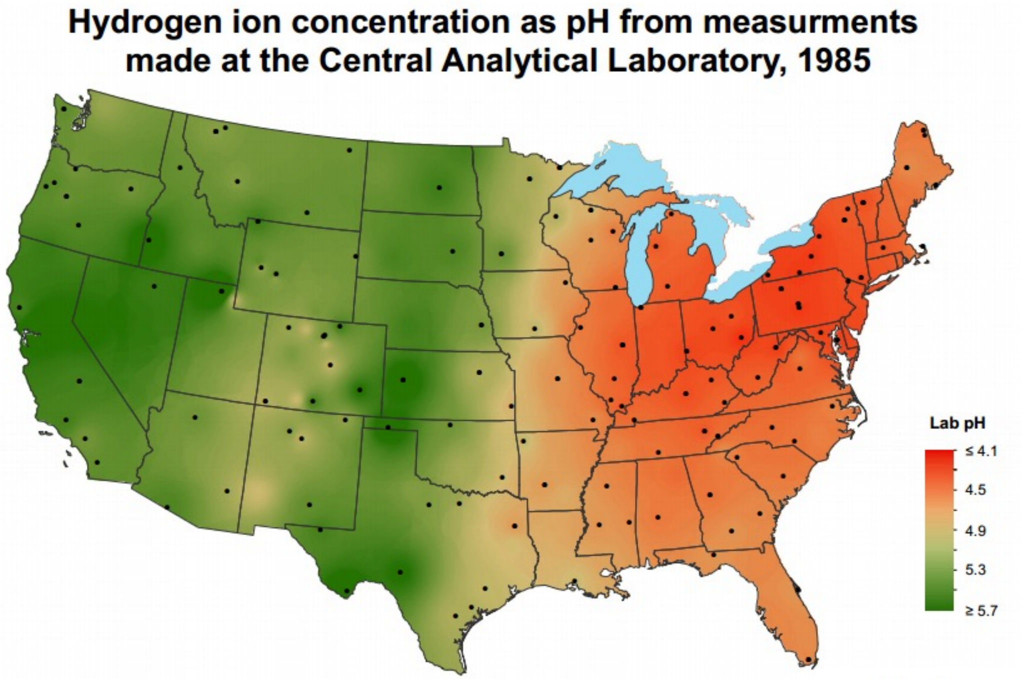
National Atmospheric Deposition Program/National Trend:
http://nadp.isws.illinois.edu

Sulfate ion concentration, 1985

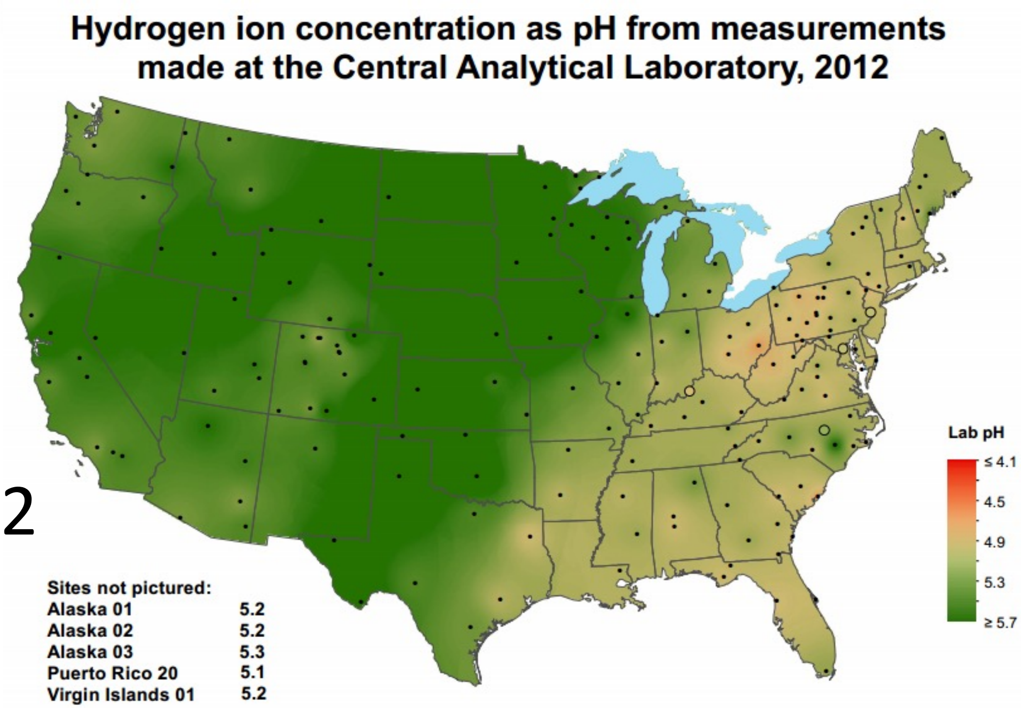


[SO_4^{2-}]

Precipitation chemistry has changed over time; e.g., rainwater pH



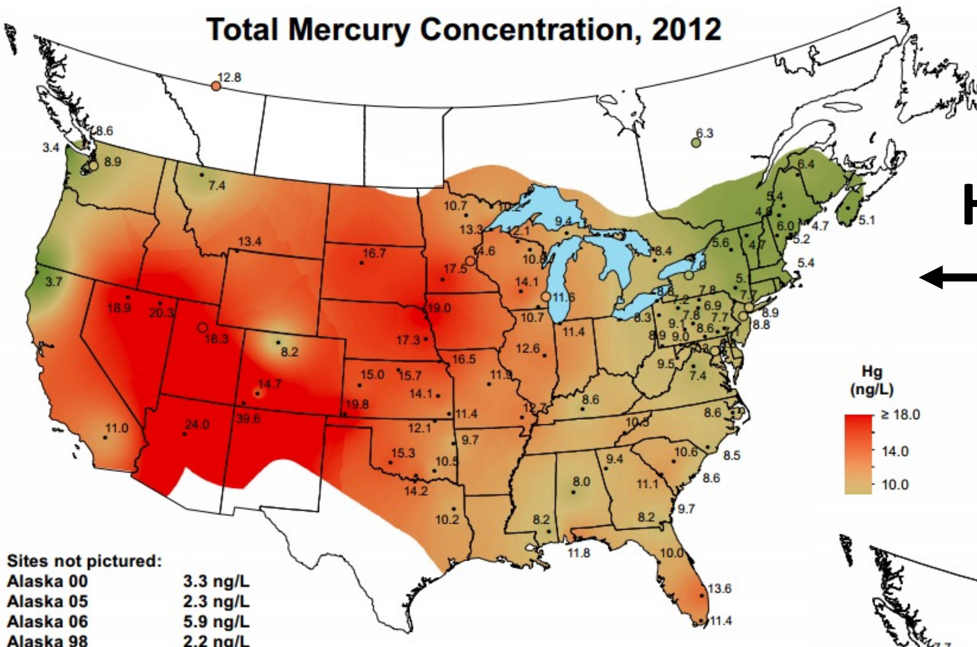
Rain pH in 1985



Rain pH in 2012

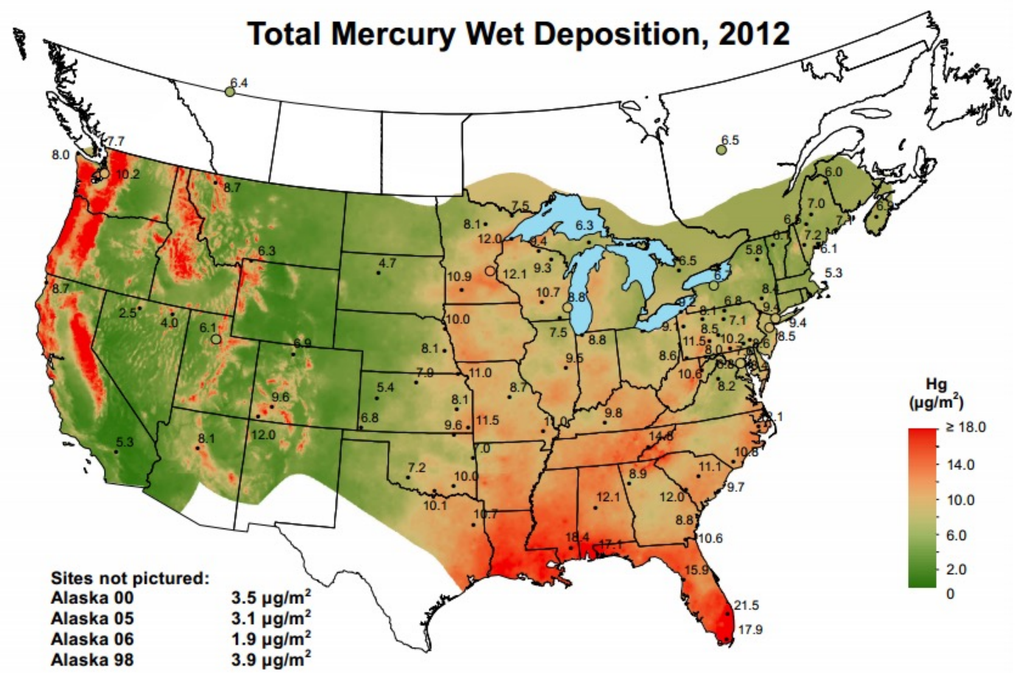
Atmospheric Deposition = Precipitation x Concentration

(mass/area) = (volume/area) x (mass/volume)



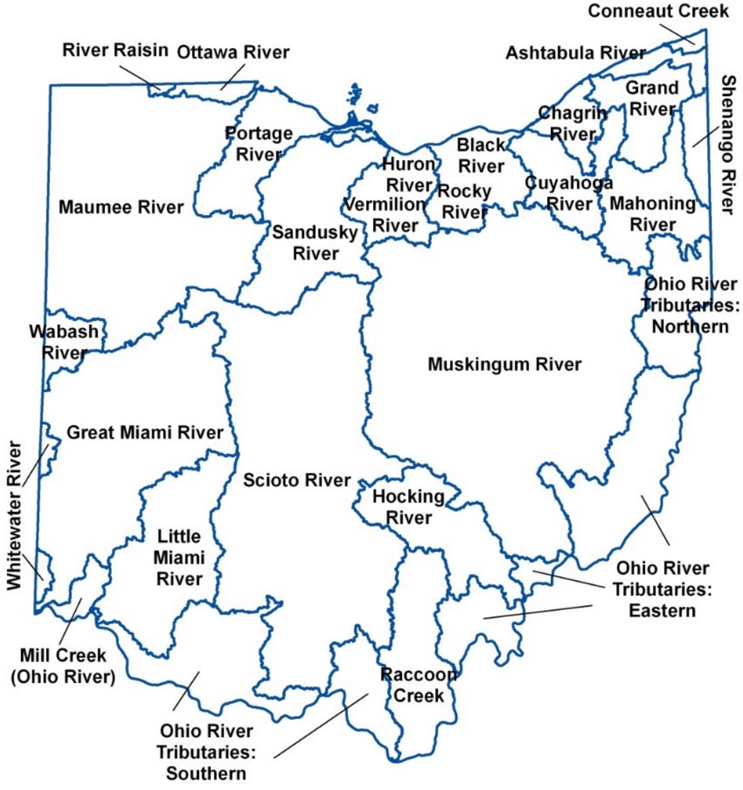
Hg concentration (ng/L)

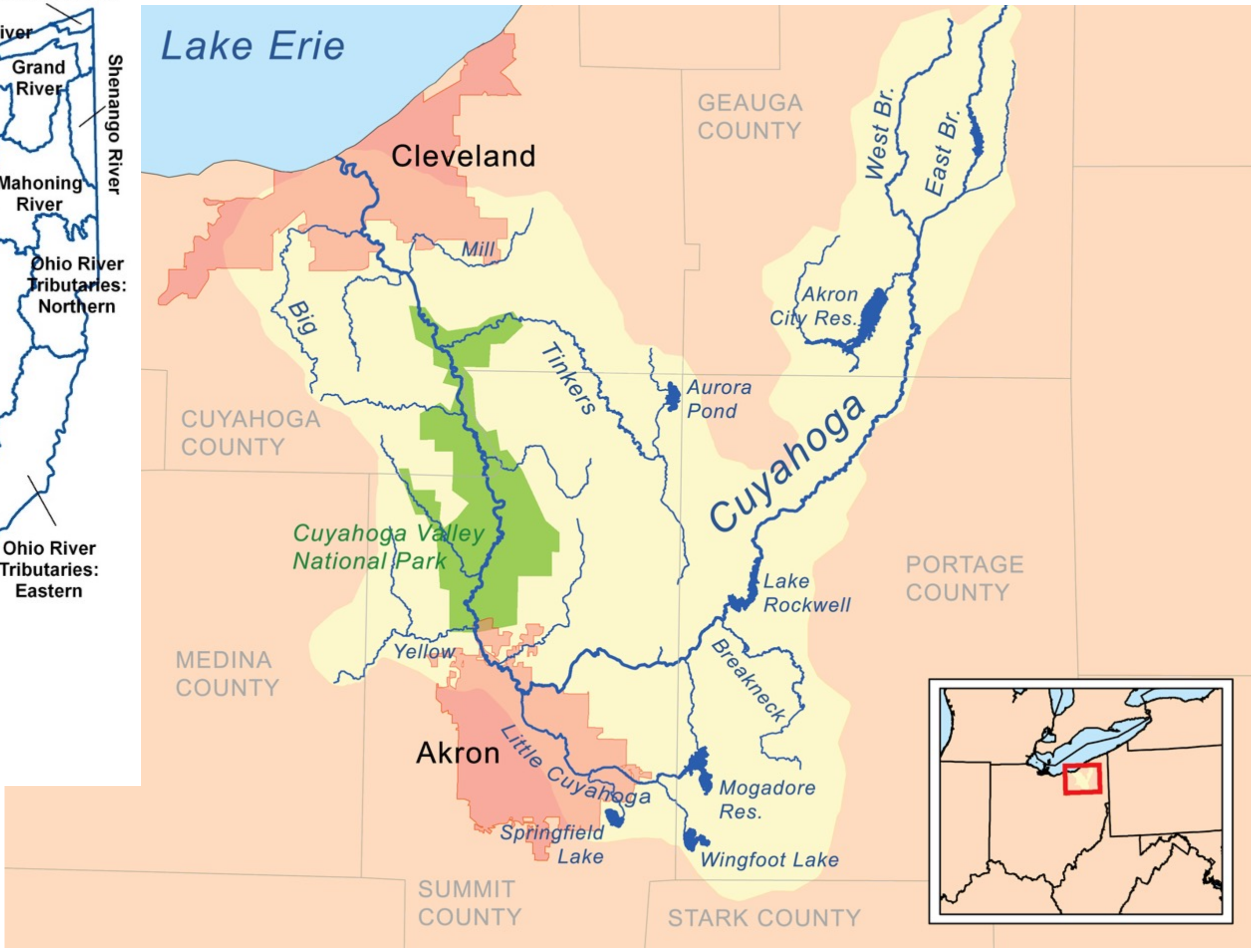
Hg deposition (µg/m²)



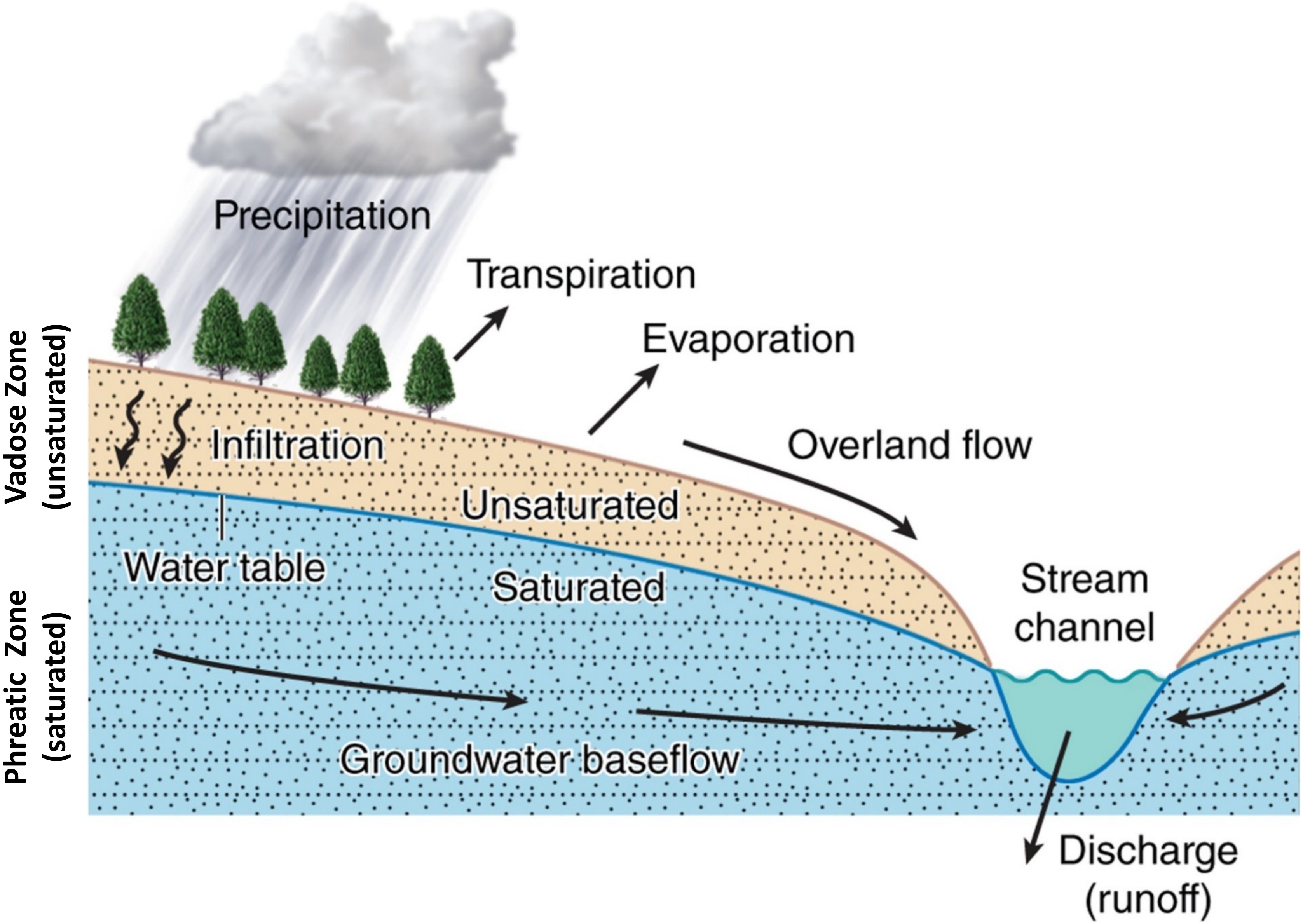
Watershed

- An area of land over which all water that falls into it drains into the same location
- also referred to as drainage basin, catchment

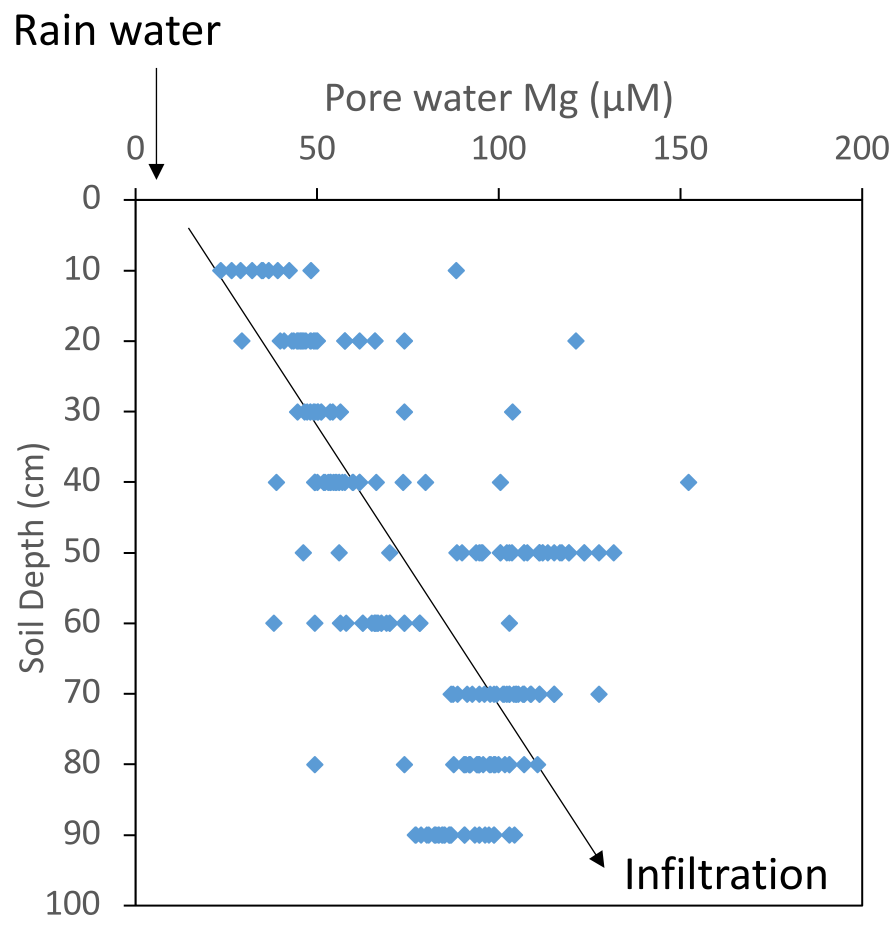




Water that is deposited to the land surface can travel to the stream through various flow paths

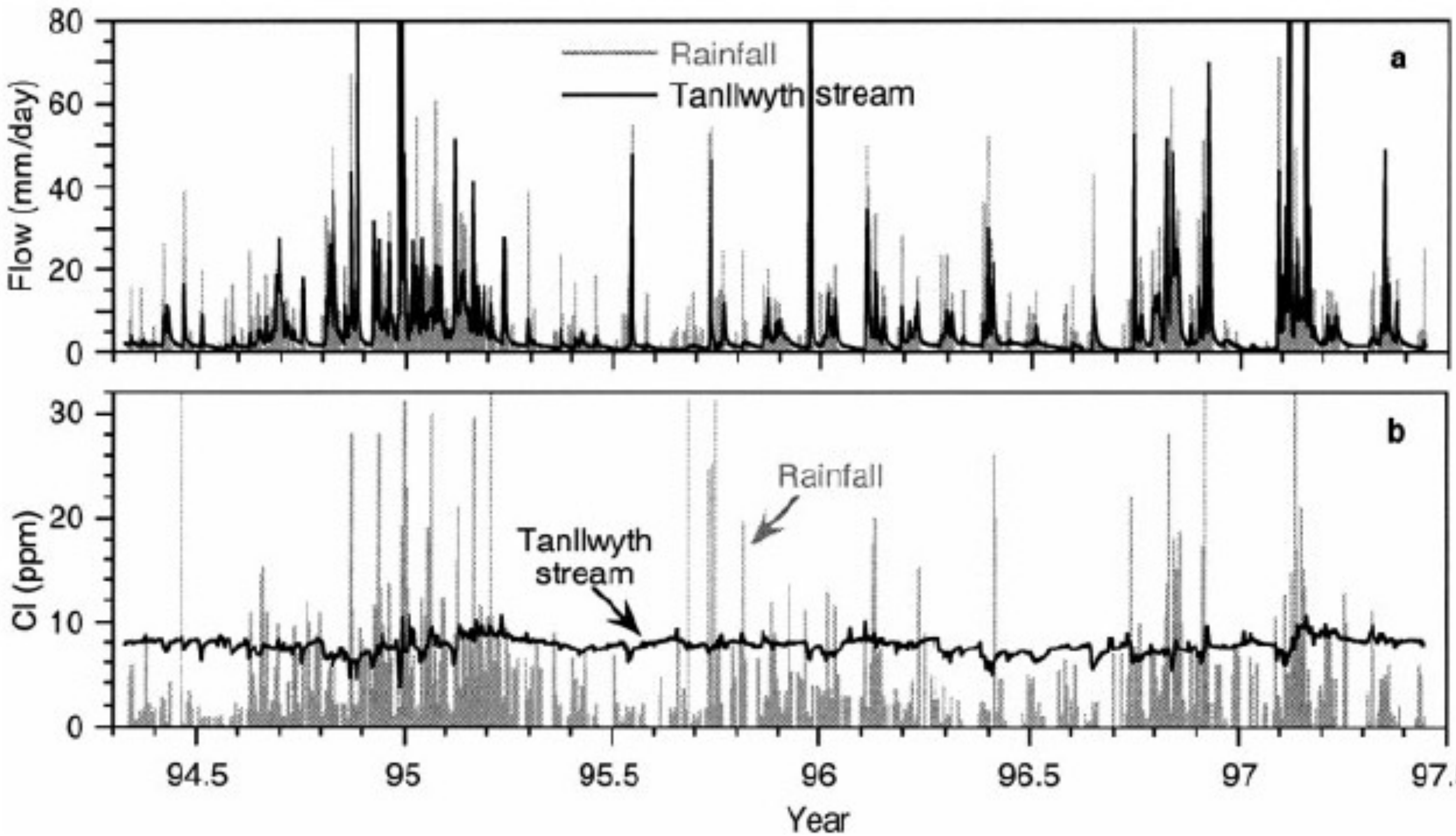


Infiltration: Meteoric water acquires solutes from the dissolution of soil minerals as it travels through watersheds



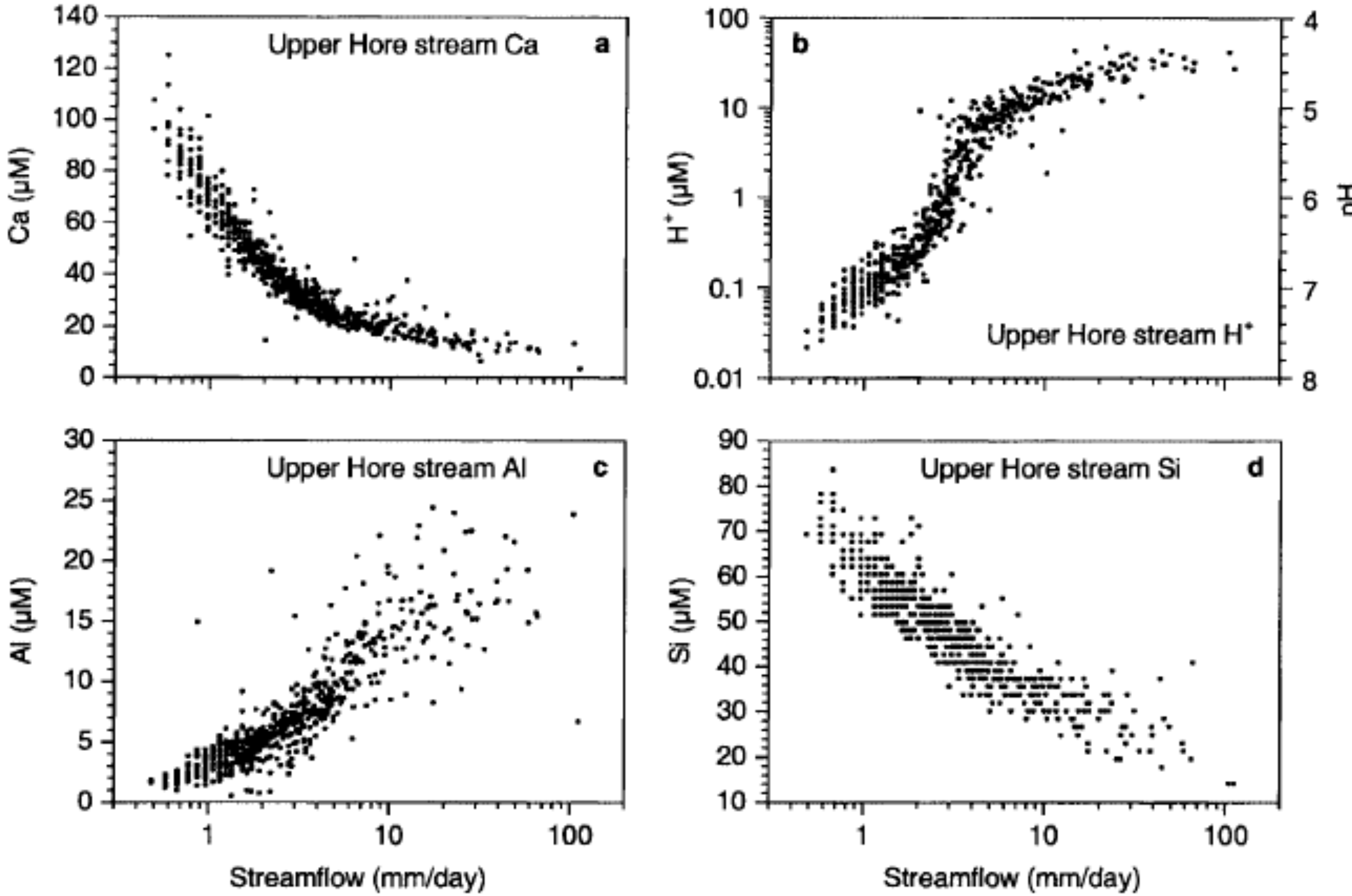
Pore water chemistry reflects silicate mineral dissolution in soil

Solute concentrations in streams remain relatively stable despite large fluctuations in rainfall and stream discharge



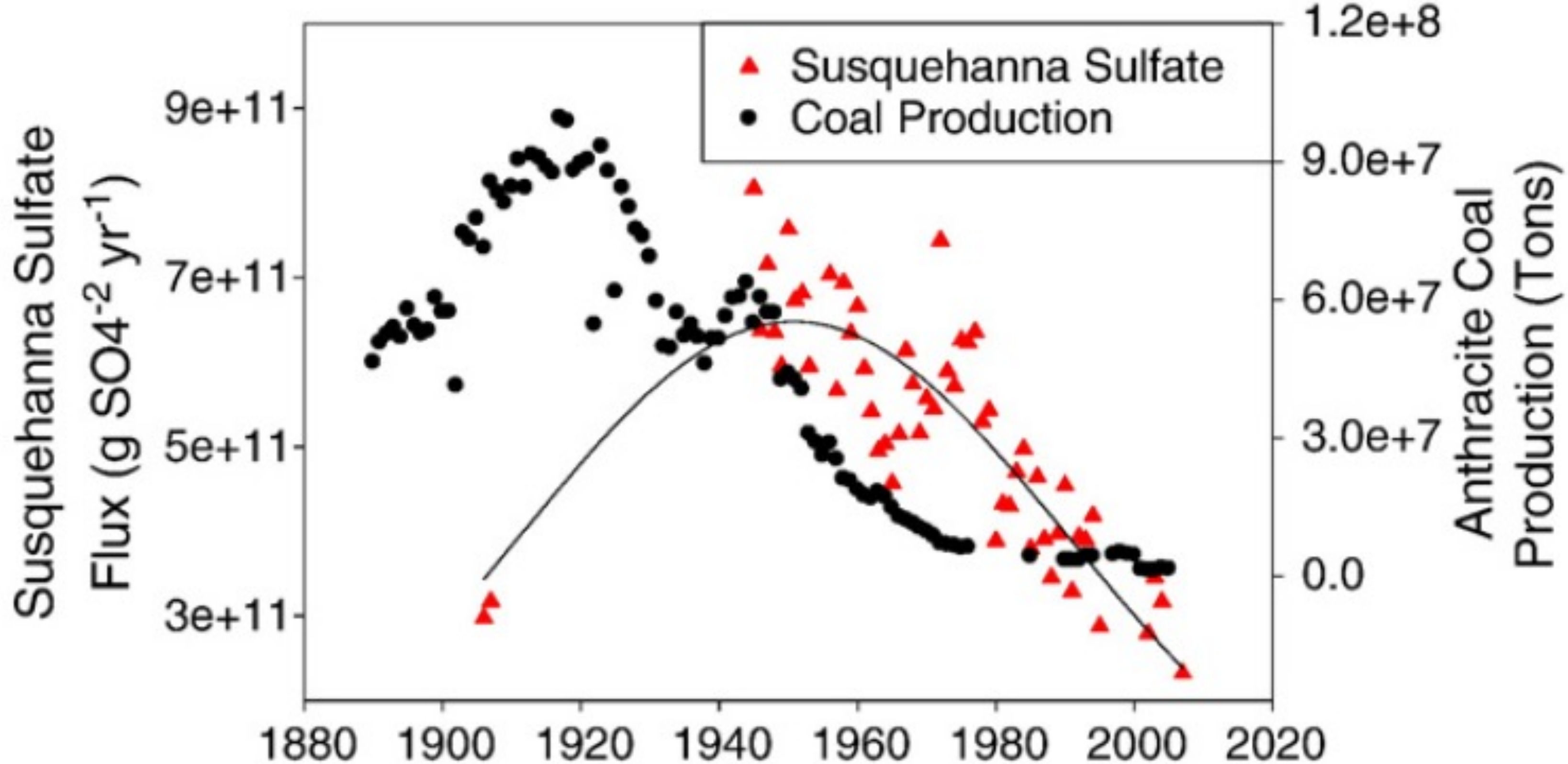
Kirchner (2003) Hydrol. Processes

Solute concentrations can also increase or decrease in response to changes in discharge depending on sources



Kirchner (2003) Hydrol. Processes

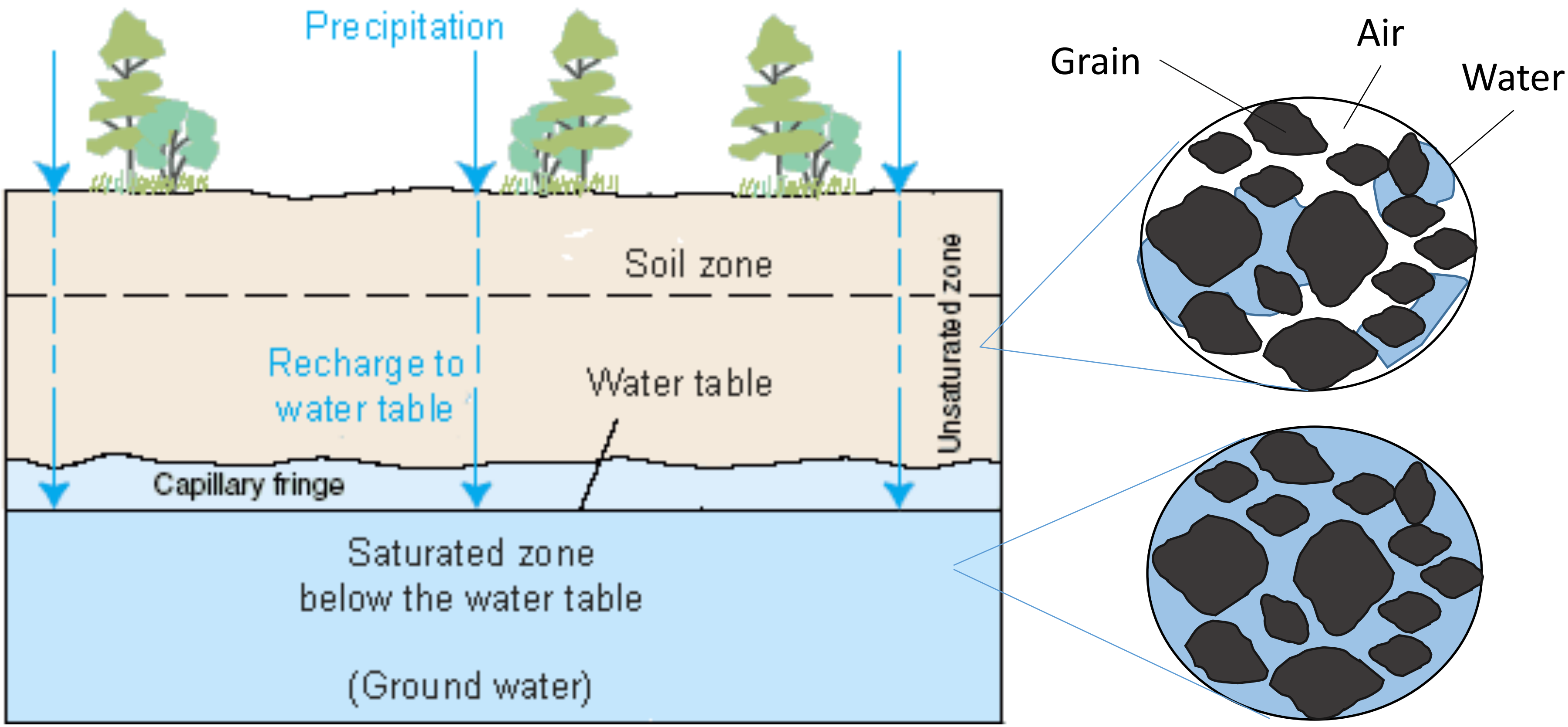
Solute concentrations in streams have changed over time in response to changing industrial inputs



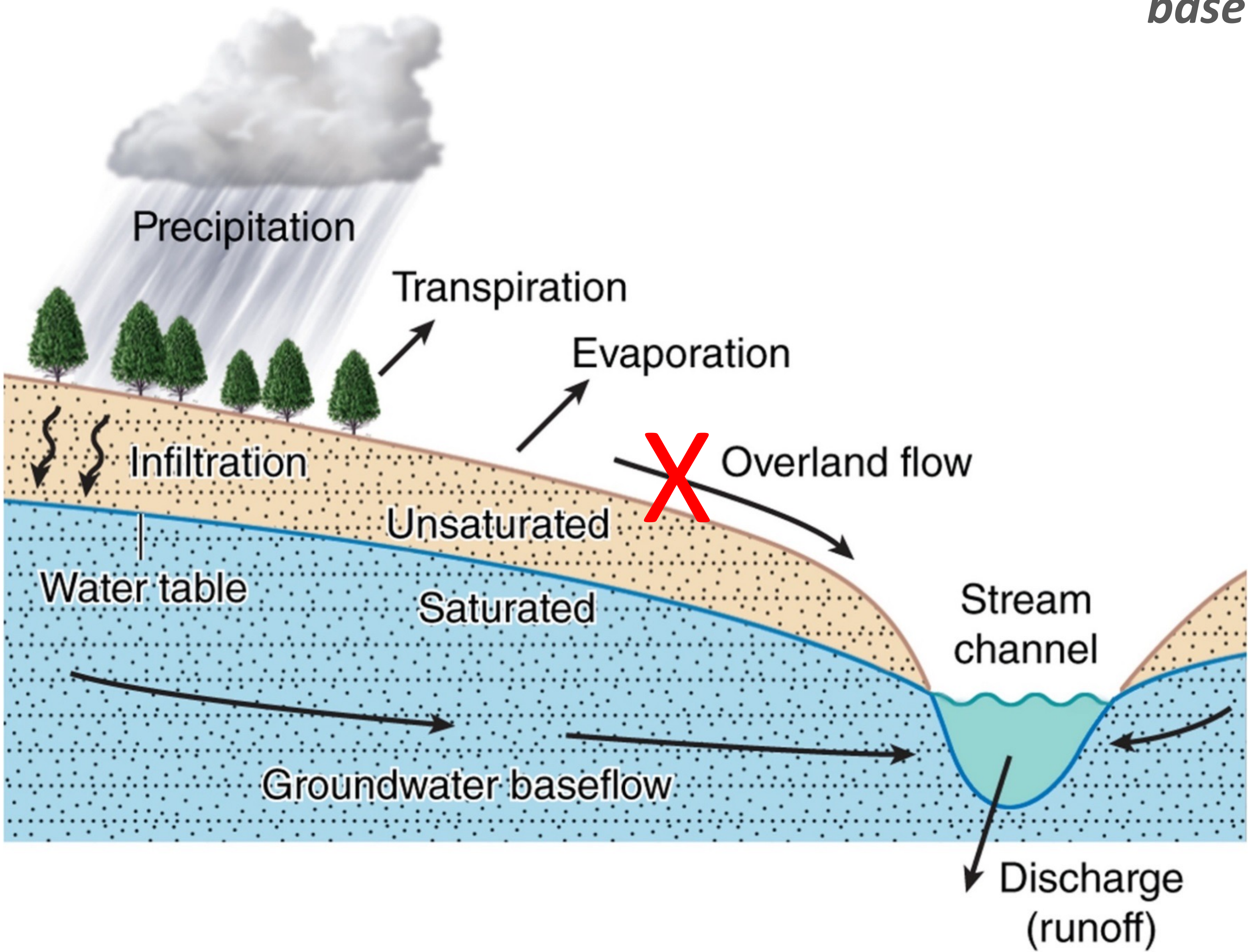
Raymond and Oh (2009) EPSL

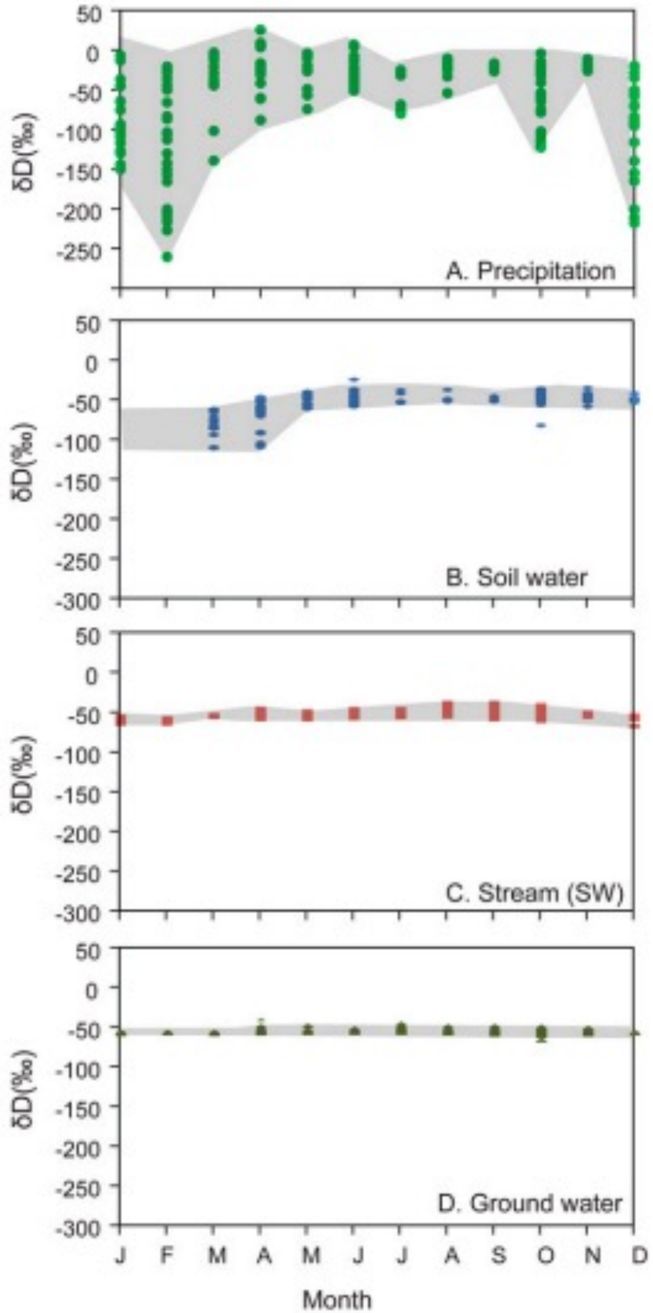
Groundwater

- **Water that infiltrates the unsaturated zone and is stored in the void spaces of rocks below the *water table*, defined as the depth at which these voids spaces are persistently, completely filled with water**



Groundwater contributes water to streams during periods when flow through the vadose zone is limited (e.g., summer); termed *base flow*





Jin et al. (2011) Vadose Zone Journal

← Groundwater integrates water chemistry over space and time and generally has a longer residence time than water in soils or streams

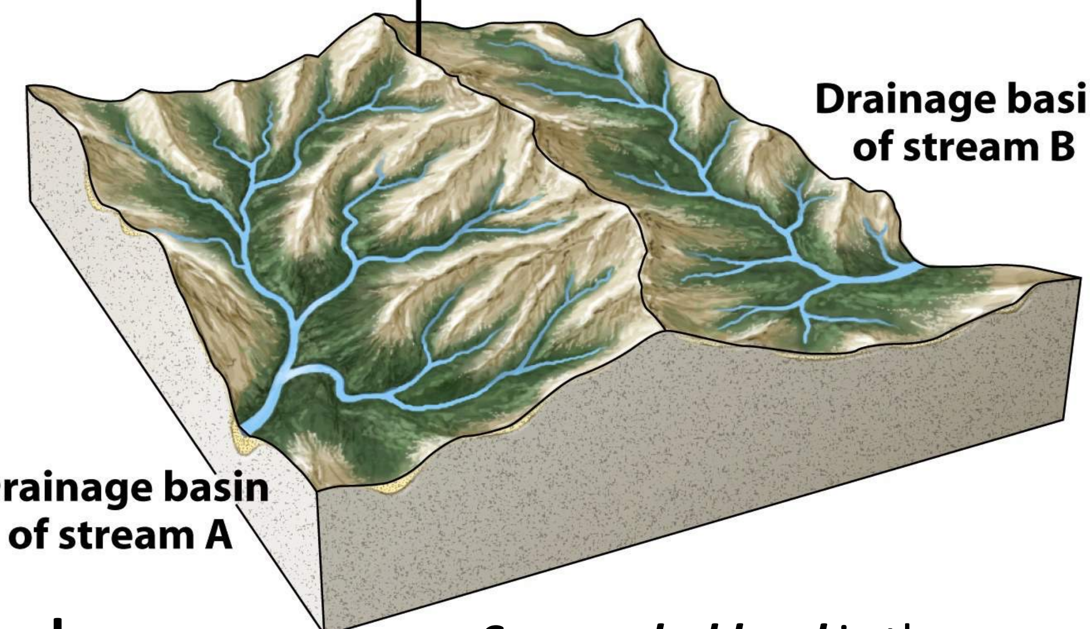
- Contains solutes derived from the vadose zone as well as solutes dissolved from deep lithological units (e.g. carbonates)

- Some chemicals are filtered out of the water during soil infiltration (e.g., contaminants)

Streams and Rivers

- Streams integrate water sources, including direct precipitation, overland flow, water that infiltrates through the soil, and groundwater, over their drainage area

- ***Discharge*** (m^3/s) is the volume of water that travels through a stream in a given unit of time
- ***Dissolved Load*** is the total mass of solutes transported in the stream per unit time (e.g., mol/s)

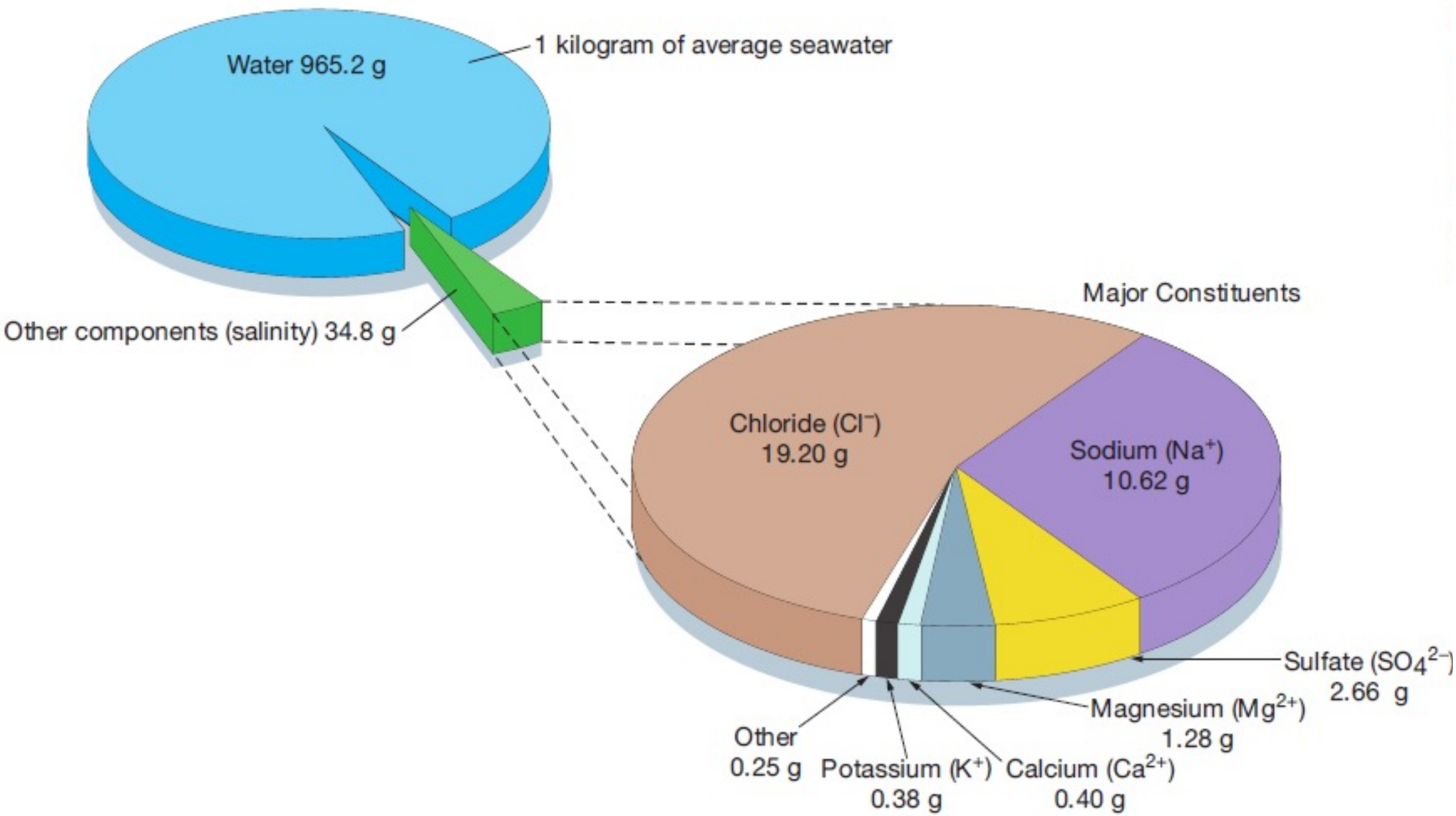


Load = Concentration x Discharge

- ***Suspended load*** is the mass of sediment transported in the stream per unit time

Terrestrial inputs to the oceans

- Watersheds deliver solutes from continents to the oceans
- Dissolved loads derive from sources including weathering of silicate and carbonate minerals



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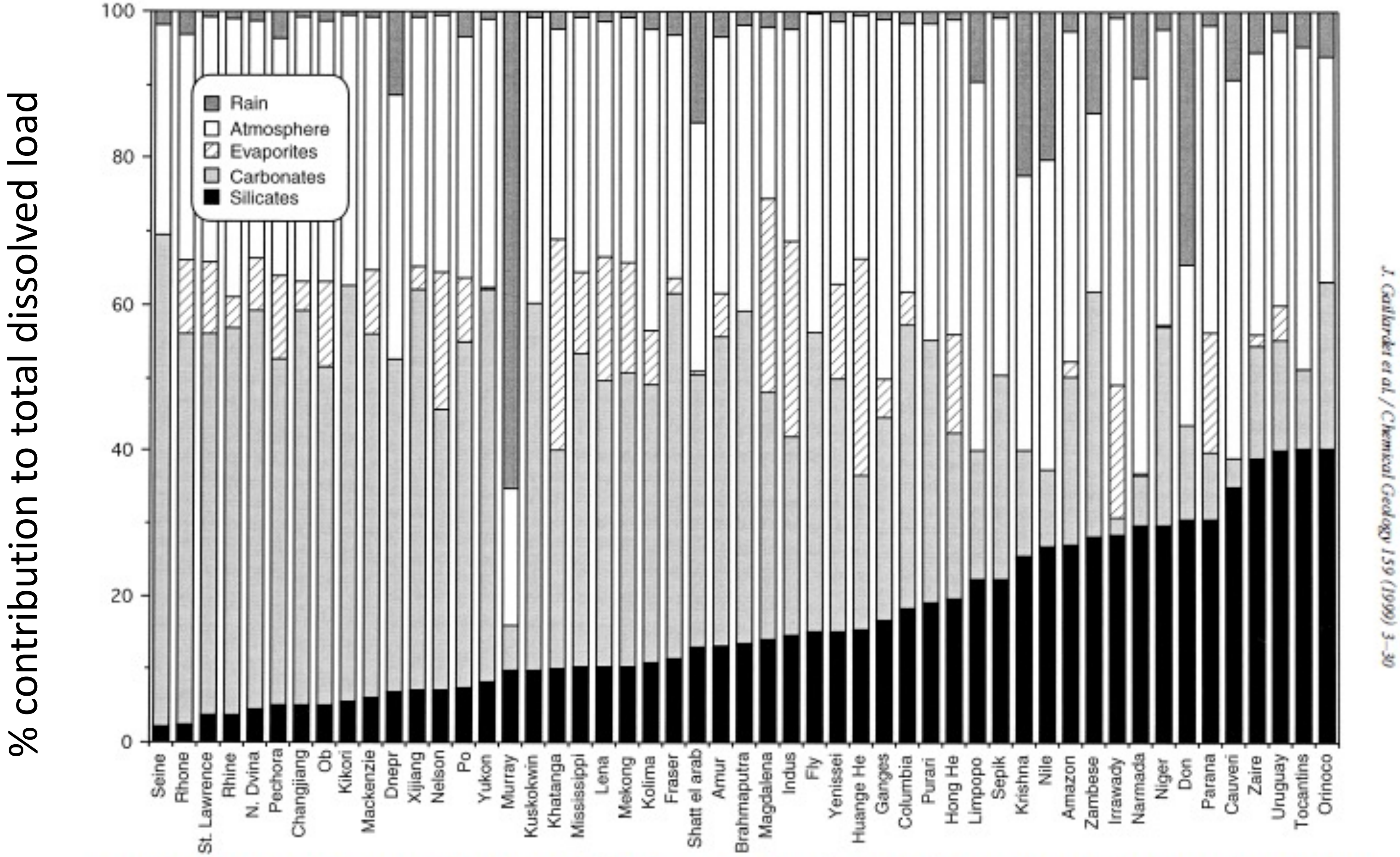


Fig. 5. Diagram showing for each river of this study, the contribution (as % of concentrations in mg l^{-1} of river water) of the different reservoirs. Rivers are ranked from left to right following the contribution of silicate weathering to total dissolved load. The atmospheric contribution corresponds to bicarbonate ions of atmospheric origin derived from carbonate and silicate weathering. The rain contribution corresponds principally to Na and Cl ions derived from seasalt dissolution.

Online databases for water chemistry

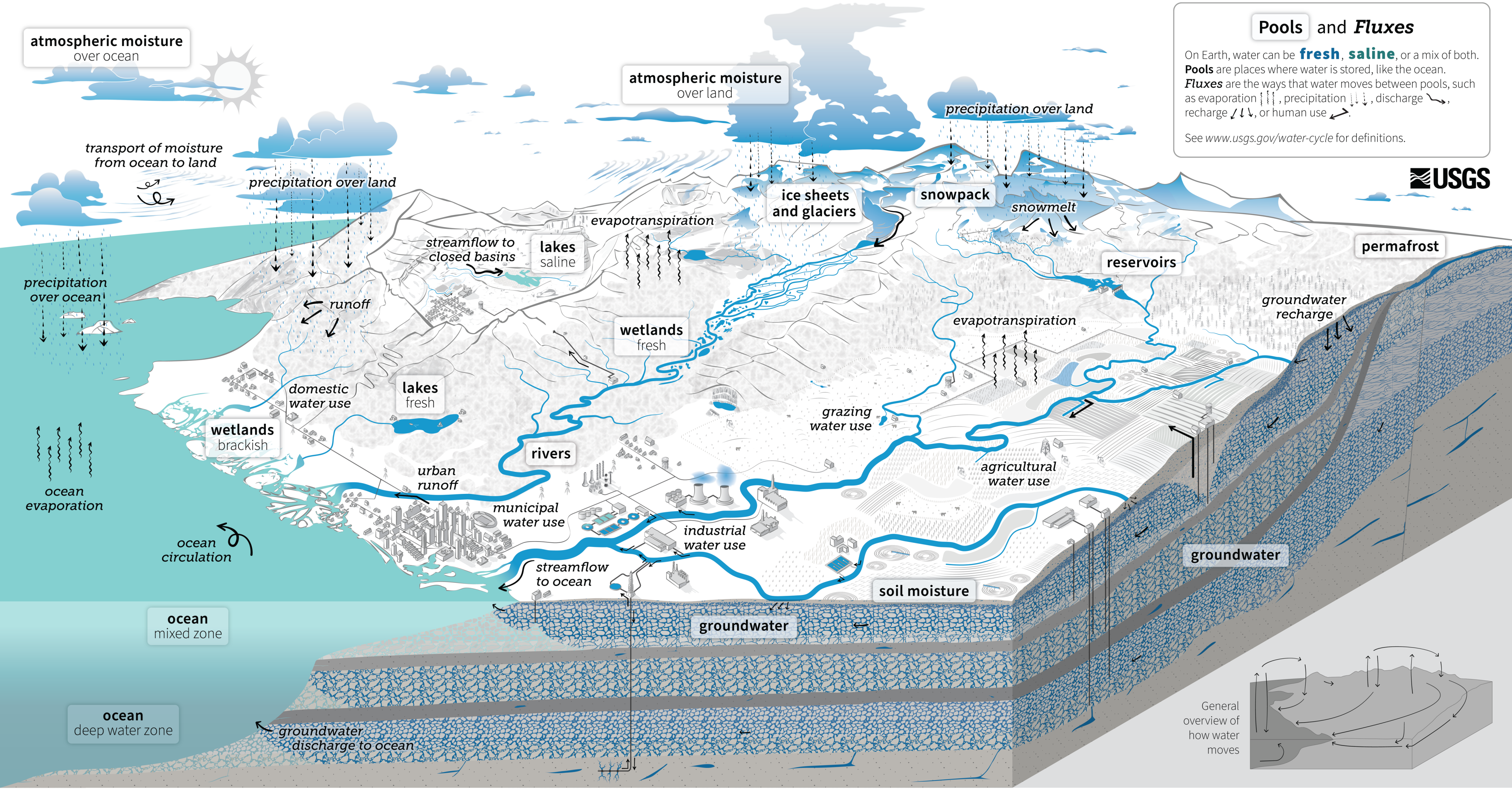
USGS National Water Information System
http://waterdata.usgs.gov/nwis

STORET: water quality data related to pollution (EPA)
https://www.epa.gov/waterdata/storage-and-retrieval-and-water-quality-exchange

Water Quality Portal
http://waterqualitydata.us/

National Atmospheric Deposition Program
https://nadp.slh.wisc.edu

HydroClient (CUAHSI)
http://data.cuahsi.org/



The Water Cycle

The water cycle describes where water is on Earth and how it moves. Water is stored in the atmosphere, on the land surface, and below the ground. It can be a liquid, a solid, or a gas. Liquid water can be fresh, saline (salty), or a mix (brackish). Water moves between the places it is stored. Water moves at large scales and at very small scales. Water moves naturally and because of human actions. Human water use affects where water is stored, how it moves, and how clean it is.

Pools store water. 96% of all water is stored in **oceans** and is saline. On land, saline water is stored in **saline lakes**. Fresh water is stored in liquid form in **freshwater lakes**, artificial **reservoirs**, **rivers**, and **wetlands**. Water is stored in solid, frozen form in **ice sheets** and **glaciers**, and in **snowpack** at high elevations or near the Earth's poles. Water vapor is a gas and is stored as **atmospheric moisture** over the ocean and land. In the soil, frozen water is stored as **permafrost** and liquid water is stored as **soil moisture.** Deeper below ground, liquid water is stored as **groundwater** in aquifers, within cracks and pores in the rock.

Fluxes move water between pools. As it moves, water can change form between liquid, solid, and gas. **Circulation** mixes water in the oceans and transports water vapor in the atmosphere. Water moves between the atmosphere and the surface through **evaporation**, **evapotranspiration**, and **precipitation**. Water moves across the surface through **snowmelt**, **runoff**, and **streamflow**. Water moves into the ground through infiltration and **groundwater recharge**. Underground, groundwater flows within aquifers. It can return to the surface through natural **groundwater discharge** into rivers, the ocean, and from **springs**.

We alter the water cycle. We redirect rivers. We build dams to store water. We drain water from wetlands for development. We use water from rivers, lakes, reservoirs, and groundwater aquifers. We use that water to supply our **homes** and **communities.** We use it for **agricultural** irrigation and **grazing** livestock. We use it in **industrial** activities like thermoelectric power generation, mining, and aquaculture. The amount of water that is available depends on how much water is in each pool (water quantity). It also depends on when and how fast water moves (water timing), how much water we use (water use), and how clean the water is (water quality).

We affect **water quality**. In agricultural and urban areas, irrigation and precipitation wash fertilizers and pesticides into rivers and groundwater. Power plants and factories return heated and contaminated water to rivers. Runoff carries chemicals, sediment, and sewage into rivers and lakes. Downstream from these sources, contaminated water can cause harmful algal blooms, spread diseases, and harm habitats. **Climate change** is affecting the water cycle. It is affecting water quality, quantity, timing, and use. It is causing ocean acidification, sea level rise, and more extreme weather. By understanding these impacts, we can work toward using water sustainably.

https://www.usgs.gov/special-topics/water-science-school/science/water-cycle-diagrams

Now let's consider a spherical cow…

Credit: Wikipedia

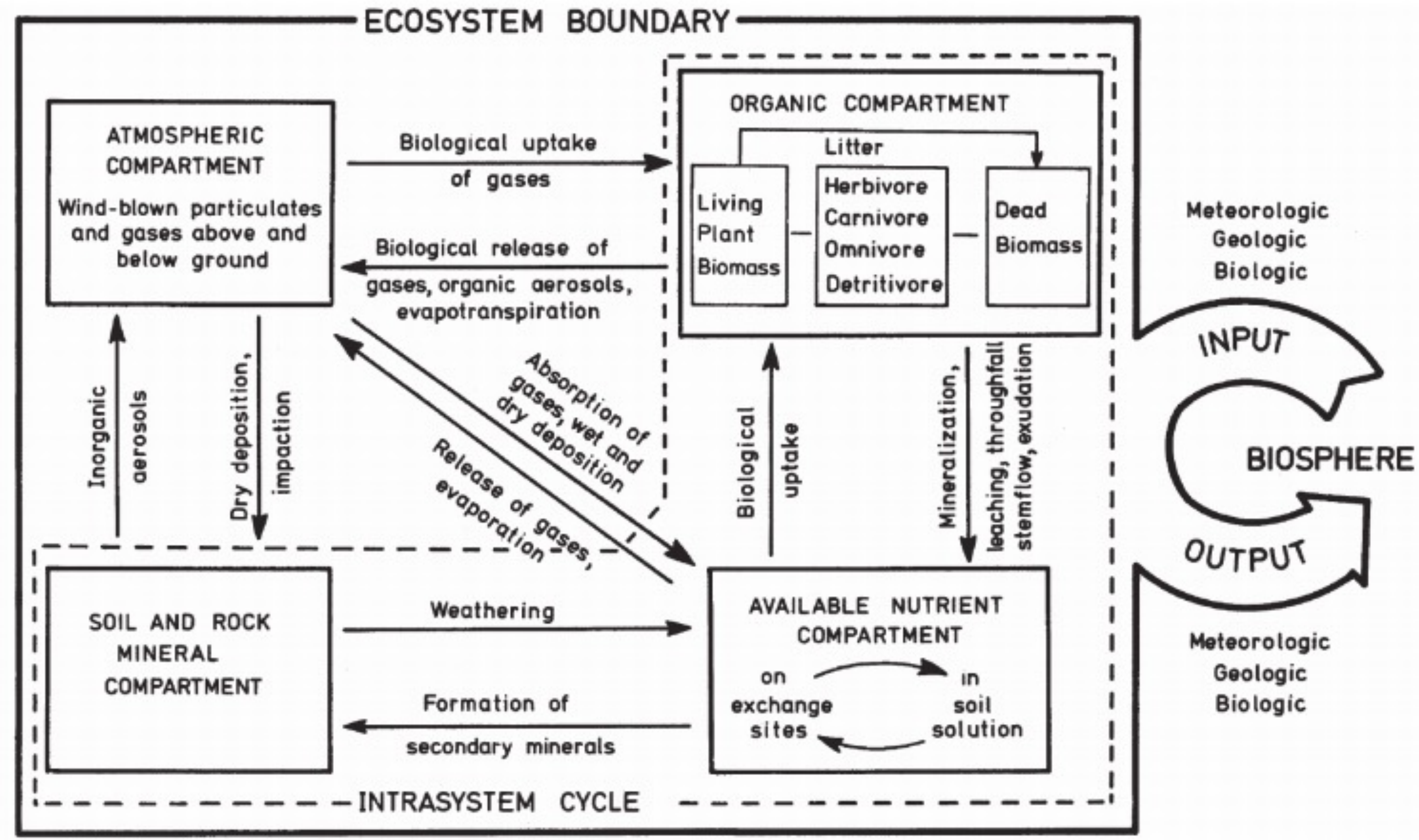
Catchment Mass Balance

A watershed can be represented as one box system with multiple fluxes:

1. define the boundaries of the system
2. define the substance of interest (water or something else)
3. define the fluxes into and out of the system
4. How do you know if the system is at steady-state?

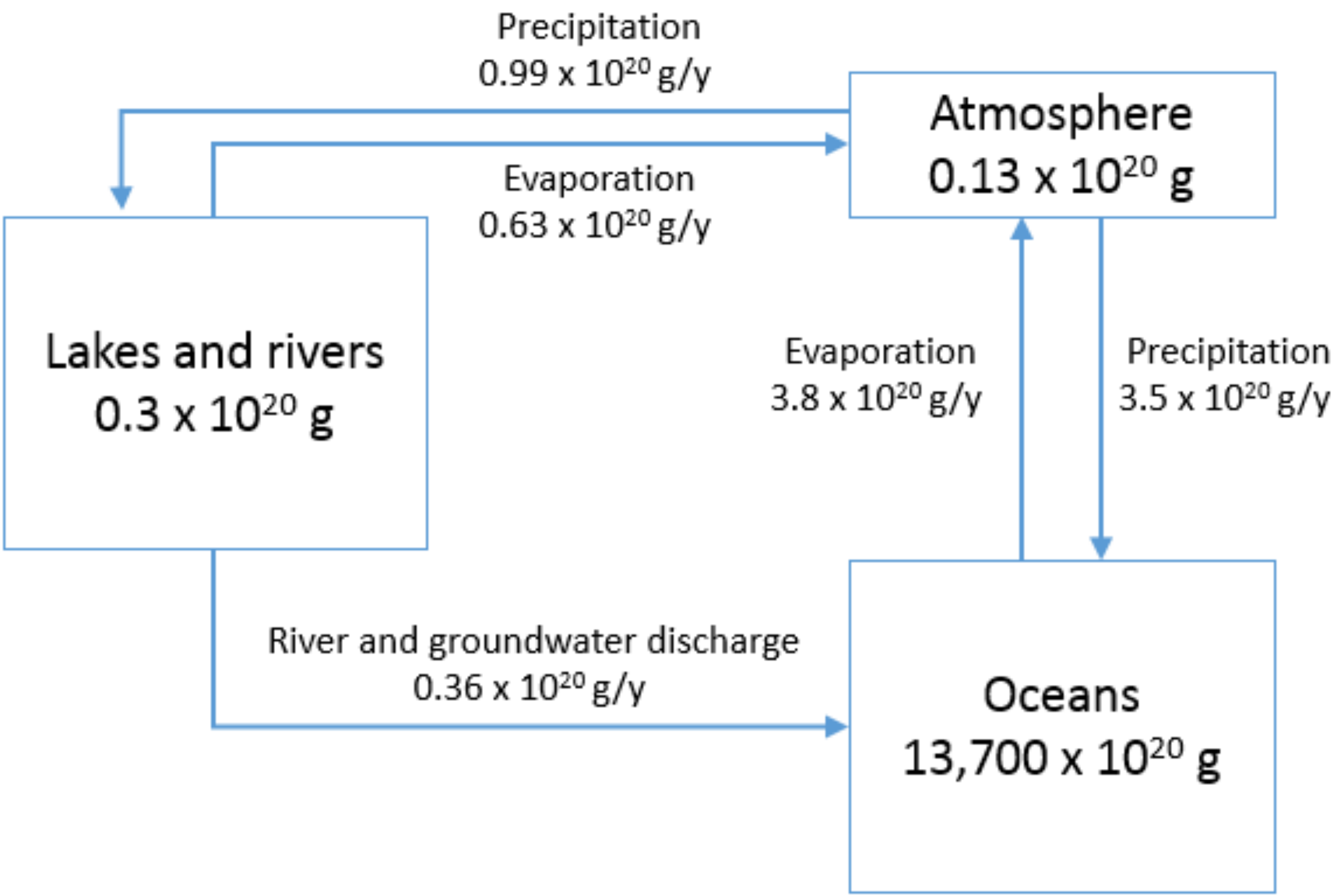
Treating a watershed as a simple box model:

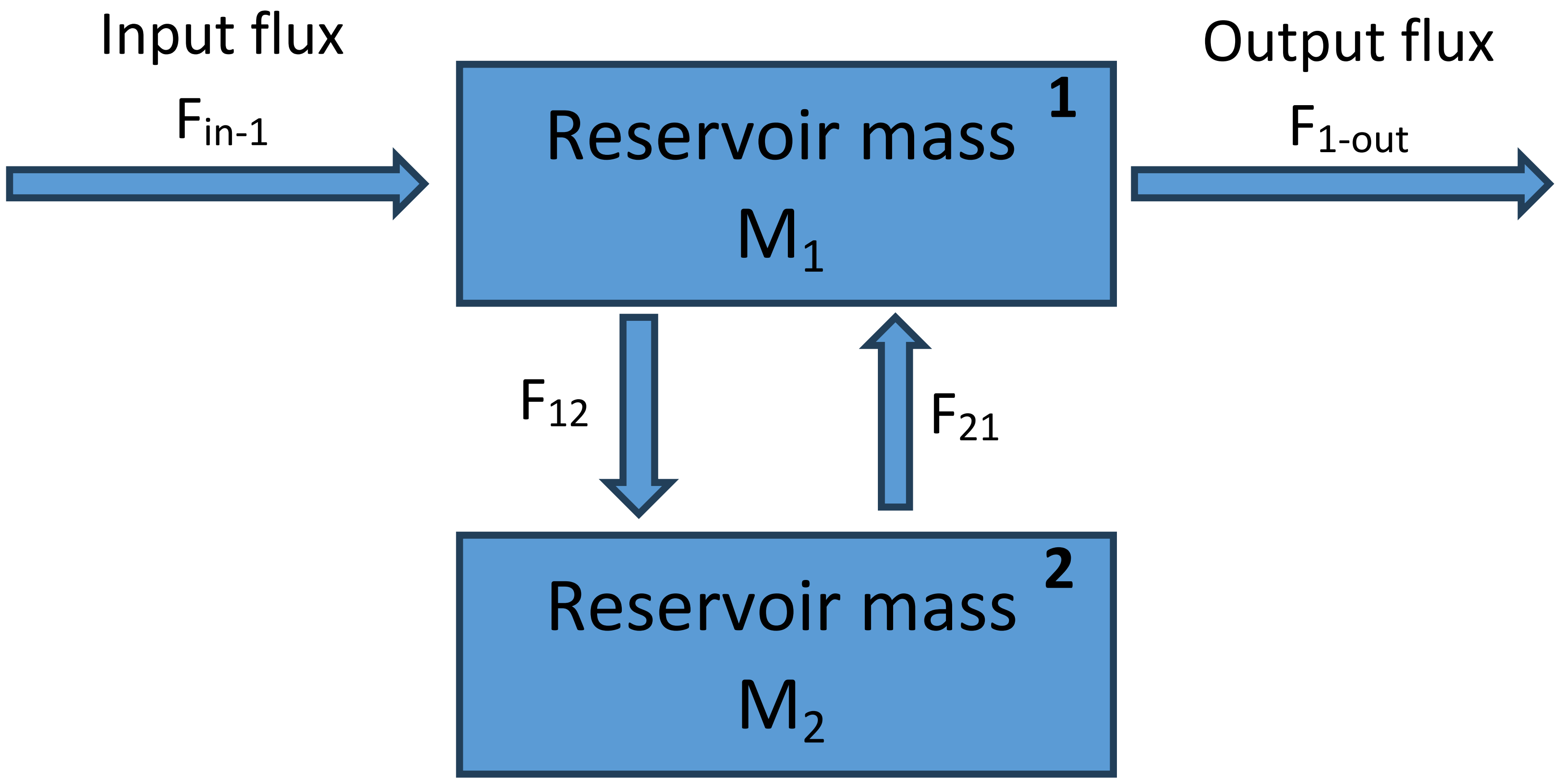
Change in storage (dM/dt) = Input (ΣF_{in}) – Output (ΣF_{out})



Likens et al. 1977

The Hydrologic Cycle: Simple Box Model for Water





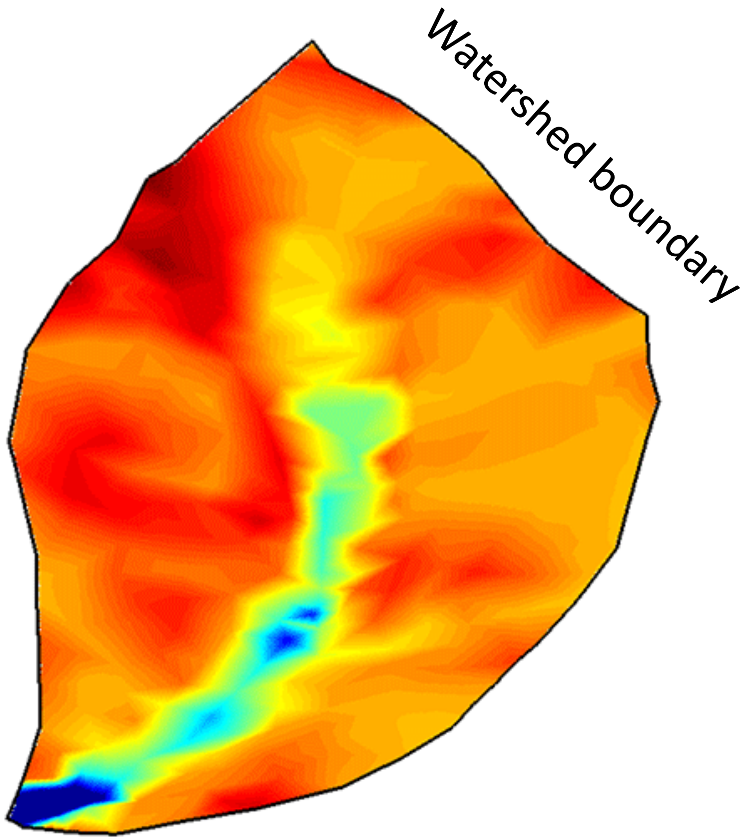
Input flux
F in-1
Output flux
F 1-out
Reservoir mass
M1
1
F12
F21
Reservoir mass
M2
2

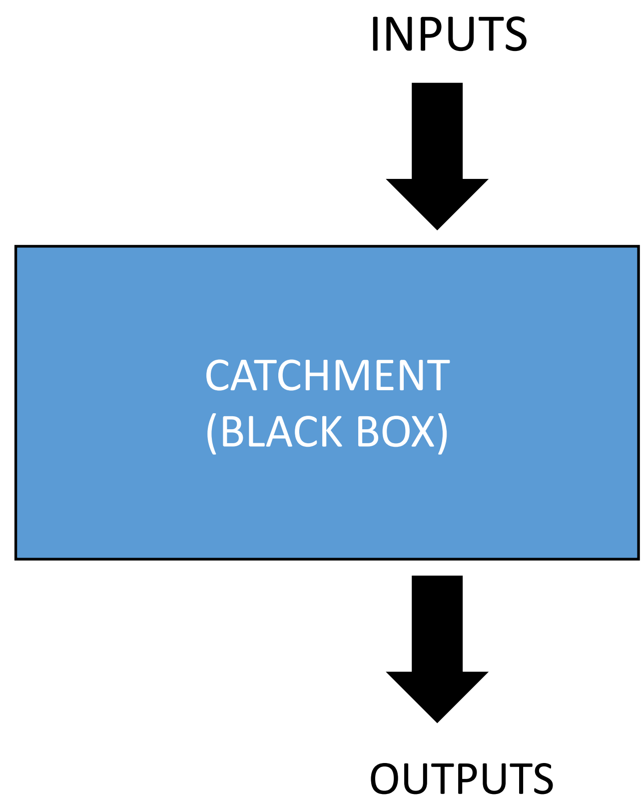
Example 4:

A stable and highly soluble pollutant is dumped into a lake at the rate of 0.16 tonnes per day. The lake volume is 4×10^7 m^3 and the average water flow through the lake is 8×10^4 m^3/d. Ignore evapotranspiration (i.e., the volume of the lake does not change) and assume the pollutant is uniformly mixed in the lake. Assuming the lake is at steady-state with respect to water, what eventual steady-state concentration will the pollutant reach?

Catchment Hydrogeochemistry

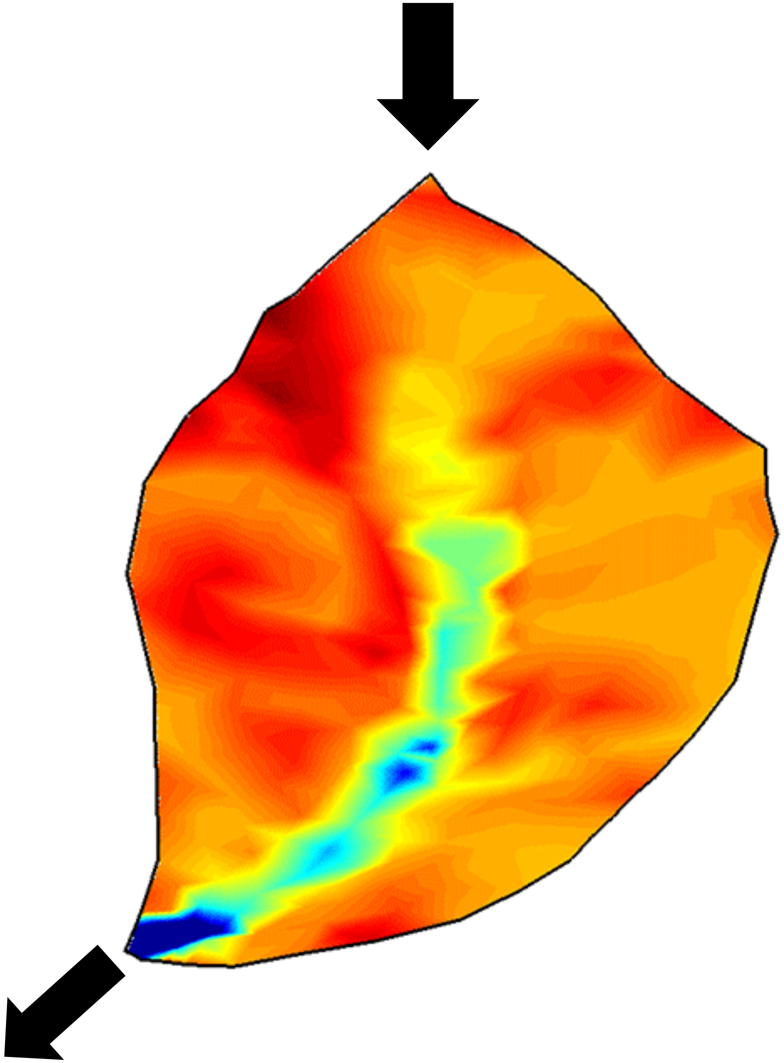
A mass balance approach is commonly used to simply biogeochemical interactions and evaluate major processes occurring within watersheds

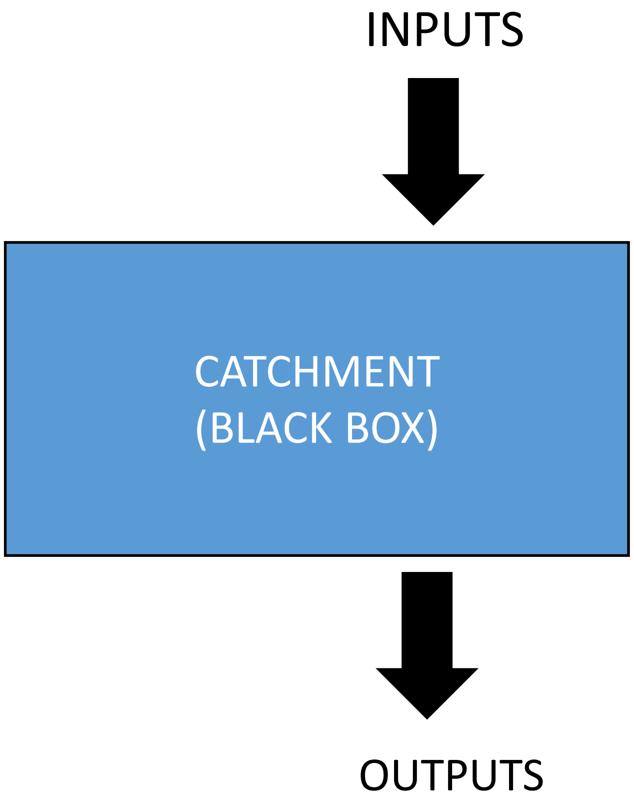




Catchment Hydrogeochemistry

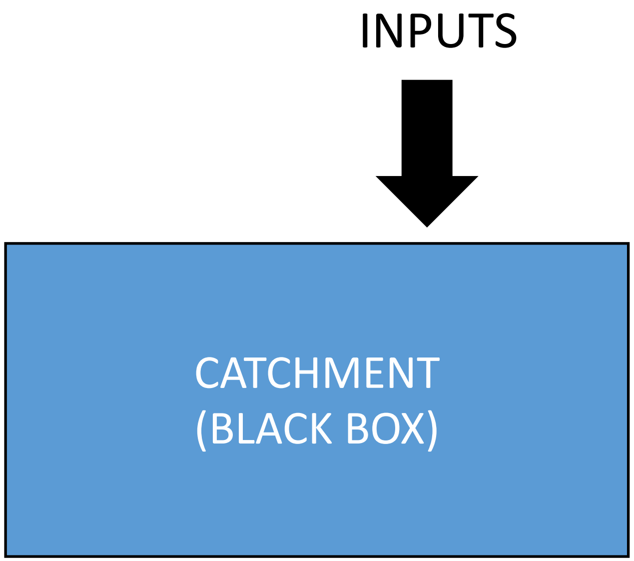
Change in storage (dM/dt) = Input (ΣF_{in}) – Output (ΣF_{out})

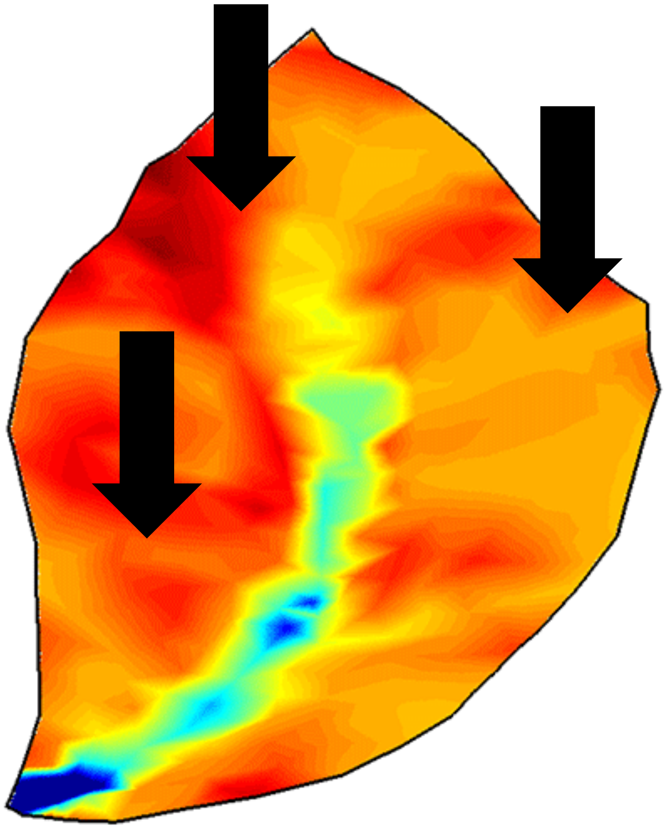




Inputs = atmospheric deposition for a headwater catchment

Atmospheric inputs include only external inputs (precipitation and dry deposition)

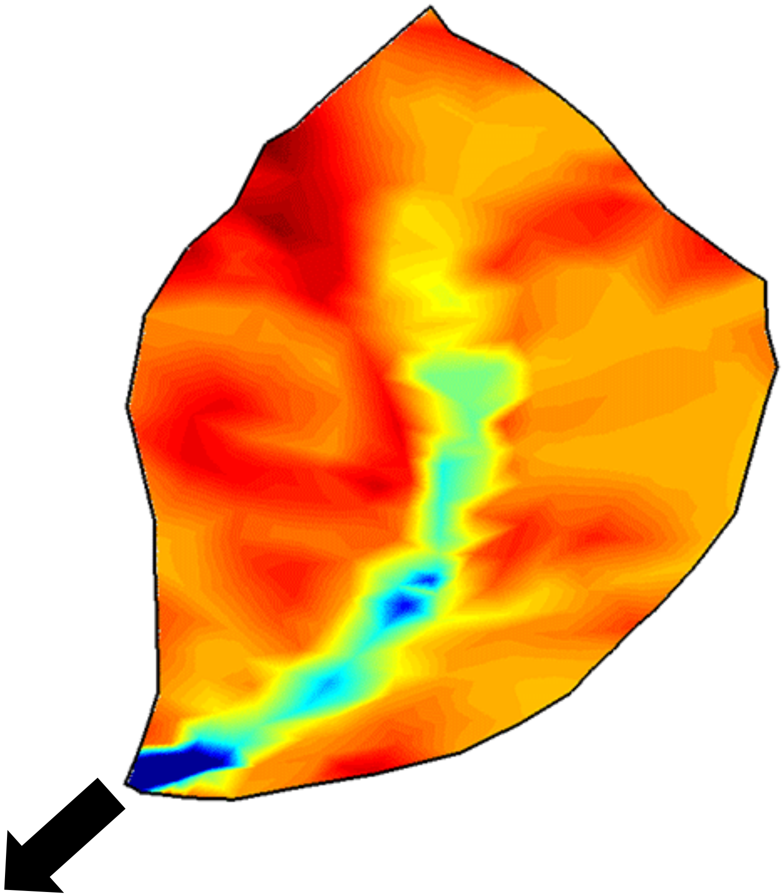


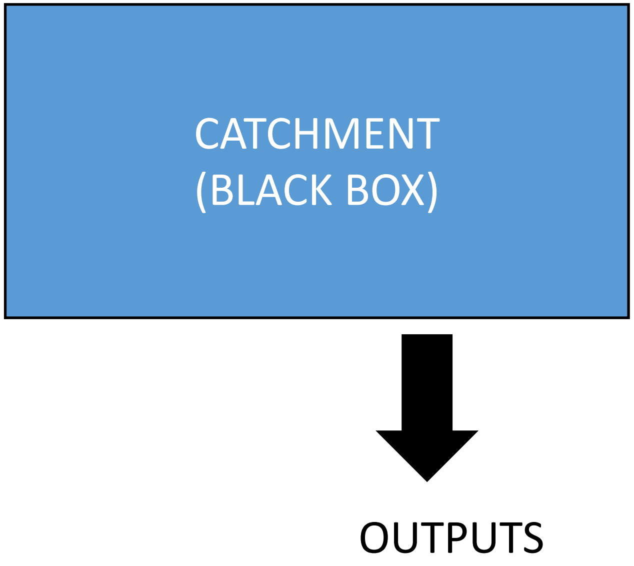


Outputs = loss in the stream at the outlet

Includes inputs from atmosphere + solutes from weathering of minerals ± solutes from change in biomass** ± change in the soil exchange pool**

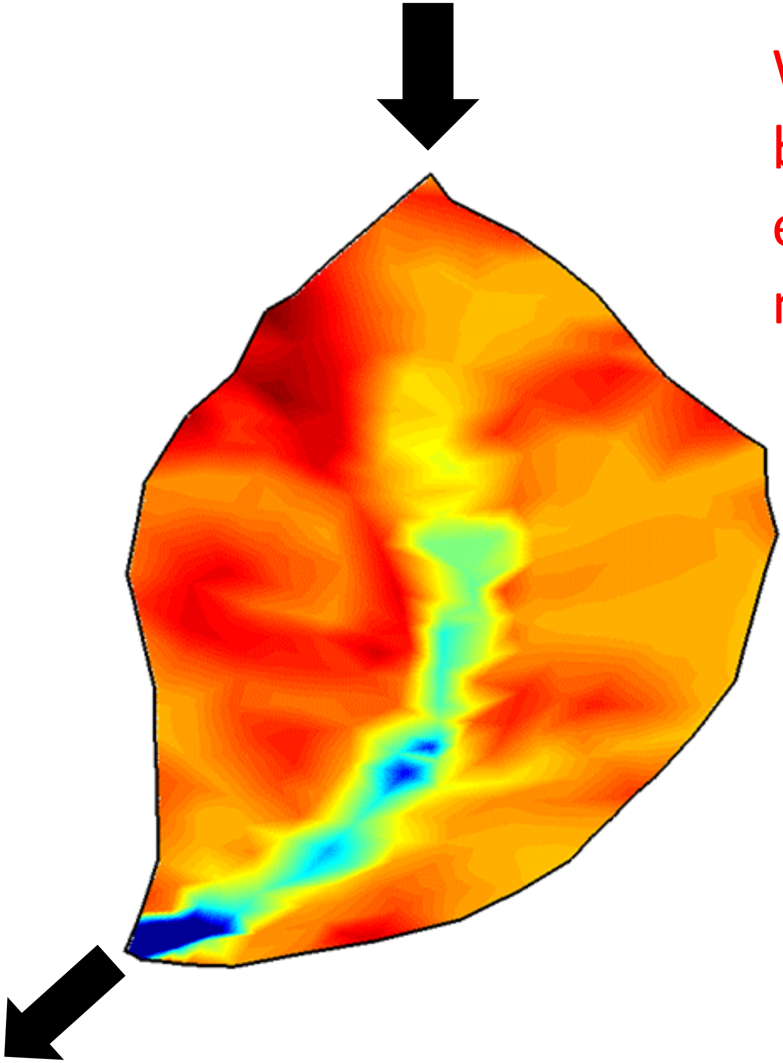
**assumed to be in steady-state on annual timescales





Catchment Hydrogeochemistry

Change in storage (dM/dt) = Input (ΣF_{in}) – Output (ΣF_{out})

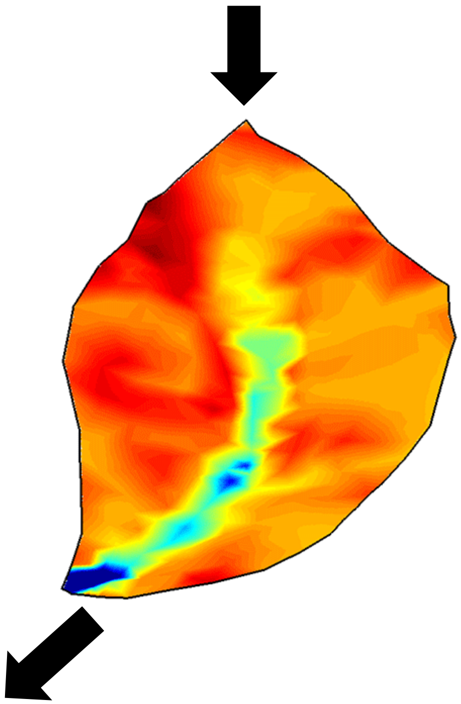


We want to calculate how much Ca is being weathered from a watershed each year (mol/year). What data do we need?

- Precipitation rate (volume/time)
- Ca concentration in precipitation (mass/volume)
- Stream discharge (volume/time)
- Ca concentration in the stream (mass/volume)
- Area of the watershed (area)

Catchment Hydrogeochemistry

Change in storage (dM/dt) = Input (ΣF_{in}) – Output (ΣF_{out})



We want to calculate how much Ca is being weathered from a watershed each year (mol/year). What data do we need?

- Precipitation = 1.0 m y^{-1}
- Ca in precipitation = 2.6 µmol/L
- Stream discharge = 31,600 m^3 y^{-1}
- Ca in the stream = 240 µmol/L
- Area = 79,000 m^2

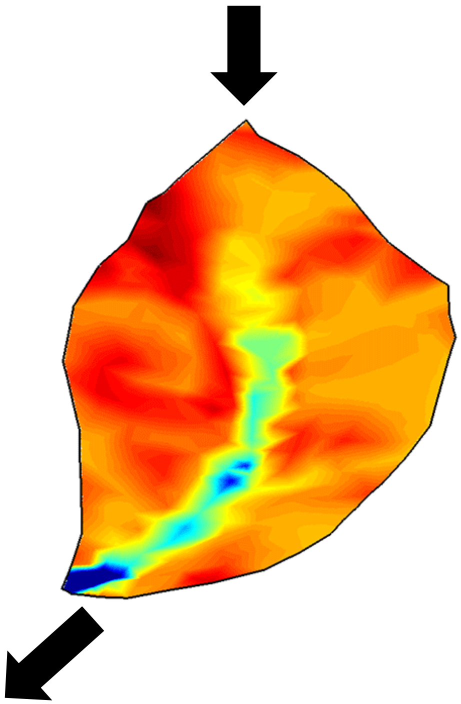
flux in outflow discharge = 3.16E4 m^3/y x 1E3 L/m^3 x 240 µmol/L x 1E-6 mol/ µmol
= 7584 mol/y

flux in inflow precipitation = 1 m/y x 7.9E4 m^2 x 1E3 L/m^3 x 2.6 µmol/L x 1E-6 mol/µmol
= 205.4 mol/y

flux in weathering = 7584 mol/y – 205.4 mol/y = 7378.6 mol/y

Catchment Hydrogeochemistry

Change in storage (dM/dt) = Input (ΣF_{in}) – Output (ΣF_{out})



Now we want to know the first order rate constant (k) for weathering of Ca from minerals stored in the catchment. What data do we need?

Now we need to know how much Ca is stored in the weathering zone (M_{ca})

- Area = 79,000 m^2
- Thickness of weathering zone = 1 m
- Bulk density of soil = 1500 kg m^{-3}
- Ca concentration in soil = 1000 mg/kg

From last slide, we know that weathering flux F = 7584 - 205.4 = 7378.6 mol/y

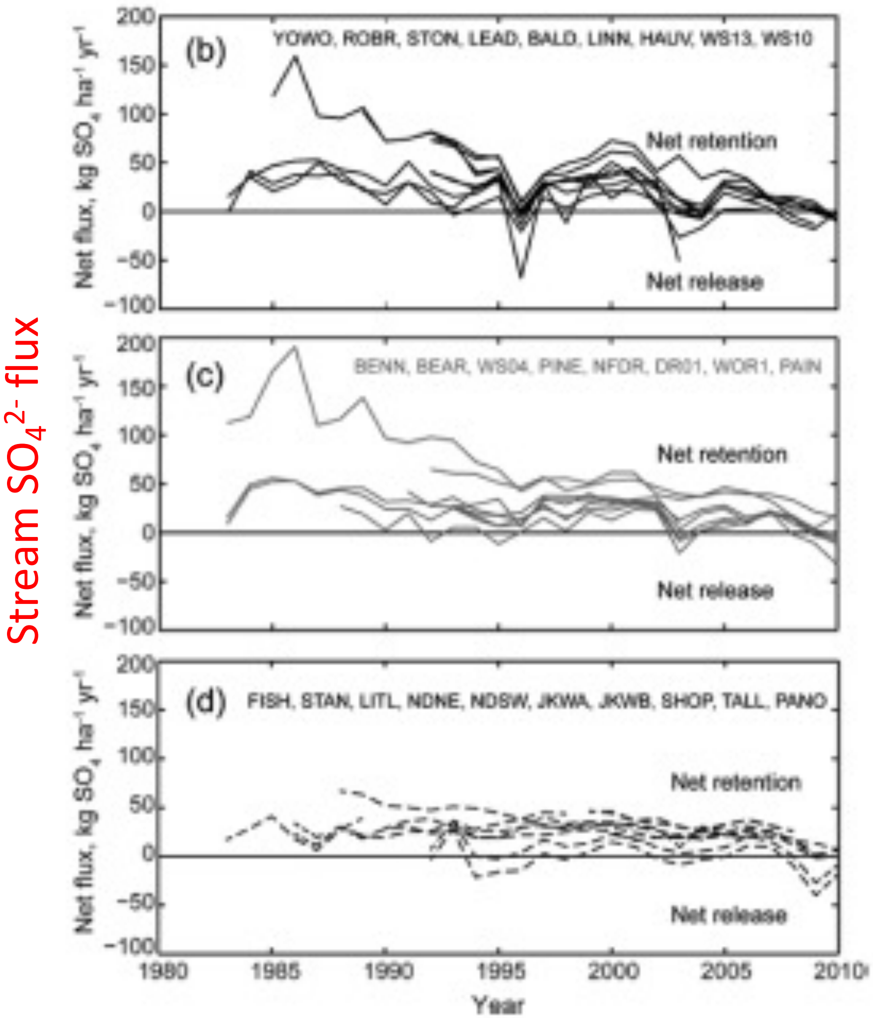
M_{ca} = 7.9E4 m^2 x 1 m x 1.5E3 kg/m^3 x 1000 mg/kg x 0.001 g/mg ÷ 40 g/mol
= 2.9625E6 mol

k = F / M_{ca} = 0.0025 y-1

Are watersheds acting as a sink or source of atmospherically deposited SO_4^{2-} in eastern US?

- SO_4^{2-} deposition has decreased since CAA
- Watersheds store SO_4^{2-} in soils
- Some watersheds still retain SO_4^{2-} (inputs > outputs) but are predicted to switch to net release (outputs > inputs)
- Some watersheds have already switched to net release (northern glaciated watersheds with thin soils)

Change in storage = inputs – outputs



Rice et al. (2014) ES&T

What are caveats to treating a catchment as a black box?