Atmospheric and Surface Water Isotopes: Processes and Applications

Gabe Bowen

gabe.bowen@utah.edu

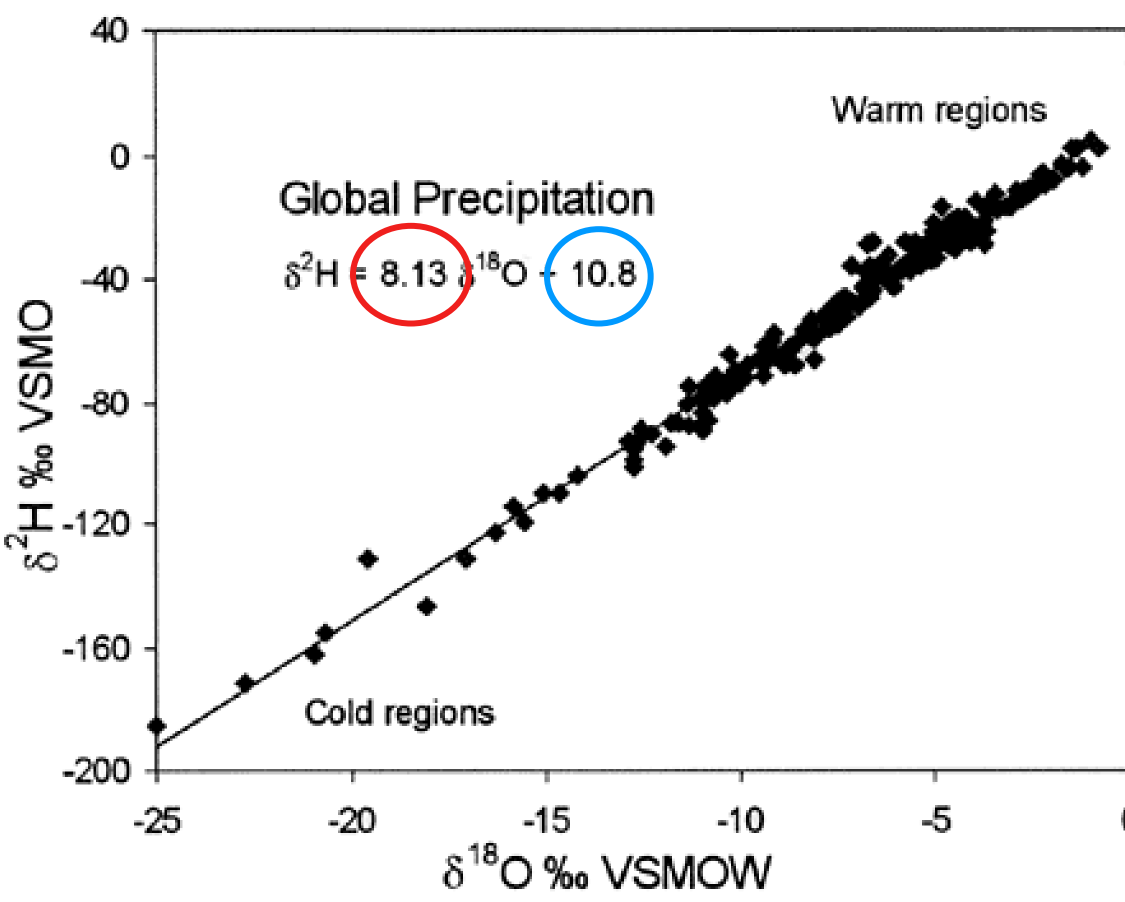
SPATIAL

University of Utah

Why Water in the Atmosphere?

- Precipitation is the source of freshwater in hydro- and eco-systems
- Most of the isotopic variation we see in freshwater systems is derived from atmospheric processes

The Global Meteoric Water Line



The slope of the GMWL is 8

The intercept of the GMWL is +10‰

Clark and Fritz, 1997; GMWL defined by Craig, 1961

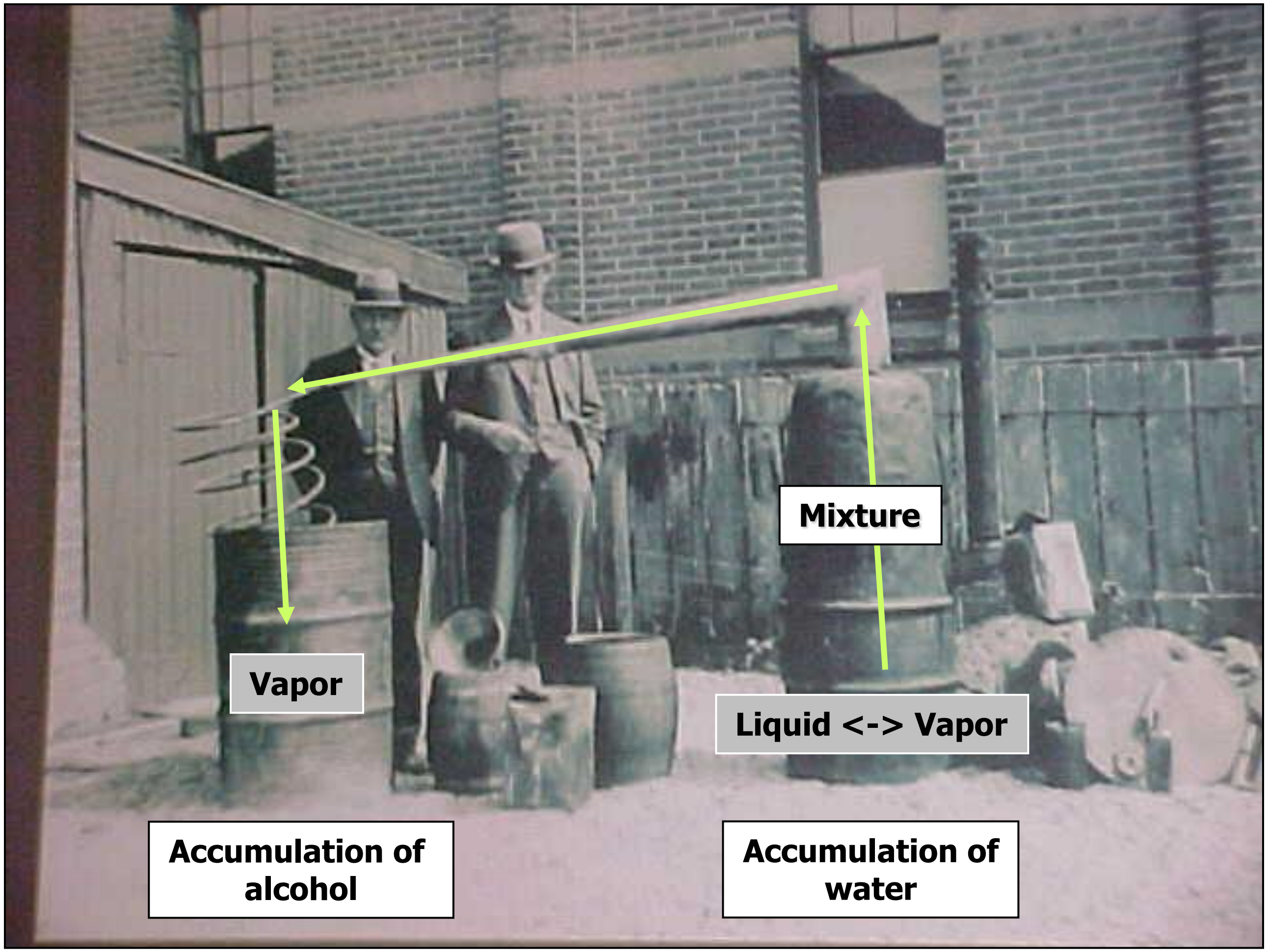
Rayleigh Distillation

- A processes by which fractionation (of isotopes, elements, molecules, elephants) leads to a change in 2-component reactant mixture
- Is it Rayleigh Distillation?
  - Open system
    - No addition of material
    - Rapidly and continuous removal of product
  - Product is fractionated relative to the reactant
- The Rayleigh equation describes the composition of the reactant pool as a function of reaction progress:

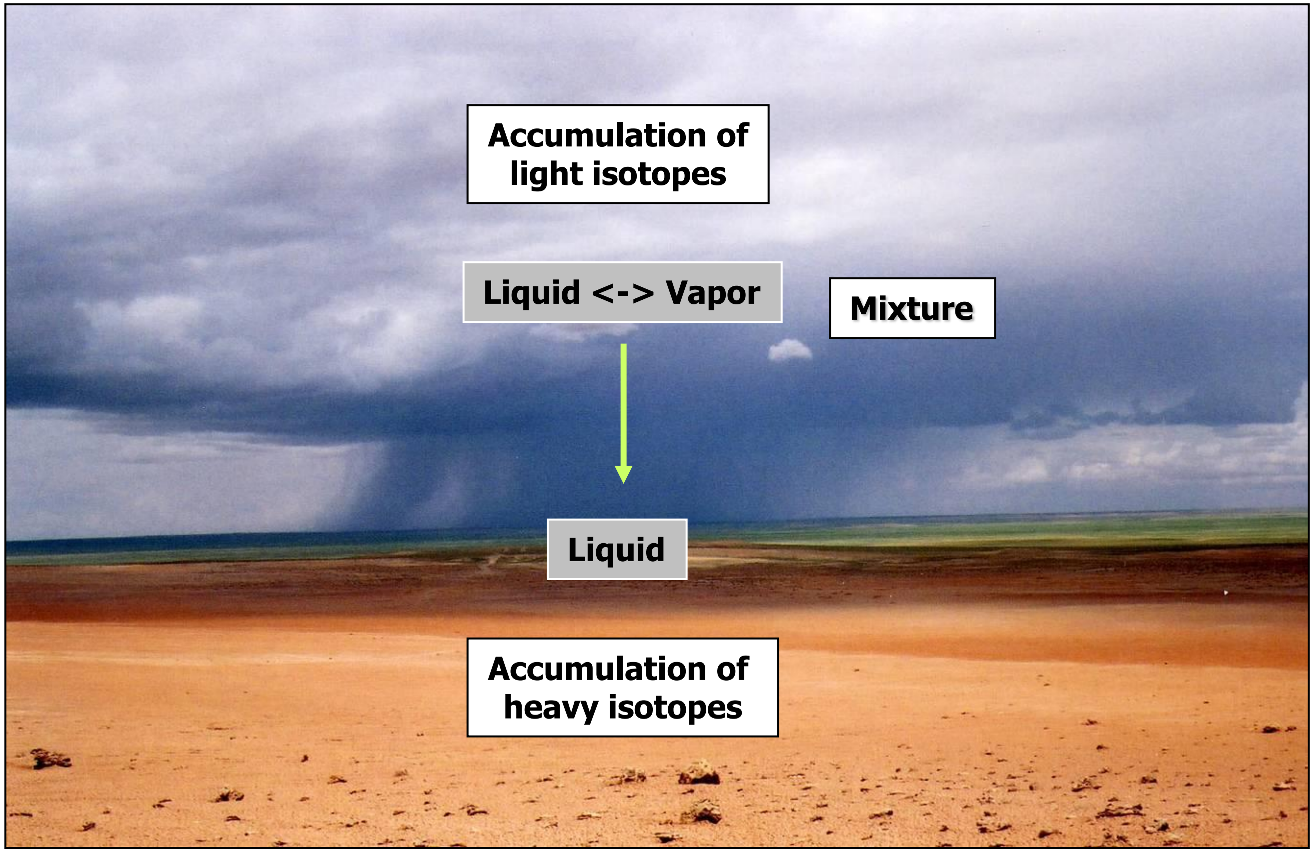
$$R = R_0 f^{(\alpha - 1)}$$

R and R_0 are current and initial isotope ratios
f is fraction of reactant remaining

Rayleigh Distillation

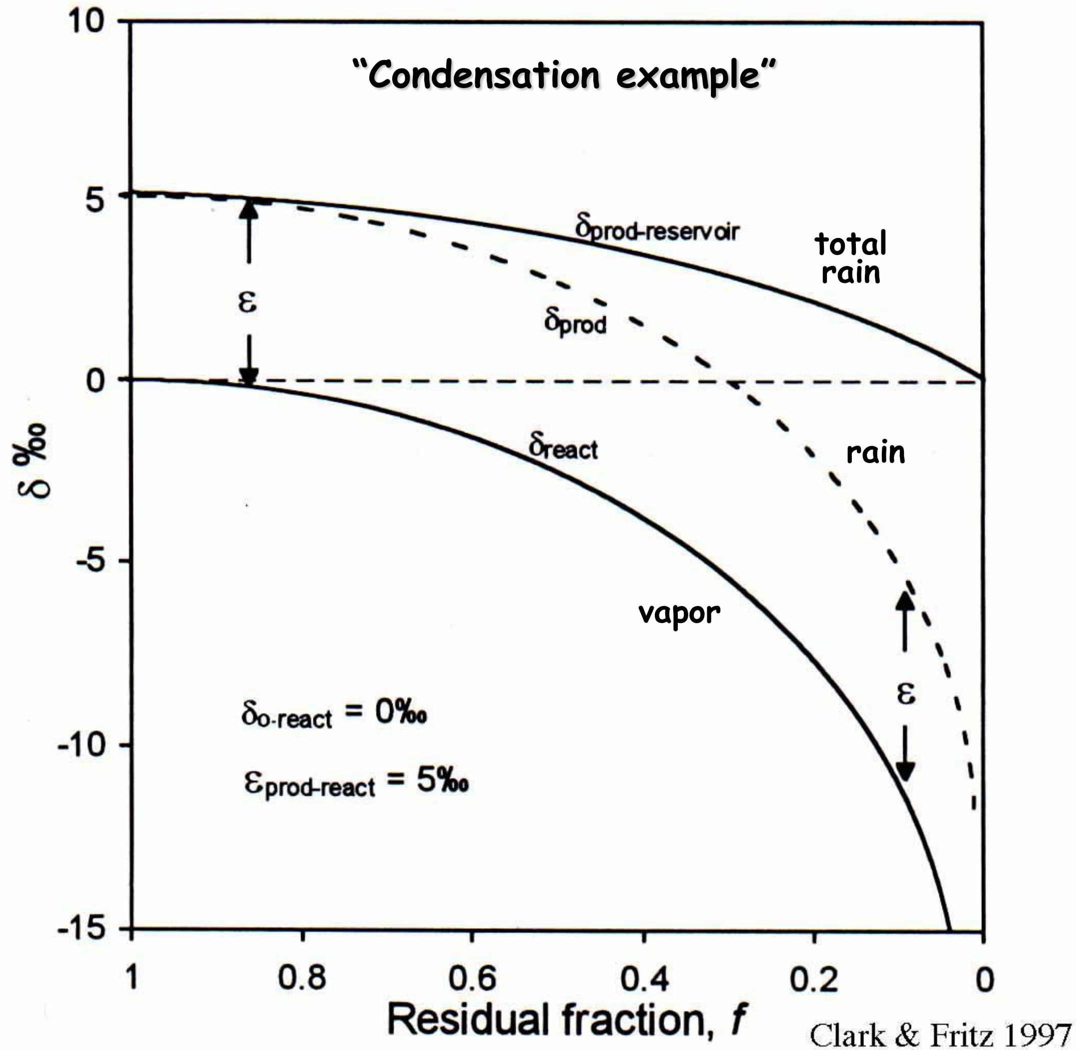


Rayleigh Distillation



Rayleigh Distillation and Precipitation

- Precipitation formed from condensation of cloud vapor
- Equilibrium process (free atmosphere RH ≈ 100%)
    - Equilibrium fractionation
- **But one element of complexity…**



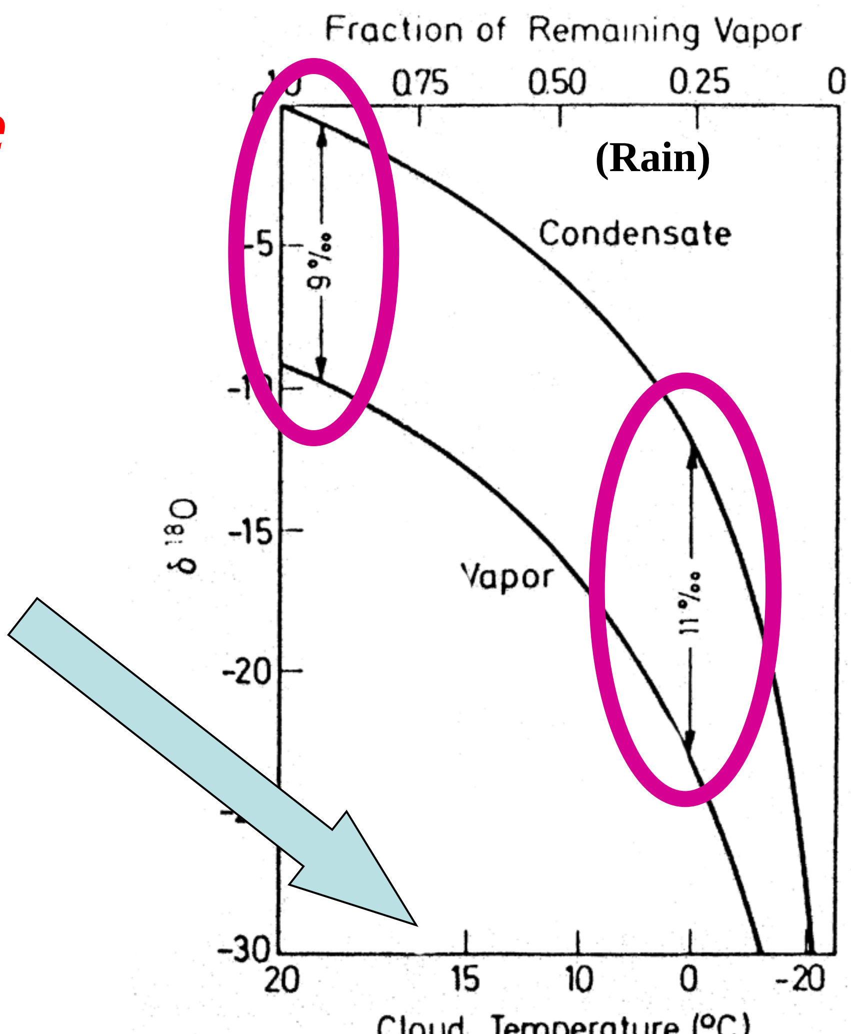
Clark & Fritz 1997

Rayleigh Distillation and Precipitation

!!!This does not cause the ‘temperature effect’!!!

As condensation proceeds, the temperature of the remaining cloud decreases.

Thus, α increases, resulting in a greater difference between cloud and rain H_2O



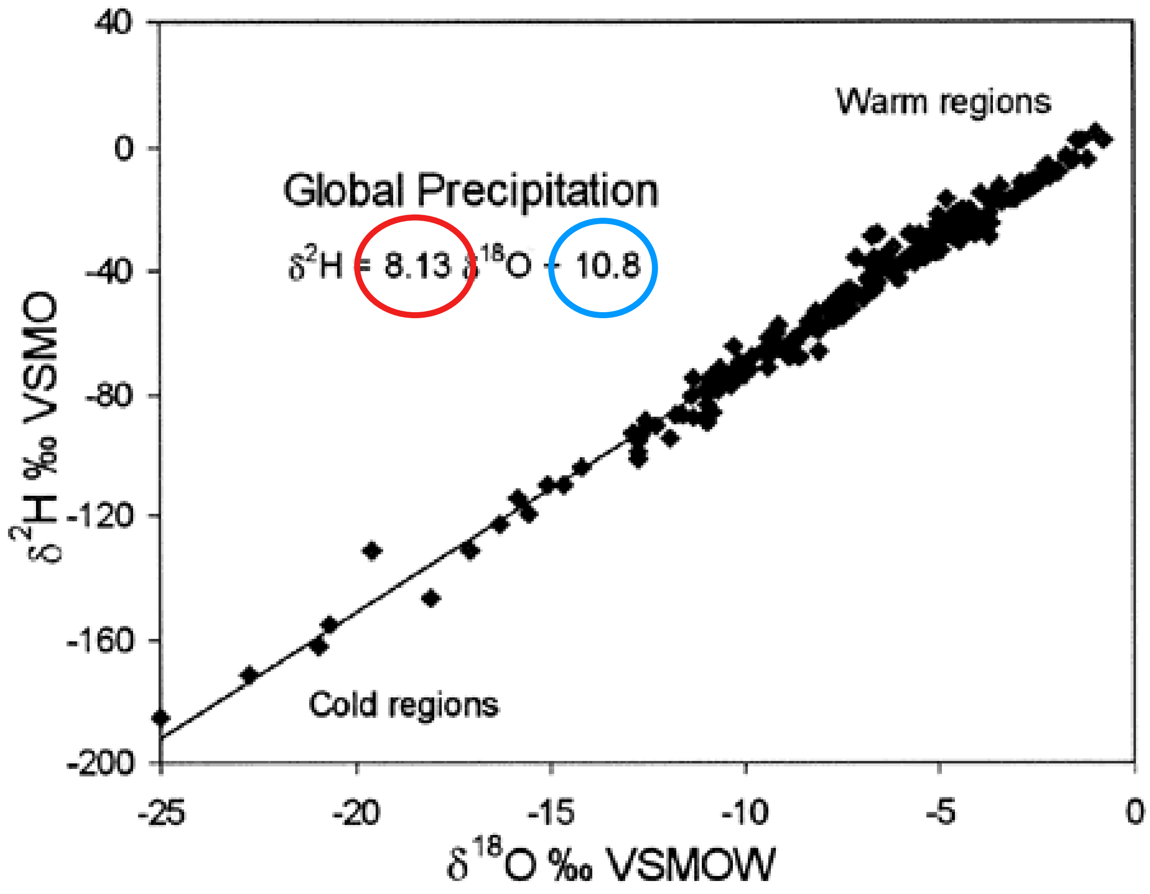
Hoefs 1997

Equilibrium Fractionation Proportionality

- at 20° C
  - $\varepsilon^{2}H = 74‰$
  - $\varepsilon^{18}O = 9.2‰$
  - $\varepsilon^{2}H / \varepsilon^{18}O = 8.0$
- at 80° C
  - $\varepsilon^{2}H = 38‰$
  - $\varepsilon^{18}O = 4.5‰$
  - $\varepsilon^{2}H / \varepsilon^{18}O = 8.4$

Equilibrium enrichment factors for H isotopes are ~8 x those for O isotopes

The Global Meteoric Water Line



Condensation is an equilibrium process

so

Most precipitation δ values lie along a Global Meteoric Water Line (GMWL) of slope 8

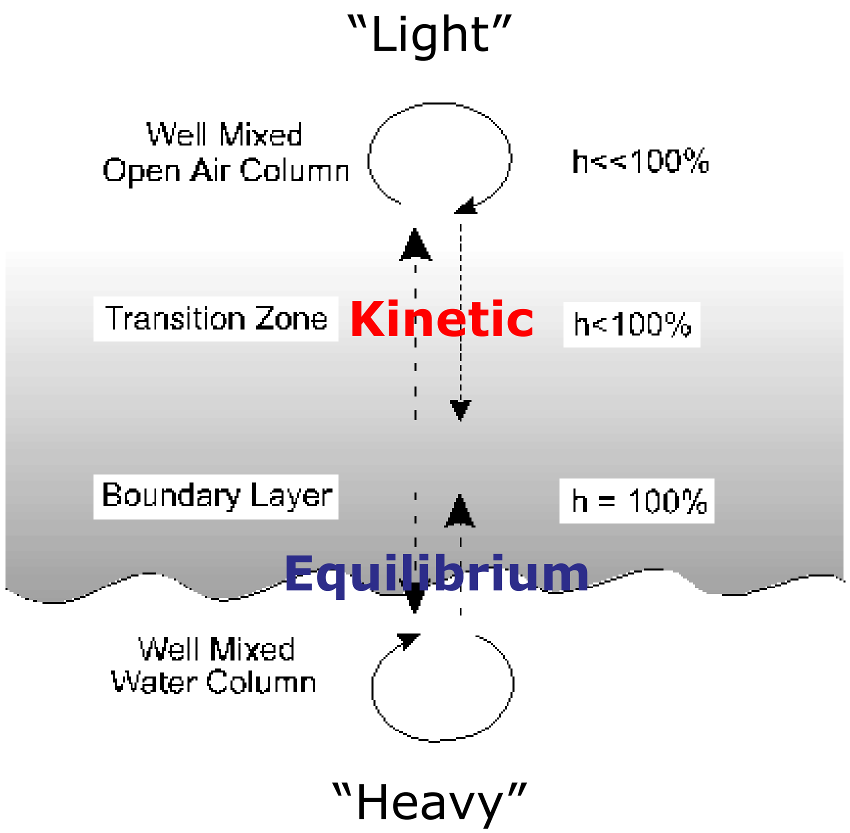
$(\varepsilon^2H / \varepsilon^{18}O = 8)$

The intercept of the GMWL is +10‰

Clark and Fritz, 1997; GMWL defined by Craig, 1961

Phase Change Reaction: Craig-Gordon

- Open air
  - Well-mixed
  - Large
- Transition zone (TZ)
  - Turbulently mixed
  - Decreasing humidity upwards
- Boundary layer (BL)
  - Thin, well-mixed layer
  - 100% RH
- Liquid
  - Large (ocean) or small (droplet) body of water
  - Mixed or stratified



$$\delta_e = \frac{\alpha^* \delta_l + \varepsilon^* - h\delta_a - \Delta\varepsilon}{1 - h}$$

Gat, 1996

Kinetic Effect

- $\Delta\varepsilon = (1-h)n\theta C_D$
  - h = relative humidity
  - n = relative strength of kinetic vs. turbulent transport
  - θ = perturbation of boundary layer humidity
  - C_D = ratio of effective diffusion coefficients for isotopologues
    - H = 25.1‰
    - O = 28.5‰

- Let’s discuss…

Equilibrium and kinetic enrichment factors

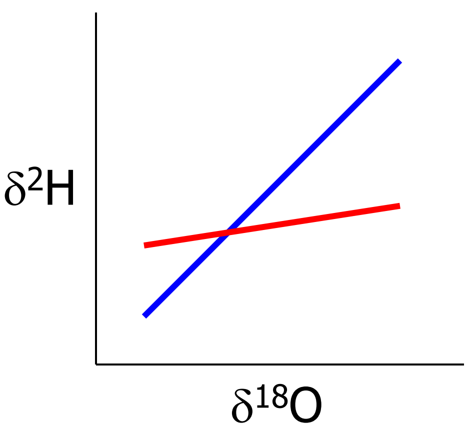
Q: What was the relationship between $\varepsilon_e{}^2H$ and $\varepsilon_e{}^{18}O$?

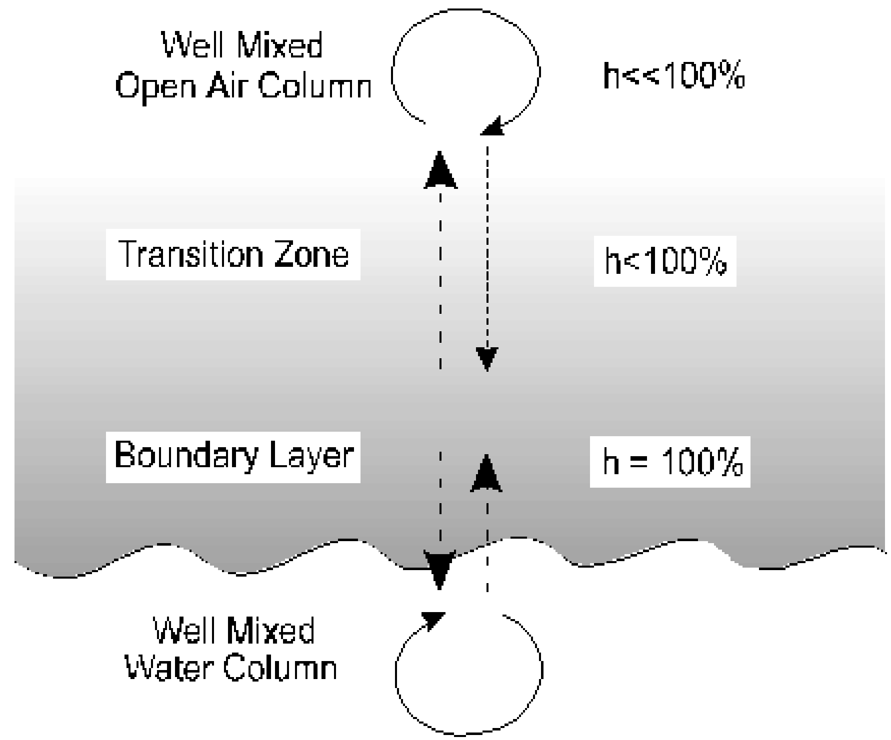
A: $\varepsilon_e{}^2H / \varepsilon_e{}^{18}O = 8$

$\Delta\varepsilon^2H$ and $\Delta\varepsilon^{18}O$ give us a different relationship

Kinetic
$\alpha^2H \approx \alpha^{18}O$

Equilibrium
$\alpha^2H = 8*\alpha^{18}O$

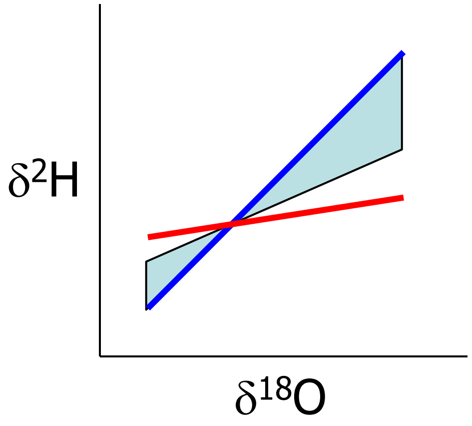


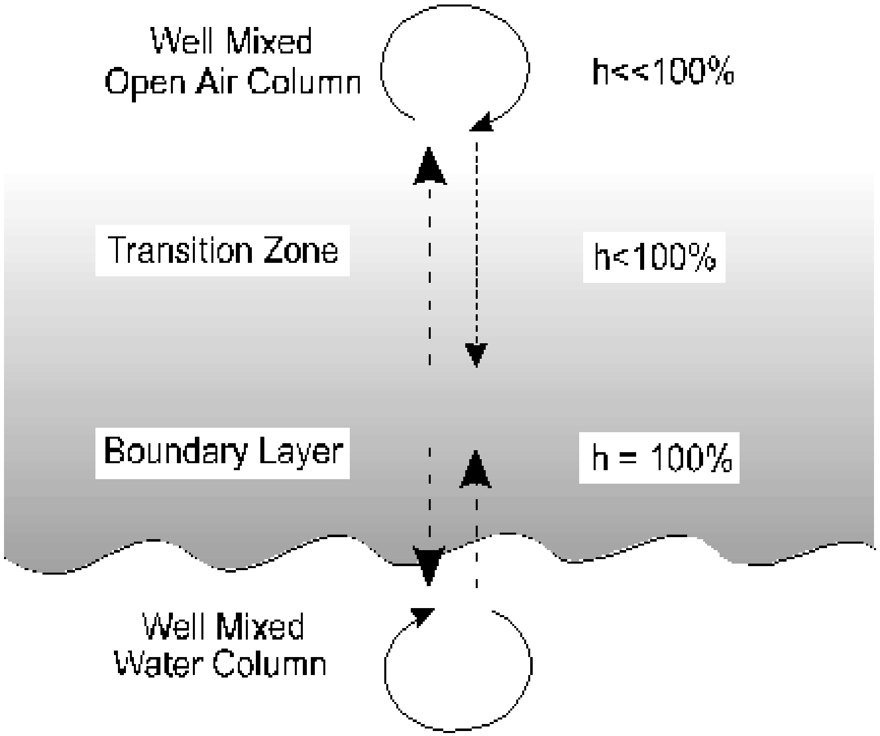


Gat, 1996

Equilibrium and kinetic enrichment factors

- The net ratio of ^2H and ^{18}O isotope effects is a blend of the Equilibrium and Kinetic ratios, typically between 3 and 8
- The coupled $^2H/^{18}O$ system gives us a "proxy" for kinetic fractionation… **deuterium excess**

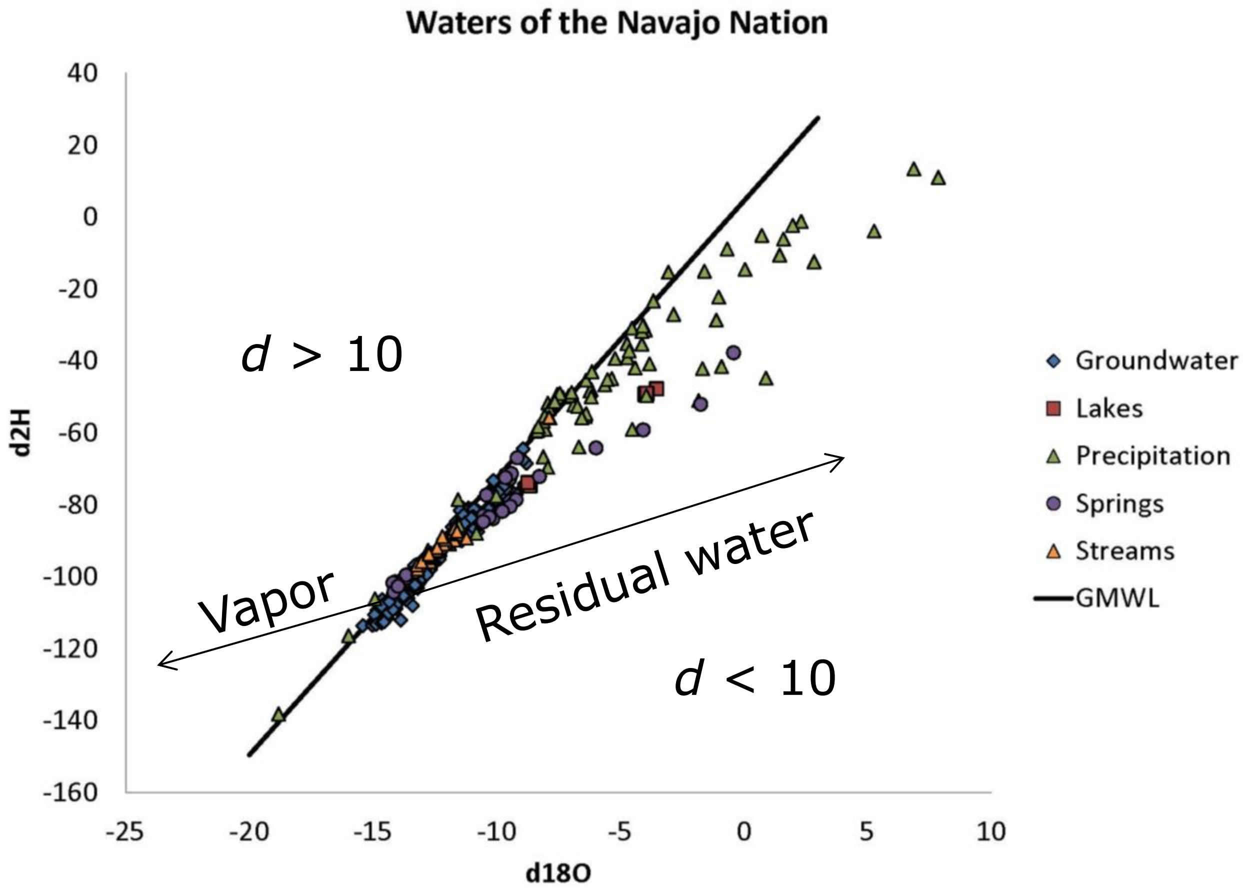




Gat, 1996

Deuterium excess

$d = \delta^2H - 8 \times \delta^{18}O$

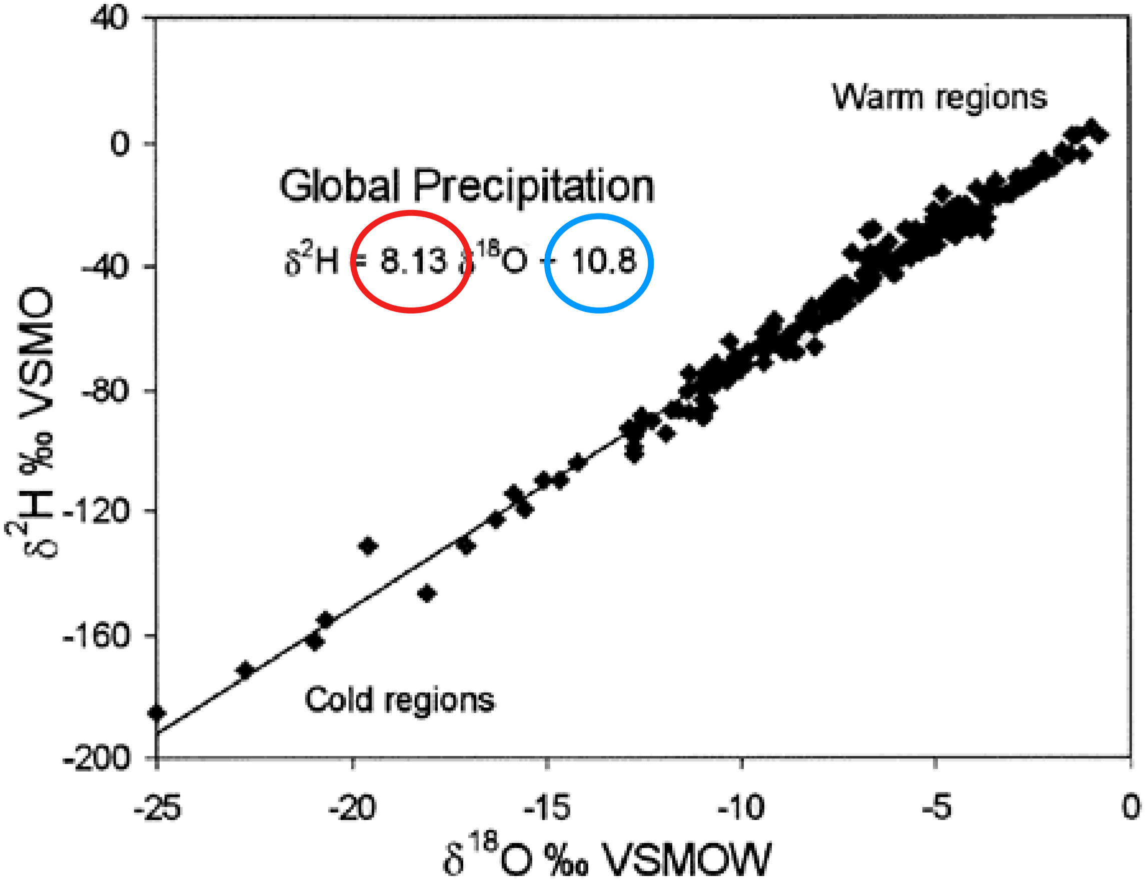


Crystal Tulley-Cordova, unpub.

GMWL Intercept

- Global precipitation
  - δ^2H = -22‰
  - $\delta^{18}O$ = -4‰
- What is the isotopic composition of global evaporation?
- So global evaporation has a *d* value of ~ +10‰
  - Implies conditions of evaporation
    - n = 0.5
    - θ = 0.5

The Global Meteoric Water Line



The slope of the GMWL is 8

Kinetic fractionation gives a *d* value for the (dominant) oceanic evaporation flux of +10‰, setting GMWL intercept

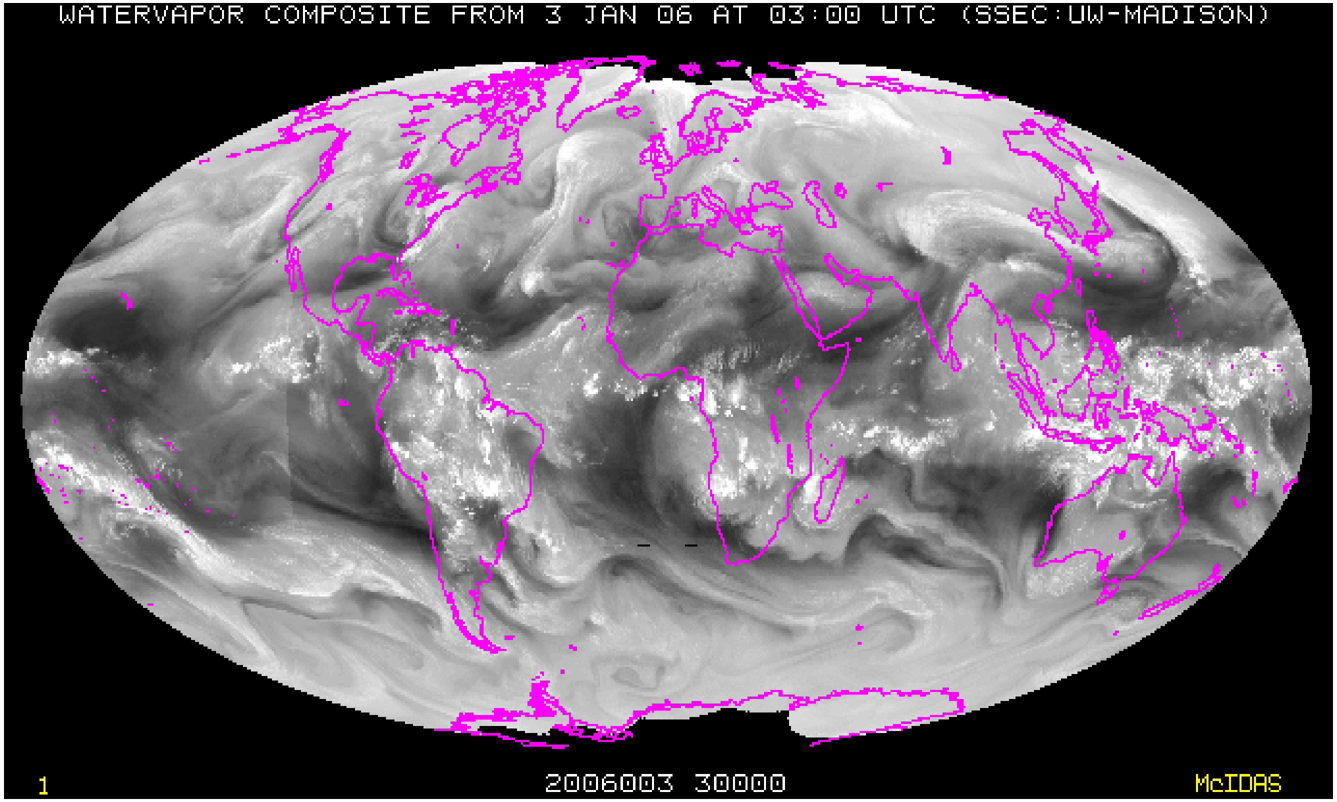
Clark and Fritz, 1997; GMWL defined by Craig, 1961

Precipitation Isotope Patterns and Rayleigh Distillation

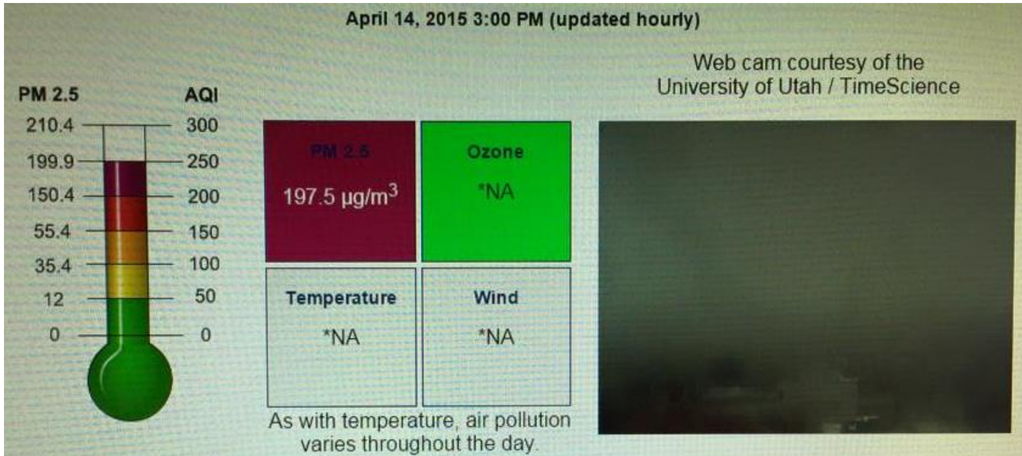
- Rayleigh distillation causes precipitation isotope ratios to get **lower** as air gets **drier**

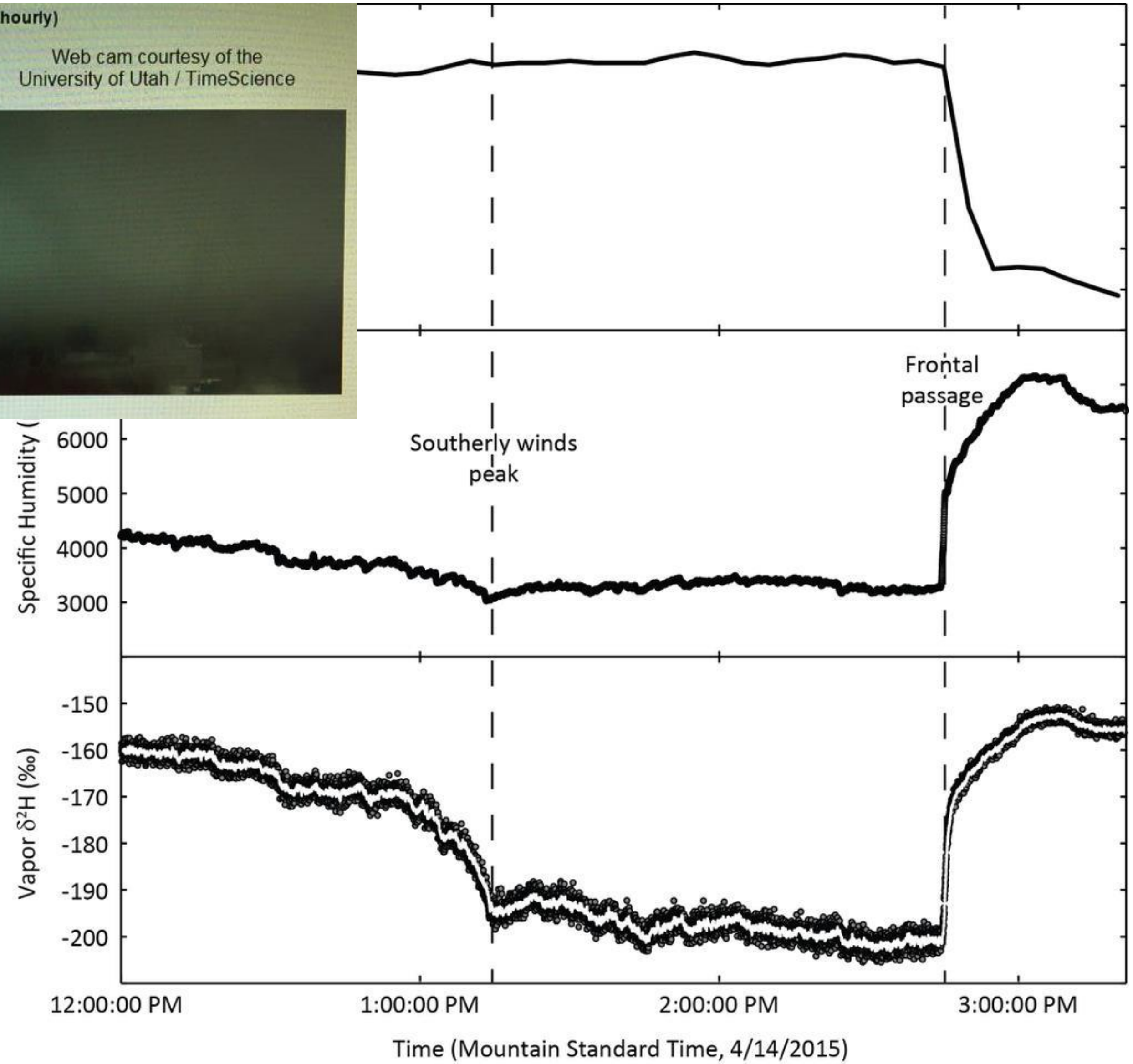
What does this imply about the spatial distribution of precipitation isotope ratios?

Patterns of Climate → Patterns of Water Isotope Ratios

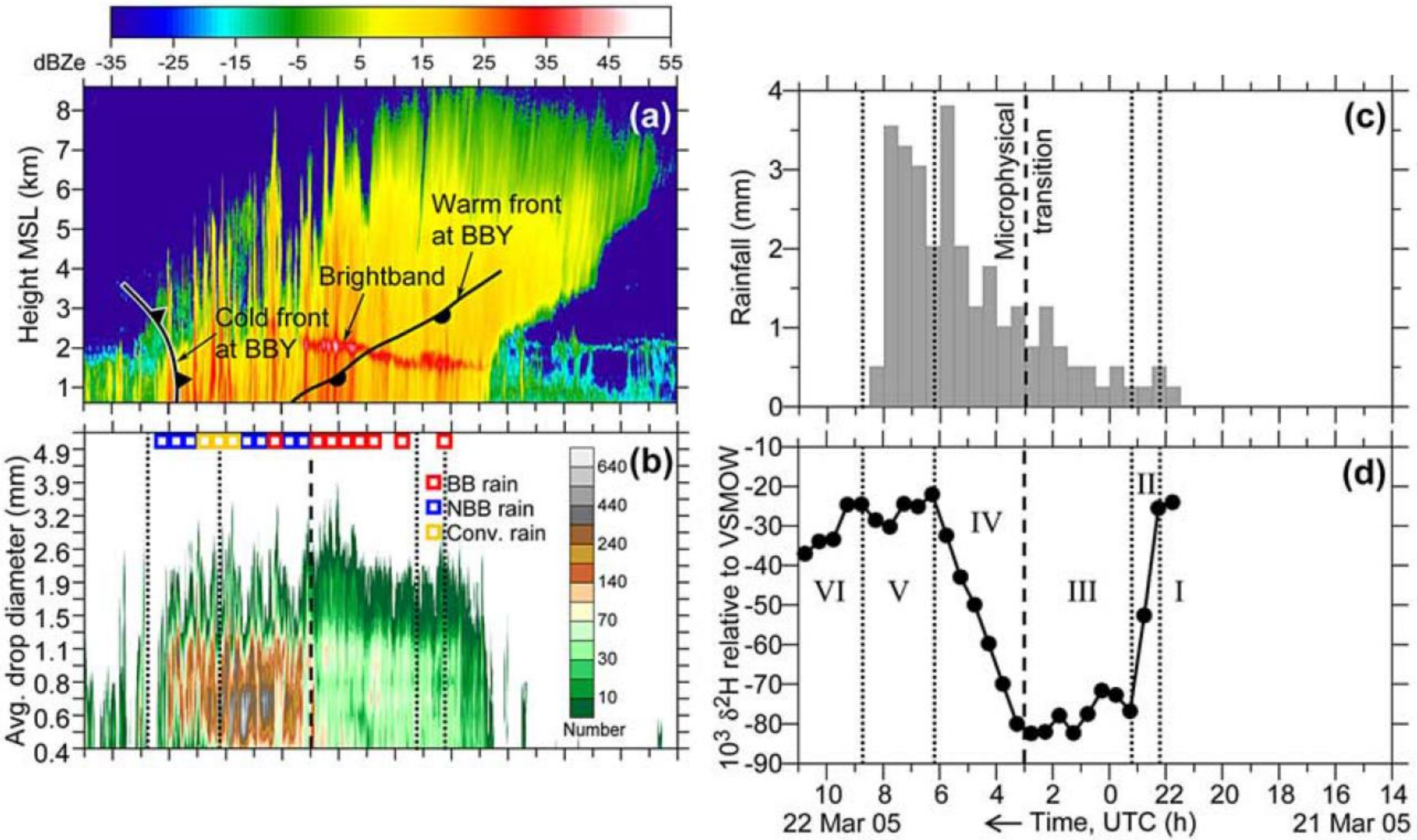


A Salt Lake City Example





Temporal Variation - Meterological

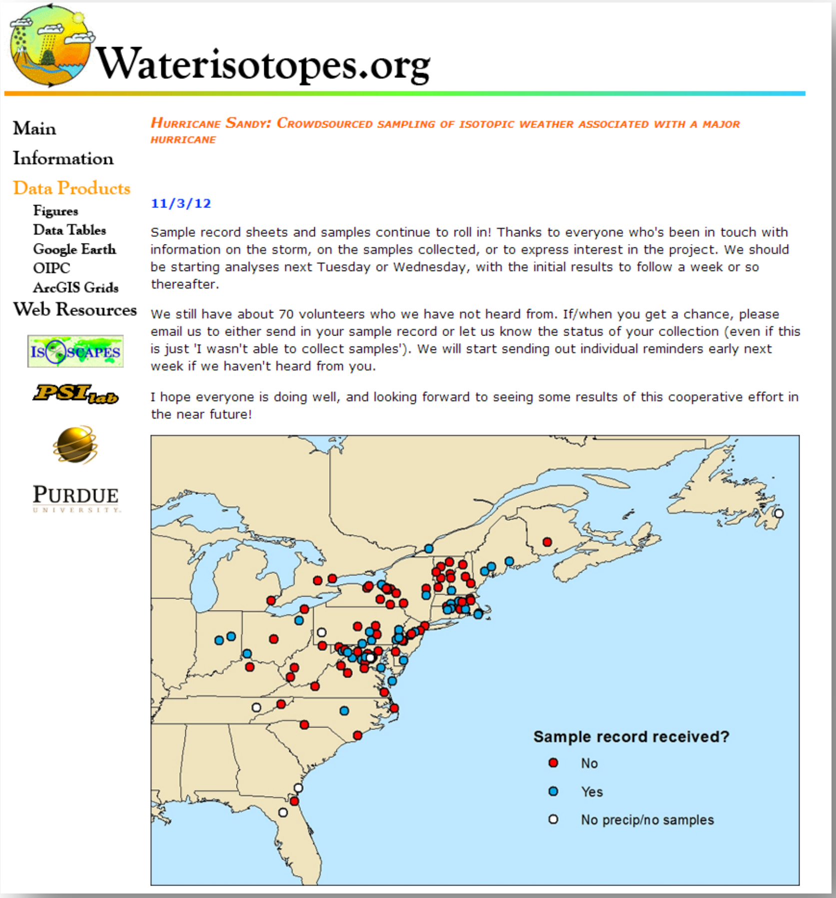


Coplen et al., 2008, *GRL*

Synoptic-scale systems (Sandy)

- October 22-31, 2012
  - ET transition October 29
  - Landfall (NJ) early on October 30
- Maximum intensity category 3, category 1 at landfall
- 2nd costliest Hurricane in US history

Crowdsourced Sampling Network


Waterisotopes.org

Main
Information
Data Products
Figures
Data Tables
Google Earth
OIPC
ArcGIS Grids
Web Resources

HURRICANE SANDY: CROWDSOURCED SAMPLING OF ISOTOPIC WEATHER ASSOCIATED WITH A MAJOR HURRICANE

11/3/12

Sample record sheets and samples continue to roll in! Thanks to everyone who's been in touch with information on the storm, on the samples collected, or to express interest in the project. We should be starting analyses next Tuesday or Wednesday, with the initial results to follow a week or so thereafter.

We still have about 70 volunteers who we have not heard from. If/when you get a chance, please email us to either send in your sample record or let us know the status of your collection (even if this is just 'I wasn't able to collect samples'). We will start sending out individual reminders early next week if we haven't heard from you.

I hope everyone is doing well, and looking forward to seeing some results of this cooperative effort in the near future!


crowdsourcing.org THE INDUSTRY WEBSITE™
EVENTS FEATURED RESEARCH SITES TOPICS CAPS
CROWDFUNDING CLOUD LABOR CROWD CREATIVITY DISTRIBUTED KNOWLEDGE OPEN INNOVATION TOOLS CONTENT SITE QUESTION

CROWDSOURCING SCIENCE FROM HURRICANE SANDY

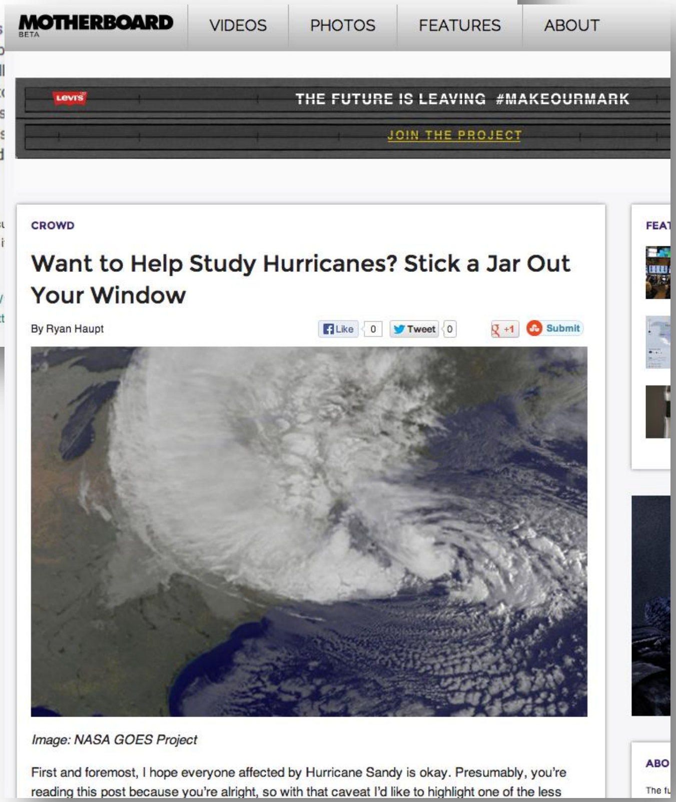
BLOG Crowd Creativity

Crowdsourcing Science from Hurricane Sandy
By Andrew Alden, About.com Guide October 27, 2012
My Bio | Headlines | Forum | RSS
Follow me on: Facebook Twitter

The eastern United States is ... weekend. If you're in the sto... a citizen-science effort to coll... it's a project to map the isoto... internal processes of major s... information about what the s... a series of samples collected...

Description
If you're in the storm's way and have a secu... from the storm. Run by waterisotopes.org, i... internal processes of major storms.

SOURCE:http://geology.about.com/b/2012/... utm_source=twitterfeed&utm_medium=twitt...


MOTHERBOARD BETA VIDEOS PHOTOS FEATURES ABOUT

THE FUTURE IS LEAVING #MAKEOURMARK
JOIN THE PROJECT

CROWD

Want to Help Study Hurricanes? Stick a Jar Out Your Window

By Ryan Haupt

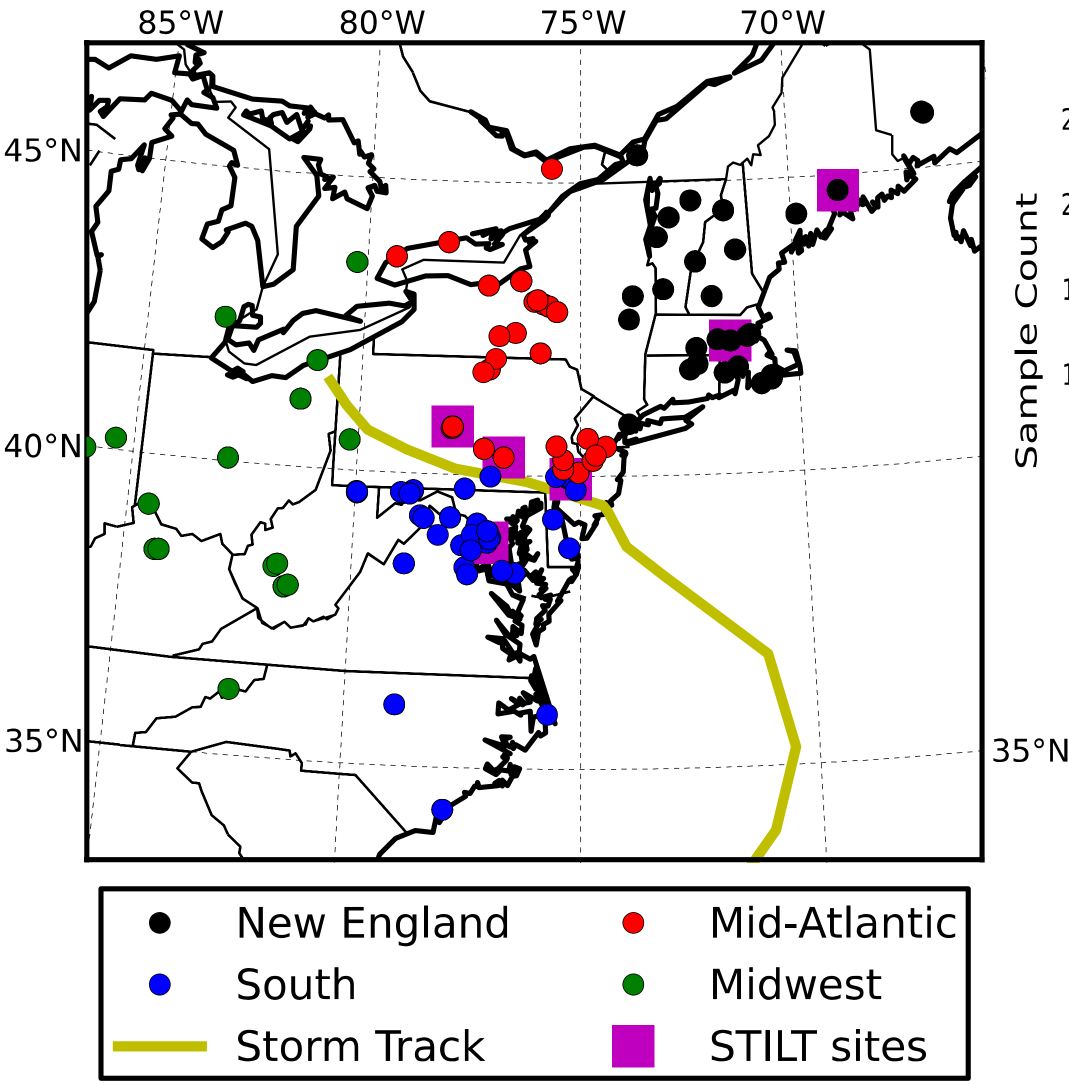
Like 0 Tweet 0 +1 Submit

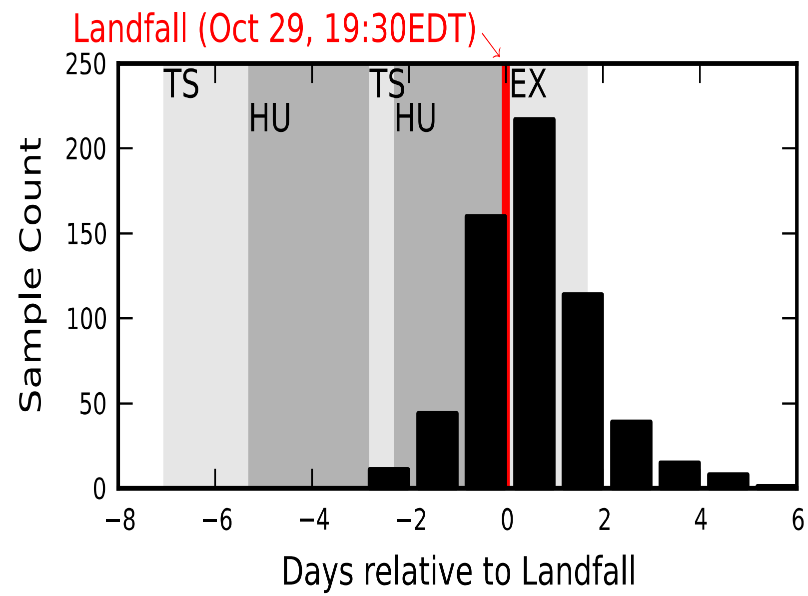
Image: NASA GOES Project

First and foremost, I hope everyone affected by Hurricane Sandy is okay. Presumably, you're reading this post because you're alright, so with that caveat I'd like to highlight one of the less


PRIORITY MAIL
PRIORITY MAIL
Top
Top
Gabriel Bowen

Sample Suite

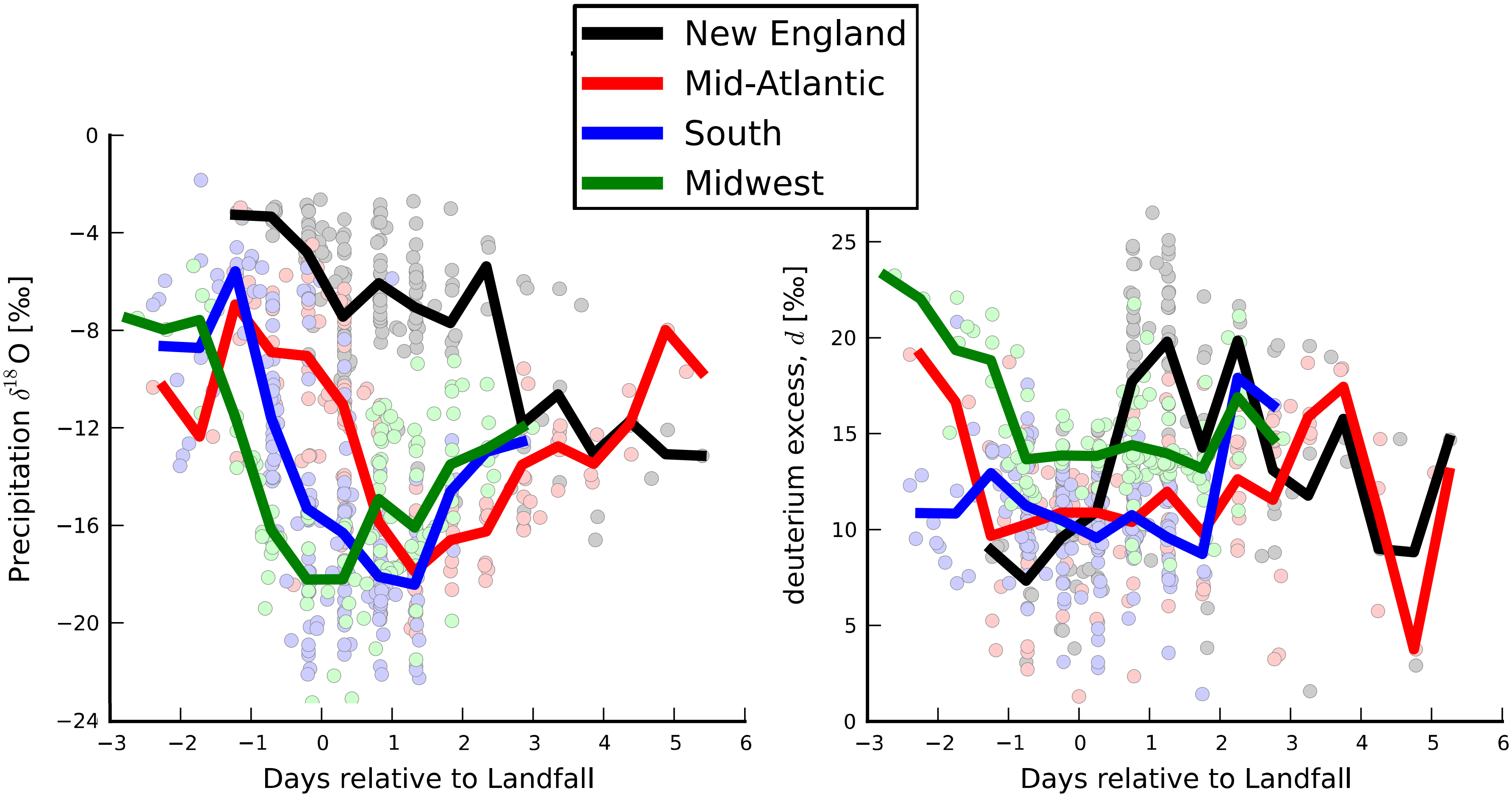




685 Samples from Over 125 Sites

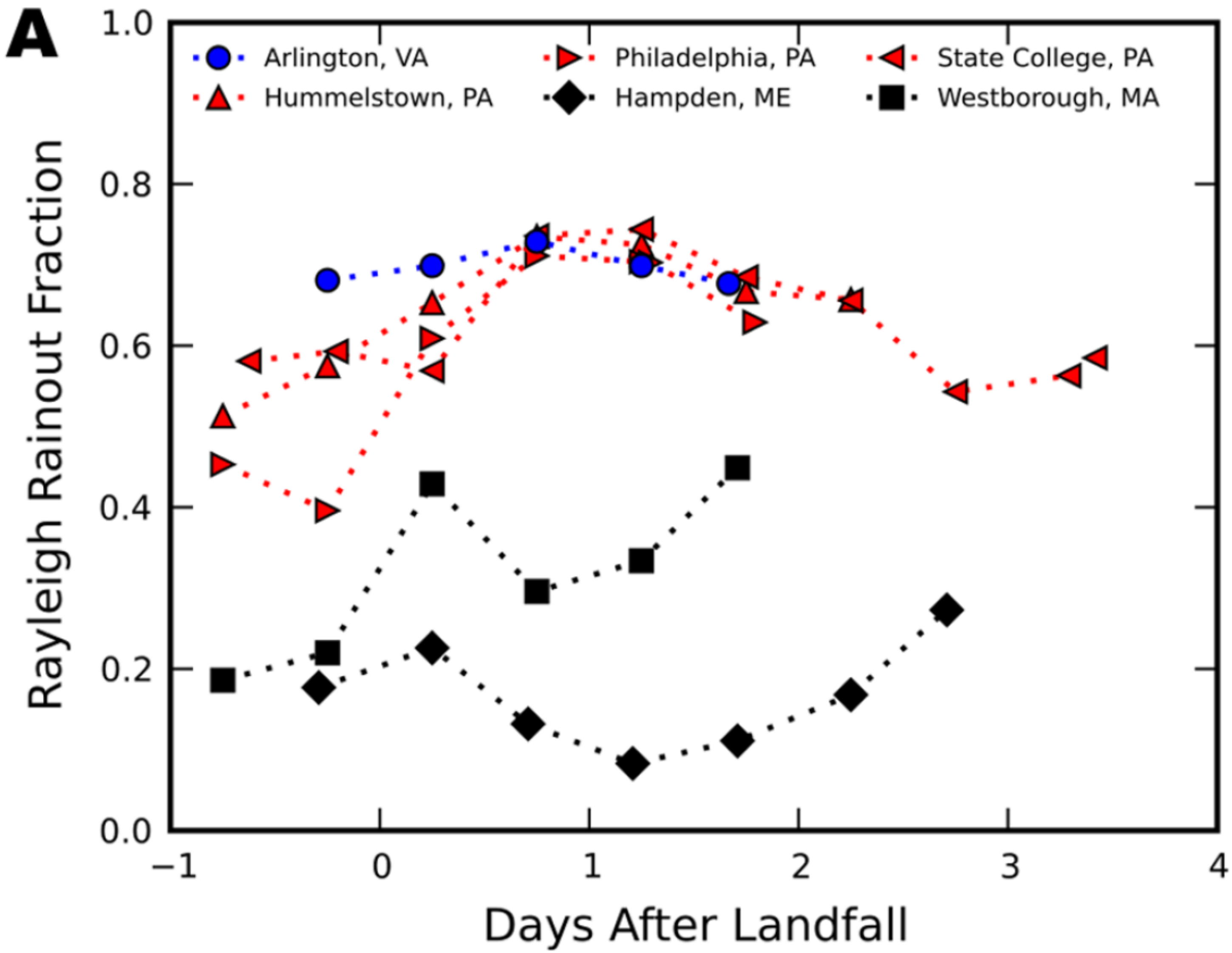
Good et al., *PLoS ONE*, 2014

Spatiotemporal Isotope Patterns

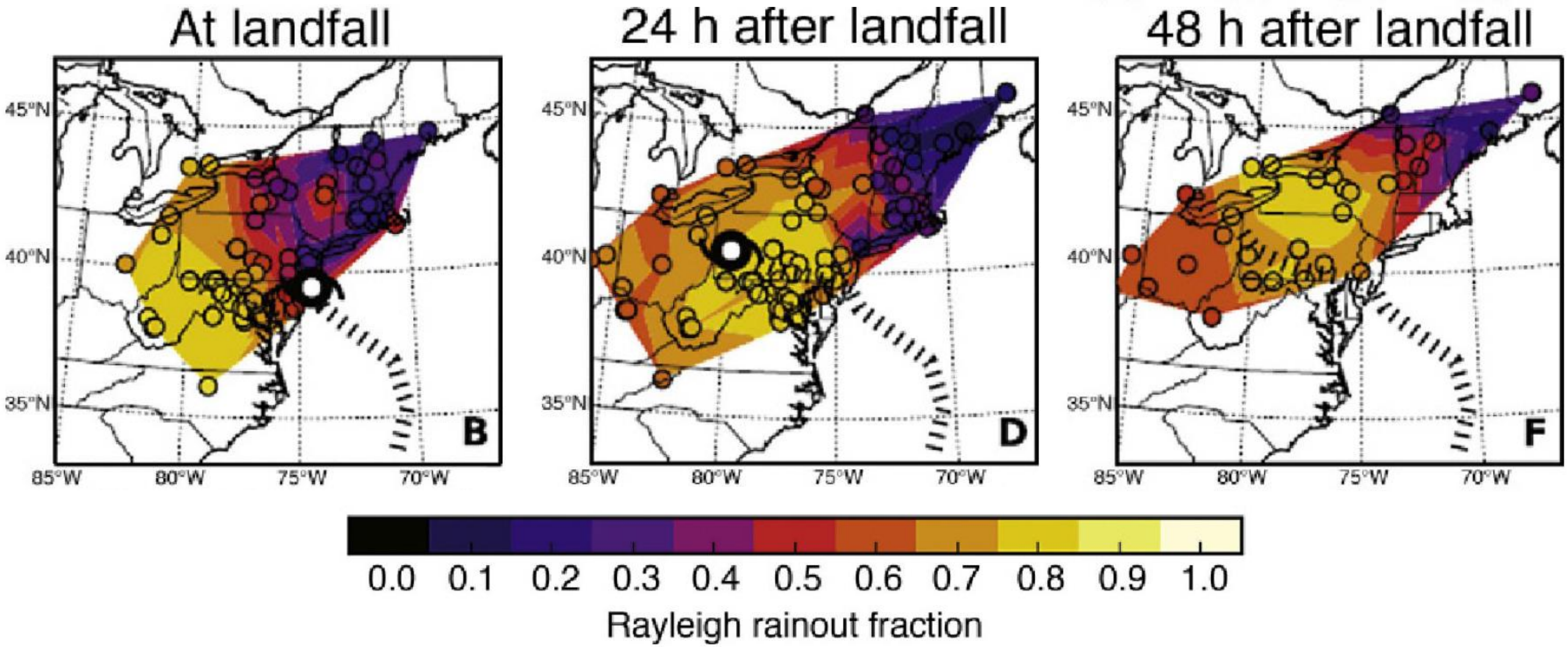


Distinct regional isotopic patterns as storm moves northwest

Rayleigh Rainout Model



Spatial Evolution of Storm Water Cycling

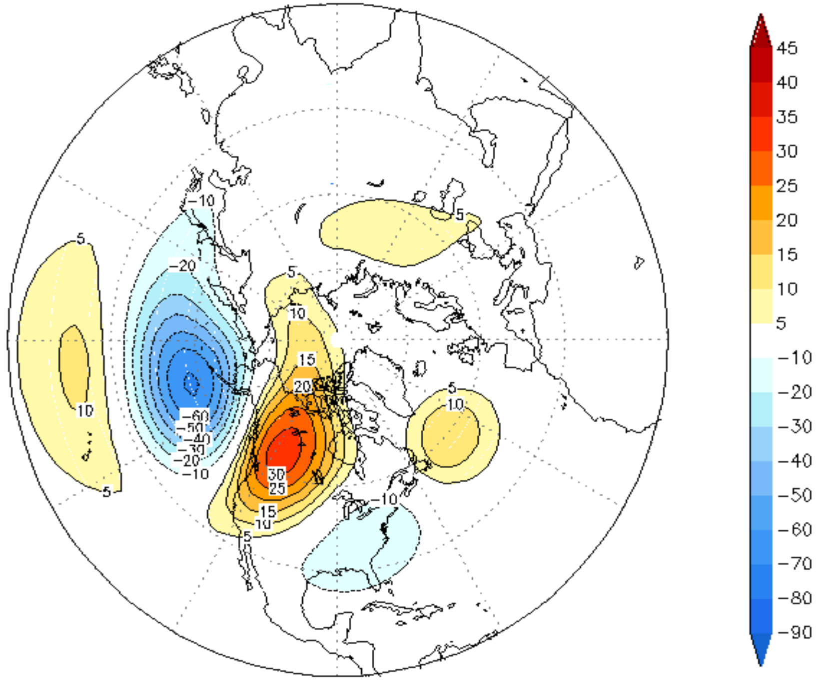


- Superstorm Sandy up to 80% rainout-'efficient'
- Over 2 days disconnects from Atlantic, adds continental moisture

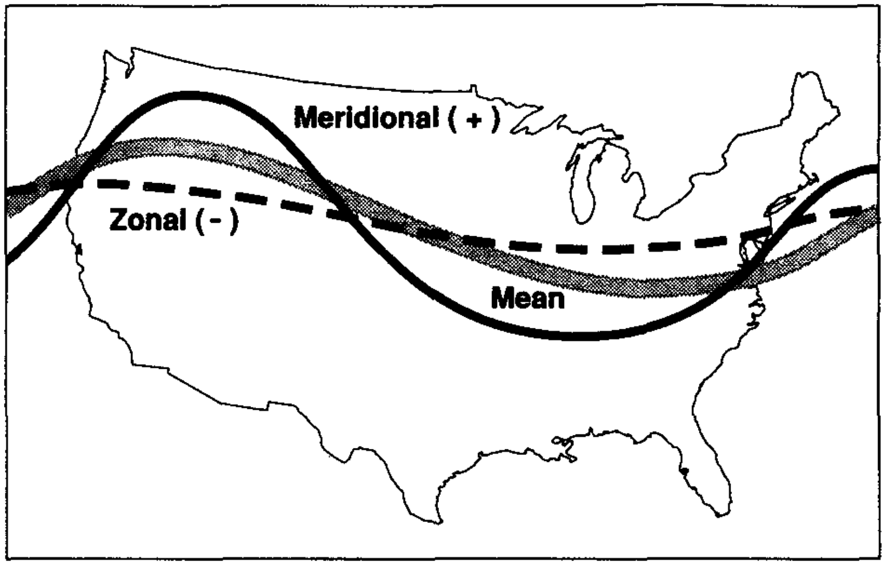
Good et al., 2014, *Sandy edited volume*

Pacific North American Pattern

Loading Pattern for the Pacific North American (PNA) Oscillation
Geopoential Height at 500 hPa (m)

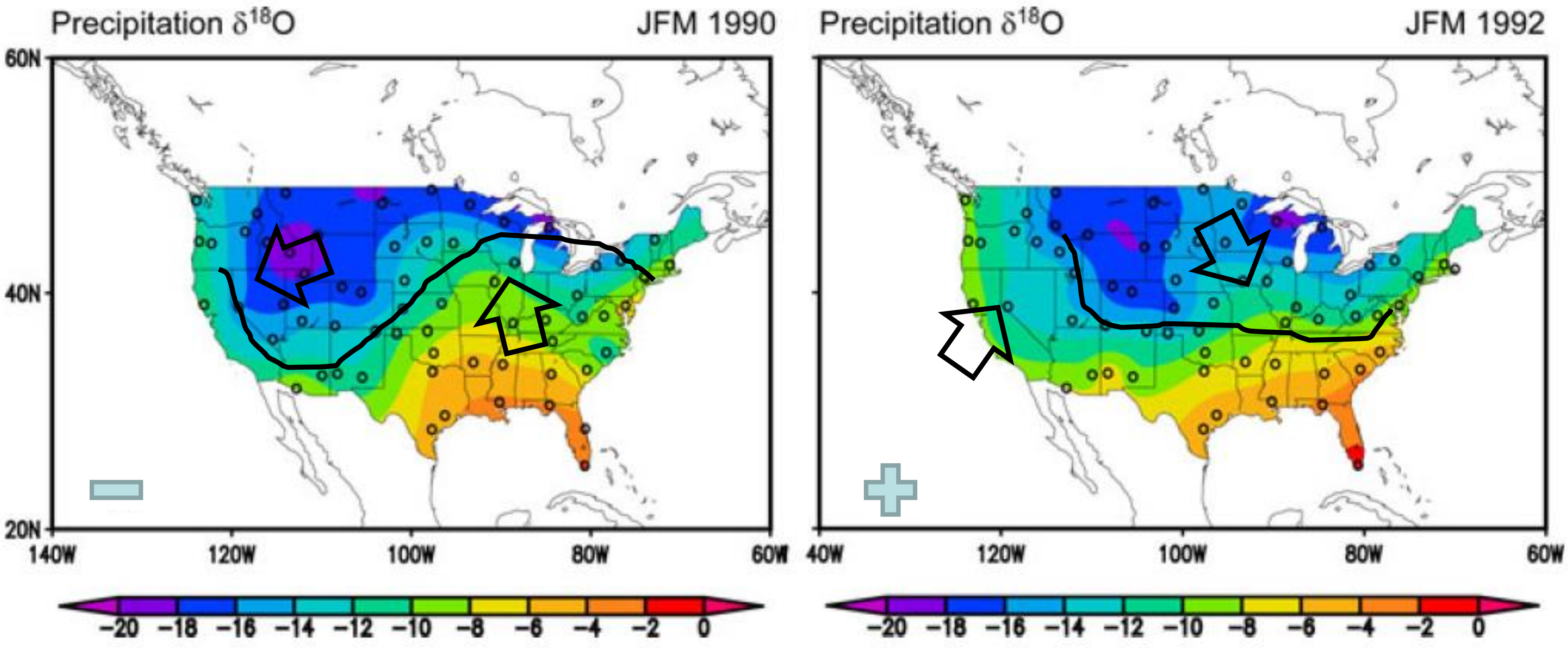


http://www.emc.ncep.noaa.gov/gmb/ssaha/



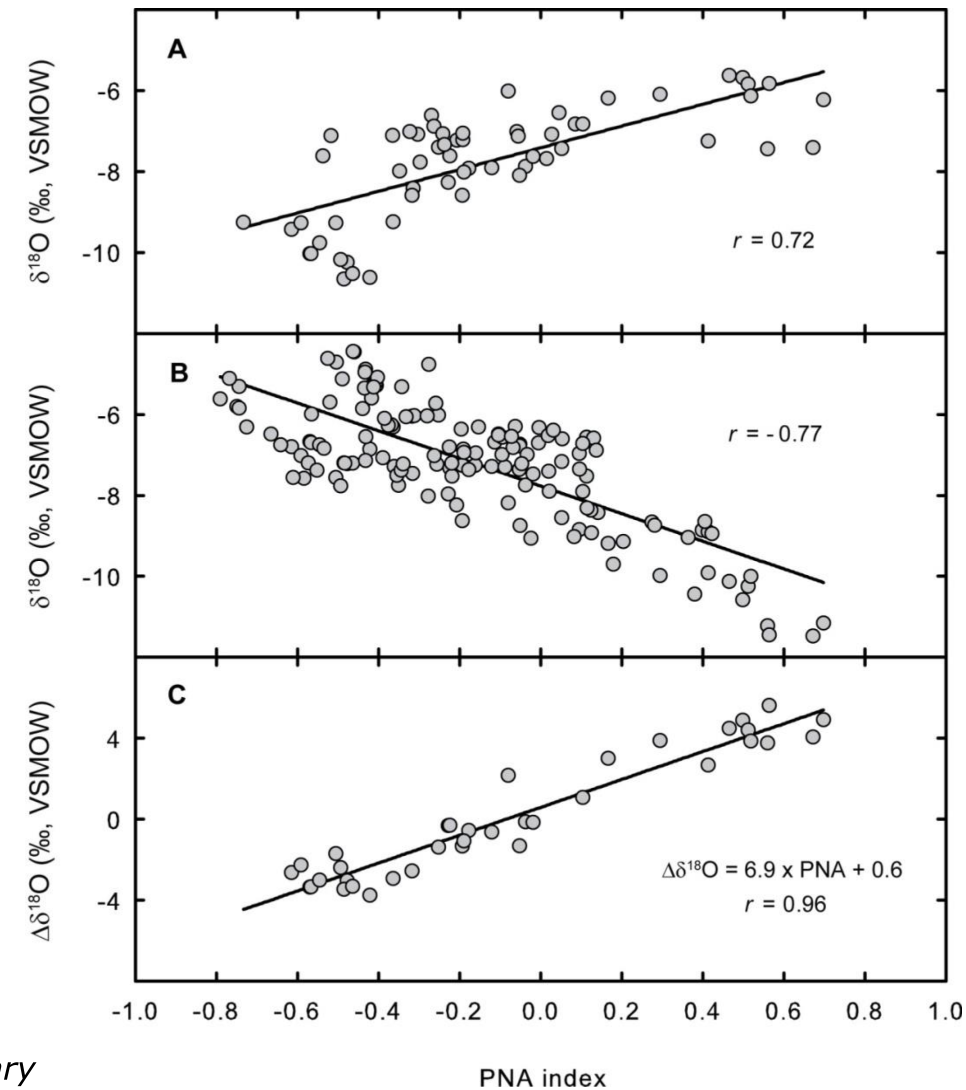
Leathers et al. Journal of Climate, 1991

PNA Pattern and Precipitation $\delta^{18}O$



Liu et al., 2013, *Clim. Dynamics*

A PNA Isotope Index



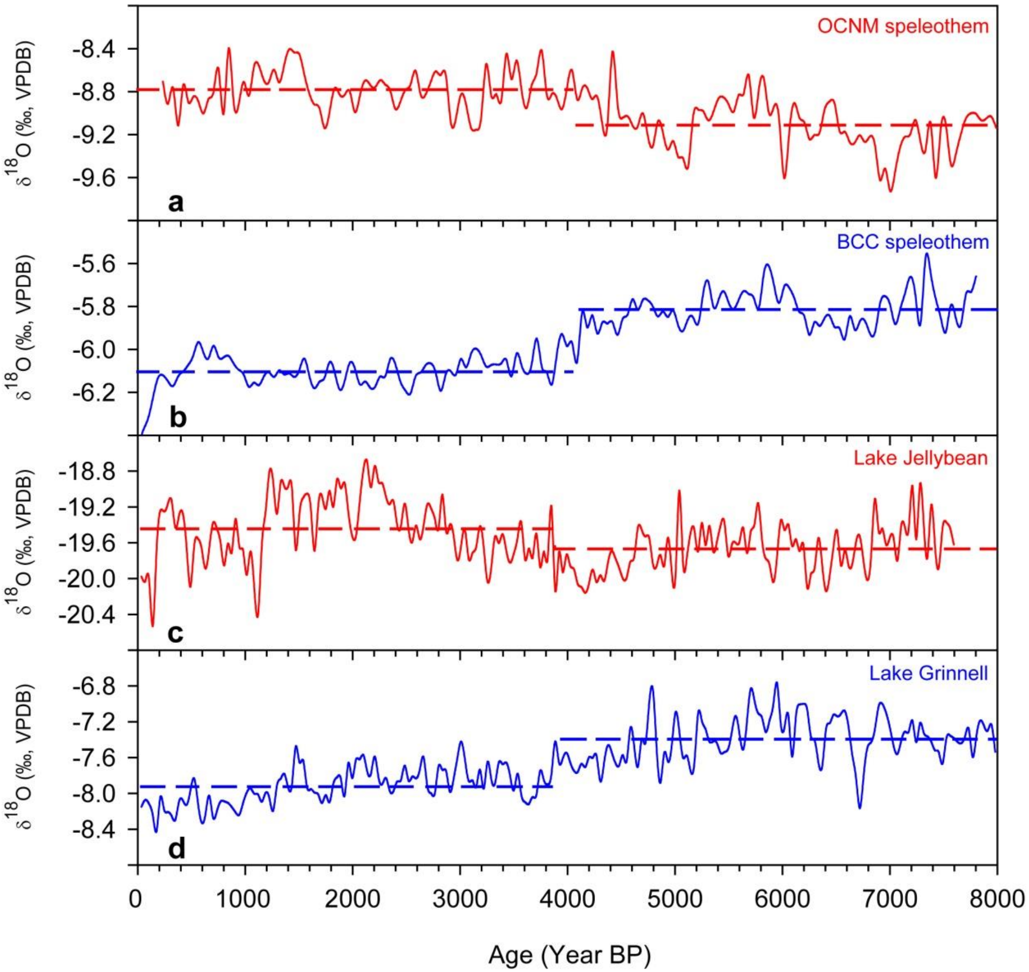
Albuquerque

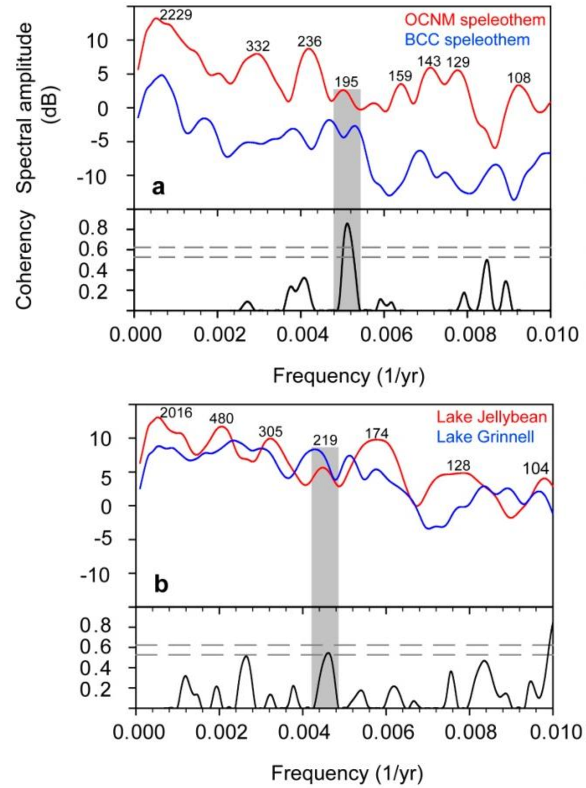
Chicago

Albuquerque
-
Chicago

Liu et al., Earth and Planetary Science Letters, 2011

Paleo-PNA





Liu et al., *Nat. Comm.*, 2014

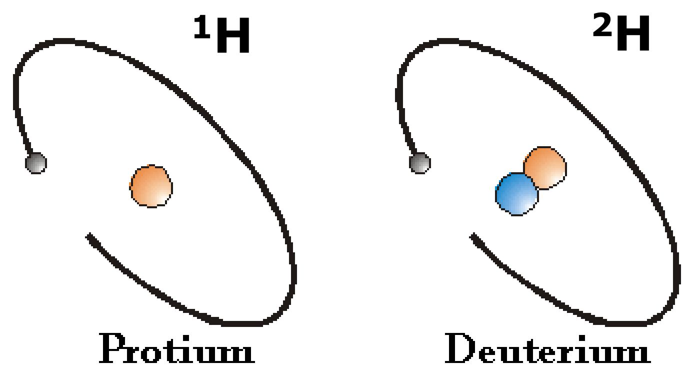
Multiple Sources of ET

Water Isotope Tracers

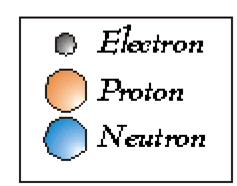
- Stable H and O isotopes inherent tracers with well-documented, well-understood behavior in the water cycle

- Transpiration does not fractionate
  - $\delta_{vapor} = \delta_{liquid} = \delta_{precipitation}$

- Evaporation fractionates
  - $\delta_{vapor} < \delta_{precipitation}$
  - $\delta_{liquid} > \delta_{precipitation}$

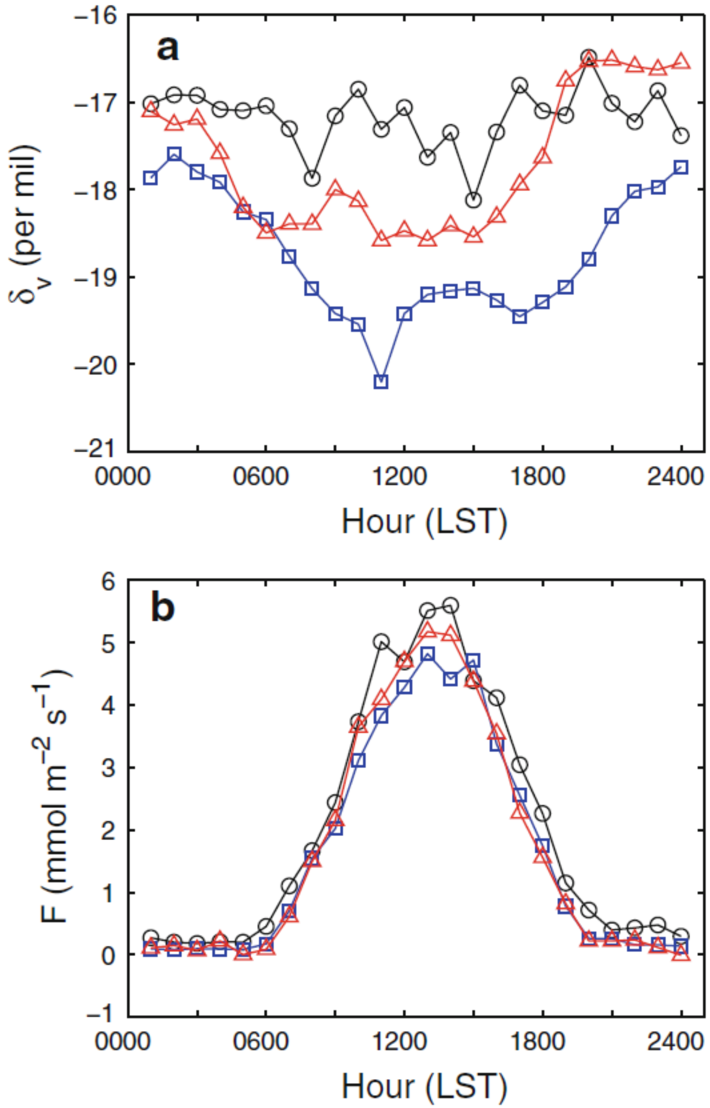


$$\delta = R_{sample}/R_{standard} - 1$$
$$R = {}^{2}H \; / \; {}^{1}H$$



2 Approaches to ET Separation

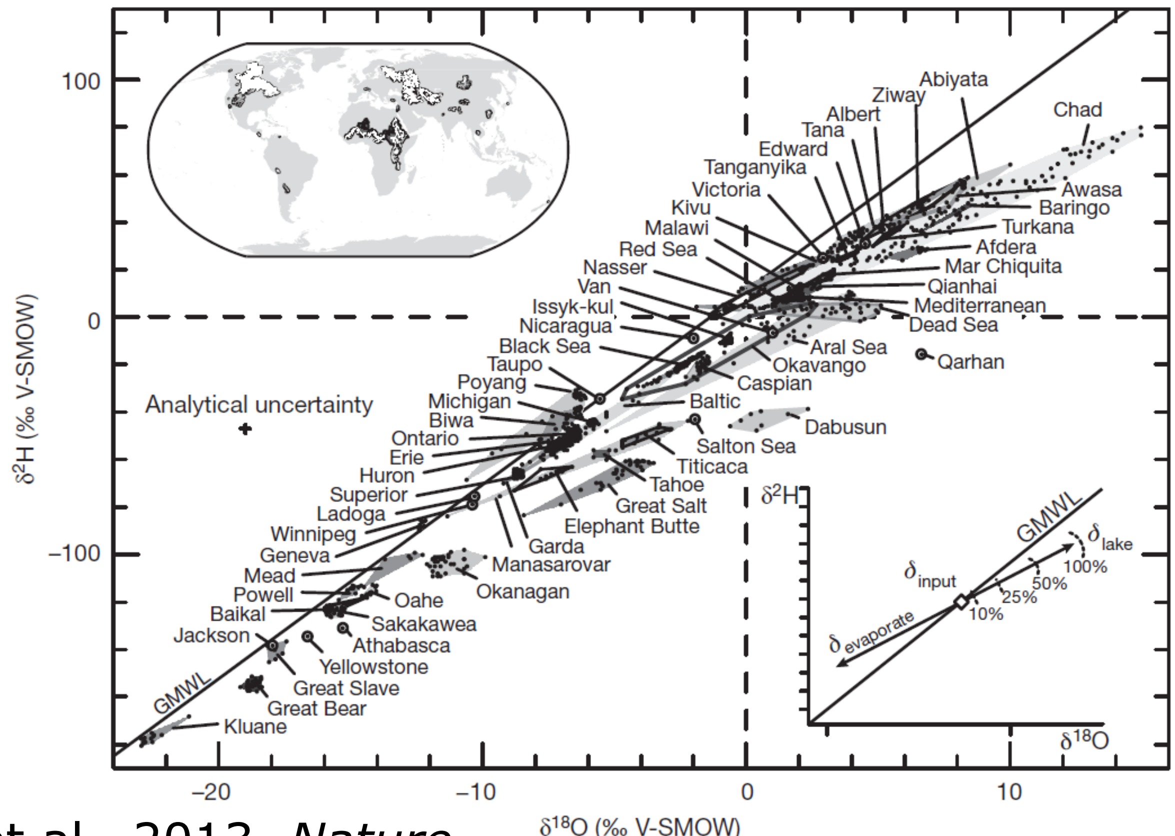
- Measure vapor
  - + Directly assess ET flux
  - - Difficult at large scales



Griffis et al., 2010, *B-LM*

2 Approaches to ET Separation

- Measure liquid
  - + Can integrate over large areas
  - - May not 'see' all processes

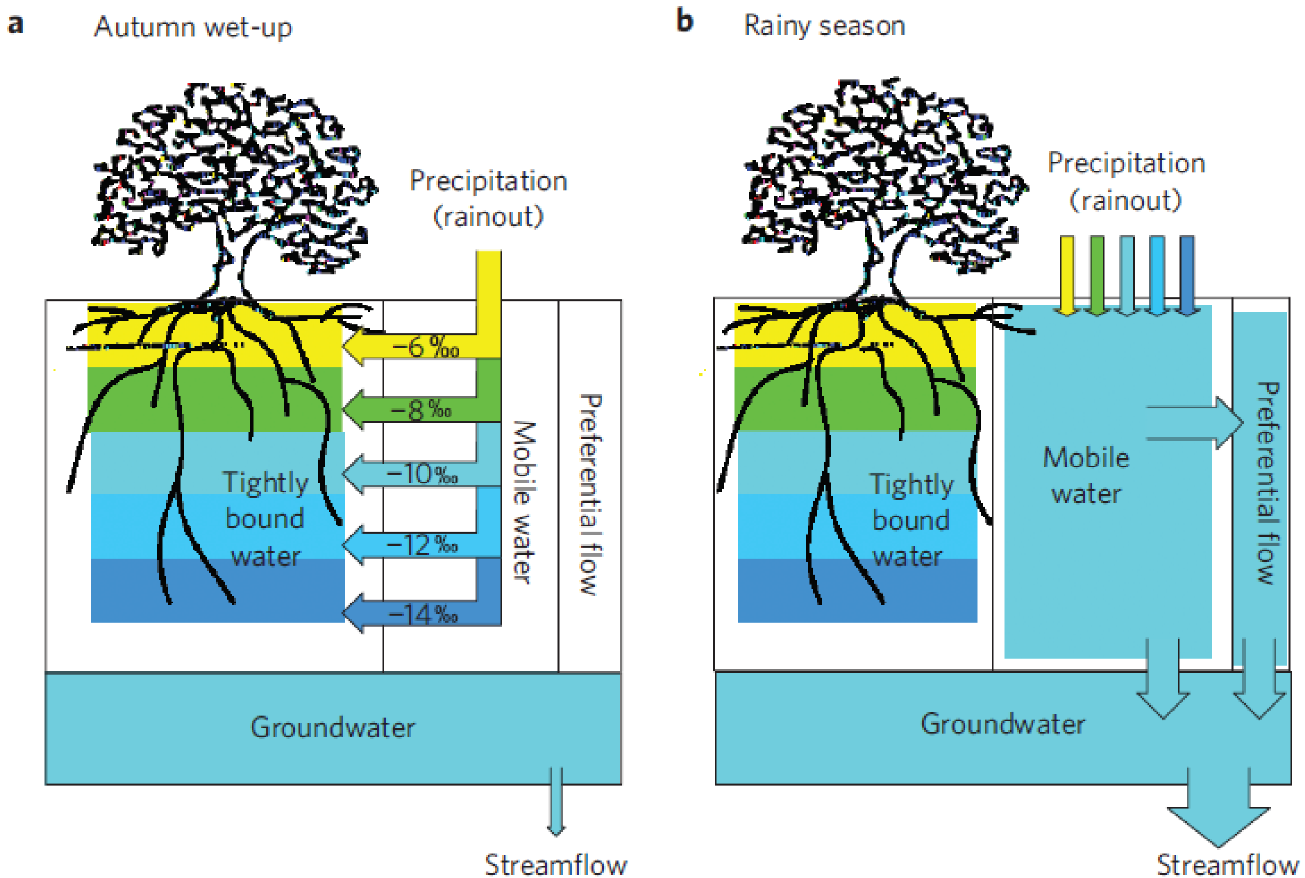


90% of ET is transpiration?

Jasechko et al., 2013, *Nature*

Ecohydrologic Connectivity

- Water in soils and plants may not be same water that enters aquifers and rivers



Brooks et al., 2009, *Nat. Geoscience*

Can we Combine Approaches?

- Need global estimates of δ for river water and ET
- Where can we get them?
  - Ocean and atmosphere mass-balance

$$dH_2O_o/dt = 0 = P_o + Q - E_o$$

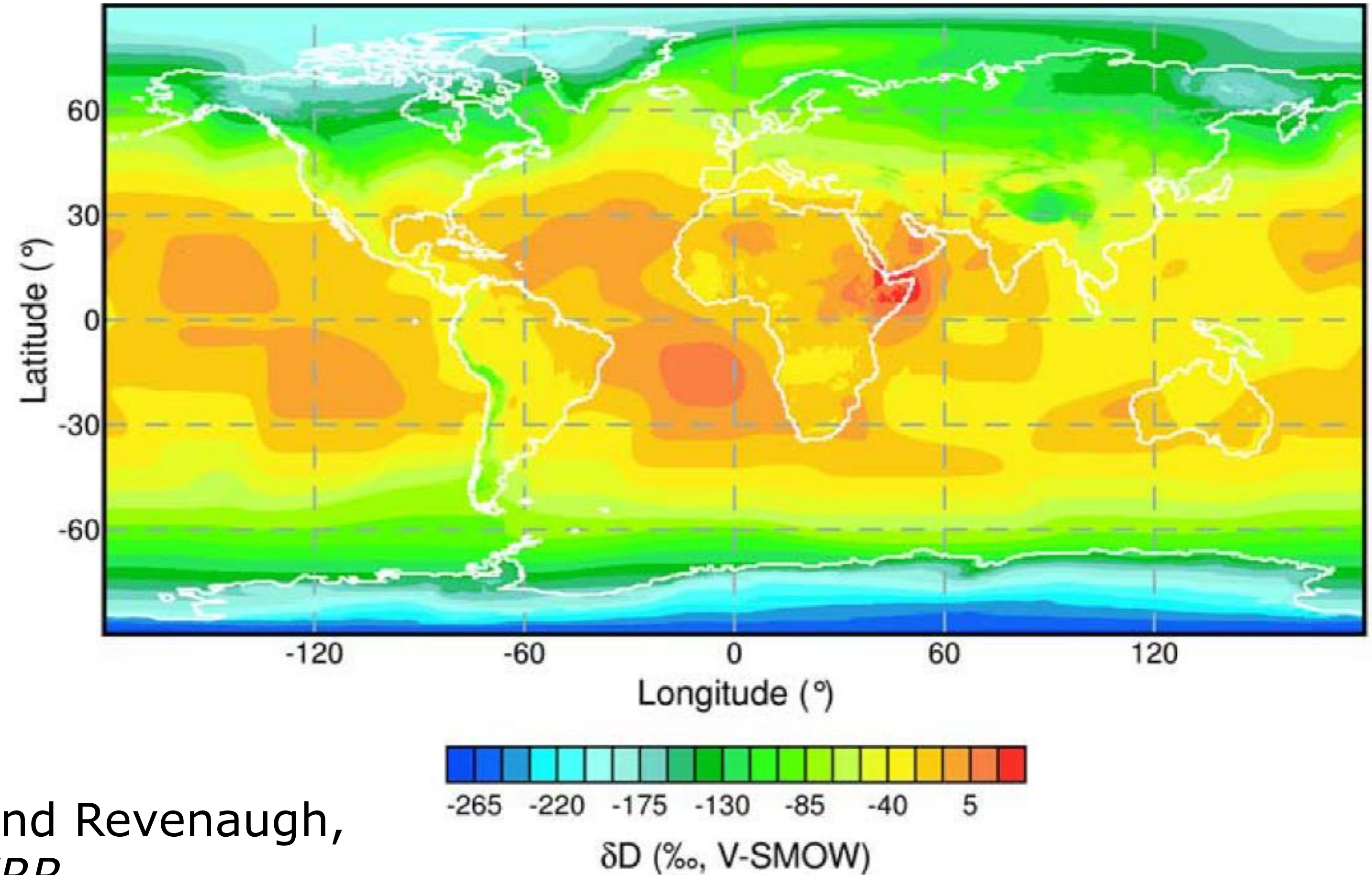
$$d\delta_o/dt = 0 = P_o*\delta_{Po} + Q*\delta_Q - E_o*\delta_{Eo}$$

$$dH_2O_a/dt = 0 = E_o + ET - P_o - P_c$$

$$d\delta_a/dt = 0 = E_o*\delta_{Eo} + ET*\delta_{ET} - P_o*\delta_{Po} - P_c*\delta_{Pc}$$

Constraints

- Good data exist on bulk water fluxes (P, E, ET, Q)
- Precipitation isotope composition from isoscapes



Bowen and Revenaugh, 2003, *WRR*

The Evaporation Isotope Problem

- Excellent model for estimating δ value of E_o, but you need to know surface layer δ_a

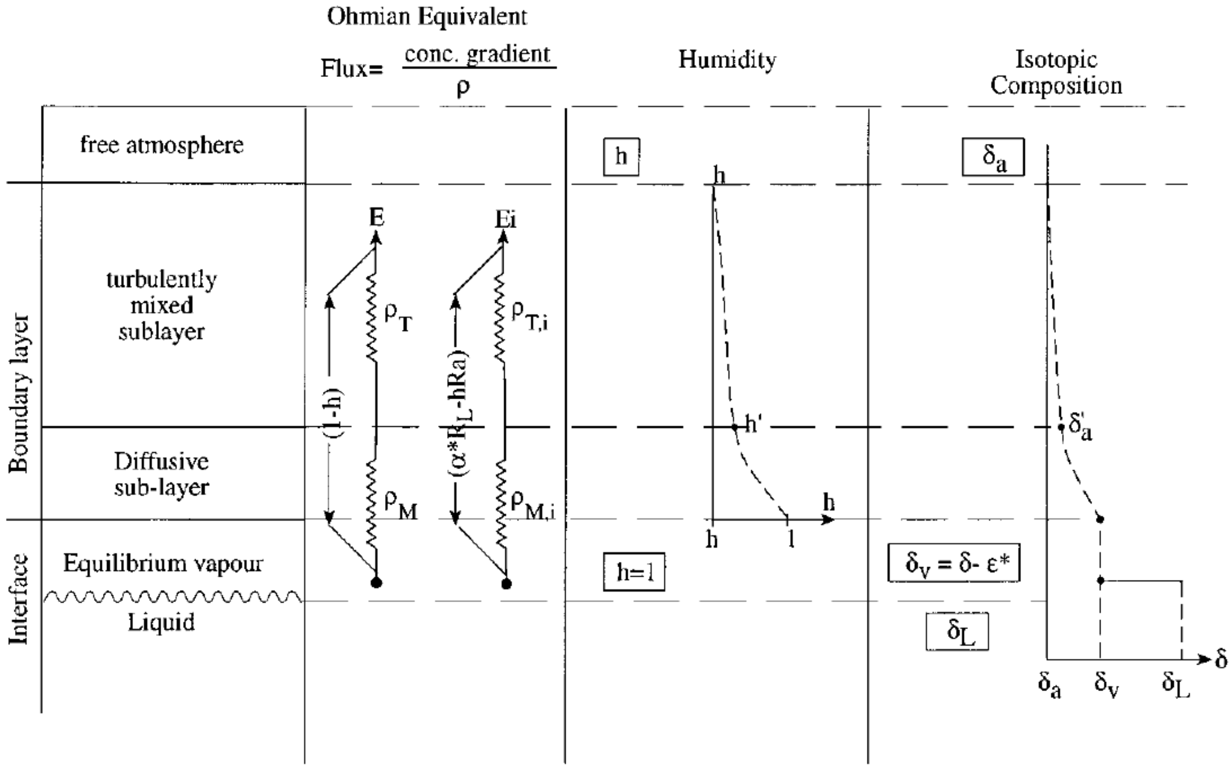
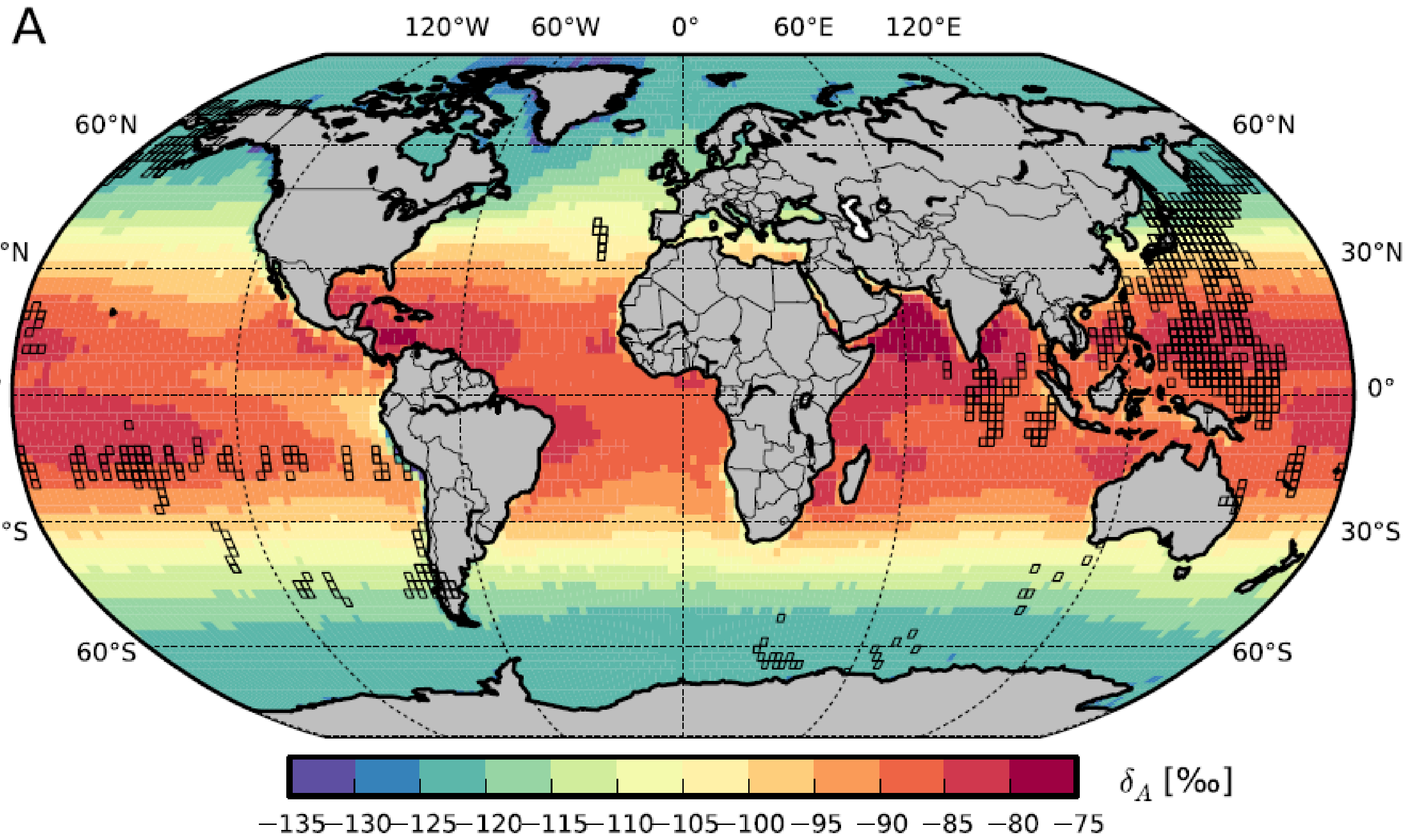


Figure 3 The Craig-Gordon evaporation model.

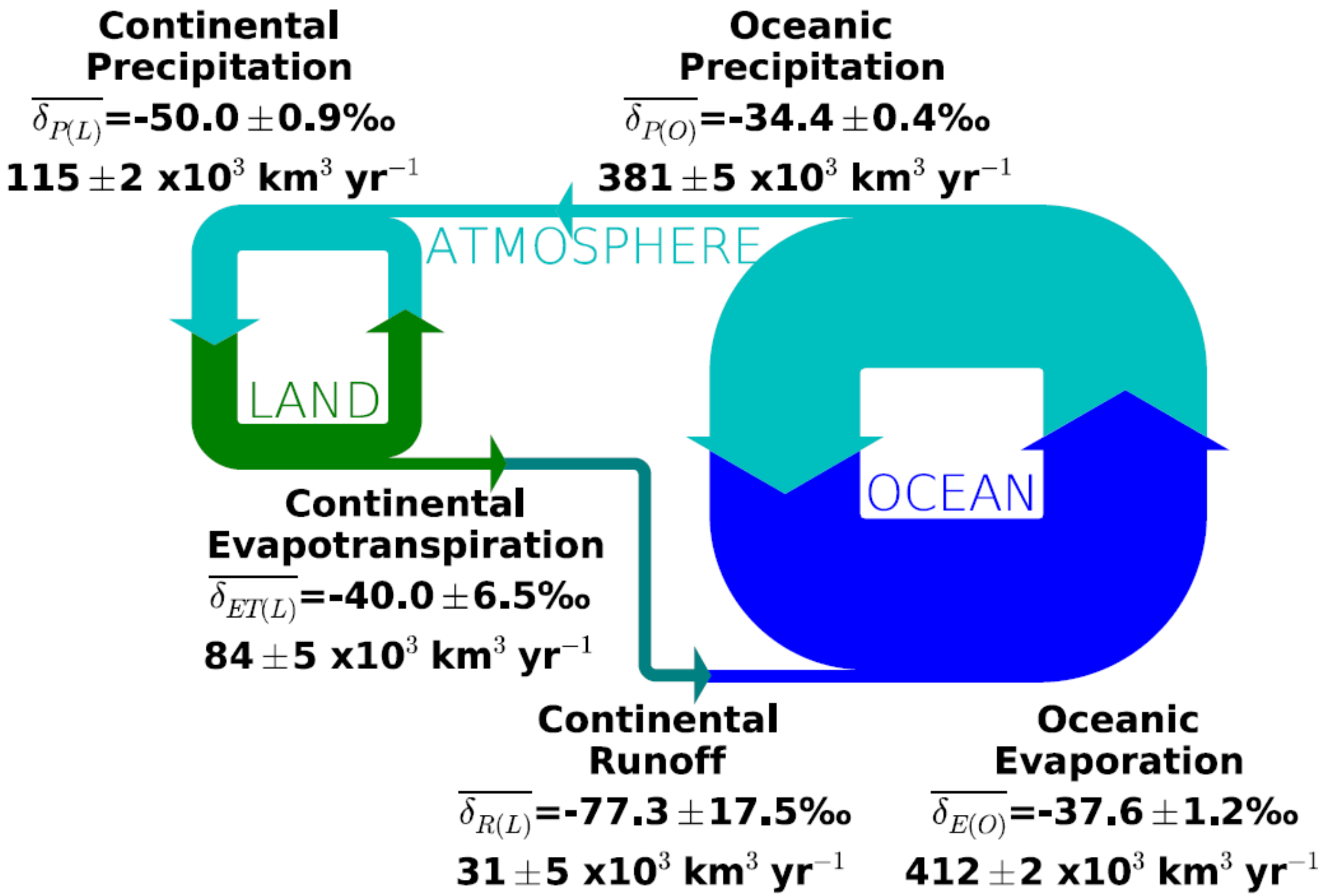
Gat, 1996, *AREPS*

New Satellite-Based δ_a Isoscape



Good et al., 2015, *GRL*

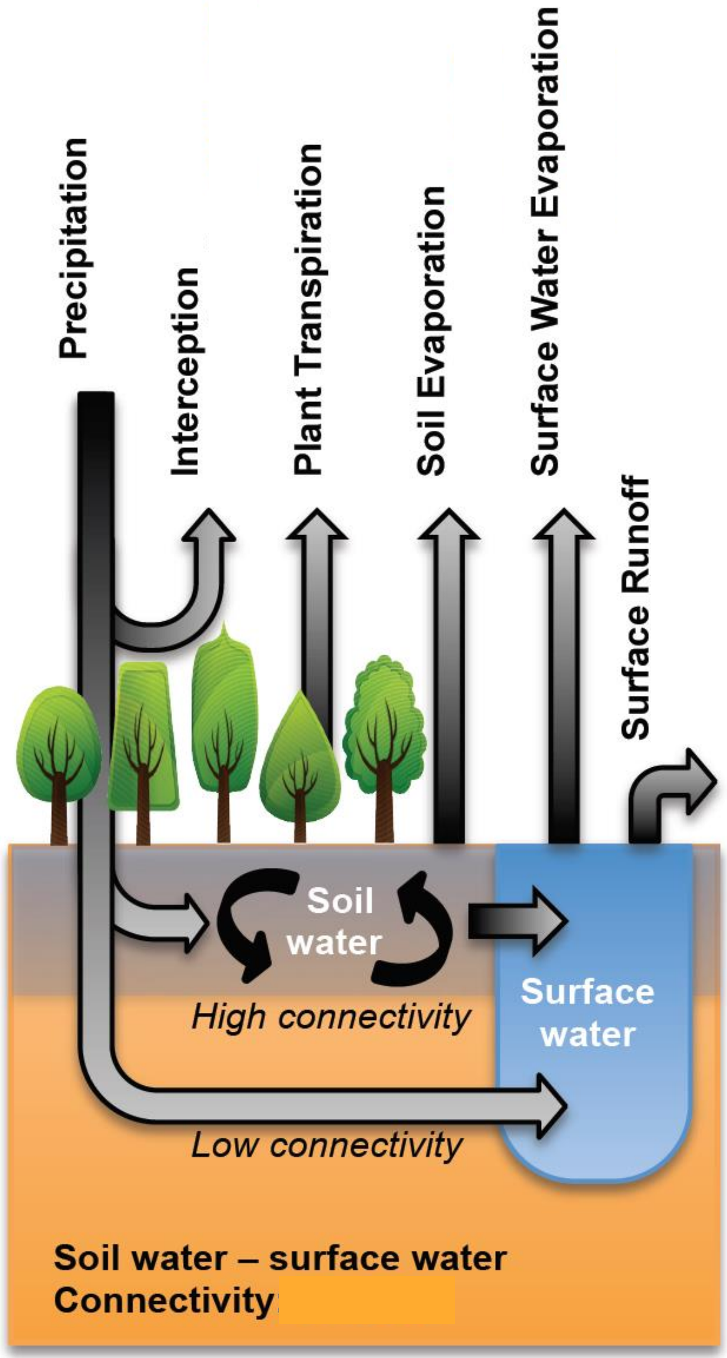
New Estimates of Global δ_Q, δ_{Eo}



Good et al., 2015, *GRL*

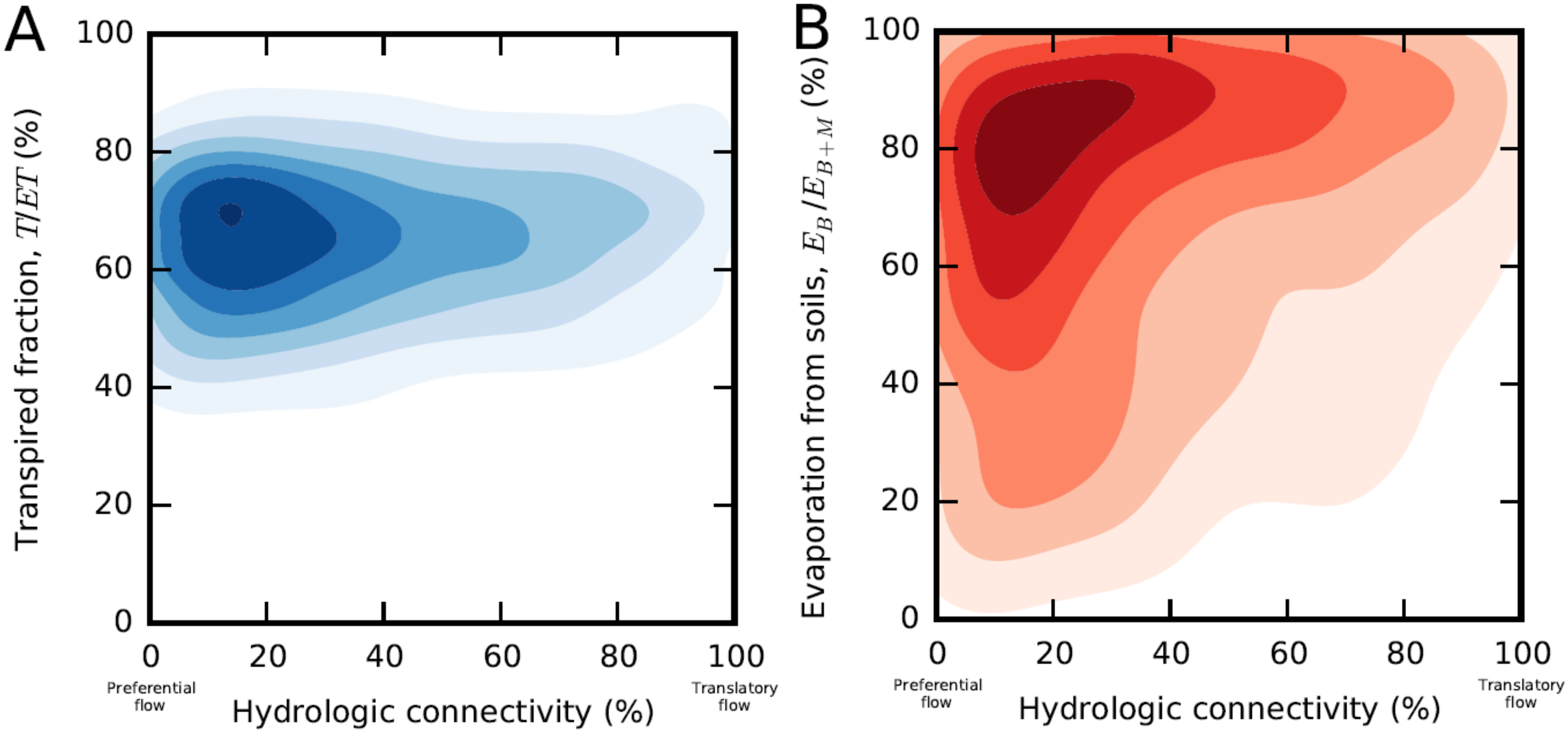
Global Analysis

- What combinations of T, soil E, open-water E, and connectivity give the estimated global values



Good, Noone and Bowen, 2015, *Science*

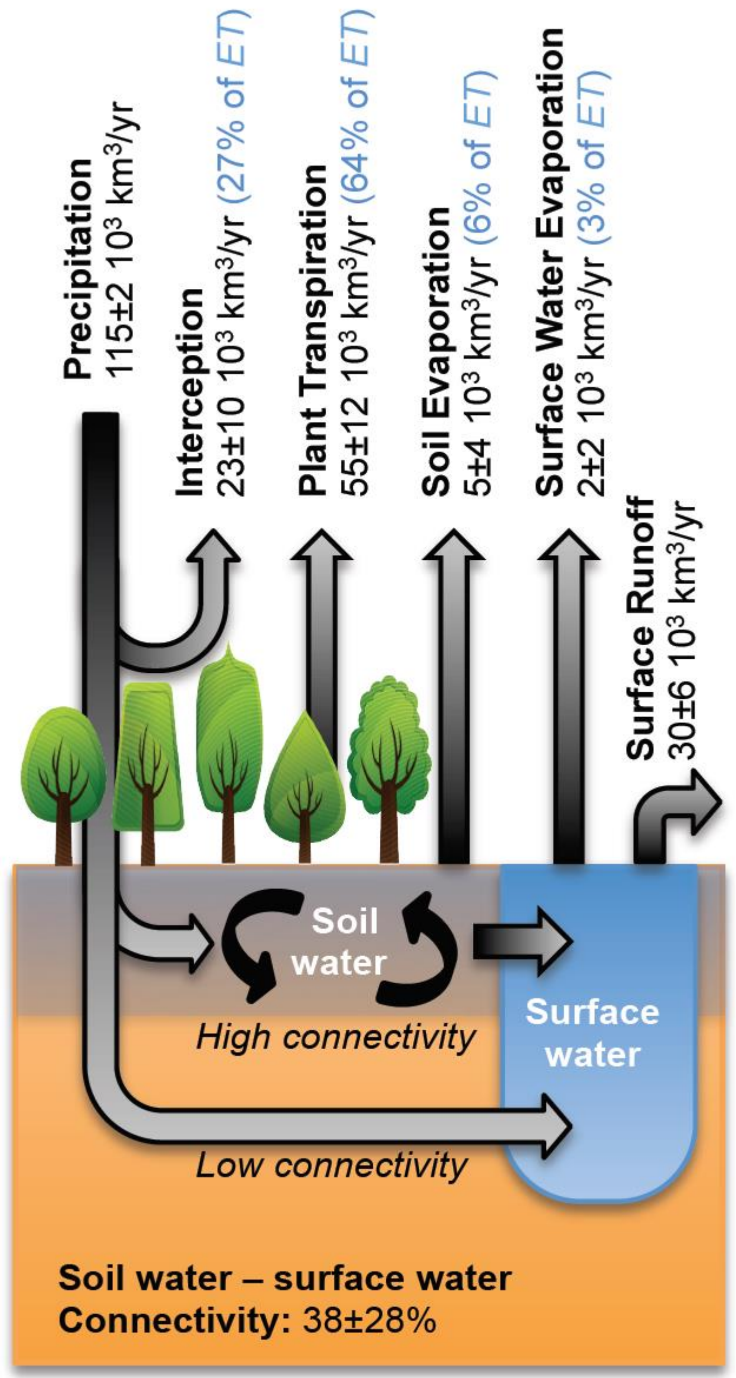
Kernel Density Examples



Good, Noone and Bowen, 2015, *Science*

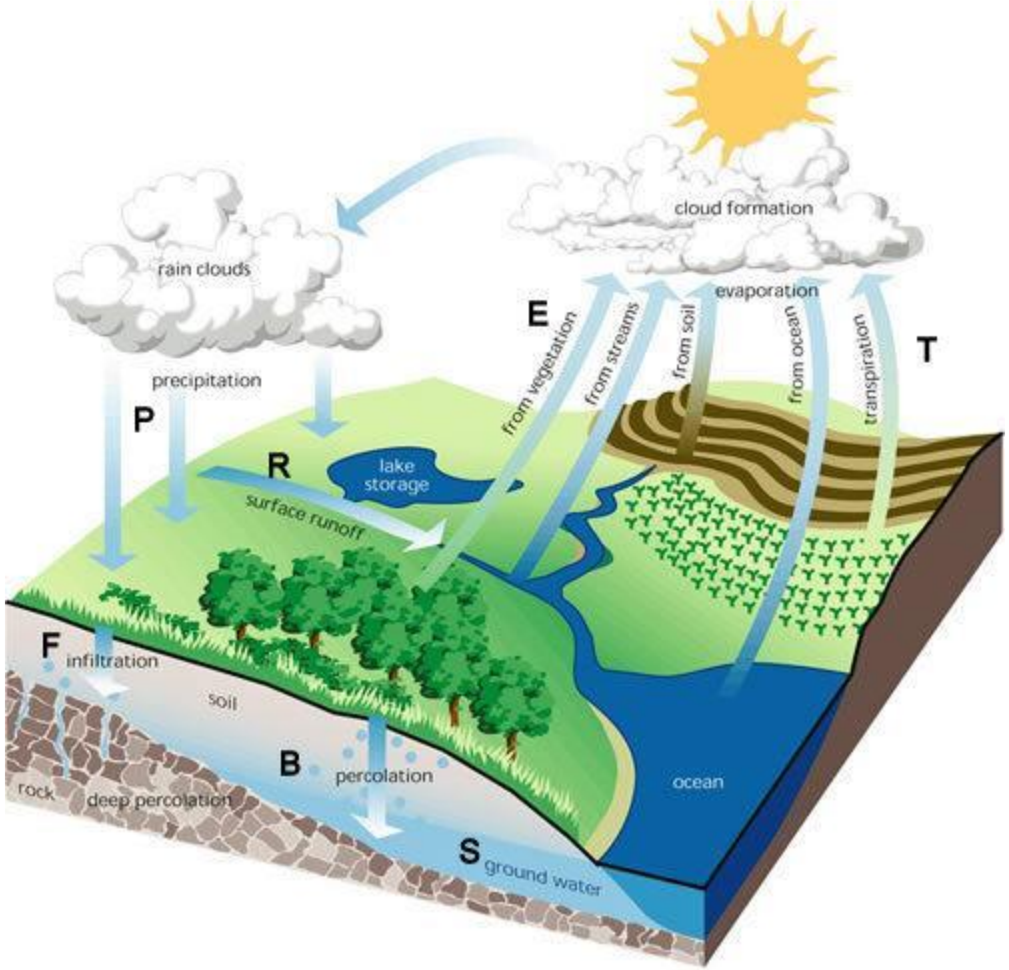
Global Result

- Globally, transpiration majority of ET but not 90%
- Low connectivity of soil and surface waters suggests dominance of preferential flow
- This, + the fact that >60% of continental evaporation occurs in soils, compromises the lake-based ET separation method



Good, Noone and Bowen, 2015, *Science*

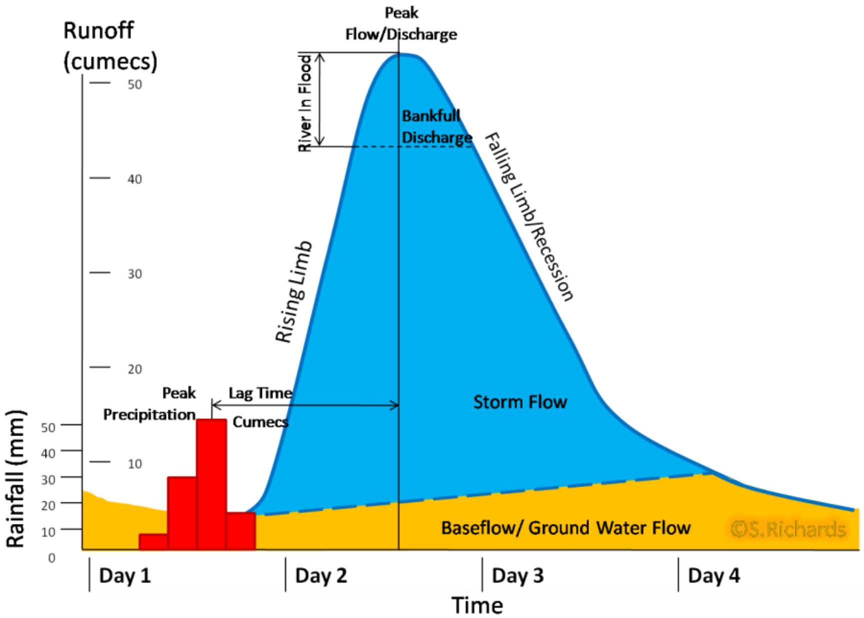
Catchment water balance



$$P = R + E + T + \Delta S$$

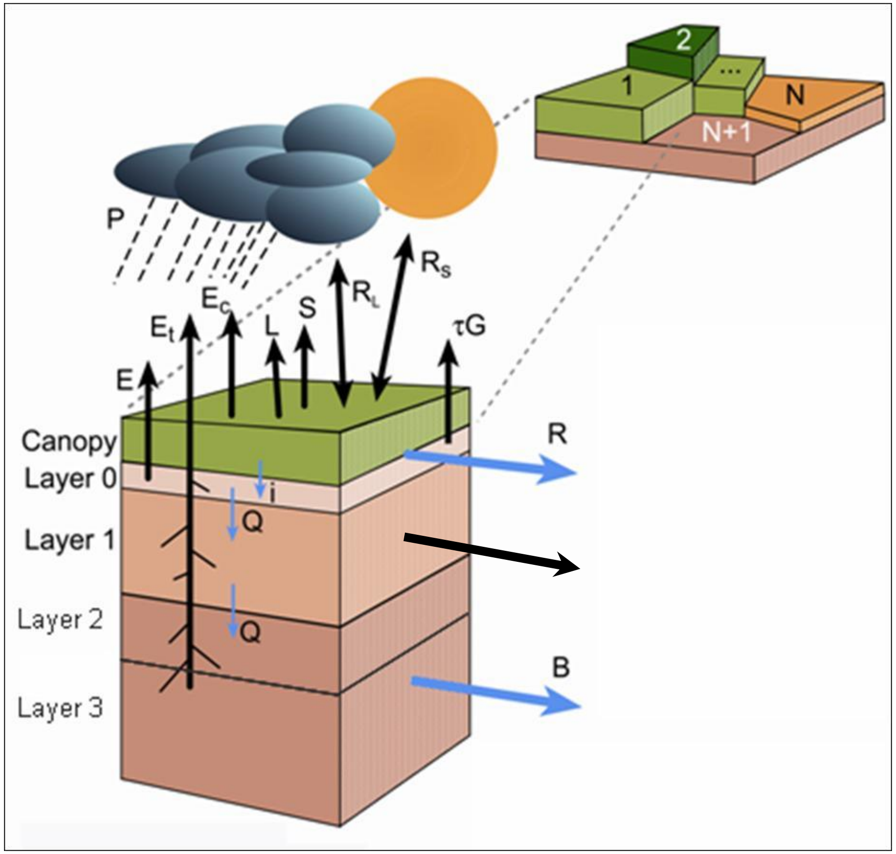
Storm Hydrograph

- Accurate rainfall-runoff models are one of the fundamental goals of catchment hydrology
  - Flood control
  - Water management
  - Water quality
- Summarized in terms of storm hydrograph



Rainfall routing

- How is storm precipitation delivered to streams?
  - Overland flow
  - Interflow
  - Groundwater recharge/baseflow
- What are the transit times associated with these flowpaths?



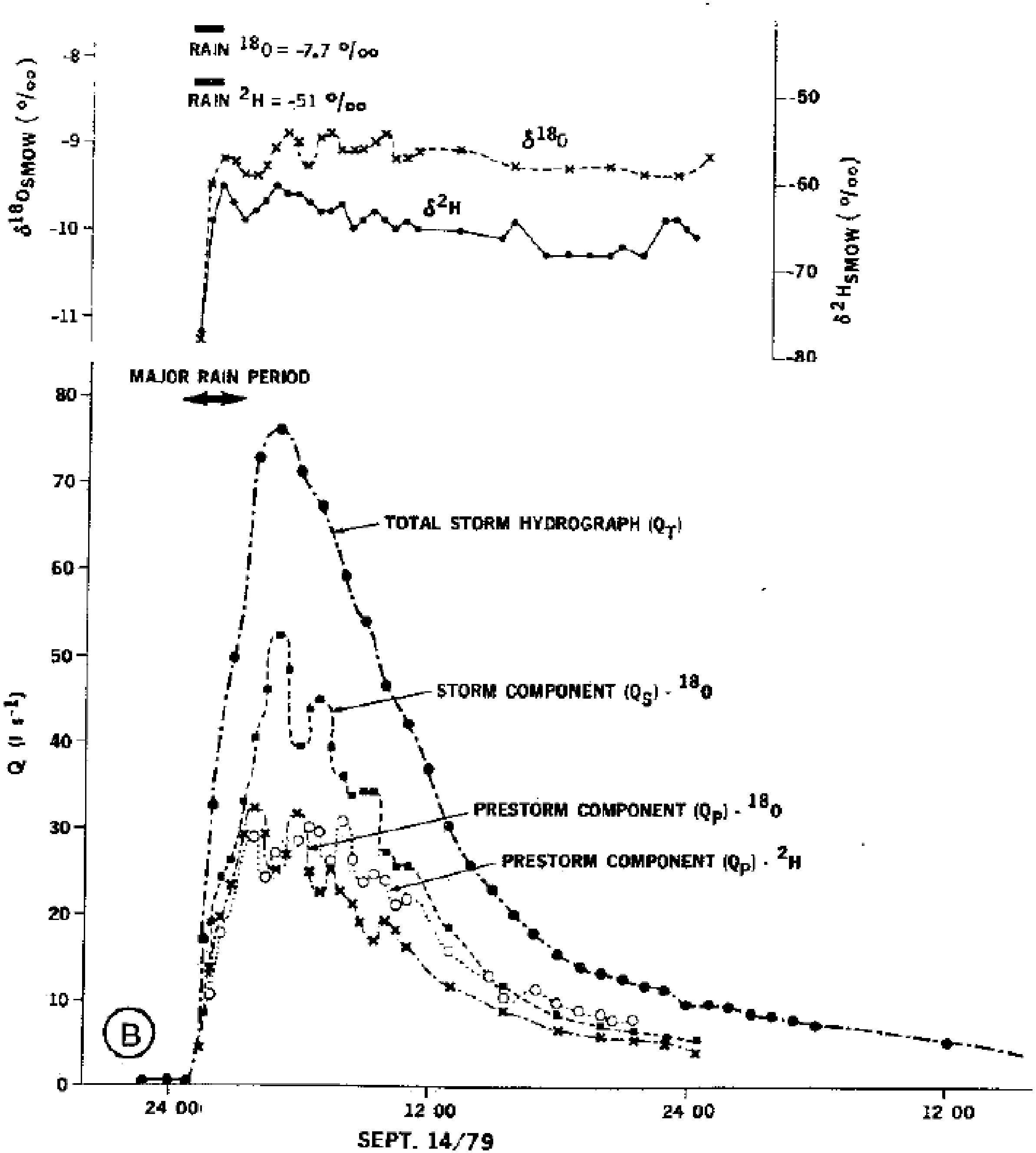
www.hydro.washington.edu

Hydrograph separation

- Given any conservative tracer that is present in different abundance in ***pre-event*** and ***event*** water, the fraction of pre-event water in storm flow at any time is

$$f_{pe} = \frac{C_s - C_e}{C_{pe} - C_e}$$

- Major assumption: C_e and C_{pe} are constant and can be accurately characterized
- Isotope hydrograph separation takes advantage of temporal variation in precipitation δ values



Bottomley et al., 1984
J Hydrol

"Old water paradox"

Study	Location	Catchment area (ha)	Tracer	Percentage pre-event water	
				peak	volume
Jordan (1994)	Switzerland	3.6	^{18}O		45, 75
Waddington et al. (1993)	Ontario	160	^{18}O	87, 93	
McDonnell et al. (1991)	New Zealand	3.8	D	92-100	
O'Gunkoya & Jenkins (1991)*	United Kingdom	1000	D		54-90
McDonnell et al. (1990)	New Zealand	310	D		21-33
Nolan and Hill (1990)	California	1060	D		57
Bonell et al. (1990)	New Zealand	218	D		59
		310	D	38	38 to >97
Blowes and Gillham (1988)	Ontario	0.75	^{18}O	9, 45	22, 50
Turner et al. (1987)	W. Australia	82	^{18}O, D		69-95
Herrman et al. (1987)*	Germany	76	^{18}O		84
Rodhe (1987)	Sweden	3	^{18}O		81, 87
		4	^{18}O		81, 96
		17	^{18}O	87	
		50	^{18}O		85-99

....

Genereux and Hooper, 1998, *Isotope Tracers*

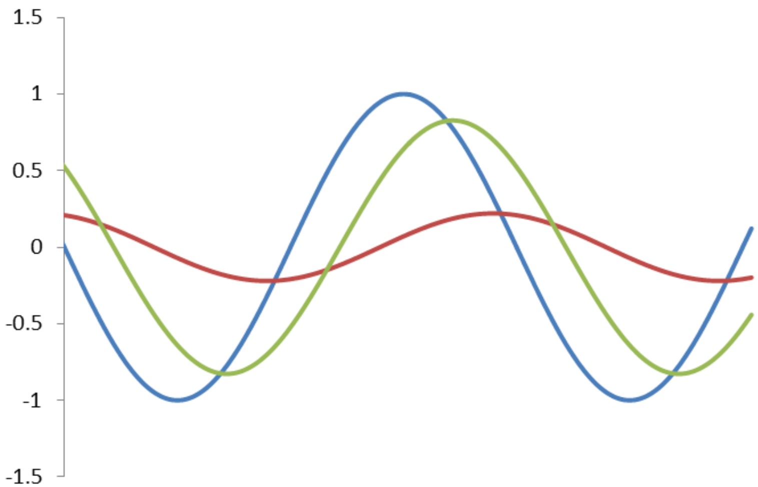
"Old water paradox"

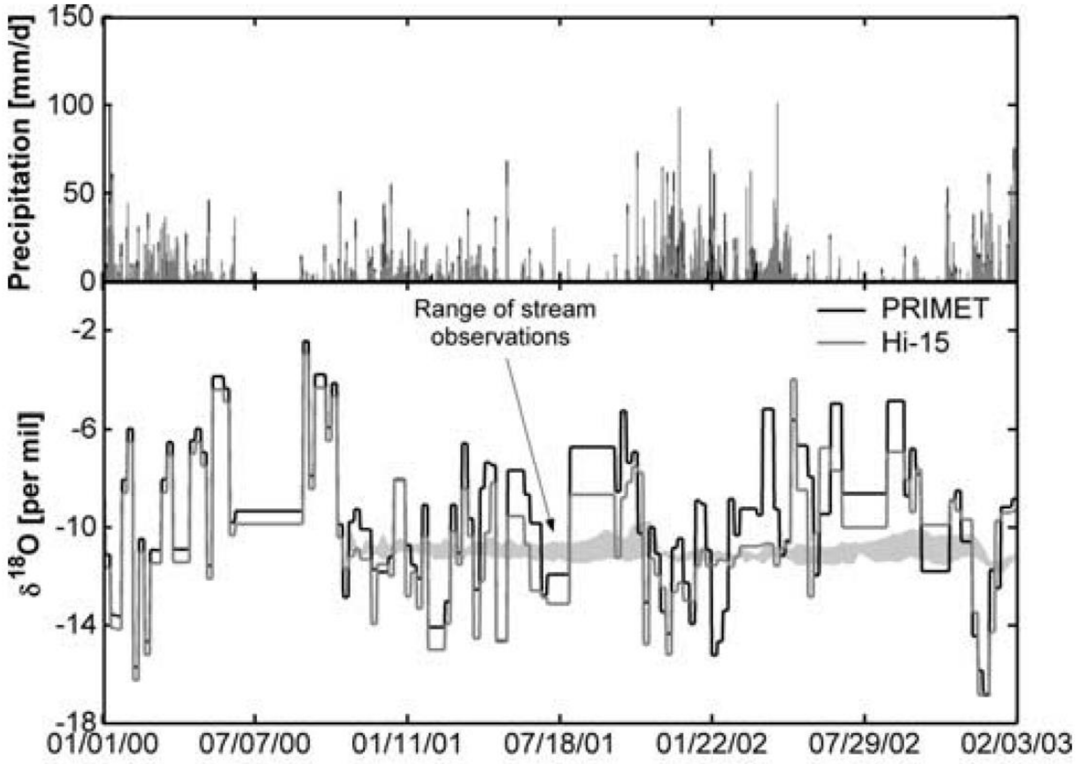
- Even in small, steep catchments, most storm flow is "old" water
- Mean residence time of water in catchments is much longer than implied by simple interpretation of storm hydrograph, rainfall-runoff models

- How does storm discharge actually work?
  - If water is not transferred directly, how does addition of precipitation rapidly force release of pre-event water?
- Hypotheses
  - Pressure waves
  - Capillary fringe
  - Macropore flow

Baseflow transit time distributions

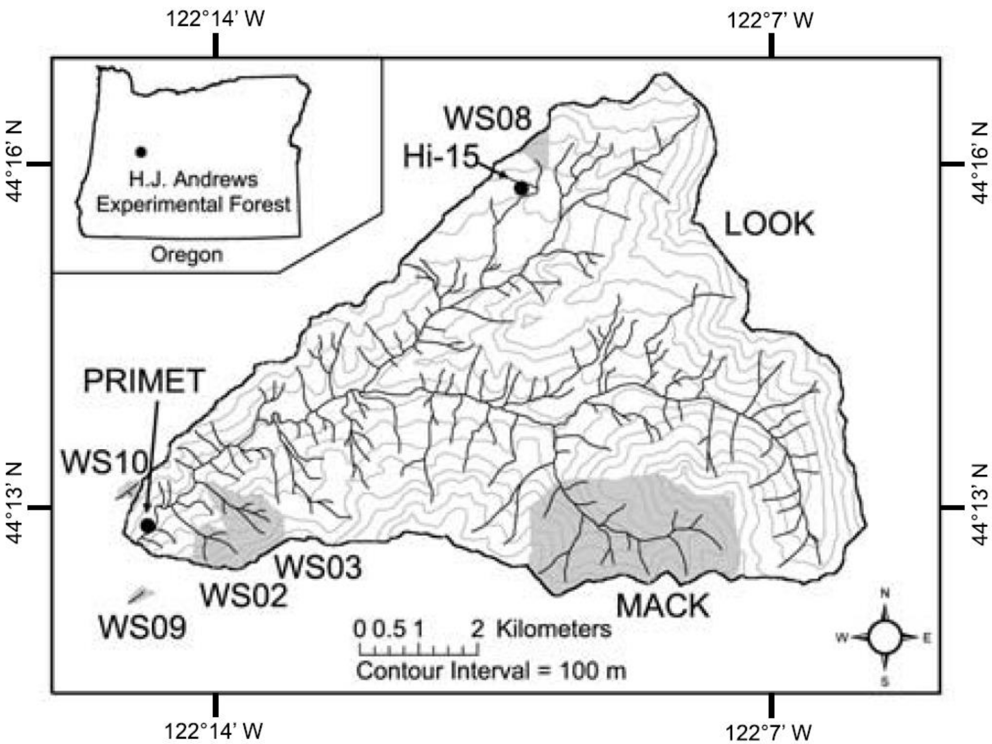
- Given measured input and output time series, optimize the function *f*(*t*) describing the distribution of transit times within a catchment



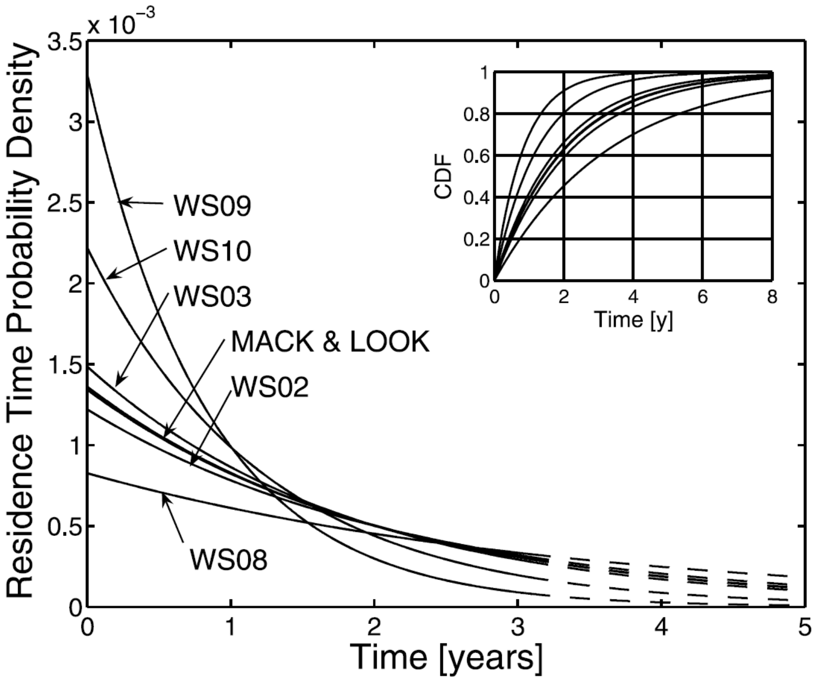


McGuire et al. 2005 *WRR*

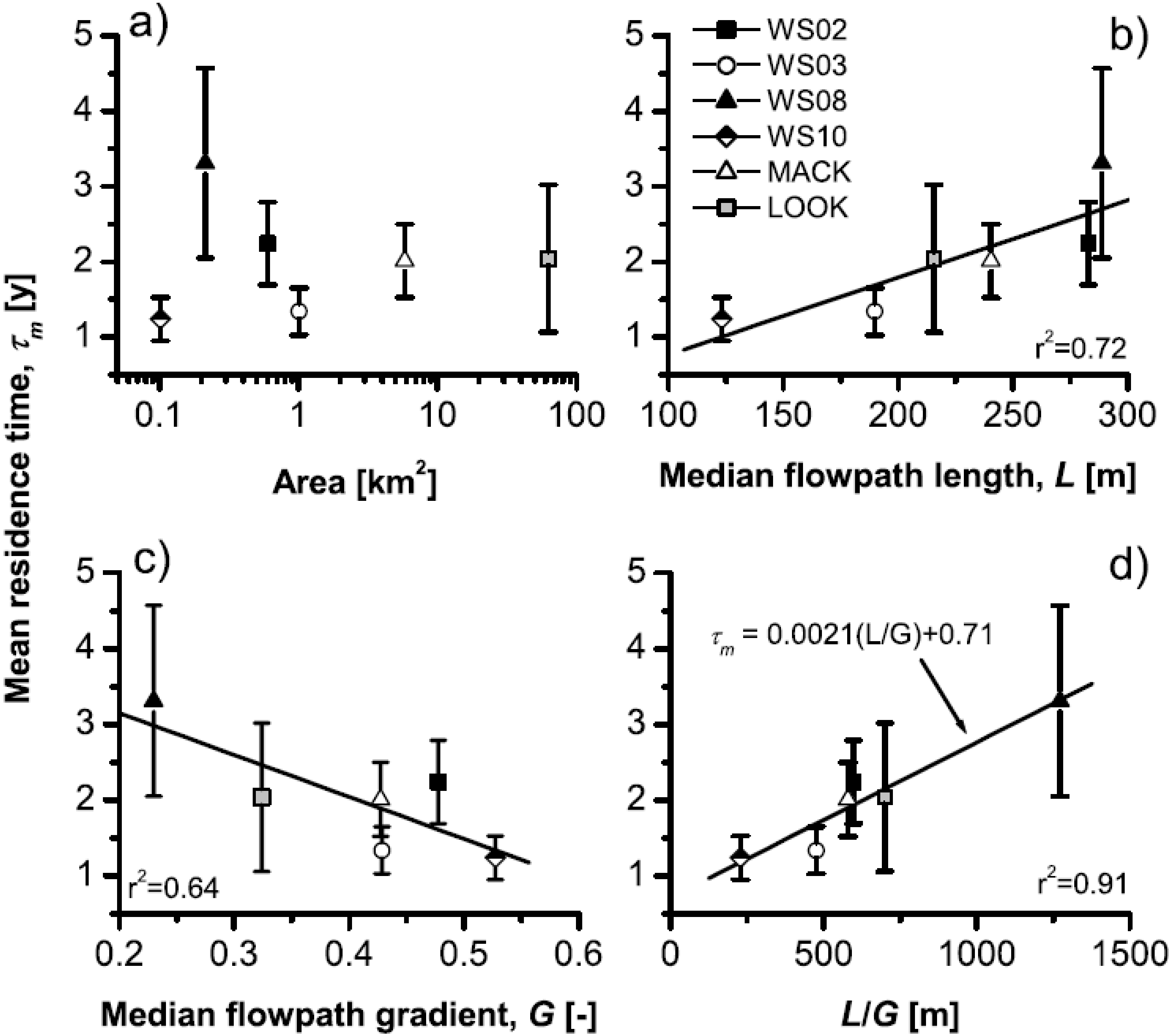
Baseflow transit time distributions



- Mean residence times are long (years)
- What catchment properties control distribution?



McGuire et al. 2005 *WRR*

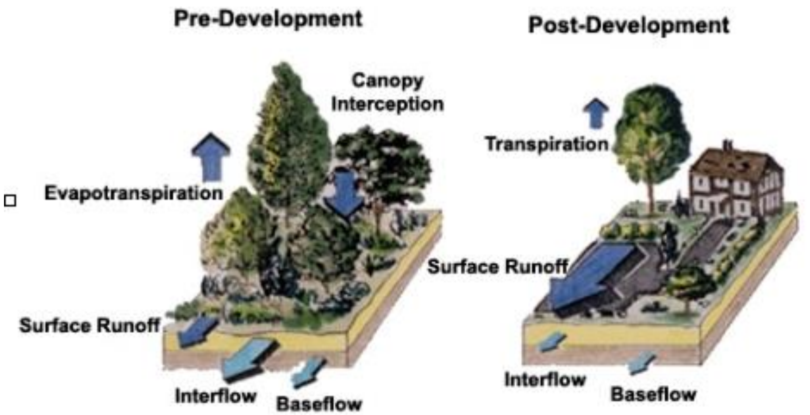


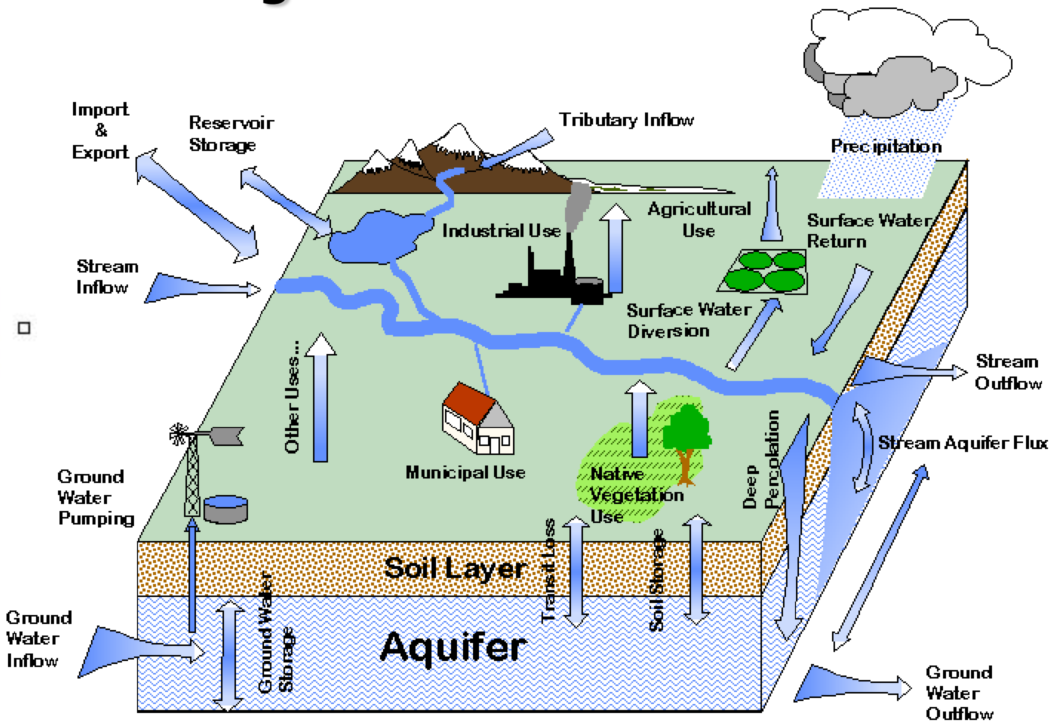
McGuire et al., 2005, *WRR*

Frontiers: Managed Landscapes

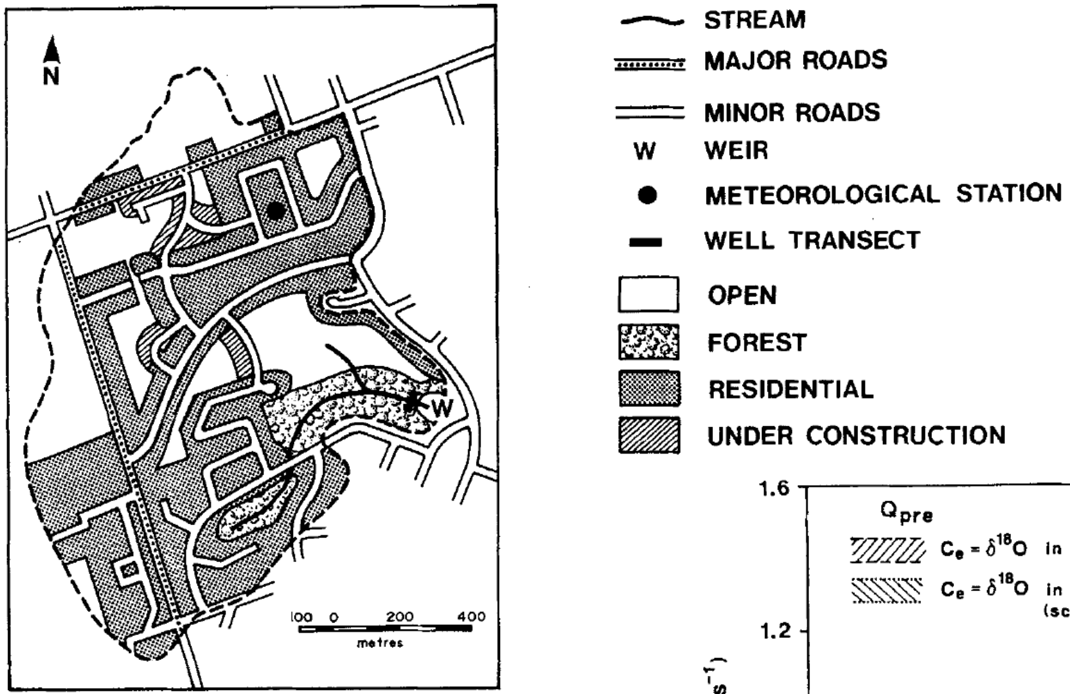
- Relatively few studies have investigated transit times and runoff routing in large catchments and human-dominated systems

- LOTS of great questions relating to land-use effects on runoff generation

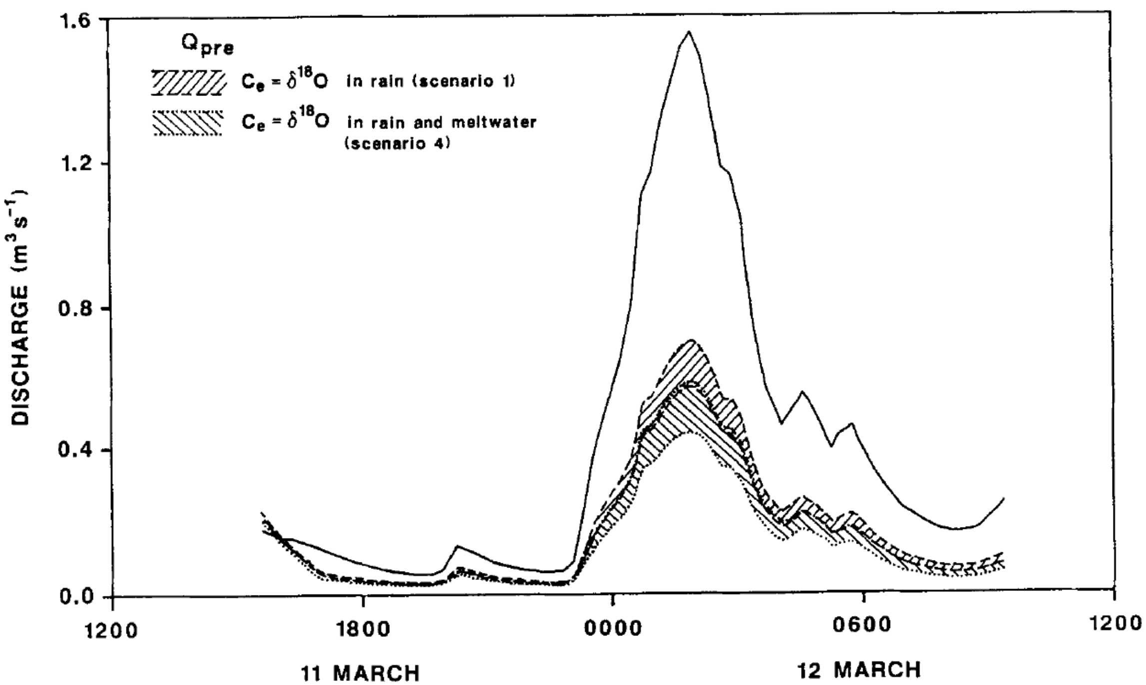




Hydrograph separation - suburban



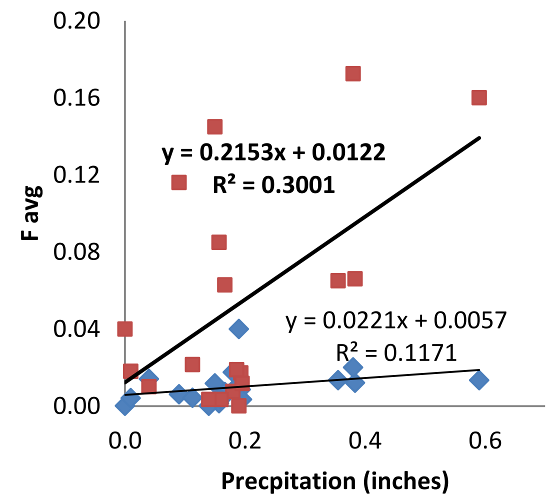
- Pre-event water <33% of storm runoff

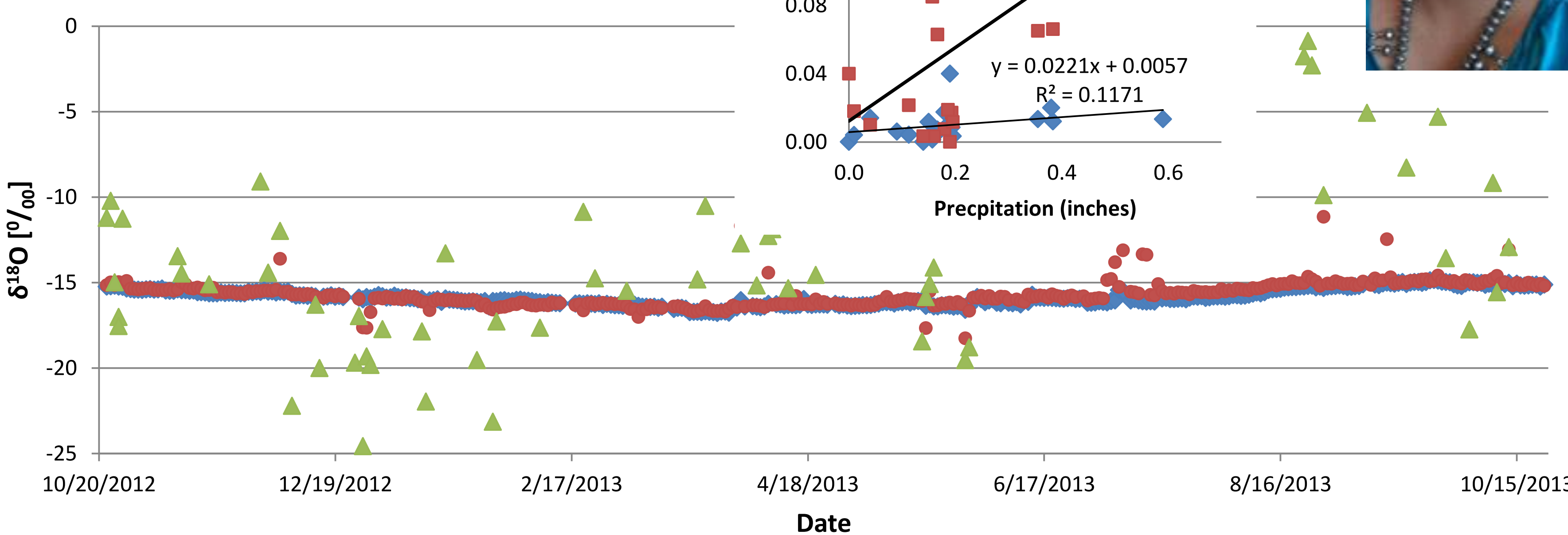


Buttle et al., 1995

Urban system – Red Butte Creek

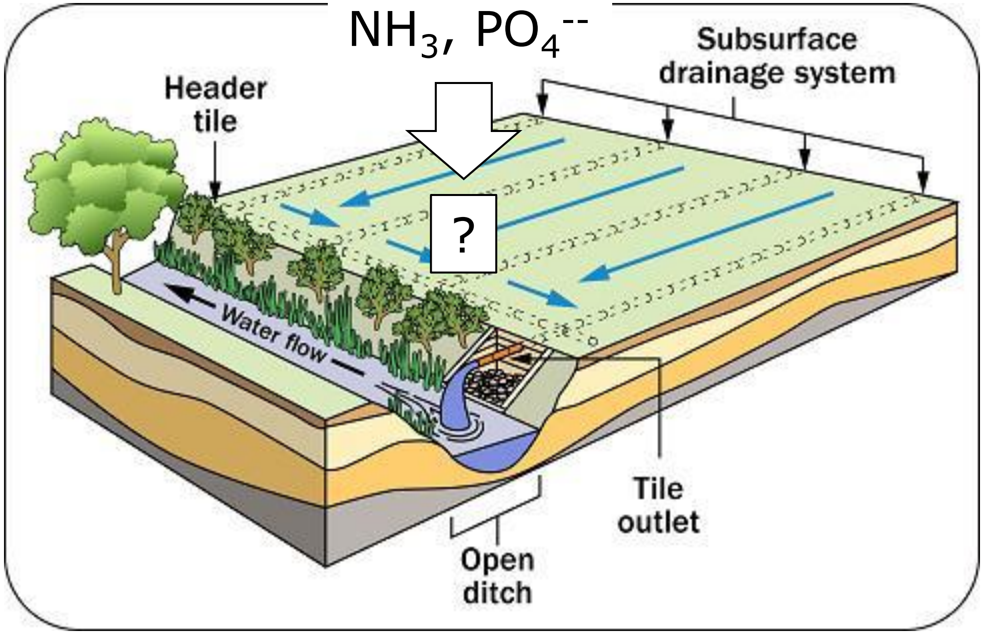
- Rapid and substantial addition of storm water in lower developed reach of catchment (UU campus)
- Seasonally variable





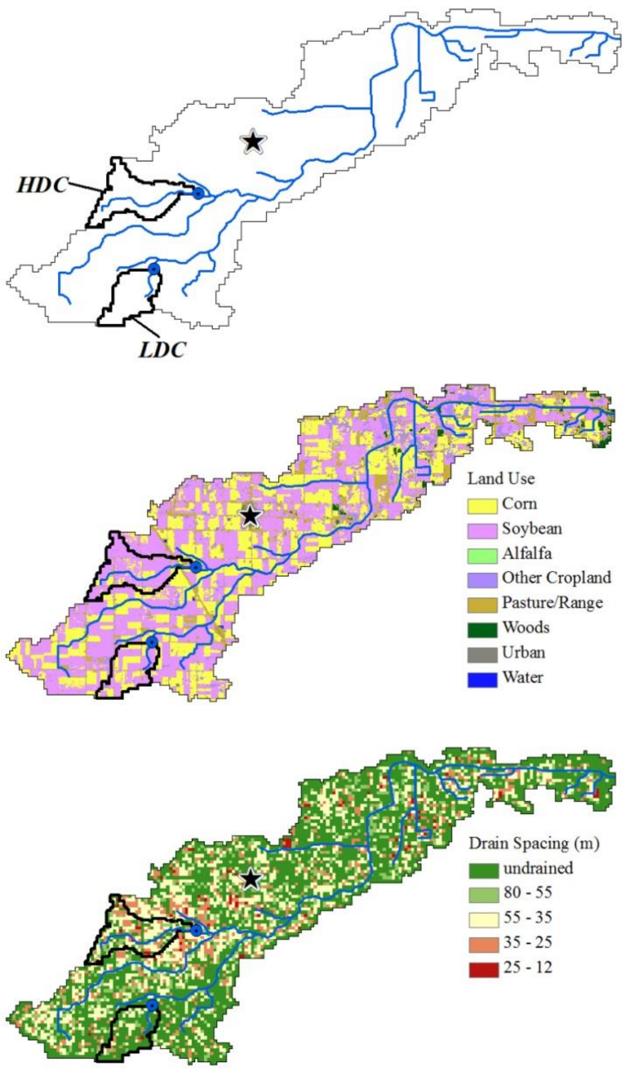
Agricultural systems – artifical drainage

- Subsurface drain network increases agricultural land quality
- Fundamentally alters hydrological flow
- What is the impact on timing, magnitude of nutrient discharge from these lands?



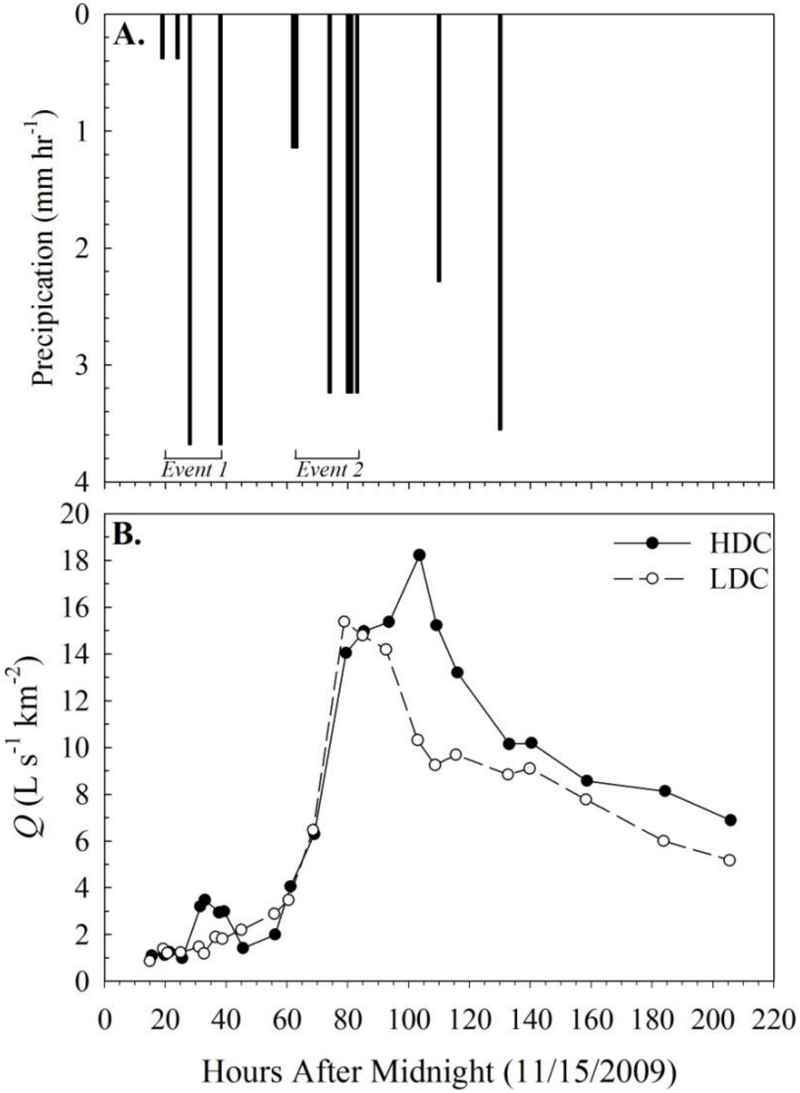
Hoagland watershed

- Paired catchment study
- High and Low drainage density catchments
- Sampling for water quality, isotopes through Nov. storm
- Student participation (EAS591 Isotope Hydrology)



Storm hydrograph

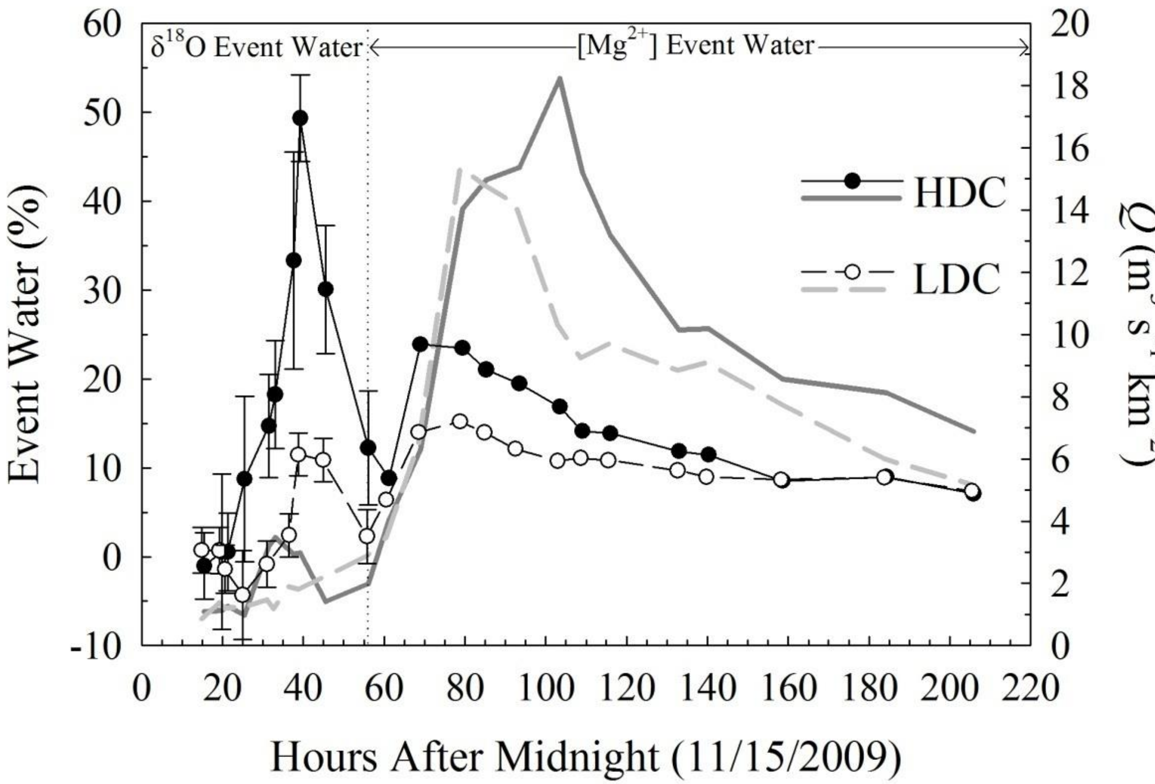
- Different timing of discharge for the high- and low-drainage catchments



Kennedy et al., 2012, *J. Hydrol.*

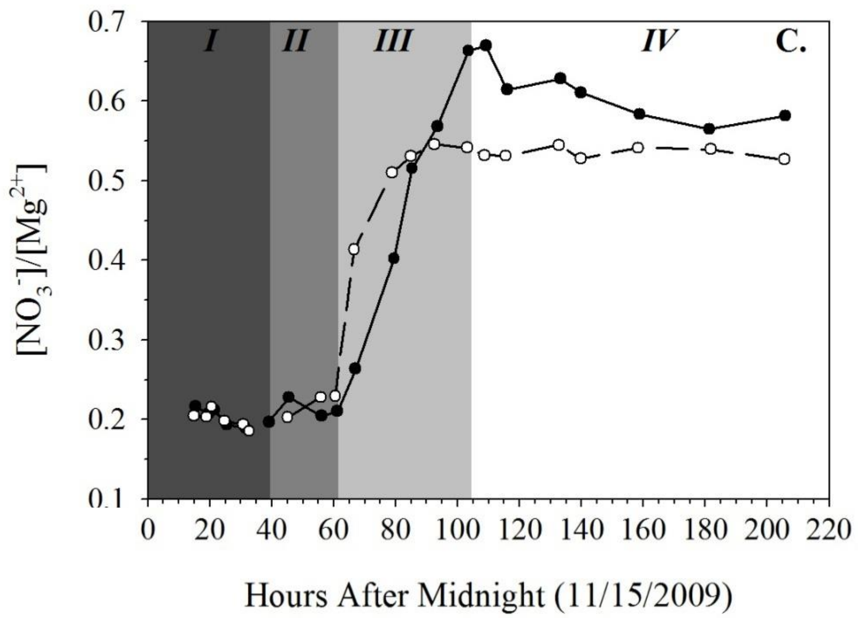
Hydrograph separation

- Partitioned storm flow into event and pre-event water components using O isotopes, Mg^{2+}
- Faster routing of storm water to stream in high-drainage catchment
- Change in storm water routing through event



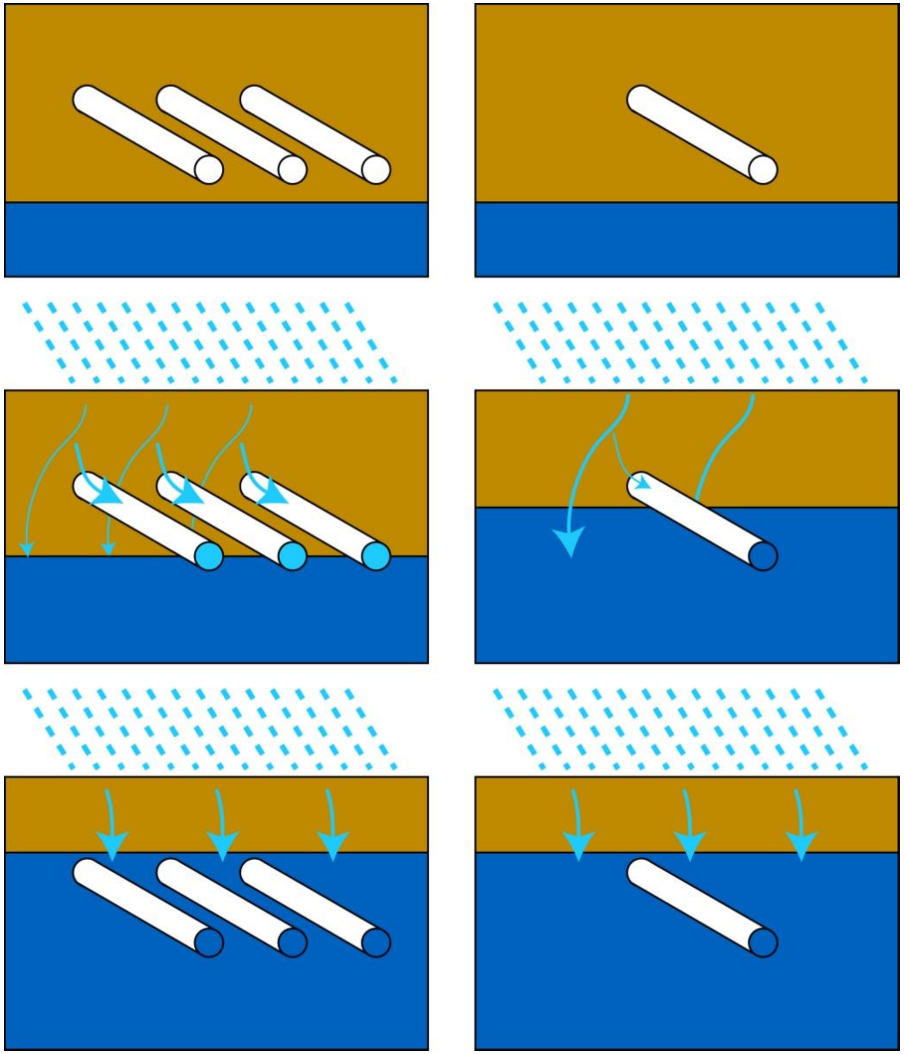
Nutrient discharge

- Timing and magnitude of peak nitrate discharge different in the two catchments

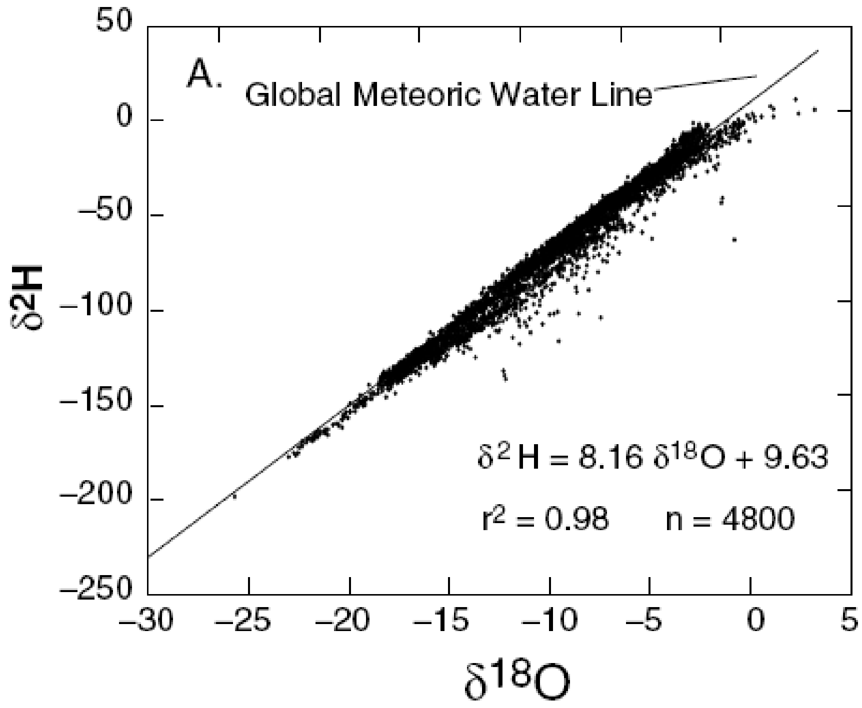


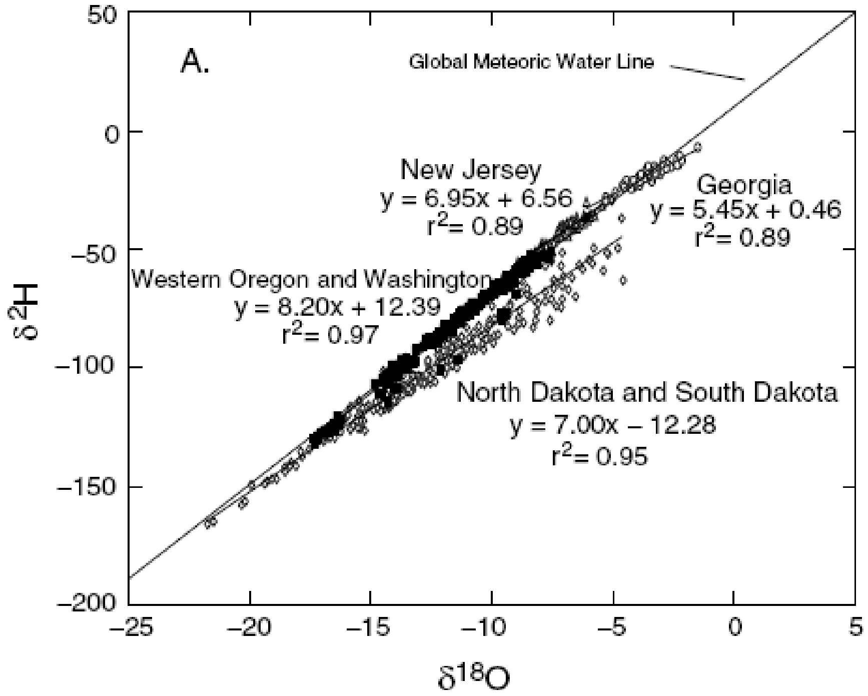
Flush/bypass model

- Late season, drains largely inactive
- Drains divert storm water, slowing water table recharge
- Drains activation and discharge of high-N groundwater lags in high-drainage catchment
- Diversion of infiltration changes ‘flashiness’ of contaminant export



River water isotopes – continental scale



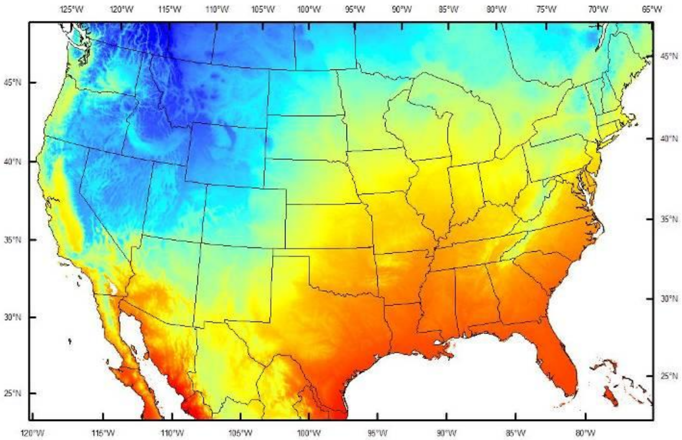


Kendall & Coplen, 2001

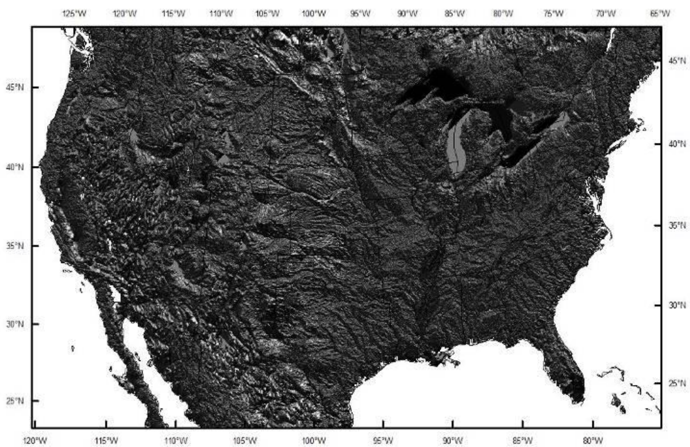
River water isotopes: rainfall-runoff model

- Can we reproduce isotope differences between surface water and precipitation using process models?

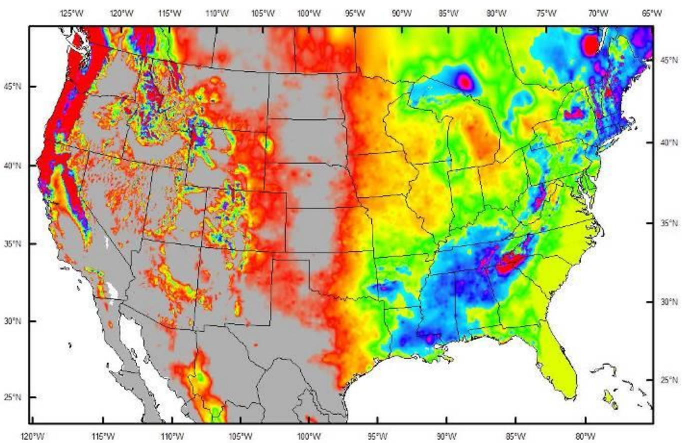
Precipitation isotopes



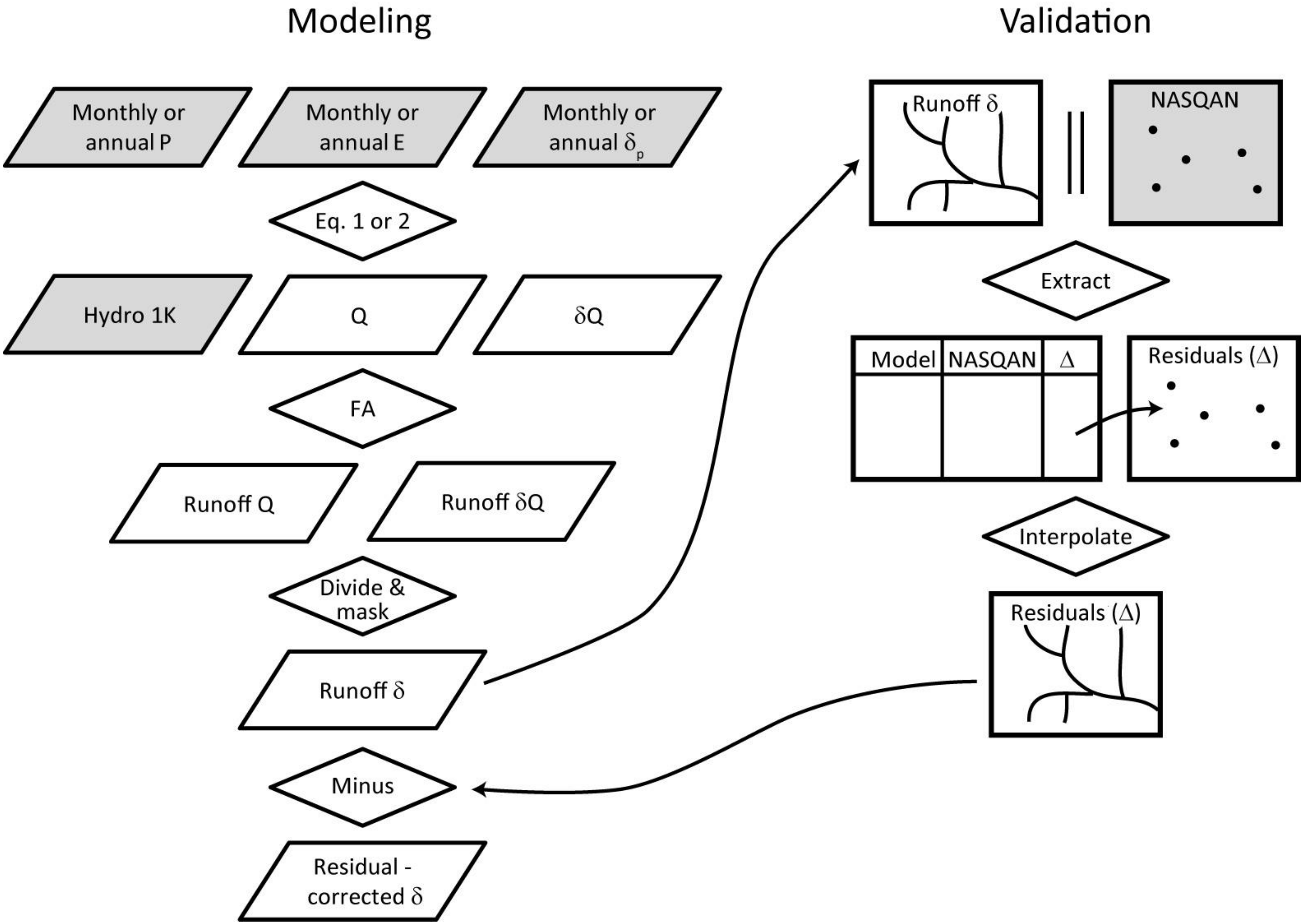
Topography



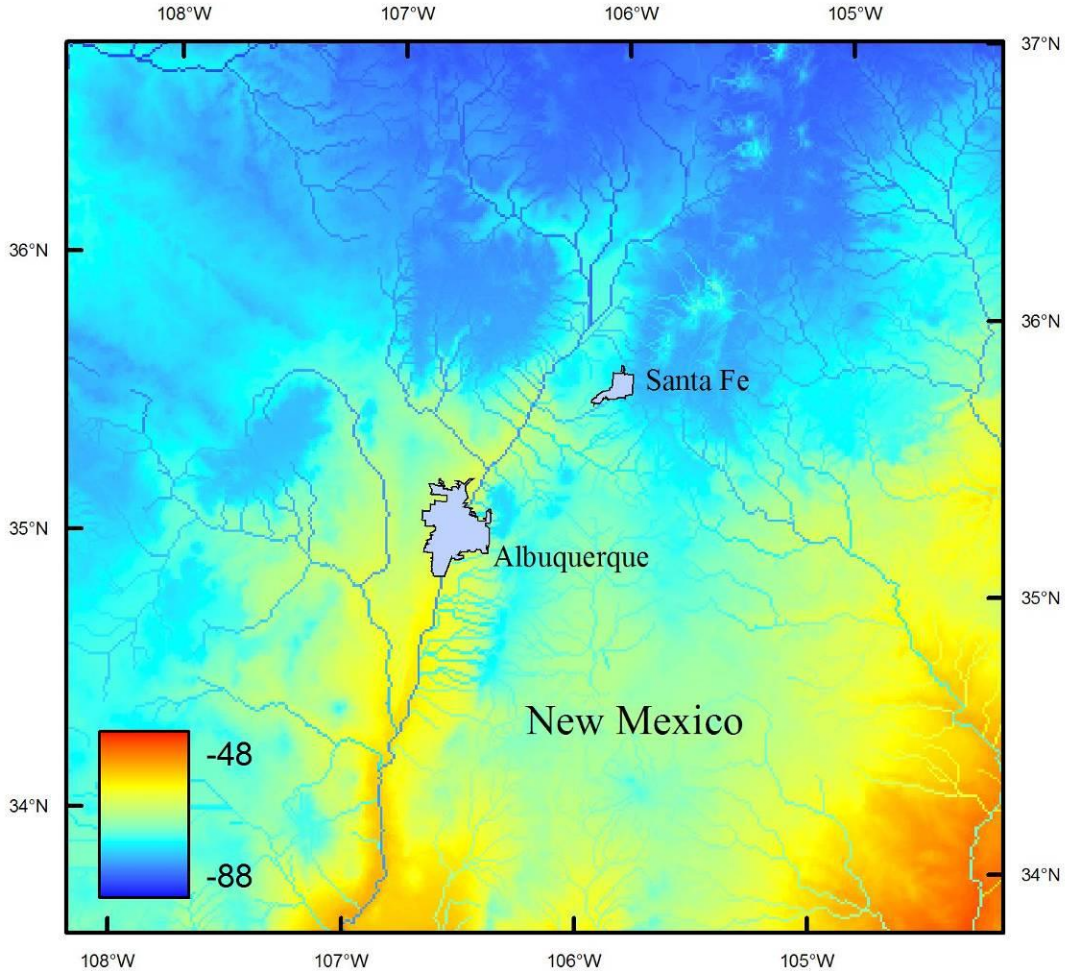
Runoff amount



Bowen et al., 2011, *JGR*

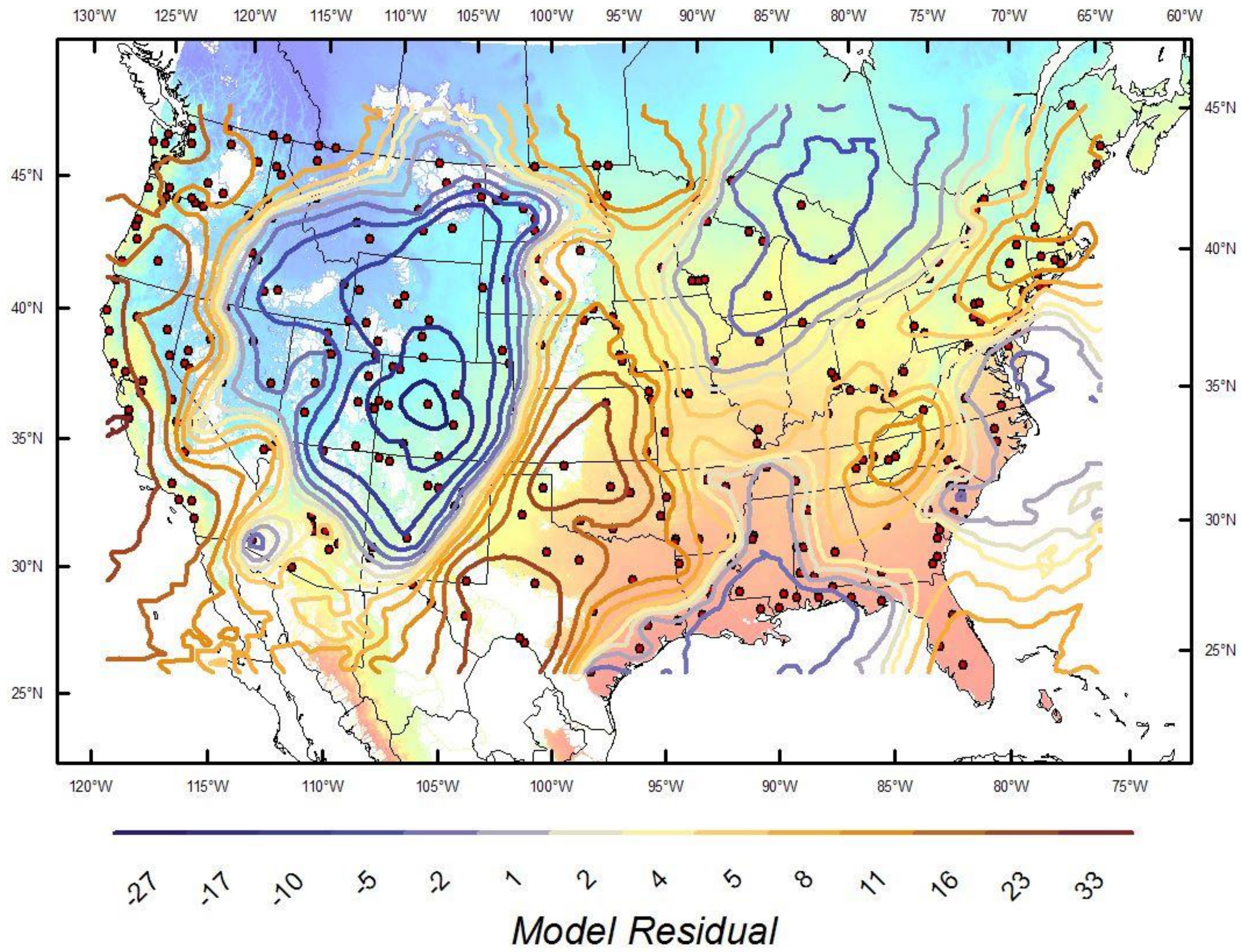

Modeling
Validation
Monthly or annual P
Monthly or annual E
Monthly or annual δ_p
Eq. 1 or 2
Hydro 1K
Q
δQ
FA
Runoff Q
Runoff δQ
Divide & mask
Runoff δ
Minus
Residual - corrected δ
Runoff δ
NASQAN
Extract
Model
NASQAN
Δ
Residuals (Δ)
Interpolate
Residuals (Δ)

Runoff model



Predicted river δ^{2}H values superimposed on precipitation δ^{2}H values

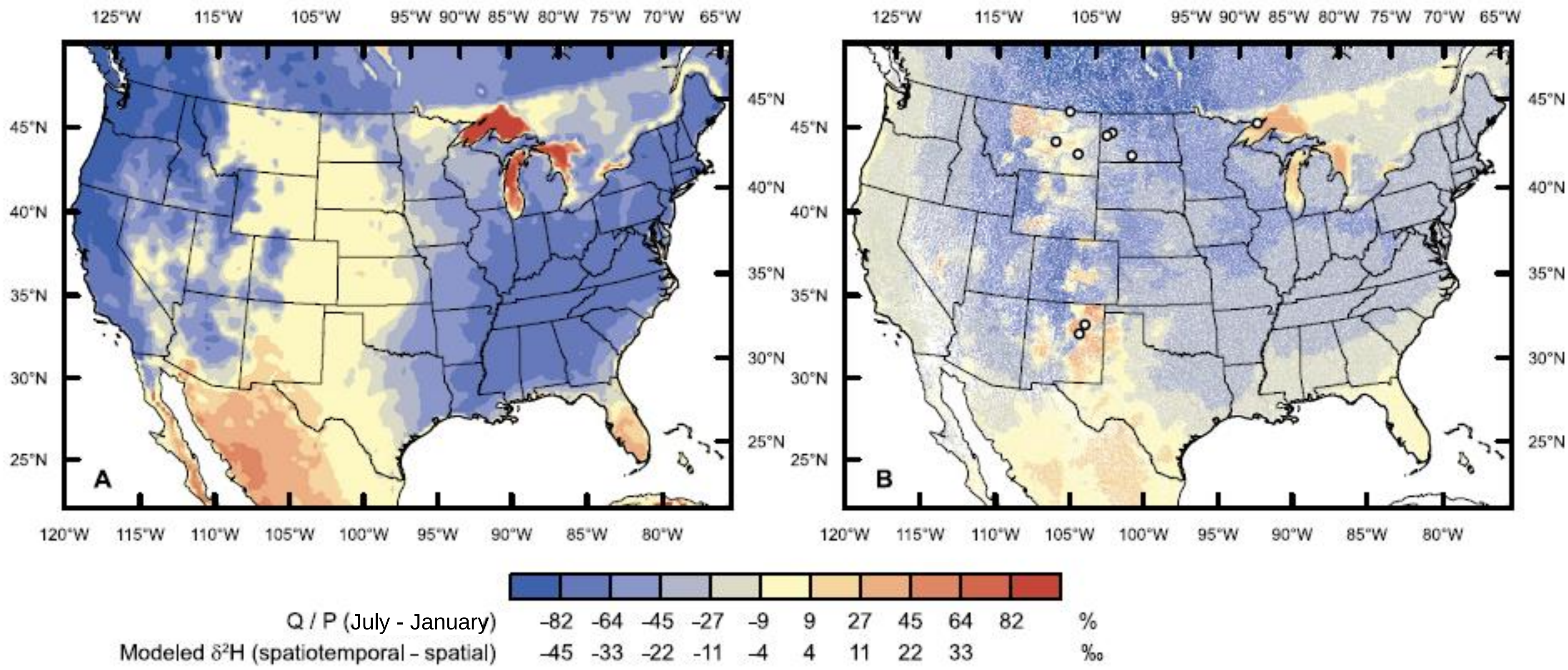
Runoff model residuals - why?



Data: Kendall and Coplen, 2001

Sensitivity testing ET patterns

Impact of accounting for different % loss of precipitation to ET by month

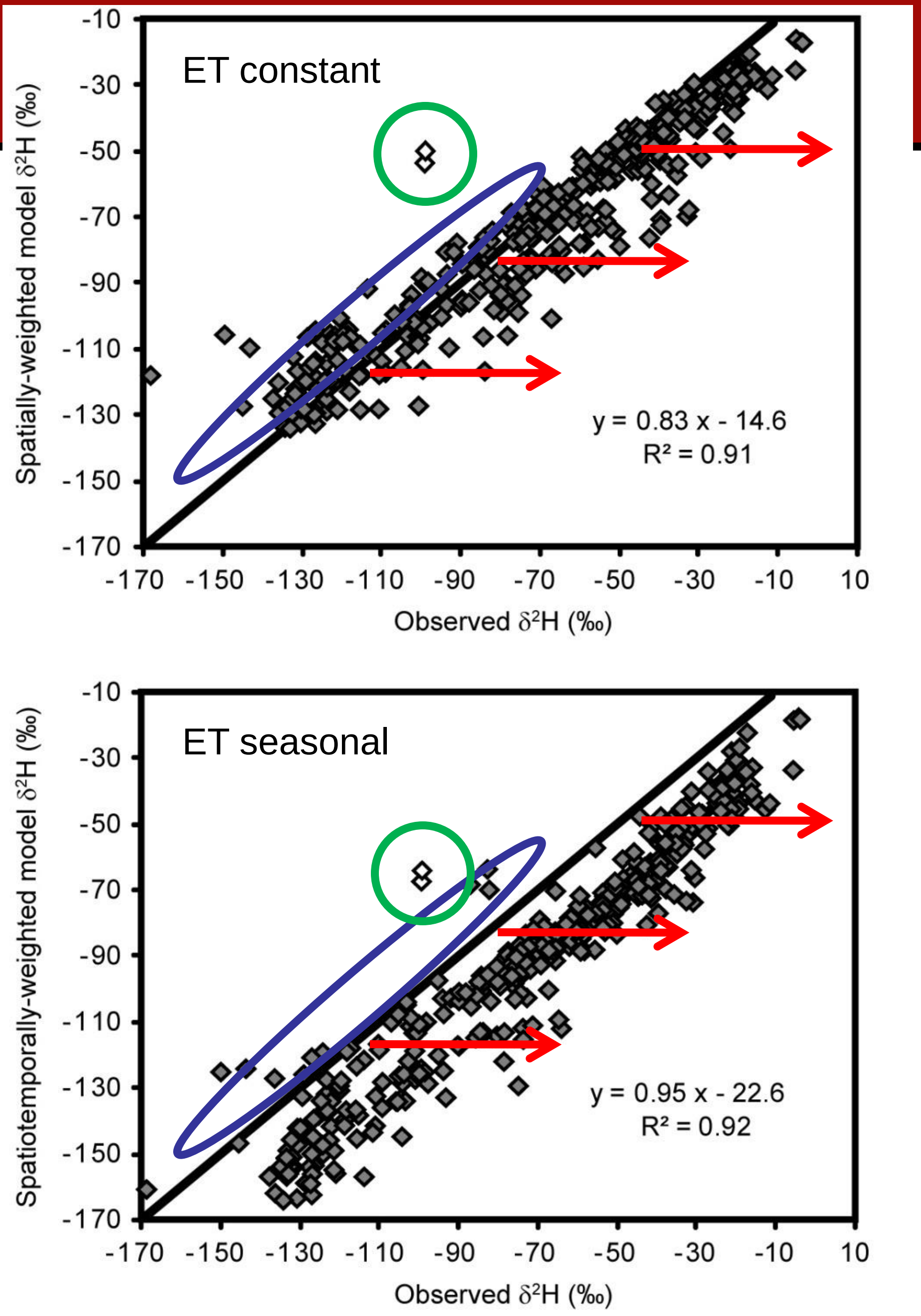


Bowen et al., 2011, *JGR*

Interrogating water source

- Evaporation
- Winter-biased runoff
- Imported water

- Provides basis for quantifying (and monitoring) seasonal or elevation bias of runoff generation
- Identifies non-local water sources

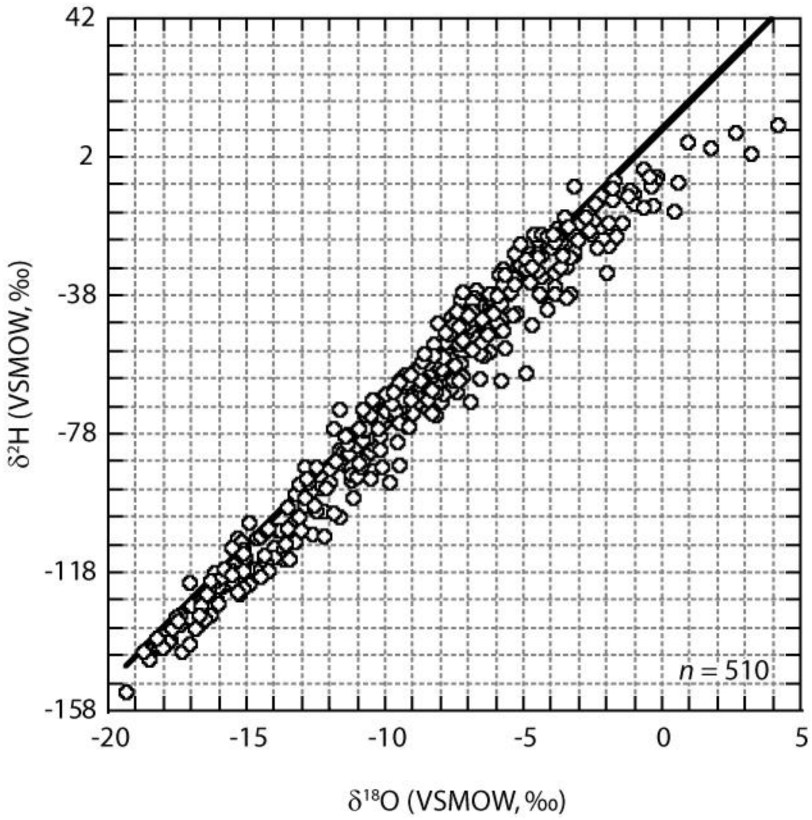


Managed waters

- Where does your water come from?
  - The faucet
  - Yes, but…
- With spatial information isotopes can
  - Establish connectivity
  - Document what happens between the source and sink

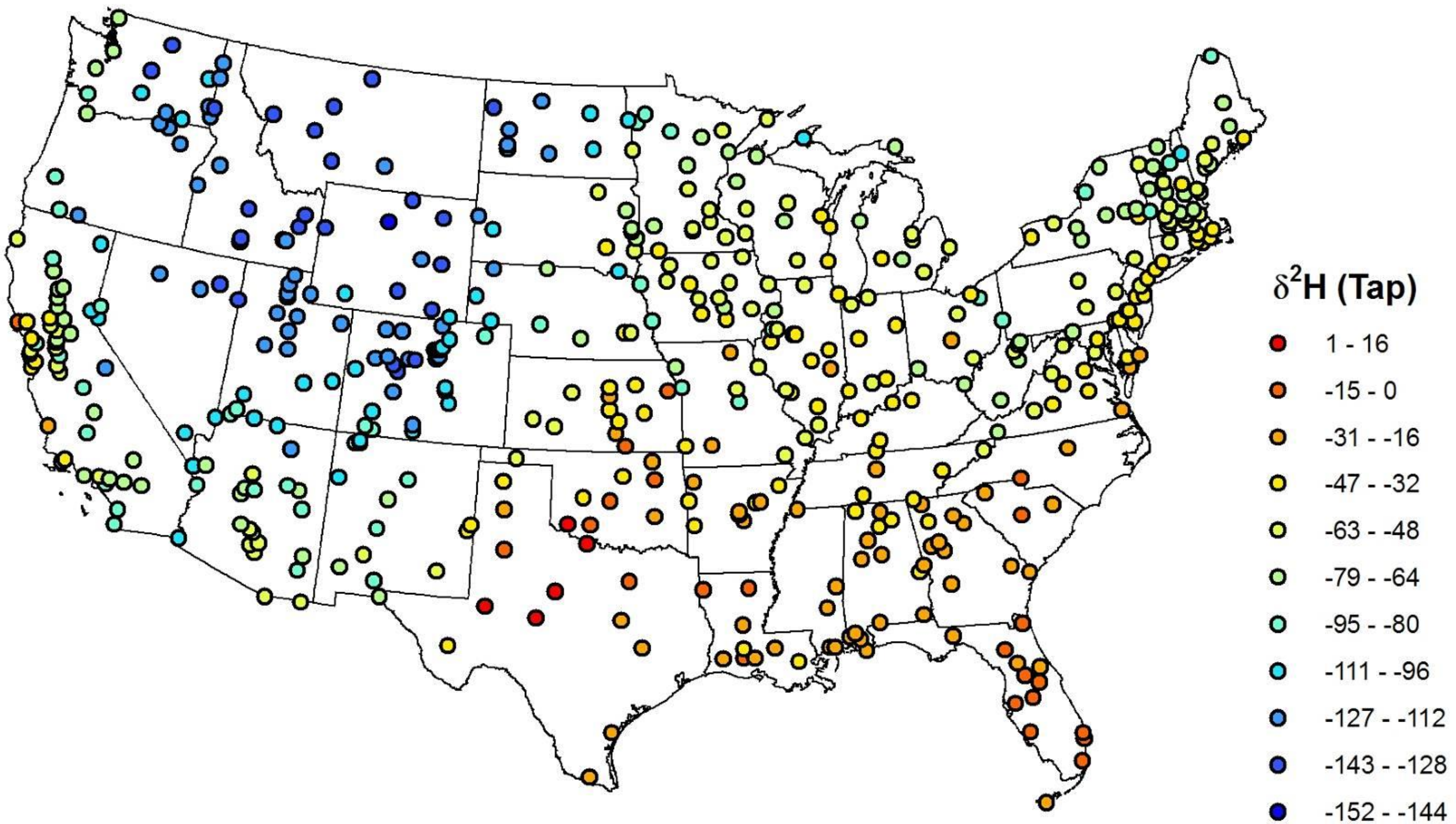
US tap water isotope ratios

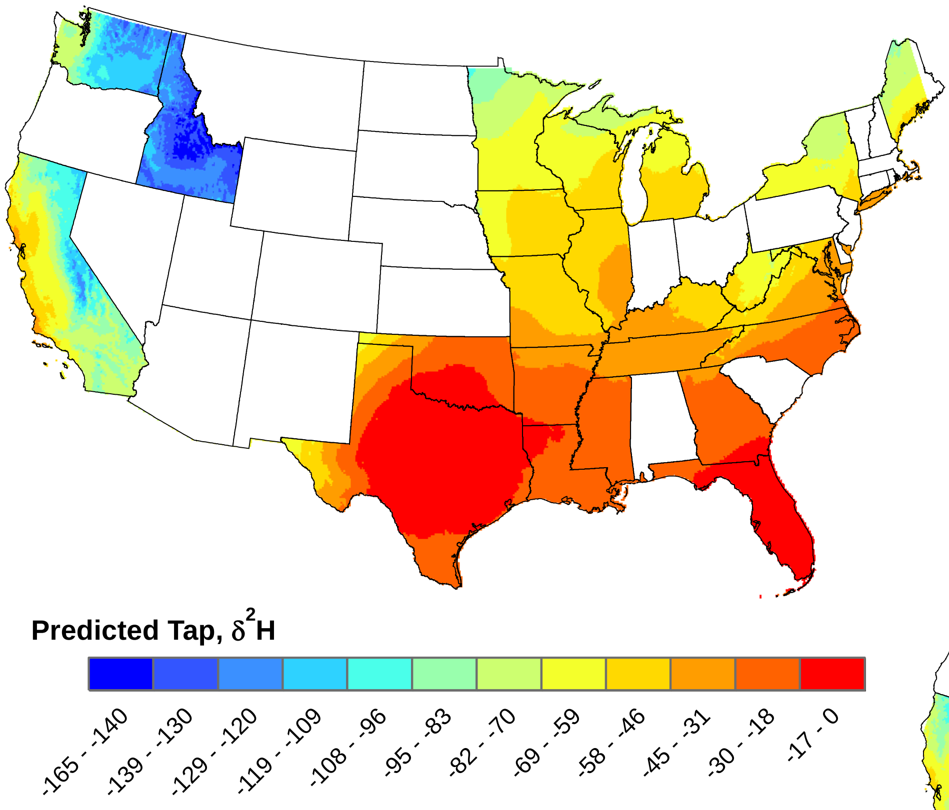
- Range
  - -152‰ < δ^2H < +11‰
  - -19.4‰ < δ^{18}O < +4.2‰
- Cluster near the GMWL
- Average d-excess value of 5 not significantly different from 10

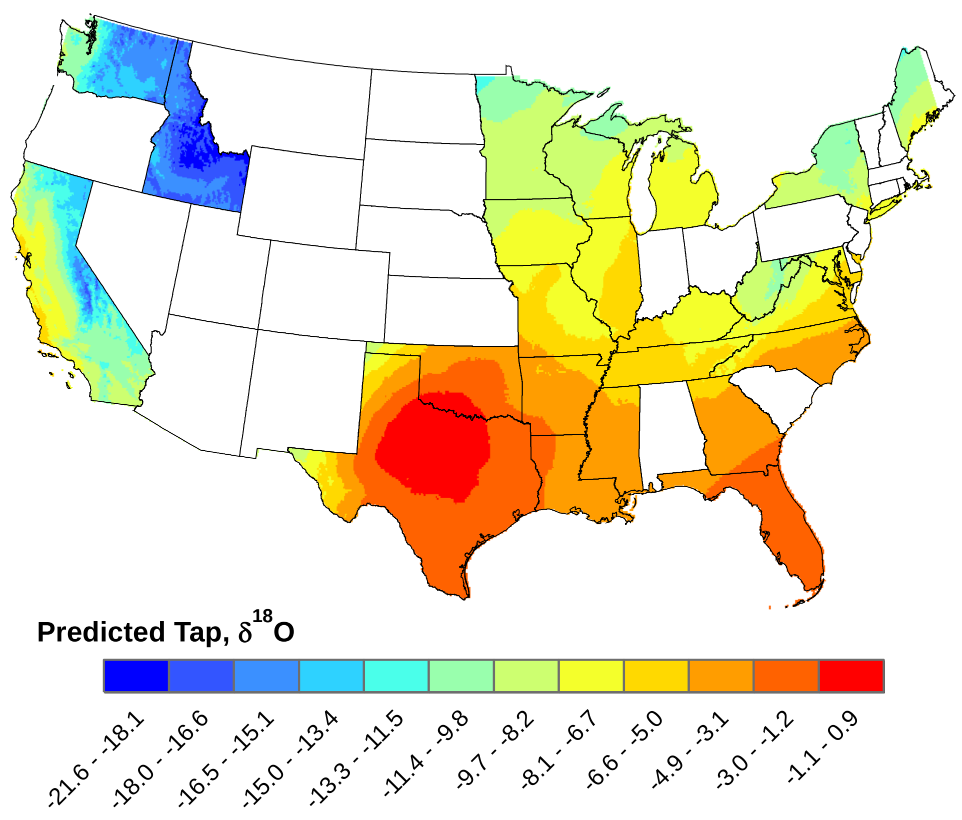


Bowen et al., 2007, *WRR*

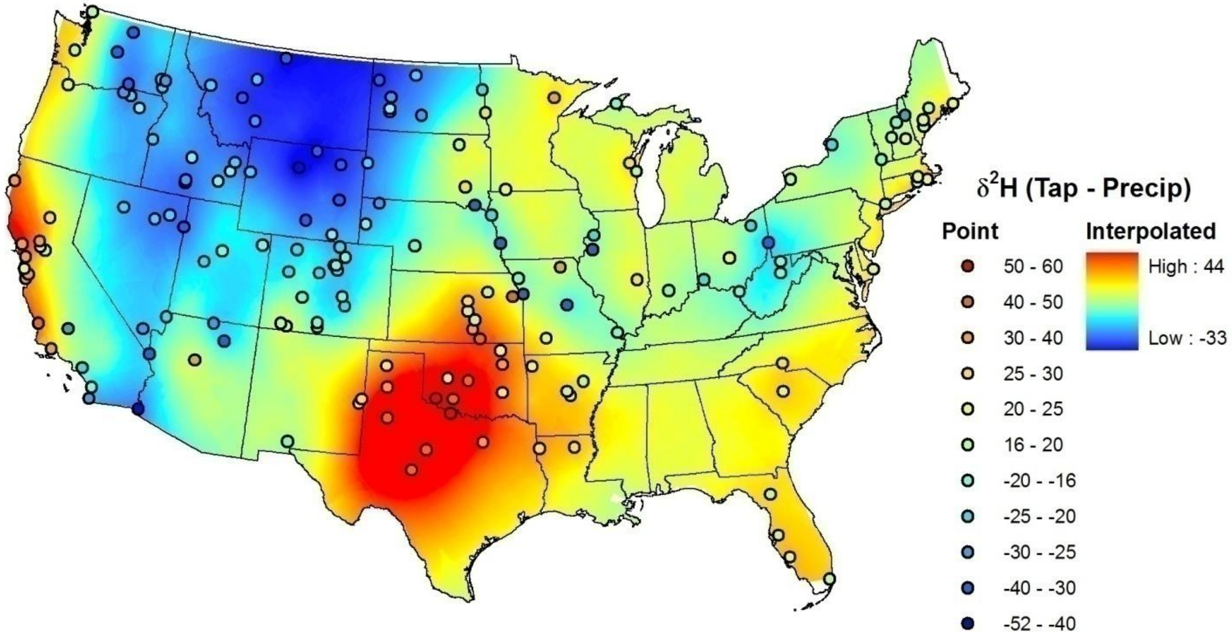
Isotope ratios of US tap waters

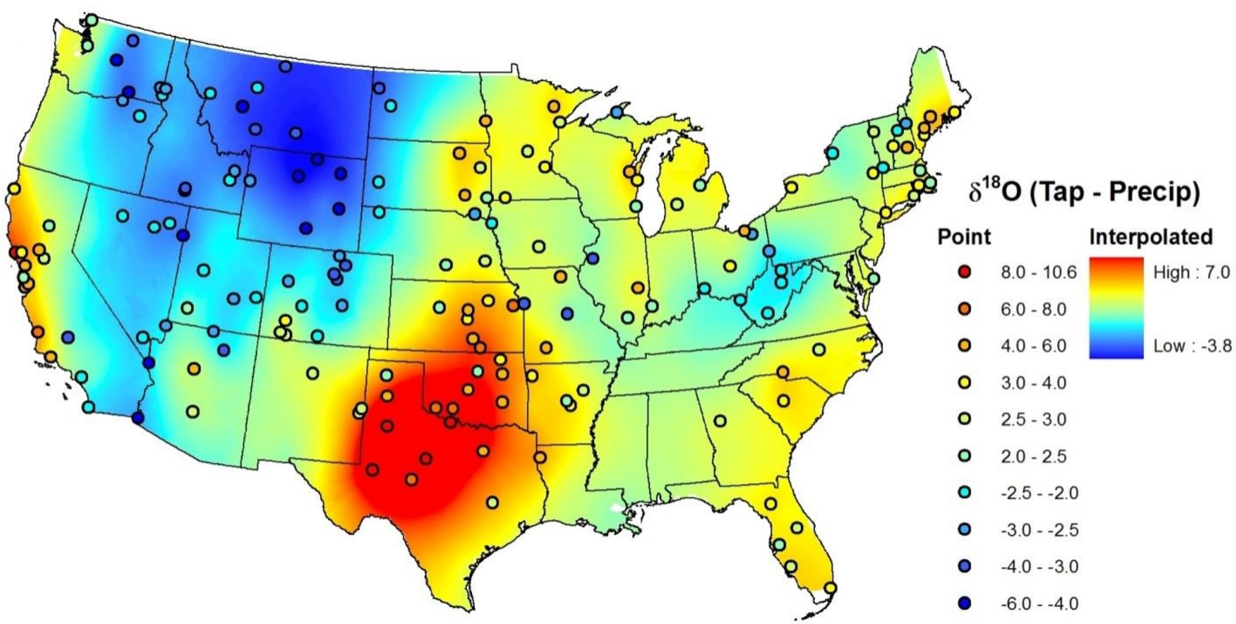



Predicted Tap, δ2H
-165 - -140
-139 - -130
-129 - -120
-119 - -109
-108 - -96
-95 - -83
-82 - -70
-69 - -59
-58 - -46
-45 - -31
-30 - -18
-17 - 0

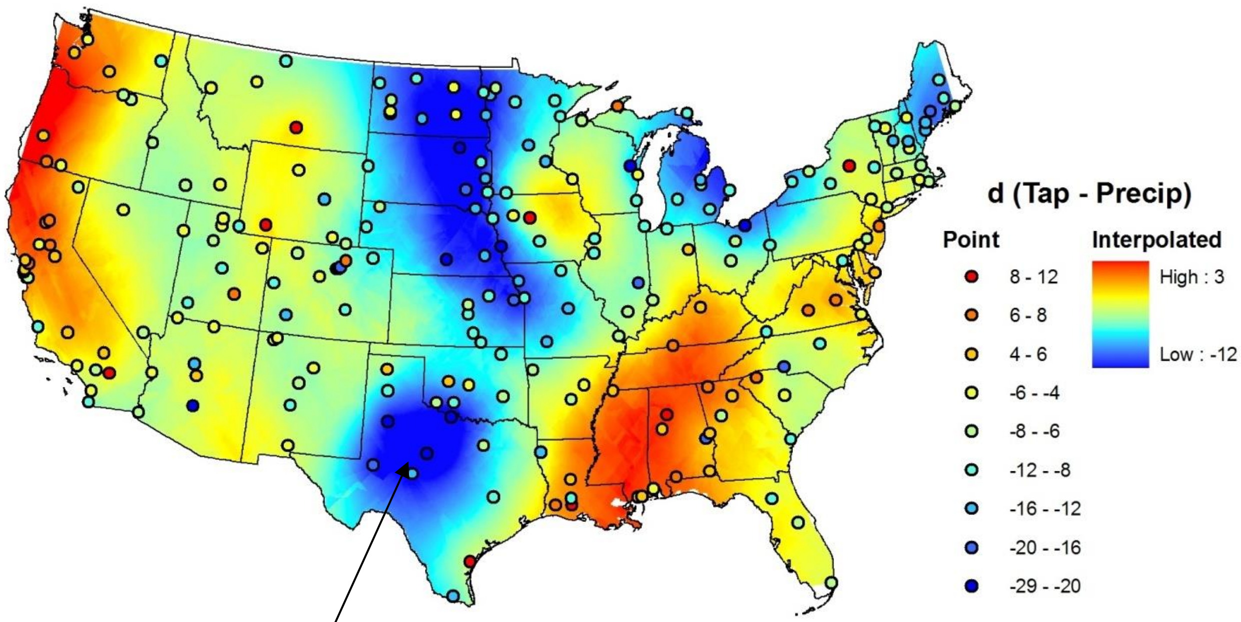

Predicted Tap, δ18O
-21.6 - -18.1
-18.0 - -16.6
-16.5 - -15.1
-15.0 - -13.4
-13.3 - -11.5
-11.4 - -9.8
-9.7 - -8.2
-8.1 - -6.7
-6.6 - -5.0
-4.9 - -3.1
-3.0 - -1.2
-1.1 - 0.9

Tap water vs. local precipitation





Tap water d values compared to precipitation

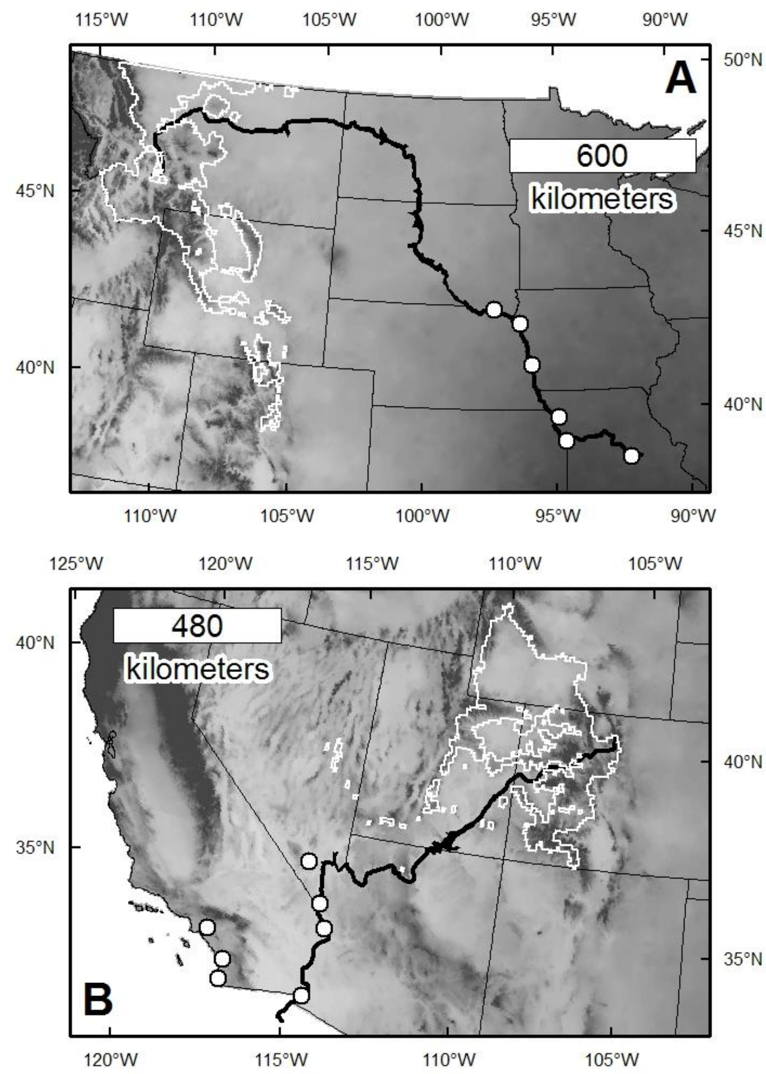


20-35%
evaporative loss

Catchment areas: source/sink connectivity

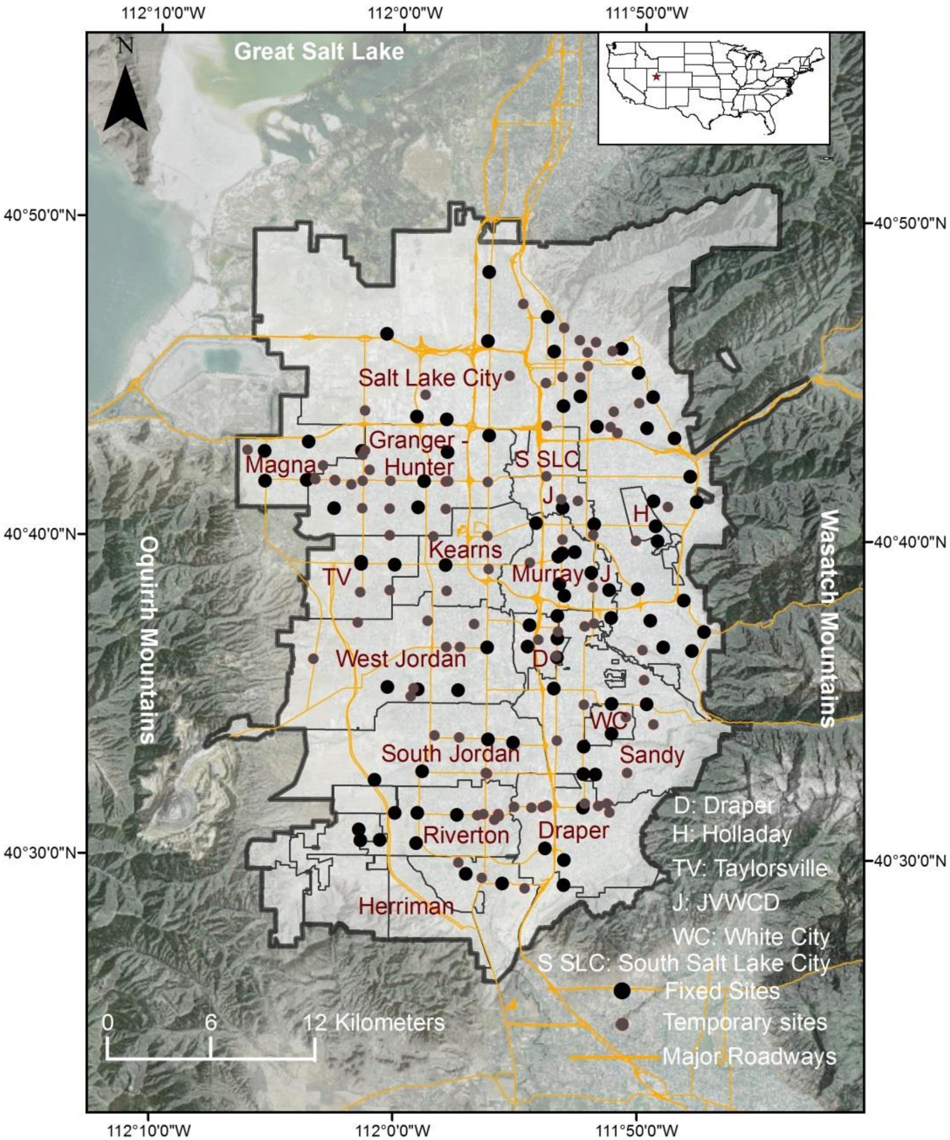
- Characterize source region for water supply
- Map supply footprint of source

- Water sinks 1000+ km removed from mean sources

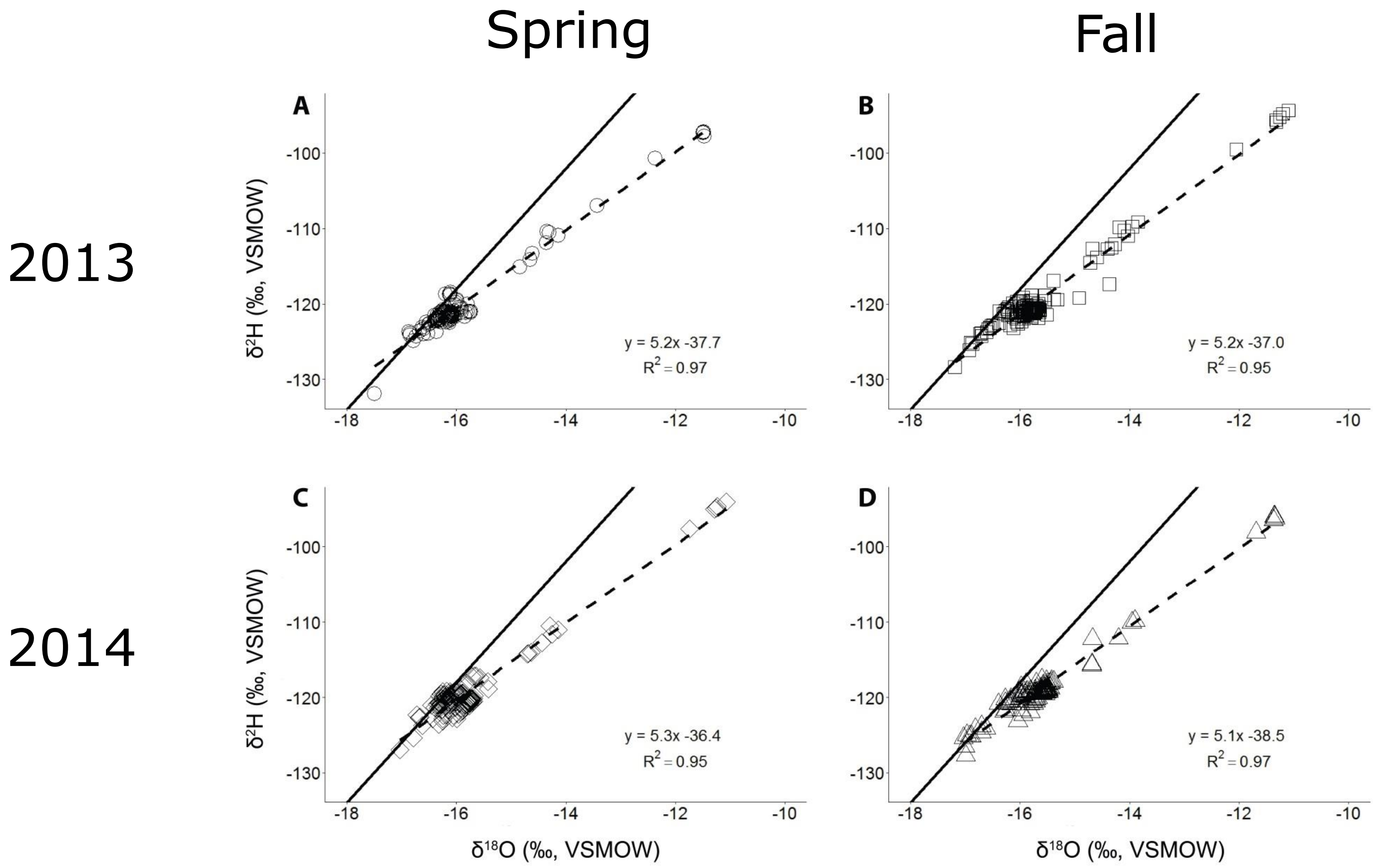


Scaling Down: Urban Structure

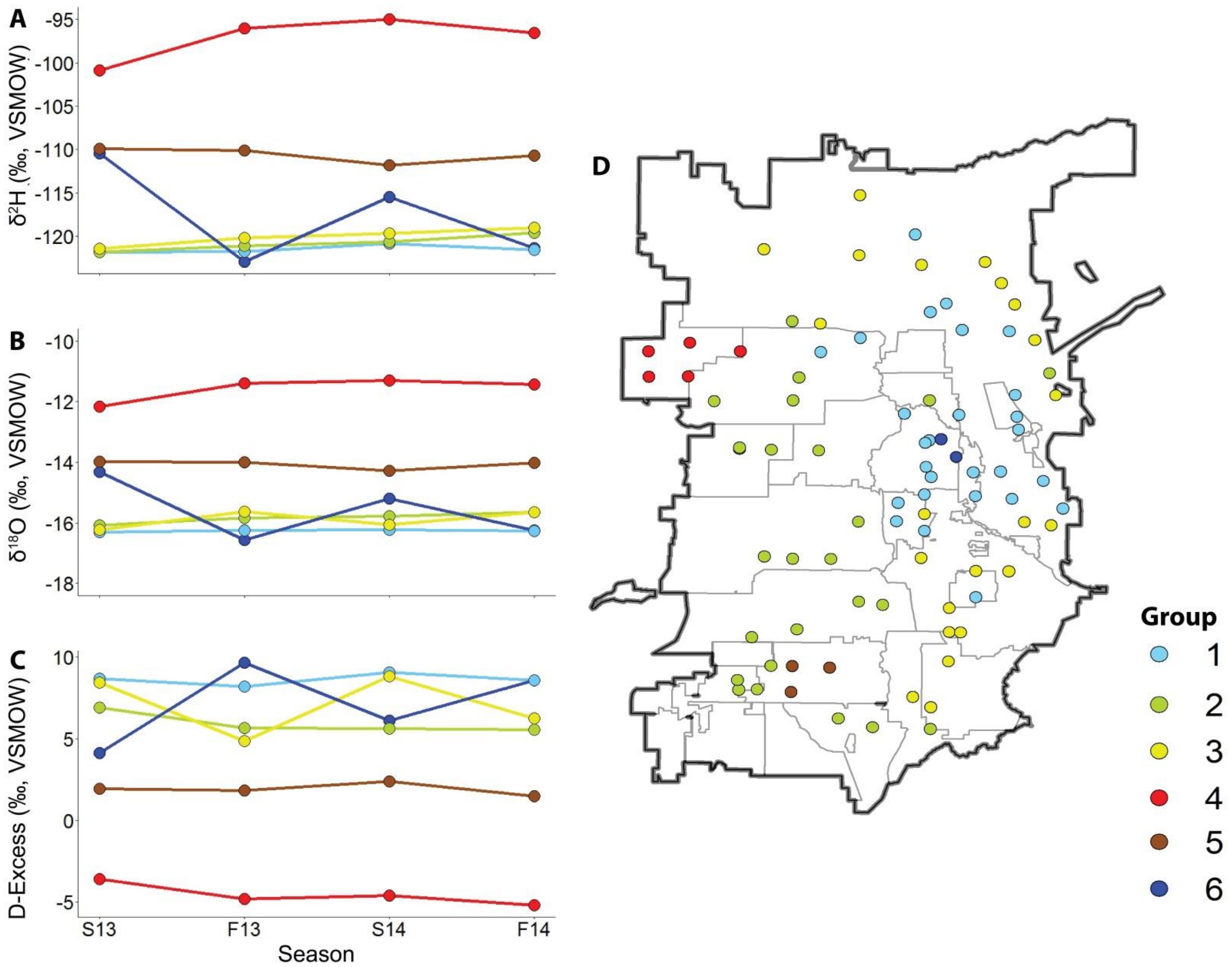
- Many urban centers have decentralized water management
- Do importation rules scale down from states to cities?
- Inference: how are resources being managed, what are controls
- Prediction: neighborhood-scale predictive isoscapes?



Salt Lake City Tap Water Isotopes



Multiple Modes of Variation



Spatiotemporal Water Isotope Patterns