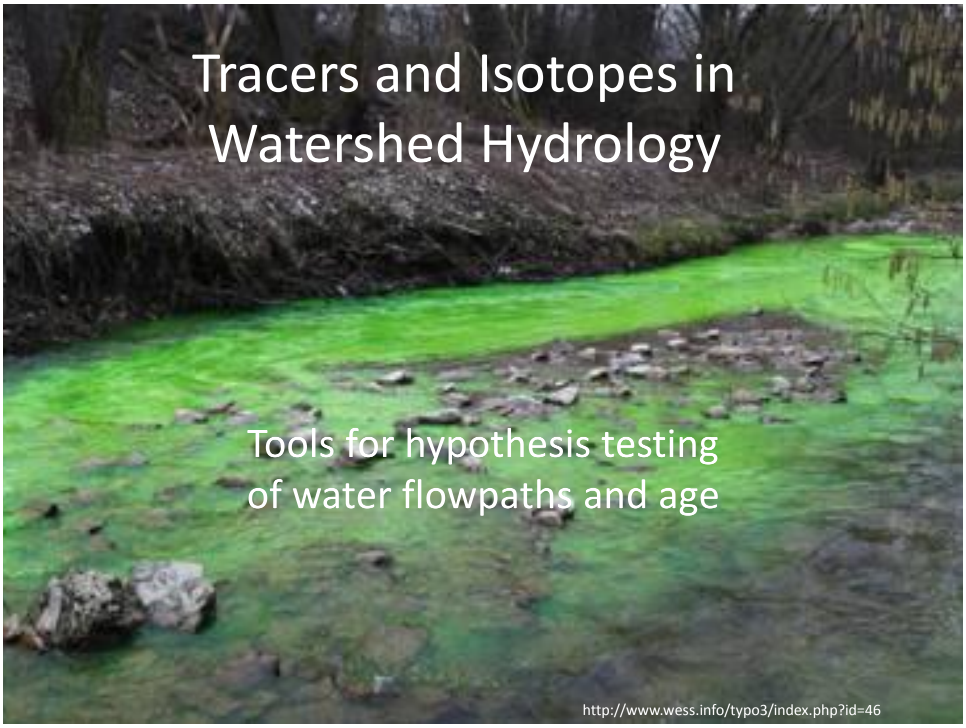


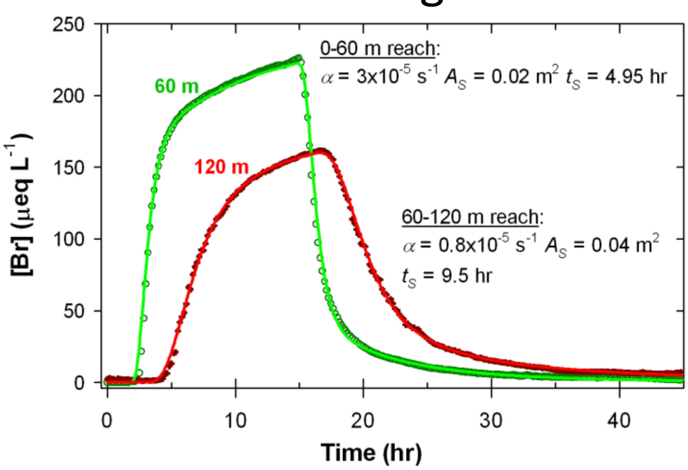
What is a hydrologic tracer?

- Any substance that can be used for tracking water movement is a *tracer*
- An *ideal tracer* behaves exactly as the traced material behaves
- A *conservative tracer* does not have sources or sinks (decay, sorption, or precipitation) in the system
- *Environmental tracers* exist in the system, *applied tracers* are added by scientists to study

Example of an applied (dye) tracer for studying groundwater-stream interactions

This tracer is non-conservative because it gets metabolized.

Applied tracer analyzed via breakthrough curve



- BTC track advection and dispersion of a tracer.
- Can be modeled to learn about flowpaths and stream behavior.

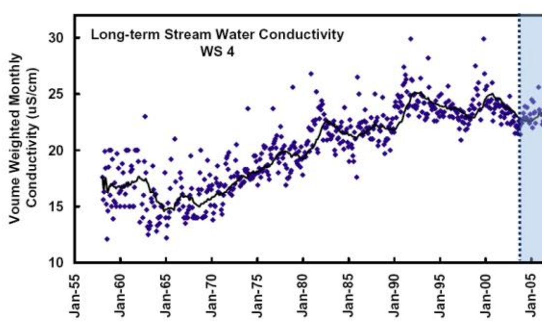
http://igwmc.mines.edu/software/igwmcsoft/otisreview.htm

Environmental tracers

- Naturally occurring substances
- Anthropogenic signals
  - CFCs/SF_6 in atmosphere and groundwater → date groundwater recharge
  - Caffeine, hormones, pharmaceuticals → "emerging contaminants" that can identify wastewater
  - Disinfection by products from wastewater treatment process
  - Fecal coliform

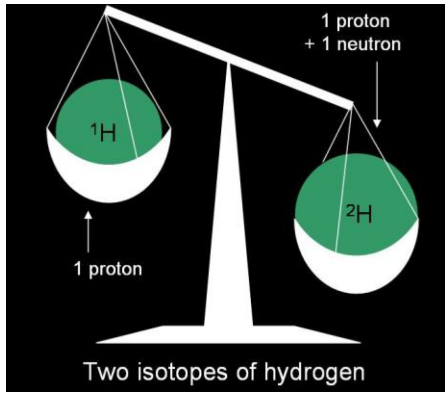
Environmental tracers: Conductivity

- Electrical conductivity –the measure of how a material accommodates the transport of electric charge.
  - In water, it varies with the amount and type of dissolved ions.
  - It varies with temperature, so we normalize and call it *specific conductance*.



Isotopes as Environmental Tracers

- Isotopes are the same element, but with different numbers of neutrons.
- Two groups of isotopes:
  - **Radioactive:** atoms that spontaneously break down their nuclei to form other isotopes
  - **Stable:** do not spontaneously break down to form other isotopes



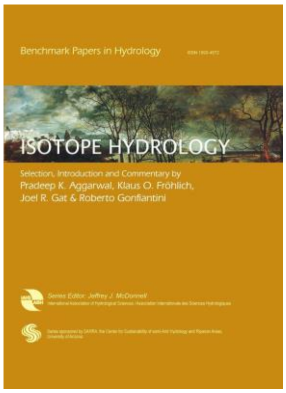
Radioactive Isotopes in hydrology

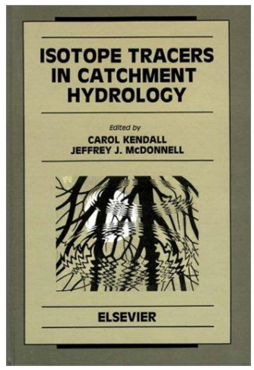
- Age of groundwater
- Measure groundwater flow rates
- Tracers for groundwater movement

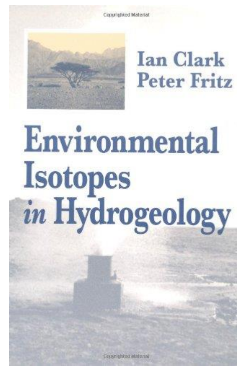
- Choose isotopic system:
  - Half-life of radioisotope
  - Reactivity of isotope in system of interest

Stable Isotopes In Hydrology

- Changes in isotope ratios in environment from physical, chemical, and biological processes due to mass differences between isotopes

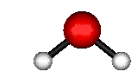


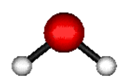


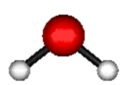


Stable Isotopes Tracing the Hydrologic Cycle

- Stable Isotopes of H_2O
  - ^{1}H, ^{2}H (^{2}D), ^{16}O, ^{17}O, ^{18}O
- Vibrational frequency (energy) differences
- Provide characteristic fingerprint of origin
- Applications in hydrogeology
  - Provenance of water
  - Identify processes that formed waters
  - Separating hydrographs into "old" and "new" water





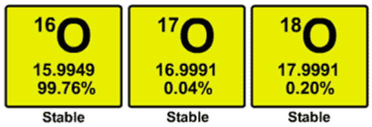


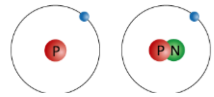
Characteristic vibrations of H_2O

Slide from E. Griffith, UT Arlington

Animations courtesy of E. Schauble (UCLA)

Isotopologues of Water





^{1}H 99.985% $^{2}H = D$ 0.015%

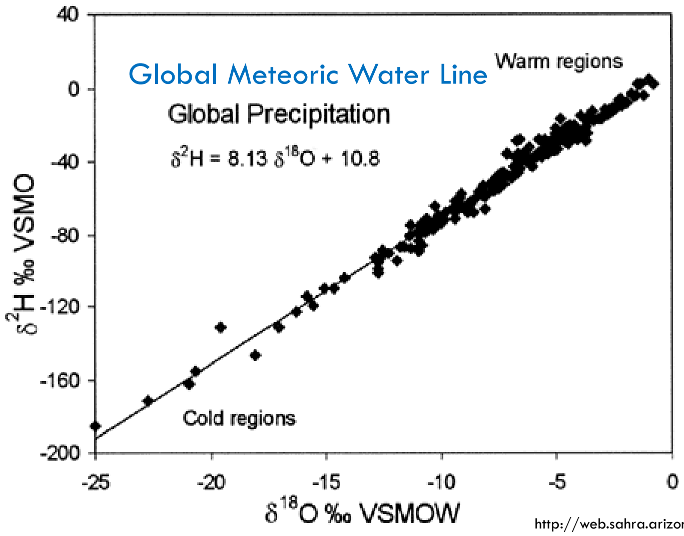
- **Isotopologues** are molecules that differ only in their isotopic content. *What are the isotopologues of water?*

Isotope Ratio notation

$$\delta^{18}O = \left[\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{standard}} - 1 \right] \times 1{,}000$$

- δ = value ‰ ‘per mil’
- O and H are normalized to SMOW – standard mean ocean water
  - $\delta^{18}O$ = 0‰, $\delta^{2}H$ = 0‰
- Positive vs. negative delta values
- Isotopically heavy vs. light, enriched vs. depleted

In H_2O, H and O isotopes ~ co-vary



General δ magnitude is a function of natural abundance.

Slope of GMWL is function of equilibrium fractionation factors.

http://web.sahra.arizona.edu/programs/isotopes/oxygen.html

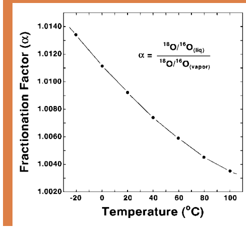
Isotopic fractionation: Detectable change in the ratio of an isotopic pair

- **Due to mass differences of isotopes**—affect vibrational frequency of atom which affects ability to make (& break) bonds w/ surrounding environment
- ^{18}O and ^{2}H content of water changes only through fractionation **associated with phase changes**
- **Conservative behavior** – once isotopes become part of water molecule, they change only through mixing

Equilibrium vs. Kinetic fractionation

Fractionation is a function of temperature.

Greater fractionation at **lower temperatures.**

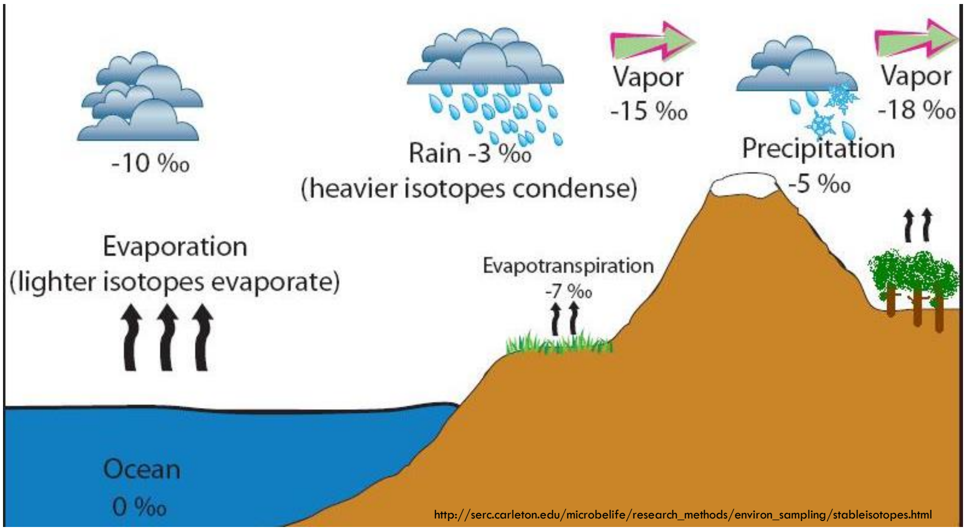


- **Equilibrium fractionation:** vapor pressure of water containing light isotopes > water containing heavy isotopes, therefore vapor is enriched in light isotopes
- **Kinetic fractionation:** rapid phase changes increase fractionation because light isotopes diffuse more rapidly than heavy ones

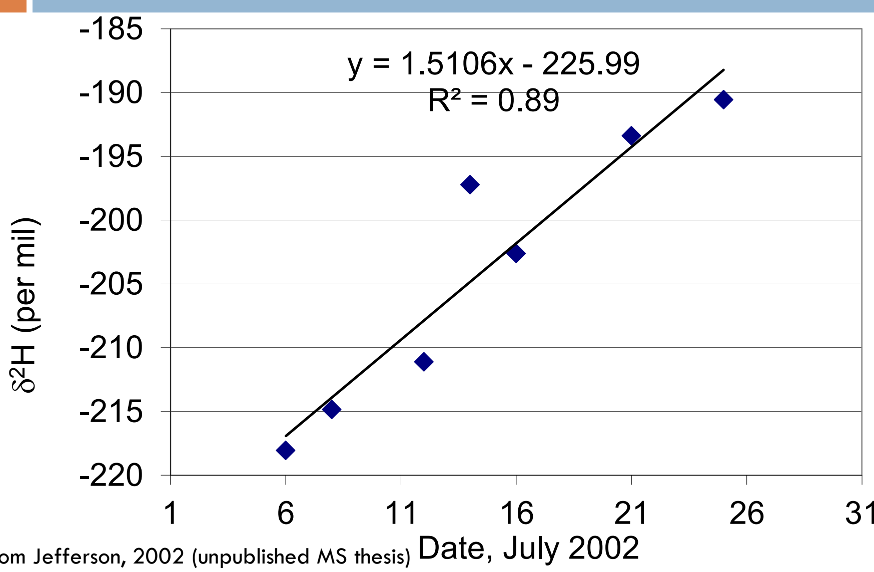
Fractionation effects associated with phase changes of H_2O

- **Condensation** – liquid that forms is heavier than surrounding water (equilibrium fractionation)
  - So, precipitation selectively removes ^{18}O and ^{2}H from the vapor phase
- **Evaporation** – vapor that forms is lighter than surrounding water (kinetic fractionation)
- **Snowmelt** – residual snowpack becomes isotopically heavier as light isotopes melt out first (equilibrium fractionation)

Fractionation effects associated with phase changes of H_2O



July snowmelt, Stenkul Fiord, Ellesmere Island, Nunavut, Canada



From Jefferson, 2002 (unpublished MS thesis)

5 key patterns in ^{18}O and ^{2}H content of precipitation

Precipitation becomes isotopically…

- lighter as air mass moves inland (**Continentality**)
- lighter towards the poles (**Latitude**)
- lighter with increasing elevation (**Altitude**) – orographic effect
- lighter in winter than summer (**Seasonality**)
- lighter as more has occurred (**Amount**)

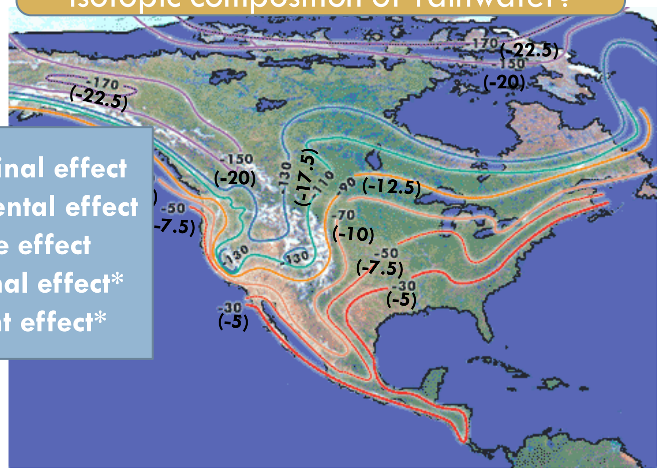
Text modified from Doug Burns and Tomas Vitvar: http://www.esf.edu/hss/IsotopeWS/Burns-Vitvar%20presentation/sld001.htm

Contours of δD and $\delta^{18}O$ in rainwater

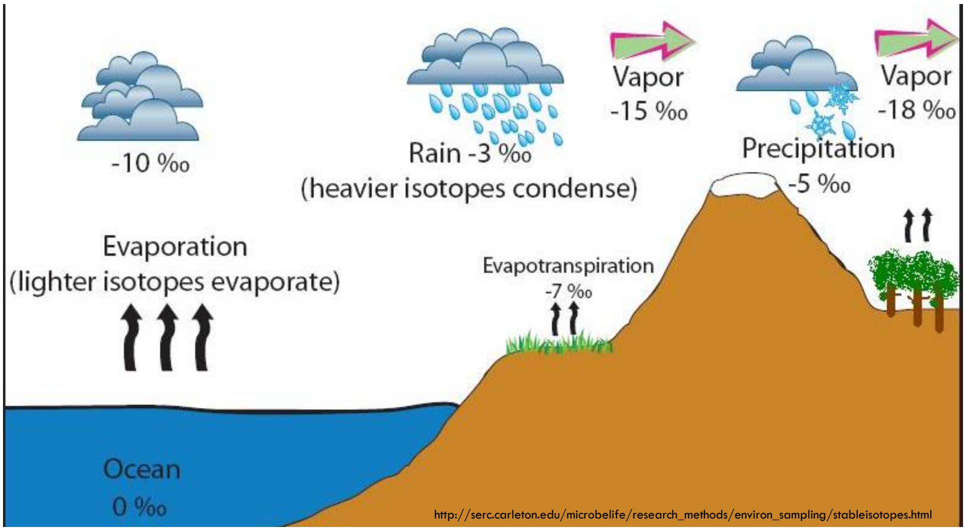
What patterns do we see in the isotopic composition of rainwater?

1) latitudinal effect
2) continental effect
3) altitude effect
4) seasonal effect*
5) amount effect*

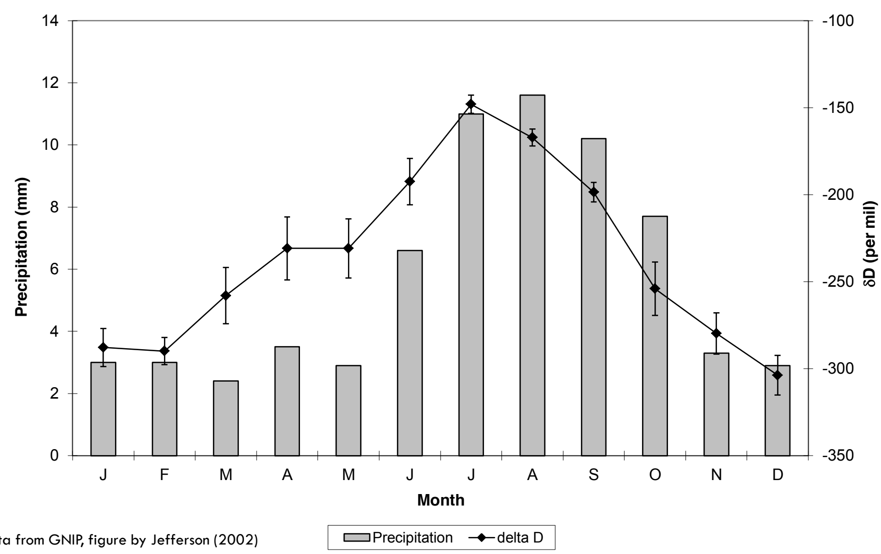
($\delta^{18}O$ values in parentheses)



Fractionation effects associated with phase changes of H_2O



Seasonality of precipitation isotopes, Eureka, Nunavut, Canada

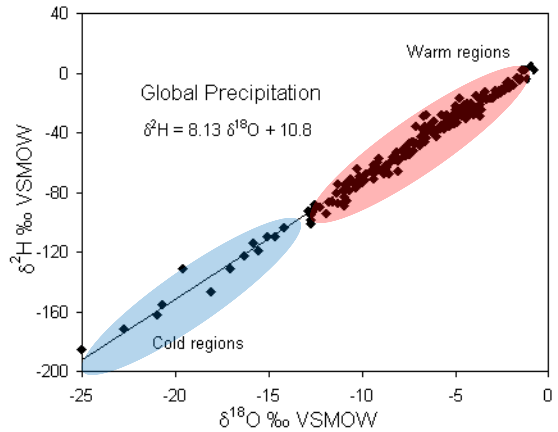


Data from GNIP, figure by Jefferson (2002)

Precipitation: Equilibrium & the "Global Meteoric Water Line"

Sam Epstein and Toshiko Maveda,1953

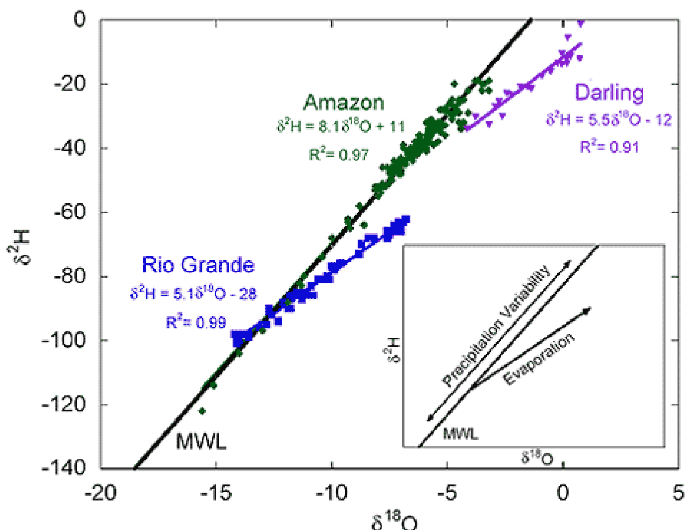
Harmon Craig (1961) defined the relationship between ^{18}O and ^{2}H in worldwide fresh surface waters.



Craig (1961); Rozanski et al. (1992)

Slide from E. Griffith, UT Arlington

Evaporation: Humidity & Local Meteoric Water Lines



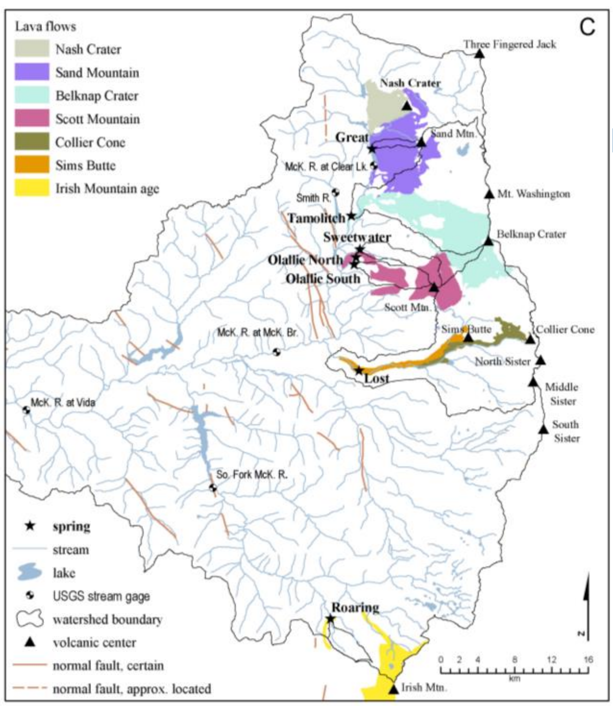
Slide from E. Griffith, UT Arlington

Use of O and H isotopes to help solve geochemical/hydrologic modeling problems

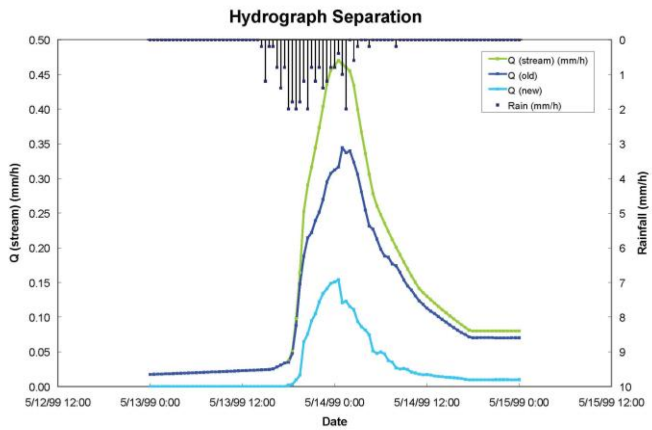
- Source of water
  - Rainwater – new or old
  - Evaporated water
  - Recharge at a certain altitude
  - Age of water
- Mixing of waters
  - Leakage from lakes, rivers, aquifers
  - Groundwater – surface water interactions
  - Contributions of snowmelt
- Salinization mechanism (plot of d vs concentration)
  - Evaporates surface water
  - Seawater
  - Dissolved evaporites
  - Mixing with connate brines
  - Reaction with rocks

Case Study: Isotopes as tracers of groundwater age **and origin**

A. Jefferson, G.E. Grant, T.P. Rose
Water Resources Research, 2006



Our use of isotopes: hydrograph separation



(data from McGlynn and McDonnell (2003)).
http://serc.carleton.edu/microbelife/research_methods/environ_sampling/stableisotopes.html

Hydrograph separation using isotope tracers

- Method takes advantage of conservative mixing of ^{18}O and ^{2}H
- Two types
  - Time source – new and old water
  - Geographic source – contributions from different landscape positions
- Punchline: Isotope methods clearly show much of stormflow or peakflow is old water stored in catchment prior to storm (*in forested watersheds*)

Text modified from Doug Burns and Tomas Vitvar: http://www.esf.edu/hss/IsotopeWS/Burns-Vitvar%20presentation/sld001.htm

Important points to remember

- Tracer separation techniques provide **components** of the hydrograph, not the same thing as a hydrologic flow path
- Usually need hydrometric data to determine contribution from a flow path
- Hydrograph separation is better for disproving than proving a streamflow generation process

Isotopes in storm-discharge analysis

Iqbal, M.Z. 1998. Application of environmental isotopes in storm-discharge analysis of two contrasting stream channels in a watershed, *Wat. Res.*32(10): 2959-2968

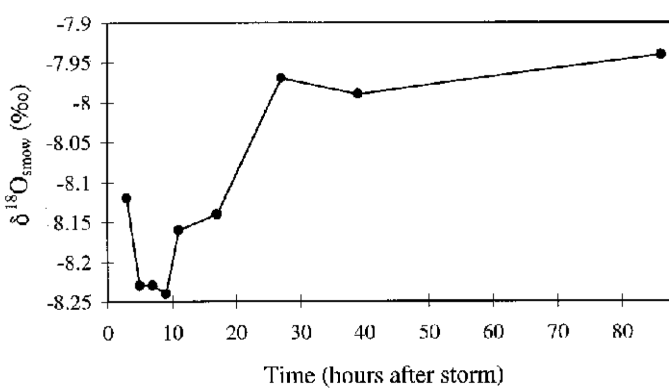


Fig. 3. Temporal variations in the oxygen isotope ratio (Cedar River).

Isotope Hydrograph Separation: How is it done?

- Simple mass balance expression
- Streamflow = new water + old water
- $Q_s\delta_s = Q_n\delta_n + Q_o\delta_o$
- Rearrange to solve for the new water discharge at any point in time
- $Q_n = Q_s \times (\delta_s - \delta_o)/(\delta_n - \delta_o)$

Text modified from Doug Burns and Tomas Vitvar: http://www.esf.edu/hss/IsotopeWS/Burns-Vitvar%20presentation/sld001.htm

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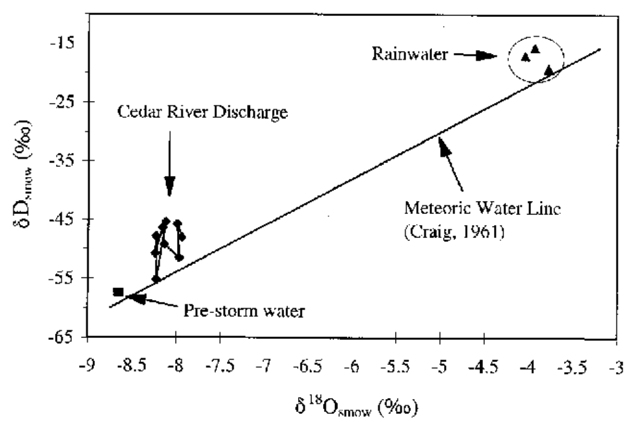

g. 4. Isotopic evolution of instantaneously discharged water in Cedar River by simple mixing

Isotopes in storm-discharge analysis

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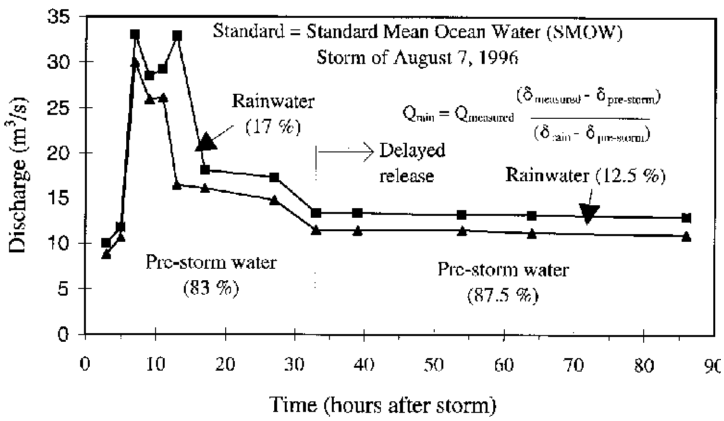

. **Storm hydrograph separation of the Cedar River using two-component mixing model oxygen isotope data).**

Assumptions of Isotope Hydrograph Separations

- Significant differences in isotopic content of new and old water
- New and old water content has a constant isotopic content in space and time, or variation can be accounted for
- Contributions of water with with isotopic content different from old water negligible – soil water, stored surface water, multiple sources of gw

Text modified from Doug Burns and Tomas Vitvar: http://www.esf.edu/hss/IsotopeWS/Burns-Vitvar%20presentation/sld001.htm

General results of hydrograph separation studies

- Old water is typically >50% of peakflow, 60-80% of total storm runoff at most sites (but humid, forested site bias)
- Agricultural and urban watersheds are dominated by new water at peak flow
- Wetlands and impoundments promote high proportion of old water in stormflow

Text modified from Doug Burns and Tomas Vitvar: http://www.esf.edu/hss/IsotopeWS/Burns-Vitvar%20presentation/sld001.htm

Where does old water originate?

- Saturation overland flow
- Macropore flow
- Transmissivity feedback – hydraulic conductivity decreases exponentially with depth, results in perched water table → subsurface stormflow
- Groundwater ridging/capillary fringe – soils near saturation close to stream, rapid water table rise