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/SF₆ 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 H₂O
  - ¹H, ²H (²D), ¹⁶O, ¹⁷O, ¹⁸O
- 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

Animations courtesy of E. Schauble (UCLA)
Isotopologues of Water

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

Isotope Ratio notation

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

- \( \delta \) = value \( \% \) `per mil`
- O and H are normalized to SMOW – standard mean ocean water
  - \( \delta^{18}O = 0\% \), \( \delta^2H = 0\% \)
- Positive vs. negative delta values
- Isotopically heavy vs. light, enriched vs. depleted
In H$_2$O, H and O isotopes $\sim$ co-vary

Global Meteoric Water Line

Global Precipitation

$\delta^2\text{H} = 8.19 \delta^{18}\text{O} + 10.8$

General $\delta$ 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 (and break) bonds with surrounding environment
- $^{18}\text{O}$ and $^2\text{H}$ 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

- **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$_2$O

- **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$_2$O

- Evaporation: vapor that forms is lighter than surrounding water
- Condensation: liquid that forms is heavier than surrounding water
- Evapotranspiration: -7 %
- Precipitation: -5 %

So, precipitation selectively removes $^{18}$O and $^{2}$H from the vapor phase

http://serc.carleton.edu/microbelife/research_methods/environ_sampling/stableisotopes.html

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

\[ y = 1.5106x - 225.99 \]
\[ R^2 = 0.89 \]

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 $\delta^D$ 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*
Fractionation effects associated with phase changes of H₂O

Evaporation – vapor that forms is lighter than surrounding water
Condensation – liquid that forms is heavier than surrounding water

So, precipitation selectively removes ¹⁸O and ³²H from the vapor phase

http://serc.carleton.edu/microbelife/research_methods/environ_sampling/stableisotopes.html

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 $^{18}\text{O}$ and $^2\text{H}$ in worldwide fresh surface waters.

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

Evaporation:
Humidity & Local Meteoric Water Lines

Evaporation Variability
Evaporation
}

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

- 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


![Graph](image)

**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

Isotopes in storm-discharge analysis


![](image.png)  

*Fig. 4. Isotopic evolution of instantaneously discharged water in Cedar River by simple mixing.*
Isotopes in storm-discharge analysis


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 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 \( \rightarrow \) subsurface stormflow
- Groundwater ridging/capillary fringe – soils near saturation close to stream, rapid water table rise