Catchment Scale

(Isotope Hydrology Primer Aside)
Primer History

Last 5 years:
For IAEA in South Africa and China
CSIRO Catchment Modeling School, Melbourne
Dept. of Civil Engineering, U. Western Australia
Dept. of Physical Geography and Quaternary Studies, Stockholm University
Dept. of Civil and Env. Engineering, Stuttgart University
Acknowledgements

Carol Kendall, USGS Menlo Park

Don Siegel, Syracuse University

IAEA Isotope Hydrology Section
Tracing the hydrologic cycle

- Rainfall and where it goes
- Lake water and its evaporation, inflows and outflows
- Water residence time, transit time, water age
- Composition of streamflow
- New ways to calibrate and test hydrologic models
- A very different data source to help structure, test and calibrate models
- A way to figure out where trees (and other vegetation) get their water

Hooper (2001)
Potential usefulness to local problems

Determining components of flow to the Swedish Rivers

Quantifying “success” in Land rehabilitation

Lake/reservoir evaporation
“The role of isotopes is like the role of the aliens in the famous sci-fi movie “The Invasion of the Body Snatchers”. Isotopes and trace elements have pervaded the entire discipline (geochemistry) and they are us now!”

K. Turekian, Editor

Geochimica et Cosmochimica Acta

....the same could now be said for Hydrology!
A recent GEOREF Search by Agarwal (2002 HP)

- **1965-1970**: 650 papers using isotope tracers
- **1995-2000**: over 6500 papers using isotope tracers in groundwater studies alone
Clark, I. and Fritz, P. 1998. Environmental Isotopes in Hydrogeology. Lewis Publisher (w/ web-link)


The classic

“...Isotope tracers have been among the most useful tools for understanding:

- Groundwater-surface water interactions
- Streamflow generation
- Flowpath dynamics”

Isotope Tracers in Catchment Hydrology
see also USGS official site

PART I. BASIC PRINCIPLES

Chapter 1: Fundamentals of Small Catchment Hydrology (by J.M. Boutle) @PDF

Chapter 2: Fundamentals of Isotope Geochemistry (by C. Kendall and E.A. Caldwell) @PDF

PART II. PROCESSES AFFECTING ISOTOPIC COMPOSITIONS
References - Internet

- USGS Isotope Interest Group Home Page (http://wwwcamnl.wr.usgs.gov/isoig/)
- ISOGEOCHEM Web Page with an E-mail Discussion List in Stable Isotope Geochemistry (http://geology.uvm.edu/geowww/isogeochem.html)
- IAEA web page and online teaching materials
Isotope Hydrology Section

Water News at the Agency

The 11th International Symposium on Isotope Hydrology and Integrated Water Resources Management

The Symposium was held at the IAEA headquarters in Vienna, 19-23 May 2003. High-level representatives from several member states and the Agency opened the Symposium.

A total of 274 participants from 69 countries and 4 international organizations attended the symposium. The number of participants set a record and was a clear indication of the keen worldwide interest in the science, as well as the relevance and role of the IAEA’s water resources programme. The
Head of IAEA Isotope Hydrology

See Summer 2005 Science Times article in NYT by Pradeep and his IAEA group
Isotopes in Hydrology

Environmental Isotopes

- STABLE
  - \(^2\text{H}/\text{H}\)
  - \(^{18}\text{O}/^{16}\text{O}\)
  - \(^{13}\text{C}/^{12}\text{C}\)

- RADIOACTIVE
  - Cosmogenic
  - Primordial
  - Fallout Products
  - Daughter Products
The Isotopes of General Hydrologic Interest in Hydrology

- Oxygen-18 and Oxygen-16
- Hydrogen-2 (Deuterium) and H-1
- Tritium (H-3)

(From Don Siegel, SU)
Isotope hydrology

Periodic Table of the Elements

H He
Li Be
Na Mg
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac

CFC

Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

Kendall (2001)
Isotope biogeochemistry

Periodic Table of the Elements

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<thead>
<tr>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
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<td>Am</td>
<td>Cm</td>
<td>Bk</td>
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Applications of Isotopes as Tracers:

1. Tracers of the water itself (D, O, T)  
   \[ = \text{Isotope Hydrology} \]
2. Tracers of solutes or reactions (C, N, S)  
   \[ = \text{Isotope Biogeochemistry} \]

This usage is **NOT** universal, but is very useful (conceptually)
Isotopes of water = history of water
Isotopes are atoms of the same element that have different numbers of neutrons.

\( ^{18}O \) and \(^{2}H \) are constituent part of natural water molecules—they *are* the water molecule.

Applied naturally during precipitation events

Conservative at ambient temperatures

Only mixing can alter concentration
Isotopes are atoms of the same element that have different numbers of neutrons.
Stable Isotopes $^2H$ and $^{18}O$

- Relative amounts in earth’s hydrosphere: $^{18}O = 0.2\%$, $^2H = 0.015\%$

- $^{18}O$ and $^2H$ content of water changes only through fractionation associated with phase exchange processes (except for saline waters)

- Conservative behavior - once isotopes become part of water molecule, they change only through mixing

<table>
<thead>
<tr>
<th>Name</th>
<th>Electrons</th>
<th>Protons</th>
<th>Neutrons</th>
<th>Abundance</th>
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<tbody>
<tr>
<td>$^{16}O$</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>99.76%</td>
</tr>
<tr>
<td>$^{18}O$</td>
<td>8</td>
<td>8</td>
<td>10</td>
<td>0.20%</td>
</tr>
</tbody>
</table>

C. Kendall, USGS
Delta Isotope = (i.e. $\delta$ in $\%_{\text{oo}}$)

\[
\text{Ratio}_{\text{sample}} - \text{Ratio}_{\text{standard}} \quad \text{Ratio}_{\text{standard}} \times 1000
\]

...in other words......

A DELTA O-18 = -10 $\%_{\text{oo}}$ means there is 10 parts per thousand less O-18 in the sample than in the standard, standard "mean" oceanic water (SMOW)

Note ratio is $^{18}\text{O}/^{16}\text{O}$ (or $^{2}\text{H}/^{1}\text{H}$ for deuterium)
Some atoms of elements can have different weights.

Fractionation—sorting the "light" from the "heavy" versions of the elements.

(From Don Siegel, SU)
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 vapor
- **So, precipitation selectively removes** $^{18}$O and $^{2}$H from the vapor phase
In other words...

\[
\begin{align*}
\text{H}_2\text{O}^{18} & \quad \text{H}_2\text{O}^{16} \\
\text{H}_2\text{O}^{18} & \quad \text{H}_2\text{O}^{16}
\end{align*}
\]

\(\text{O}^{18}\) is preferentially removed relative to \(\text{O}^{16}\) by precipitation.

\(\text{H}_2\text{O}^{16}\) evaporates slightly easier than \(\text{H}_2\text{O}^{18}\)
Fractionation in $\delta^{18}O$ and $\delta D$ during the hydrologic cycle

Anderson and Burt, 1990
**Commonly Used Terms:**

- **heavy vs. light isotopes**
  the “heavy” isotope is the one with more neutrons; it is also generally the less abundant isotope.

- **enriched vs. depleted**
  remember to state what isotope is in short supply:
  does “enriched sulfate” mean that:
  the sulfate is enriched in heavy sulfur
  **OR**
  the sulfate is enriched in light sulfur?

- **positive vs. negative**
  -10 \(^\circ\) is more positive than -20 \(^\circ\)
Glossary of Terms

α - the Greek symbol for alpha, used to symbolize the fractionation factor. See fractionation.

β - the Greek symbol for beta.

δ - the Greek lower case symbol for delta, used for light isotopes to designate per mil (‰) deviation from a standard.

Δ - the Greek upper case symbol for delta, used as the measurement of the difference between a product and a reactant.

d - the symbol used for deuterium excess, defined as the intercept of the meteoric water line (MWL): δD = 8 δ¹⁸O + d

D - used as an abbreviation for deuterium (²H). δD is the variation of ¹H and ²H relative to SMOW.

ε - the Greek symbol for epsilon. Used as the per 10⁴ deviation of sample from a standard. Also used in fractionation studies to symbolize enrichment.
Fractionation Effects on $^{18}\text{O}$ and $^2\text{H}$

- **Equilibrium fractionation** - vapor pressure of water containing light isotopes > water containing heavy isotopes, therefore vapor is enriched in light isotopes
  - E.g. at 100% humidity when the air is still and the system is almost chemically closed

- **Kinetic fractionation** - rapid phase changes increase fractionation because light isotopes diffuse more rapidly than heavy ones
  - E.g. this is more typical in hydrological systems where the system is out of chemical equilibrium (<100% humidity) or the products become slightly separated from the reactants (i.e. the resultant vapor is blown downwind).
Figure 2.3. Isotopic change under open- and closed-system Rayleigh conditions for evaporation with a fractionation factor c = 1.01. Initial vapor and water compositions: solid line (A) all increase during single-phase, open-system, evaporation with an initial water composition of $^8\delta^{18}O = 0$. The $^8\delta^{18}O$ of the remaining water (solid line, B) all increase during evaporation. The $^8\delta^{18}O$ of the accumulated vapor (dashed line, E) all increase during evaporation under equilibrium conditions. The $^8\delta^{18}O$ of the instantaneous vapor (dashed line, D) and vapor (dashed line, E) in a single-phase, closed system also increase during evaporation.

Modified from Cat and Gorfant (1981).
Example of a Rainfall Event: Fractionation in $\delta^{18}O$ during the hydrologic cycle

(Siegenthaler, 1979)
Fractionation Effects Associated with Phase Changes of $\text{H}_2\text{O}$ -- summary

- **Evaporation** - vapor that forms is lighter than surrounding water
- **Condensation** - liquid that forms is heavier than surrounding vapor
- **So, precipitation selectively removes** $^{18}\text{O}$ and $^2\text{H}$ from the vapor phase
Fractionation in the hydrological cycle

**EXPLANATION**
- Water flux involving no isotopic fractionation
- Water flux involving isotopic fractionation
- Water table
- Surface water flux assumed to be zero for kettle lakes in sandy outwash
Some “Effects”

◆ Amount Effect:
   The more rainfall, the more depleted the rain

◆ Apparent Temperature Effect:
   Approximately 0.5% for every °C for oxygen

◆ Evaporation:
   As rain falls through dry air, it may evaporate, resulting in heavier rain

Kendall (2001)
Some “Effects”

◆ Altitude effect:

On the windward (not leeward) side of a mountain, the rain gets lighter with increasing altitude.

**GRADIENTS**

\[
\begin{align*}
\text{O}: & \ -0.15 \text{ to } -0.5\% \ O/100 \text{ meters} \\
\text{D}: & \ -1.5 \text{ to } 4\% \ O/100 \text{ meters}
\end{align*}
\]

◆ Continental Effect:

Delta values decrease inland.

Kendall (2001)
Geography and Seasonality of $^{18}\text{O}$ and $^2\text{H}$ Content of Precipitation

- Precipitation becomes lighter as air mass moves inland
- Precipitation becomes lighter with increasing elevation - orographic effect
- Precipitation becomes lighter towards the poles and is lighter in winter than summer
Altitude Effect

Fig. 4.7 Example of the altitude effect on precipitation for the eastern slopes of the Andes mountains, as deduced from samples of undepth groundwater/soilwater, collected from springs. The magnitude of the effect is increasing from −0.2 to −0.6‰/100m (Vogel et al., 1975).

Source: IAEA
Fig. 4.8  Time sequence of the isotopic composition of precipitation during showers; examples are shown for two cases of convective storms: A) rain intensity in mm/2 hours (Mook et al., 1974); B) cumulative rain over variable periods.

Source: IAEA
Temperature Effect

Fig. 4.9  Weighted average annual values of $^{18}\delta$ in precipitation (pcpt) vs the mean surface air temperature, showing the variations from year to year (data from the GNIP network).

Source: IAEA
Continental effect

Mean O18 of Columbia River
Continental Effect

Mean $\delta^{18}O$ of the Columbia Watershed vs distance from the West Coast

Errorbars = 2x Stdev $O^{18}$

Starke, McDonnell and Kendall, in prep
Elevation Effect

Mean $\delta^{18}O$ of Columbia Watershed vs elevation

Errorbars = 2x Stdev

Starke, McDonnell and Kendall, in prep
Air Temperature “Effect”

Air Temp. (°C) vs. Delta O-18

- 40 - 30 - 20 - 10 0

- 20 - 10 0 10 20

Athens
Vienna
Northern Sweden

(after Don Siegel, SU)
Latitudinal Controls
Northern Hemisphere
Latitudinal Controls Southern Hemisphere
Fig. 4.5 Seasonal influence on the \((^{18}\delta, ^2\delta)\) relation for average monthly precipitation at a number of stations, arctic, tropical, coastal and continental (data from the same series as in Fig. 4.4).
Latitudinal Effect

\[ \delta^{18}O (\%o) \]

-40.00 -30.00 -20.00 -10.00 0.00

J F M A M J J A S O N D

Months

Lowest, Warmer Latitude

Waco, Texas

Chicago, Illinois

Barrow, Alaska

Higher, Colder Latitude

\( \delta^{18}O (\%o) \) variations

(from Don Siegel, SU)
Some spatial data

\[ \delta^{18}O \ (\text{‰}) \]

- > - 2
- -4 to -2
- -6 to -4
- -8 to -6
- -10 to -8
- -12 to -10
- -14 to -12
- -16 to -14
- -18 to -16
- < -18

(Kendall and Coplen, 2001)
Why are 18-O and D so similar?
Global Meteoric Water Line

...because they are related
\( \text{dD} = 8 \text{d}^{18}\text{O} + 10 \) (Factoids)

- The slope is 8 (actually, different data sets give slightly different values) because this is approximately the value produced by equilibrium Rayleigh condensation of rain at about 100% humidity.
- The value of 8 is also close to the ratio of the equilibrium fractionation factors for H and O isotopes at 25-30°C. At equilibrium, the d values of the rain and the vapor both plot along the MWL, but separated by the \( 18\text{O} \) and \( 2\text{H} \) enrichment values corresponding to the temperature of the cloud base where rainout occurred.
- The y-intercept value of 10 in the GMWL equation is called the deuterium excess (or d-excess, or d parameter) value for this equation. The term only applies to the calculated y-intercept for sets of meteoric data "fitted" to a slope of 8; typical d-excess values range from 0 to 20.
- The fact that the intercept of the GMWL is 10 instead of 0 means that the GMWL does not intersect \( \text{d}^{18}\text{O} = \text{dD} = 0 \), which is the composition of average ocean water (VSMOW).
- The GMWL does not intersect the composition of the ocean, the source of most of the water vapor that produces rain, because of the 10‰ kinetic enrichment in D of vapor evaporating from the ocean at an average humidity of 85%.
Figure 2.5. The effect of humidity on the $\delta^{18}O$ and $\delta D$ values of the residual water fraction during evaporation. Higher humidities result in less fractionation because of back exchange between the water and the vapor, and evaporation lines with higher slopes. Modified from Gat and Gonfiantini (1981).
The diagram illustrates the relationship between δ²H and δ¹⁸O, focusing on the input signal, ocean water, and atmospheric moisture. Key processes include:

- **Input signal**
- **Continental Discharge**
- **Ocean Water**
- **Atmospheric Moisture**

The diagram highlights the influence of mean precipitation, seasonality, continental discharge, and evaporation loss from rivers, reservoirs, lakes, and contributing sources on the δ²H and δ¹⁸O values.
Global Atmospheric Circulation System
Distills Water Isotopes

Evaporation

"Light" water vapor

Condensation

Heavier Rain Falls

"Heavier" Water Remains

Solar Heat

Raleigh Distillation

(From Don Siegel, SU)
Jan. Weighted $^{18}\text{O}$

Precipitation in mid-latitude regions
The δD and δ¹⁸O taken from the GNIP database were amount-weighted according to:

\[
\delta x_w = \frac{\sum_{i=1}^{n} P_i \delta_i}{\sum_{i=1}^{n} P_i}
\]

where \( P_i \) and \( \delta_i \) are the monthly precipitation amount (mm) and the isotopic composition (‰), respectively, and \( n \) is the number of months.
Characteristics of $\delta D$ and $\delta^{18}O$ of Precipitation:

- Consistent average compositions over time and space.
- Annual cycle of compositional changes—heavy in summer and light in winter.
- Large variations among storms.
- Often considerable variability within storms.
- Snow often plots along lines of higher d-exess than rain.
- Storms derived from different storms tracks may have consistently different meteoric water lines.
• Global Network for Isotopes in Precipitation

http://www.iaea.or.at/programs/ri/gnip/gnipmain.htm
Fig. 4.2  Relation between weighted average $^{18}\delta$ and $^2\delta$ values of total precipitation over periods of at least one decade from the same stations of the GNIP network as represented in Fig. 4.1. The data confirm the general validity of the Global Meteoric Water Line (GMWL) reasonably well.
People wanted to use the Lake water for irrigation, but wanted to make sure that using lake water would have no adverse effect on the discharge of nearby springs whose waters were already being utilized. (i.e., they didn’t want to “rob Peter to pay Paul”)

e.g. Lake Chala in Kenya

Can they tap lake water without affecting spring flow?

Carol Kendall, USGS
MWL at a single site – Woods Lake USA

Doug Burns, USGS
Fig. 4.2  $\delta^{18}O$-$\delta^{2}H$ relationship for water samples collected from the Titicaca Lake and the rivers feeding the lake. Titicaca is a large tropical lake, located on the border between Bolivia and Peru, at an elevation of 3800 m above sealevel. There is a remarkable isotope enrichment of the lake water with respect to the river inflow, by more than 10% in $\delta^{18}O$ (modified from Fontes et al., 1979).
Groundwater Isotopes Same as that for Average Precipitation

(From Don Siegel, SU)
Groundwater Isotopes Different than that for Average Precipitation

(From Don Siegel, SU)
Seasonal Variation in $^{18}$O of Precipitation

**Neversink watershed, 1993 - 1996**

- **$^{18}$O (per mil SMOW)**
- **Air temperature (°C)**

Vitvar, SUNY-ESF
What you might see in the Spring

Meltwater δO-18‰ From Four Snowmelt Lysimeters
Individual Rainfall Events

Kendall (2001)