

# Forest Hydrology: Lec. 17

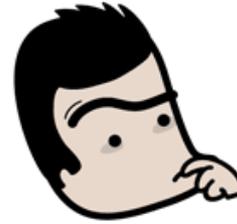
## Lecture content

- Use of tracers and isotopic analyses in hillslope hydrology
  - Fundamentals on isotopes;
  - Measurement principles;
  - Use and potential in hillslope/forest hydrology

# Objectives



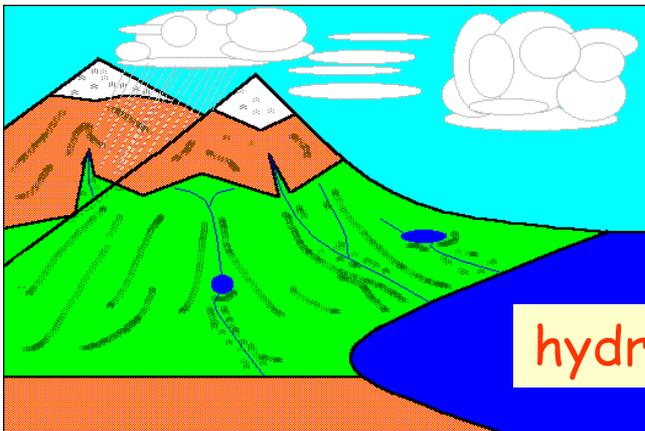
1. isotopes: who are these guys?



2. how can they be measured in water samples?



3. what are their potentials as tracers in environmental studies?



hydrogeology



plant ecology



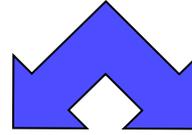
**Environmental tracers:** natural or anthropogenic compounds or isotopes that are widely distributed in the near-surface environment of the Earth, such that variations in their abundances can be used to determine **pathways** and **timescales** of environmental processes (Cook & Herczeg, 2000, Environmental tracers in subsurface hydrology).

**More specifically, in hydrology...**

**Tracers:** experimentally measured substances which, dissolved in water, **can be tracked** in order to study its **flowpaths** and **velocity** in a porous media.

Tracers are used when the properties of the analyzed system do not allow a direct measurement (Flury and Wai, 2003, Rev. of Geophysics).

# Tracers



**Conservative:** substances which do not react with the system they are injected in and remain constant in the fluid.

**Non conservative:** substances which react with other system components and grow or decay over time.

**Conservative tracers:**  
are neither produced nor consumed during their permanence in the system



useful tools in hydrogeological and ecological studies

# Isotopes



- atoms of the same element with **different number of neutrons**
- **same electric charge** but:
  - different atomic mass\*
  - different bond strengths
  - different chemicals and physical properties

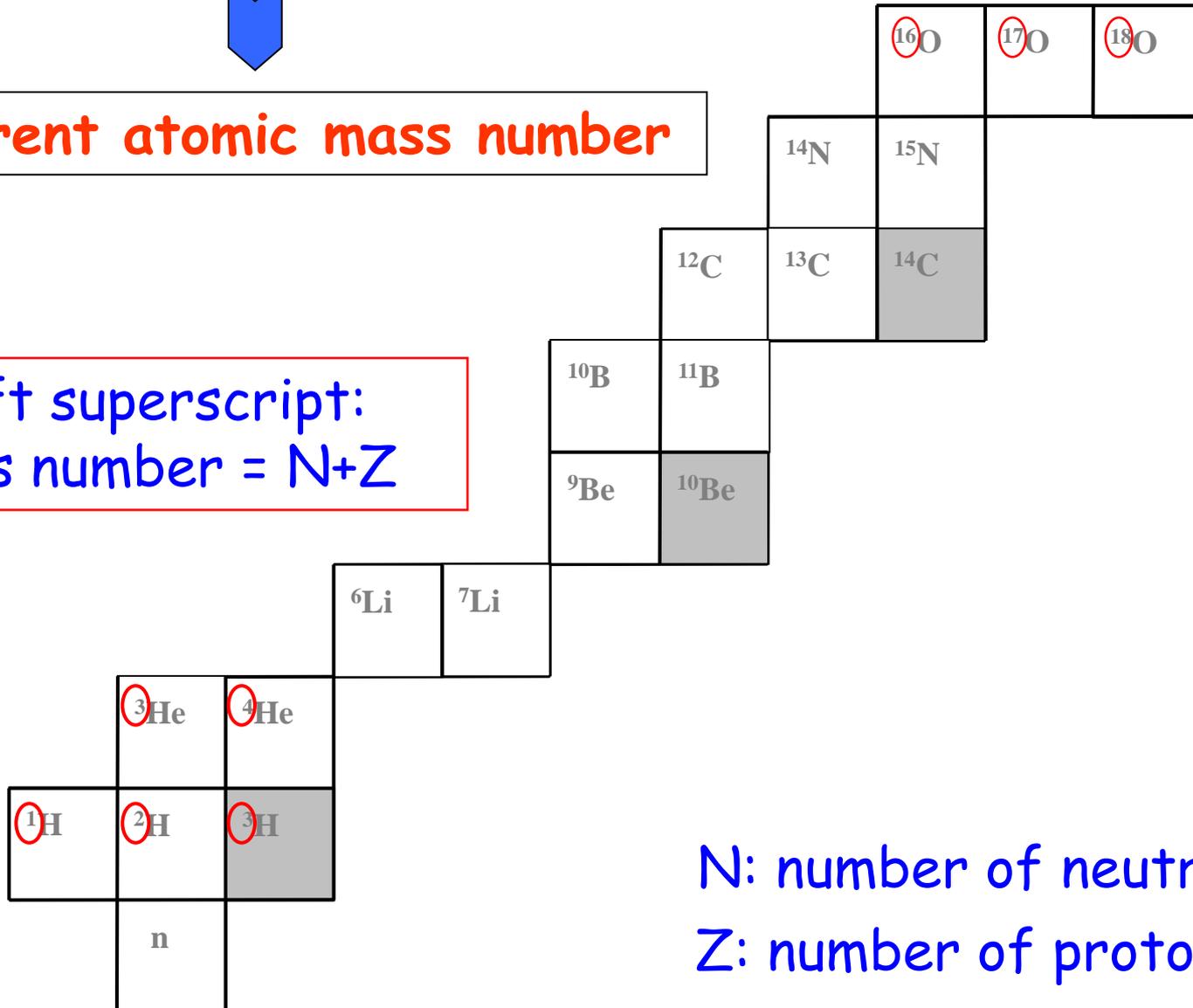
\*Atomic mass= number of neutrons (N) + number of protons (Z)

# Isotopes of the same elements



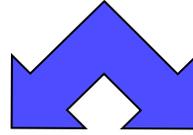
different atomic mass number

Left superscript:  
mass number =  $N+Z$



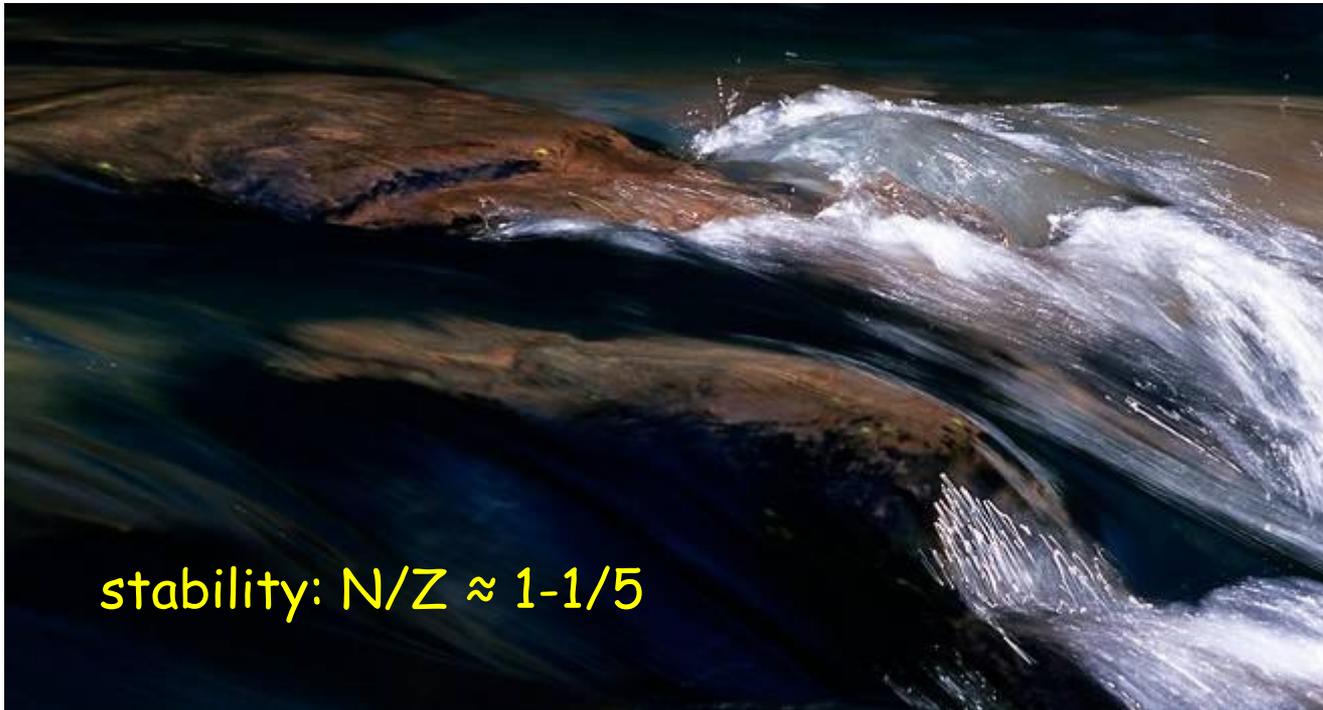
N: number of neutrons  
Z: number of protons

# Isotopes



**unstable:** radioactive isotopes which decay naturally to other atomic forms at a characteristic rate.

**stable:** isotopes which do not decay over time, they can be produced by decay of unstable isotopes.



stability:  $N/Z \approx 1-1/5$



# Water isotope relative abundance

isotope	natural abundance (%)	stability
$^1\text{H}$ (protium)	99.985	stable
$^2\text{H}$ (deuterium)	0.015	stable
$^3\text{H}$ (tritium)	trace	radioactive
$^{16}\text{O}$	99.76	stable
$^{17}\text{O}$	0.04	stable
$^{18}\text{O}$	0.20	stable

- tritium: produced in small concentrations by natural processes, in larger concentrations by nuclear reactions
- tritium decay: 12.5 years  $\rightarrow$   $^3\text{He}$
- ratio between  $^{18}\text{O}/^{16}\text{O}$ ,  $^2\text{H}/^1\text{H}$

Note: ( $^2\text{H} = \text{D}$ )

# Why isotopes in hydrology?



- $^{18}\text{O}$  e  $^2\text{H}$  form the water molecules (rainfall, snowfall, streams, rivers, lakes, groundwater...) → naturally applied during precipitation events.
- Oxygen and hydrogen isotopes: conservative → when they move across the catchment, any interaction of water molecules with the organic/lithological components of the watershed has a negligible effect on the isotopic ratio.

# Isotopes



**water isotopes  $\Rightarrow$  natural "signature" = water history**

Useful tools for investigation of processes regarding:

- interaction between surface and subsurface runoff
- runoff generation
- flowpath dynamics



# Terminology



$$\delta_x (\text{‰}) = \frac{R_x - R_{std}}{R_{std}} \cdot 1000$$

$R_x$  = sample isotopic ratio ( $^{18}\text{O}/^{16}\text{O}$ ,  $^2\text{H}/^1\text{H}$ )

$R_{std}$  = reference standard

**SMOW** (Standard Mean Ocean Water), later defined as

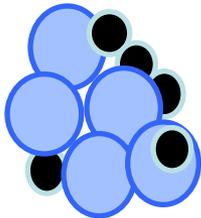
**VSMOW** (Vien Standard Mean Ocean Water)

according to **IAEA** (International Atomic Energy Agency) in Vienna.

# Stable isotopes

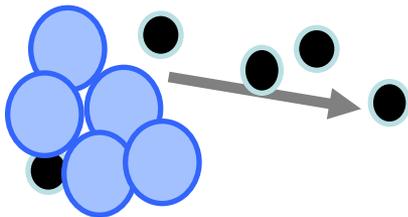


## Variation of isotopic composition in natural systems fractionation



The atoms of some elements can have different atomic weight

- light
- heavy



Chemical, physical and biological processes separate light isotopes from the heavy ones in the same element  $\Rightarrow$  **fractionation**

# In the atmosphere...

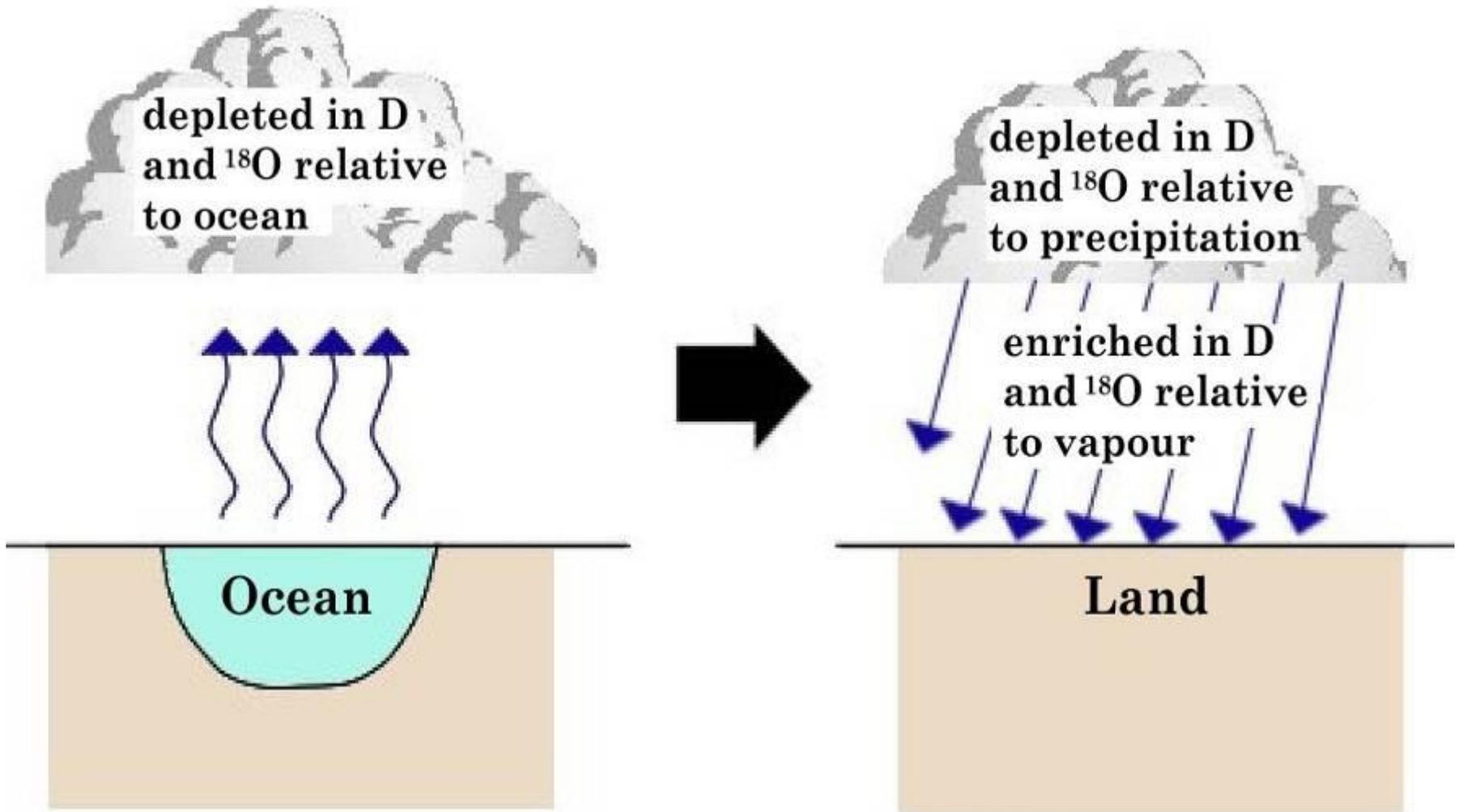


Two kinds of fractionations: kinetic and equilibrium

**Evaporation** (**kinetic** fractionation): the **liquid** phase is progressively **enriched in heavy** isotopes, the **gas** phase is **depleted in heavy** isotopes. The process is mainly influenced by atmospheric air humidity.

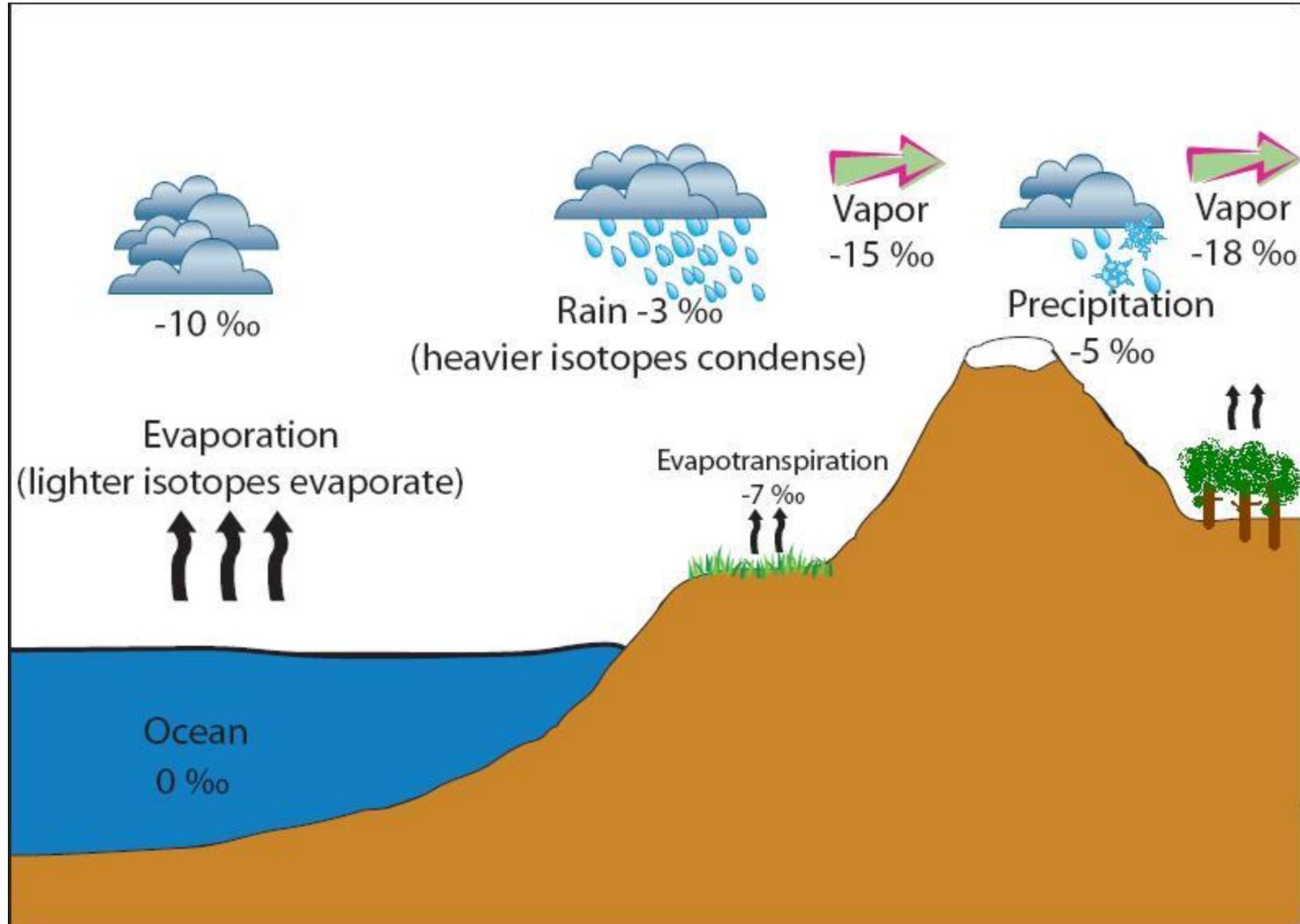
**Condensation** (**equilibrium** fractionation): the **liquid** phase is **enriched in heavy isotopes** relatively to the gas phase (cloud). This process is mainly influenced by temperature variations (100% humidity and reach of dew point).

...fractionation  $\delta^{18}\text{O}$  e  $\delta\text{D}$ ...



Anderson and Burt, 1990

# ...fractionation $\delta^{18}\text{O}$ e $\delta\text{D}$ ...



## ...and on the land surface: tracer function



- **Temperature** → the main factor controlling the isotopic composition of precipitation during condensation processes.
- **During meteoric events:**

The longer the exposition of meteoric water to atmospheric conditions ⇒ the higher the evaporation → greater enrichment in heavy isotopes in the liquid phase.

- Another possible process occurring on the land: **mixing** (surface/subsurface waters) → change in the isotopic composition.

- **Mixing:** a linear process.

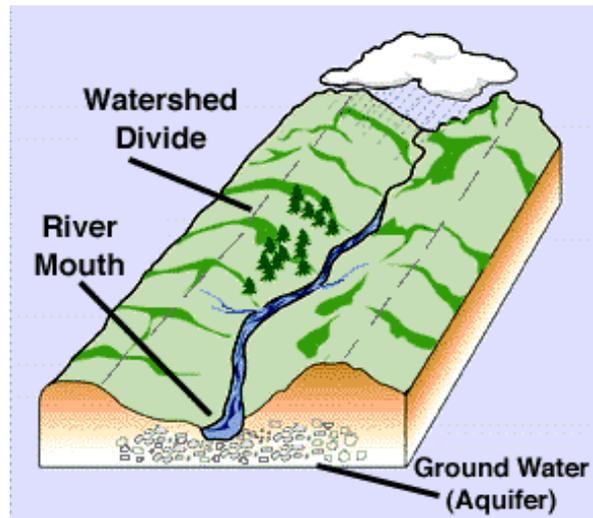
Ex:  $\delta^2\text{H}$  sample 1:  $-80\text{‰}$ ,  $\delta^2\text{H}$  sample 2:  $-60\text{‰}$

50% of sample 1 + 50% sample 2 =  $\delta^2\text{H}$   $-70\text{‰}$

## ...and on the land surface: tracer function 2



At the catchment scale:



- meteoric waters infiltrated at **high elevation** find low T and undergo short expositions to atmospheric conditions  $\Rightarrow$  less evaporation  $\Rightarrow$  **depleted** in heavy isotopes.
- meteoric waters infiltrated at **low elevation** find higher T and undergo long expositions to atmospheric conditions  $\Rightarrow$  evaporation  $\Rightarrow$  **enriched** in heavy isotopes.

# Therefore...



• Less negative values ( $\delta D$ : -5 ~ -10‰;  $\delta^{18}O$ : -2 ~ -3‰):

warm regions, low elevations/latitudes  $\Rightarrow$  removal of light isotopes through **evaporation**  $\Rightarrow$  enrichment in heavy isotopes of liquid phase  $\Rightarrow$  "heavy" sample.

• Very negative values: ( $\delta D$ : -100 ~ -150‰;  $\delta^{18}O$ : -20 ~ -30‰):

cold regions, high elevations/latitudes, snow, rainfall condensed at high elevations  $\Rightarrow$  **reduced/no evaporation**  $\Rightarrow$  no removal of light isotopes  $\Rightarrow$  "light" sample.

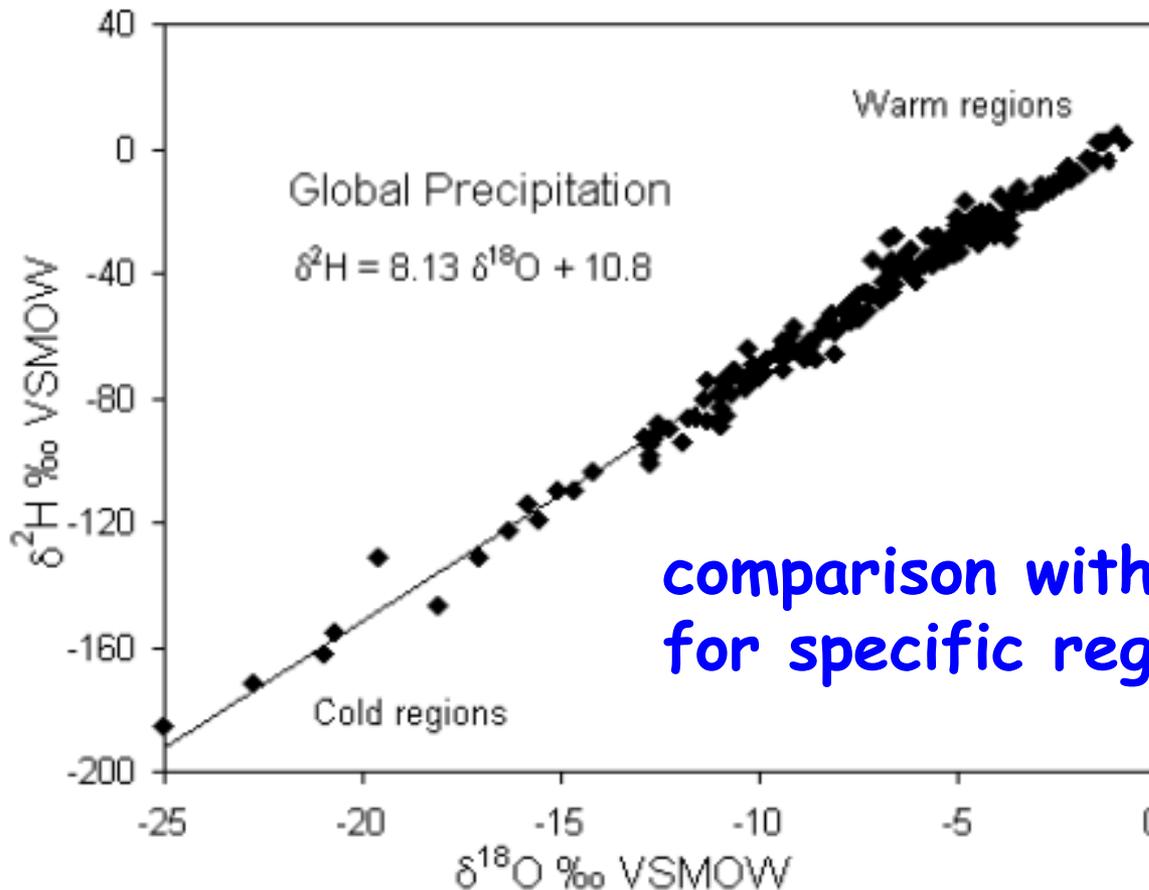
sample	$\delta D$ ‰	$\delta^{18}O$ ‰
tap water, PD	-56	-8
alpine stream	-85	-12
fresh snow	-125	-18
Antarctic core	-425	-55



# Global Meteoric Water Line

Covariance of oxygen and hydrogen isotopes in precipitation: strong correlation of rainfall from all over the world (Craig, 1961, Science).

$$\delta D = 8.13 \delta^{18}O + 10.8 \text{ ‰} \text{ (GMWL, Global Meteoric Water Line)}$$



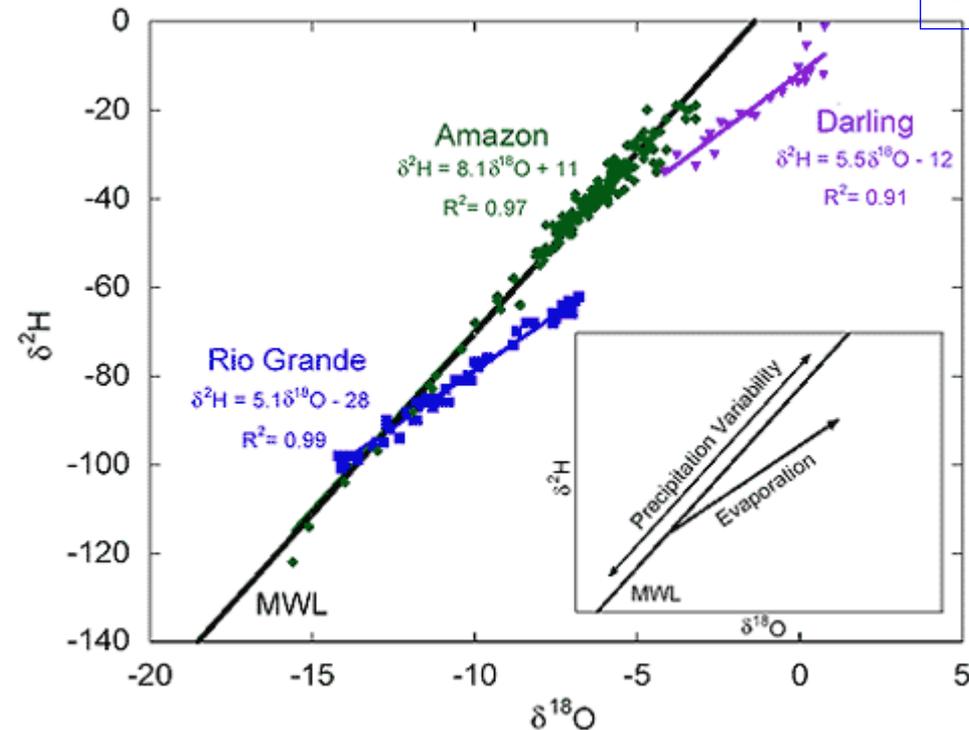
# GMWL

$$\delta D = 8.13 \delta^{18}O + 10.8\text{‰}$$



slope ~ 8: equilibrium conditions during condensation of precipitation in clouds.

intercept ~ 10‰: deuterium excess (DE): mean relative humidity during evaporation from the ocean  $\Rightarrow$  DE depends on humidity during evaporation.

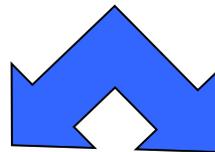


indicator of conditions in moisture source region.

# Hydrological applications at hillslope/basin scale...



- spatial & temporal variability of isotopic composition in rainfall/snowfall/snowpack
- spatial variability within the drainage network  $\Rightarrow$  different origin of waters
- runoff generation processes
- preferential flowpaths
- catchment and hillslope residence and transit time
- contribution of pre-event/event water to total stormflow  $\Rightarrow$  hydrograph separation



rainfall input

snowmelt input

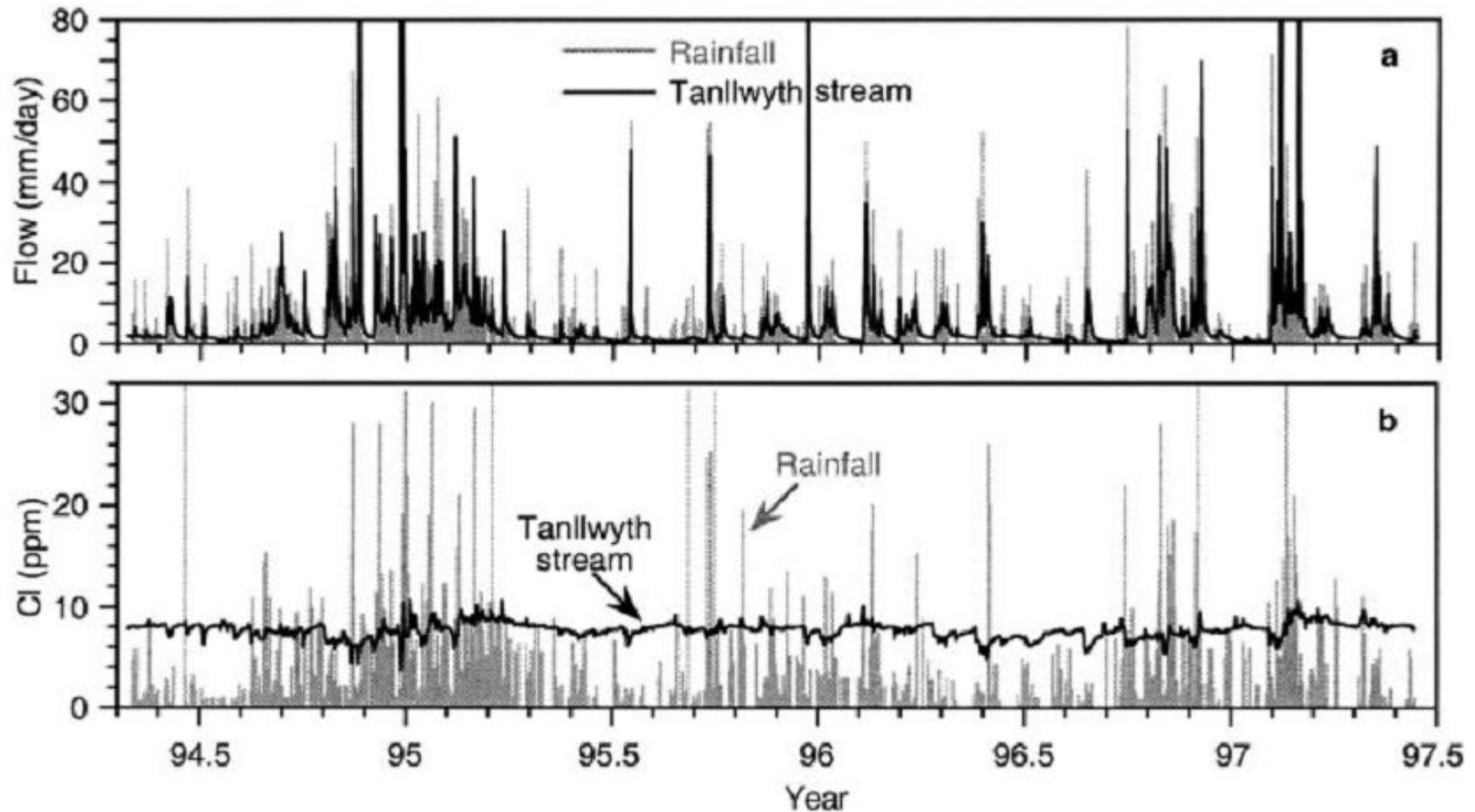
## ...and at regional scale.



- history and age of water supplies
- location of water recharge
- velocity of groundwater flow
- degree of water mixing



# The old water paradox



streamflow is highly responsive to recent rainfall, but passive tracers that move with the water are largely indifferent to recent rainfall?

Kirchner 2003, HP

# The old water paradox (= rapid mobilization of old water)



" In many small catchments, streamflow responds promptly to rainfall inputs but fluctuations in passive tracers [isotopes...] are often strongly damped. This indicates that storm flow in these catchments is mostly 'old' water".

"old" water  $\Rightarrow$  stored in the catchment  
"new" water  $\Rightarrow$  rain and surface runoff

*Main question: how do these catchments store water for weeks or months but then release it in minutes or hours in response to rainfall inputs?*

mechanisms by which catchments store water for extended periods are still not well understood.



# Hydrograph separation: Two-component mixing model

"old" water = pre-event water  $\Rightarrow$  stored in the catchment

"new" water = event water  $\Rightarrow$  rain and surface runoff

**Key concept:** the isotopic content in a stream section reflects the proportion of runoff of different origins.

$$Q_t = Q_o + Q_n$$

$$Q_t \delta_t = Q_o \delta_o + Q_n \delta_n$$

$$Q_o = Q_t (\delta_t - \delta_n) / (\delta_o - \delta_n)$$

(Sklash & Farvolden ,  
1979, JoH)

where  $Q_t$  = total runoff

$Q_o$  = old water

$Q_n$  = new water

# Assumptions for hydrograph separation



1. **groundwater** and **baseflow** are equivalent and have a constant isotopic composition.
2. the **rain** or **snowmelt** can be characterized by a single isotopic composition.
3. the rain water is significantly different from the pre-storm water.
4. contributions from **soil water** are negligible, or the composition is identical to groundwater.
5. surface-water storage contributions are negligible.

## Favourable conditions for HS through isotope application:

- short duration of stormfall;
- quick catchment response

(Sklash & Farvolden , 1979, JoH)

# Hydrograph separation

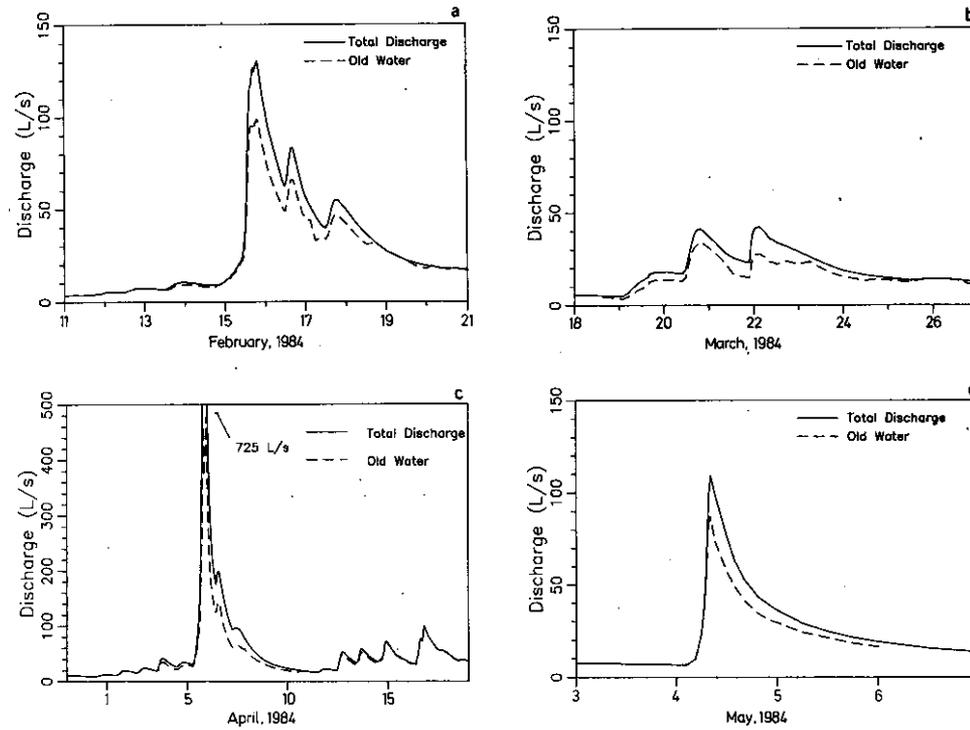


Fig. 10. Hydrograph separation for the four events during the study period using dissolved silica tracer. (a) February thaw, site 1. (b) March thaw, site 1. (c) Spring thaw, site 1. (d) Spring storm, site 0.

In all storms, "old" water dominates hydrograph.

(Hooper & Shoemaker, 1985, WRR)

Groundwater is the main component of flood hydrographs  
80%-90%.

(Sklash & Farvolden, 1982)

# Hydrograph separation: Three-component mixing model



One of the assumptions of two components hydrograph separation is that contributions from soil water are negligible, or the composition is identical to groundwater.

Is that true?

Three-component hydrograph separation through isotopes + chemical tracers

$$Q_t = Q_{cp} + Q_s + Q_{gw}$$

$$Q_s / Q_t = \left[ \frac{C_t - C_{gw}}{C_s - C_{gw}} \right] Q_{cp} / Q_t \left[ \frac{C_{cp} - C_{gw}}{C_s - C_{gw}} \right]$$

where

cp: channel precipitation (rain falling directly onto saturated areas);

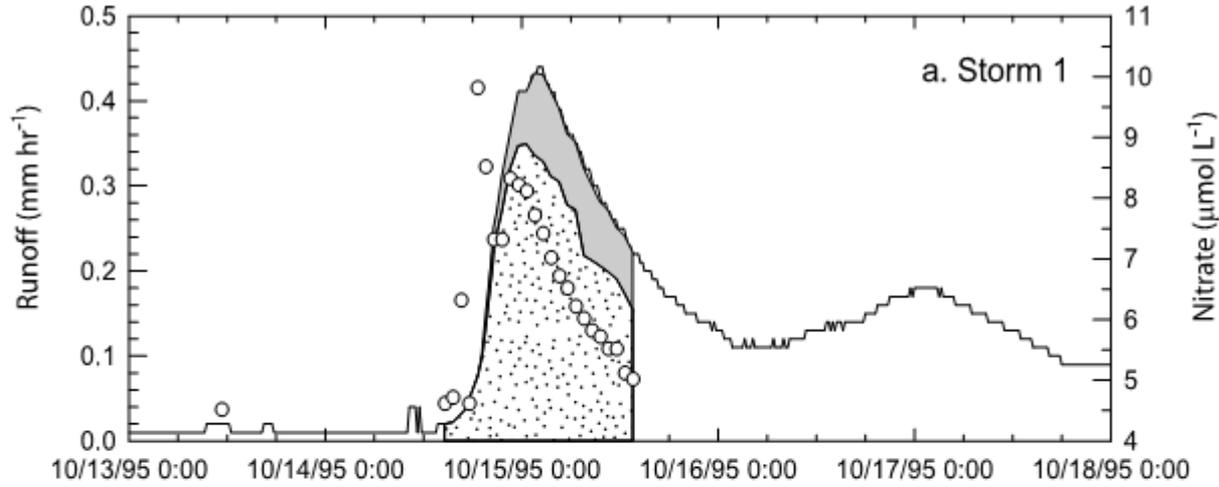
s: soil water (unsaturated zone);

gw: ground water (saturated zone).

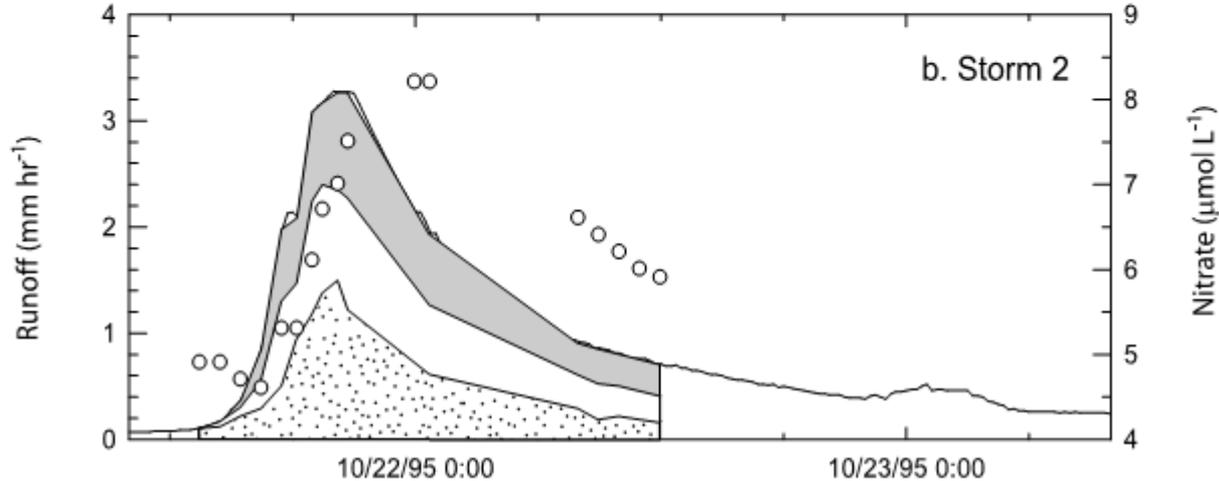
(Dewalle et al., 1988, JoH)



# Three-component hydrograph separation



→ 2-comp. HS



→ 3-comp. HS

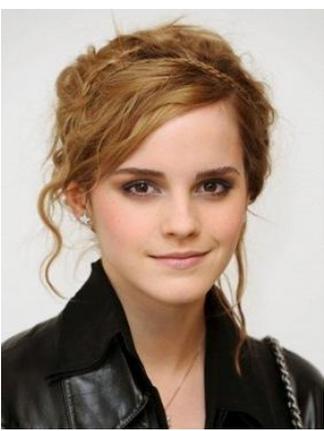
contribution to total runoff

gw: 74-90%

sw: 6-25% (Swistock et al., 1989, WRR):



EMMA...?



## End-Members Mixing Analysis

Technique for prediction of the proportions of contributing sources to the storm hydrograph.

(Christophersen et al., 1990, JoH, Hooper et al., 1990, JoH)

**End-Members:** the chemical compositions of source waters existing within a catchment that undergo physical mixing only during travel time to the stream channel.

# Emma: End-Members Mixing Analysis



**End-Members:** water sources in the catchment whose **concentration** is **more extreme** (very low or very high) than stream.

Usual end-members:  
first horizon soil water, hillslope gw, floodplain gw

EMMA relies on the assumptions of **linearity of the mixing process**, the **conservative behaviour** of tracers, and the **time invariance** of end-member compositions (Hooper 2001, HP)

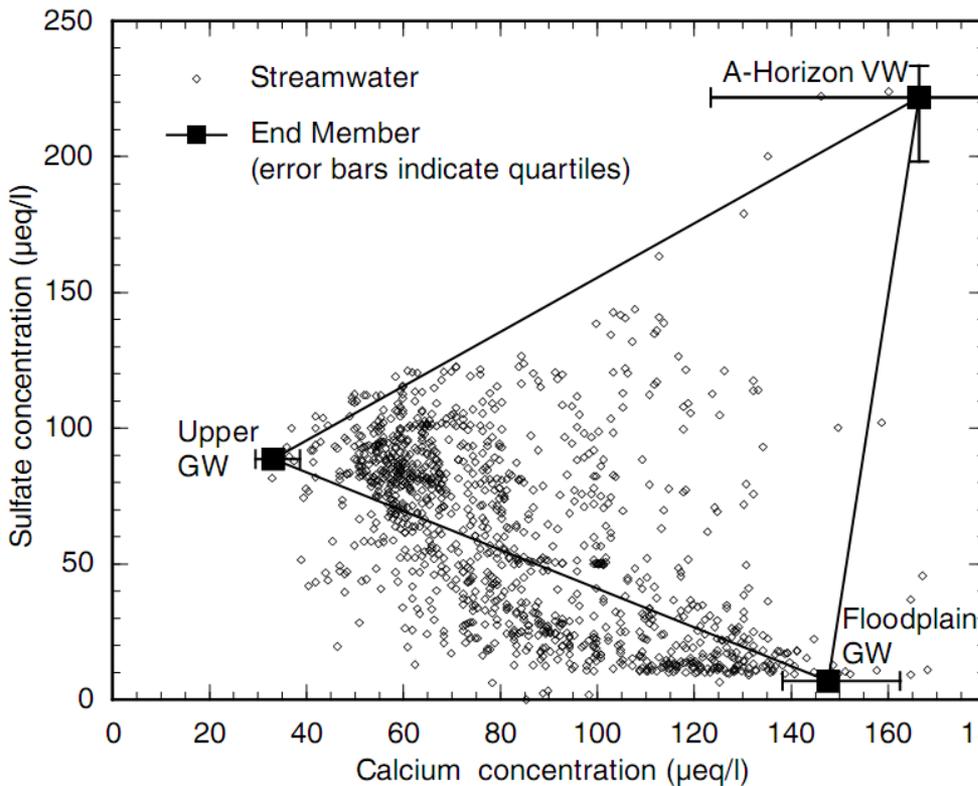
# EMMA: End-Members Mixing Analysis



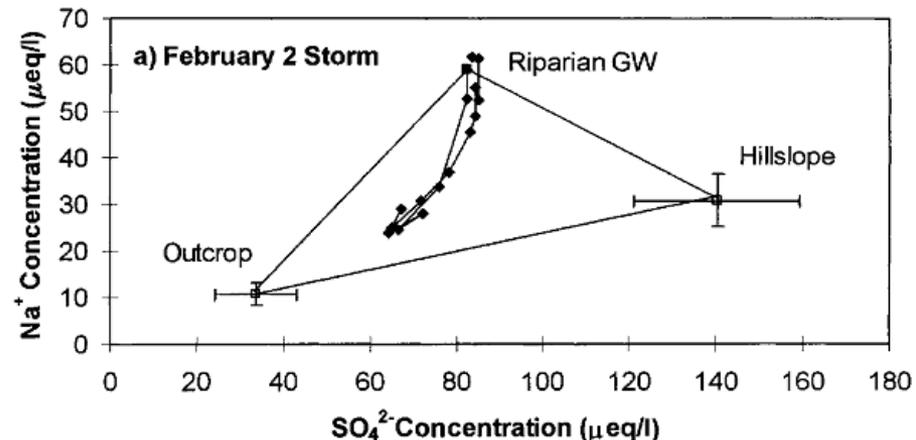
Graphical plotting of the concentrations of one environmental tracer against that of another, so that all streamwater samples fall within a triangular space bounded by three waters of extreme concentration.

major contributing sources to the storm hydrograph

(Burns et al., 2001, HP)



(Hooper 2001, HP)





# Mean Residence Time



event water  
contribution

soil water  
contribution

ground water  
contribution

# Mean Residence Time: the age of water in the catchment

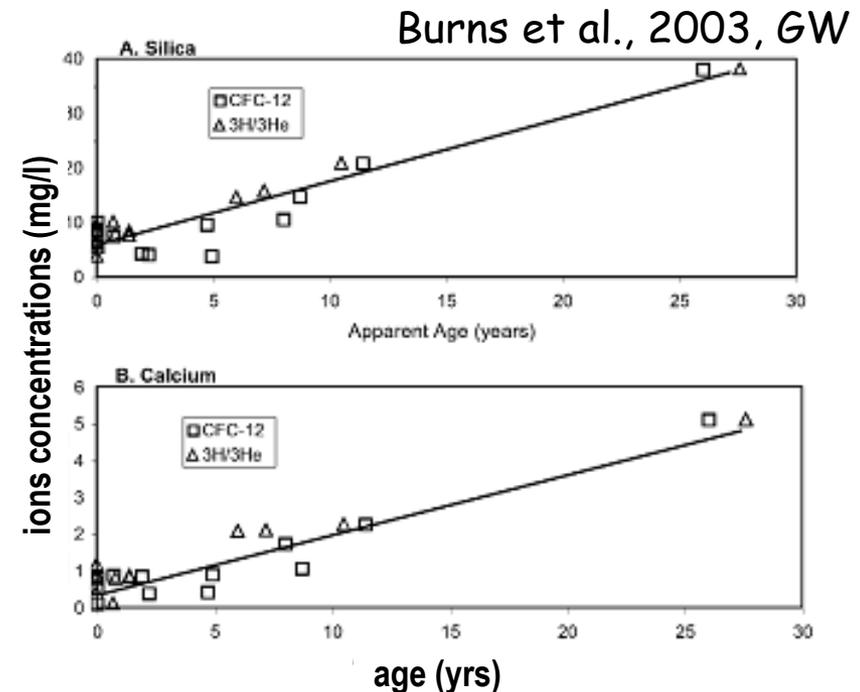


**Residence Time:** at any point along a flowpath in a catchment, the time that has passed since a water molecule entered the catchment (Maloszewski and Zuber, 1982, JoH).

In other words...the time (since entry) that water molecules **have spent inside** a flow system (McGuire & McDonnell, 2006, JoH).

## Why is MRT important?

Because chemical weathering and many biogeochemical processes vary over time  $\Rightarrow$  composition of water chemistry.



# Importance of MRT



- fundamental catchment **descriptor**: information about storage, flow pathways, source of water;
- easy scalable (Sivapalan 2003, HP) and directly related to internal catchment processes;
- how catchments **retain and release** water and solutes  $\Rightarrow$  they, in turn, control geochemical and biogeochemical cycling and persistence;
- longer MRT  $\rightarrow$  more time for biogeochemical reactions during/after rainfalls.

**stable isotopes** are the main tracers available for determining MRT of catchment systems and young groundwater (Moser, 1980, Interamer. Symp. on Isot. Hydrol.).

# MRT determination: isotopes method



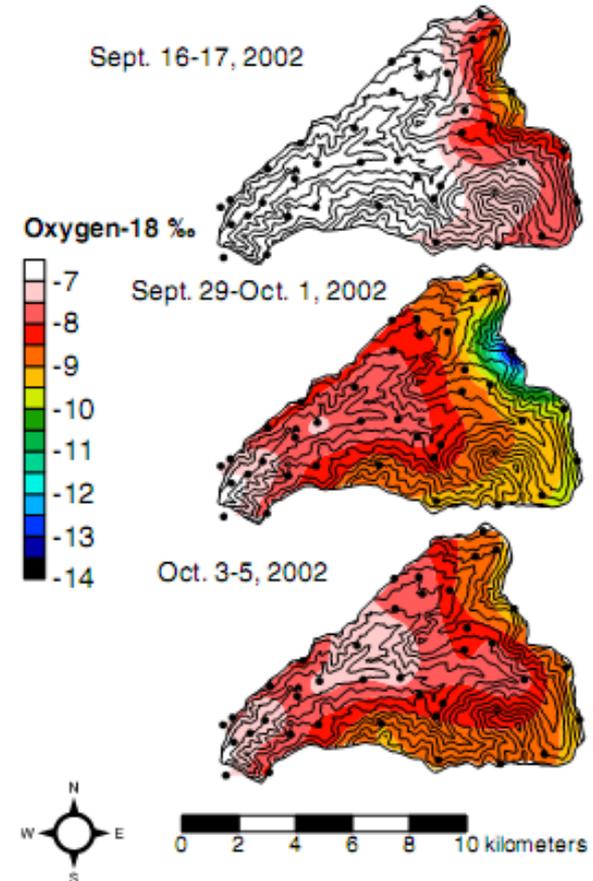
## Observation:

- spatial and seasonal variation of  $^{18}\text{O}$  and  $^2\text{H}$  in precipitation;
- some rainfall inputs transported along various flowpaths to stream network, other remain in storage or less mobile phases.



## Assumptions:

- linear input-output relations;
- uniform recharge;
- time-invariant residence time distribution;
- contribution from the entire catchment area.



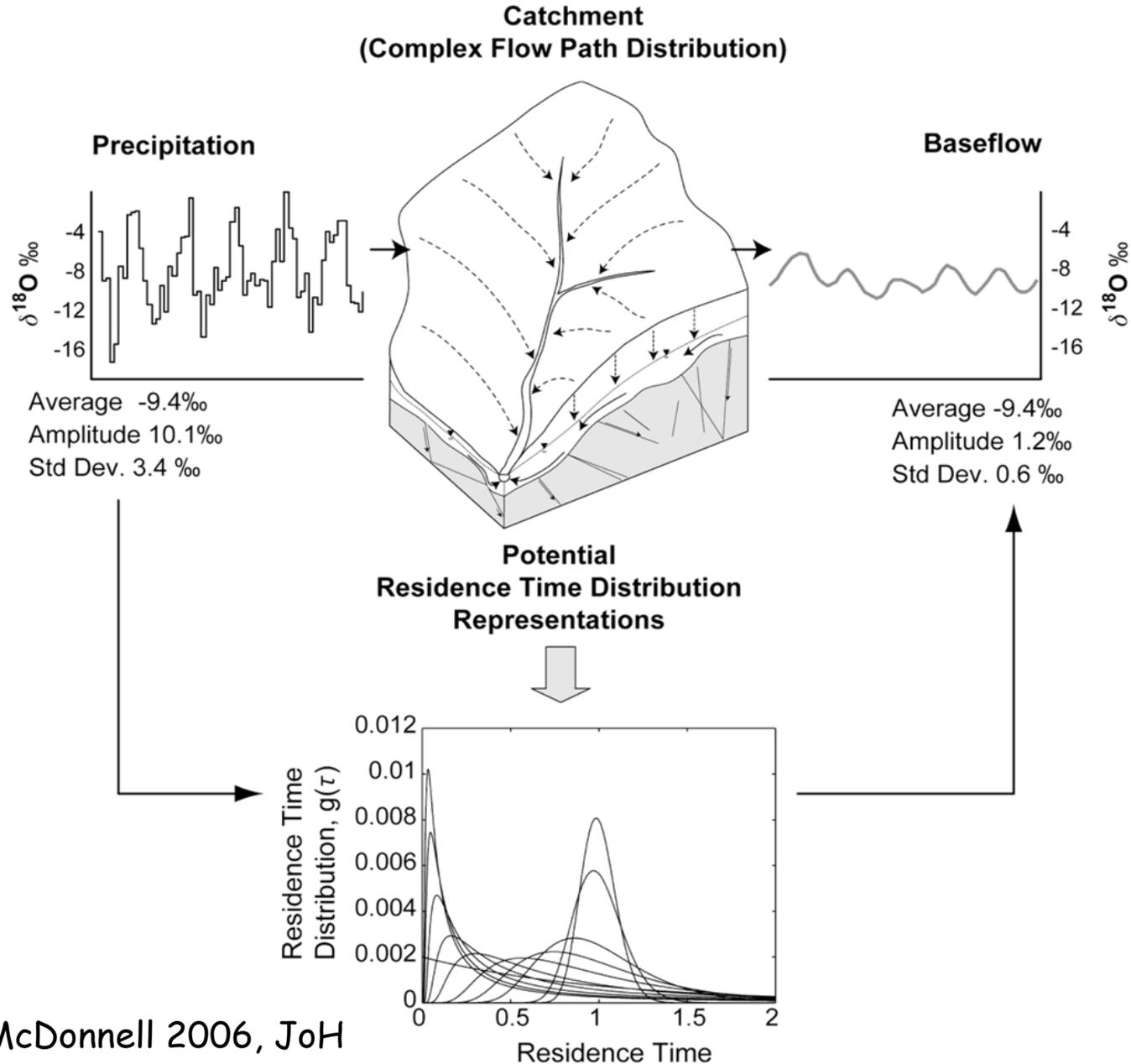
McGuire & McDonnell  
2006, JoH, modified

# MRT determination: conceptual model



1. catchment receive temporal **tracer inputs**;
2. tracer is transported along diverse **flowpaths** in the unsaturated/saturated zones migrating from the subsurface toward the stream network;
3. the result of differential transport within the catchment is a tracer **output signal** (baseflow) that is damped and lagged compared to the input signal (dispersion).
4. the complex distribution of catchment flowpaths is represented by a distribution of residence times,  $g(\tau)$ , that describes the **integrated behaviour** of tracer transport through the catchment.

# MRT determination: conceptual model



# Model Theory: The Convolution Integral

(Barnes & Bonell, 1996, HP)



$$\delta_{out}(t) = \int_0^{\infty} g(\tau) \delta_{in}(t - \tau) d\tau$$

$\delta_{out}(t)$ : streamflow isotopic composition at any time

$\delta_{in}(t-\tau)$ : tracer that fell uniformly on the catchment in the past

$g(\tau)$ : residence time distribution

$\tau$ : lag times between input and output tracer composition

Stream outflow isotopic composition at any time consists of tracer that fell uniformly on the catchment in the past which becomes lagged according to its residence time distribution.

# MRT



**MRT** duration at the small catchment scale:  
usually <1-5 years

More specifically:

- surface runoff: hours-days
- shallow groundwater<sup>\*</sup>: up to 2-3 years
- deeper groundwater<sup>\*\*</sup>: 6-9 years

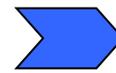
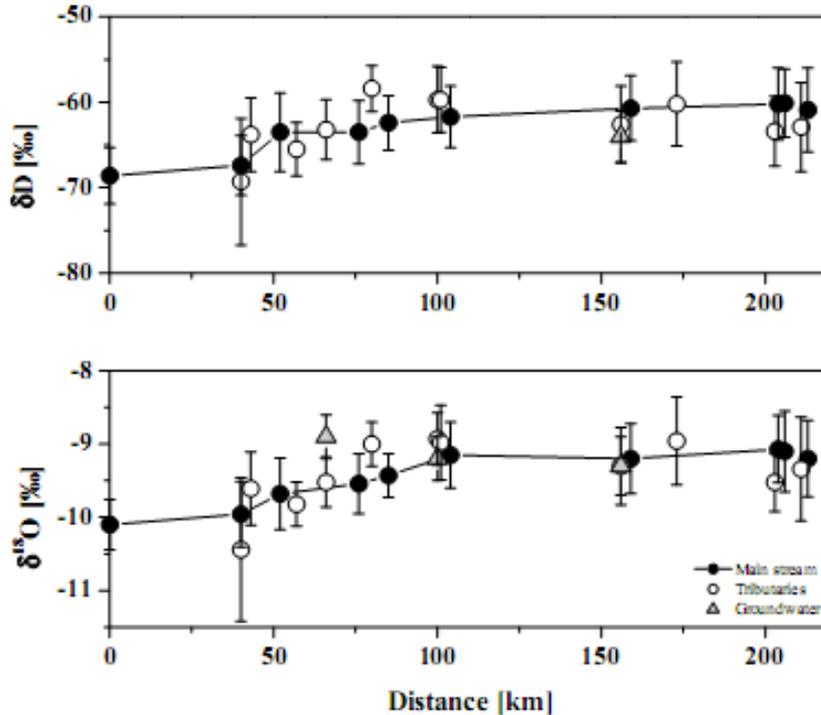
<sup>\*</sup>it still has an influence on runoff generation at the event scale, by moving soil water ("piston-flow" model)  
(Uhlenbrook et al., 2002, WRR)

<sup>\*\*</sup>it does not seem to contribute to hydrograph storm runoff  
(Uhlenbrook et al., 2000, IAHS )

# Other applications...

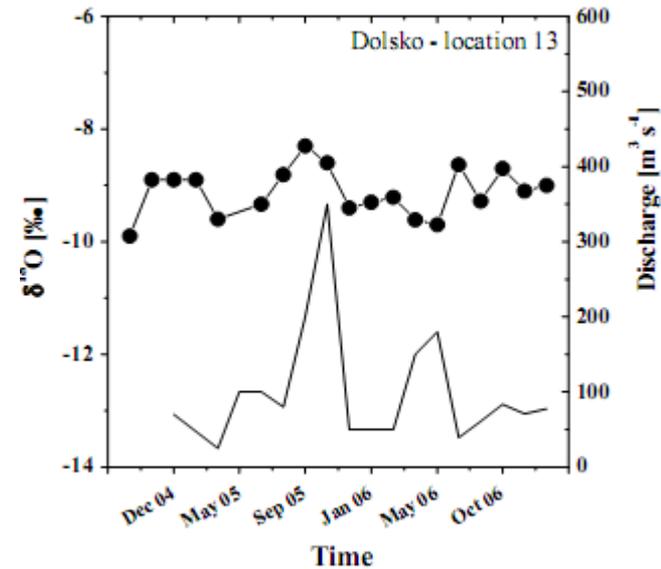


- **spatial** and seasonal variability of isotopic content in rivers



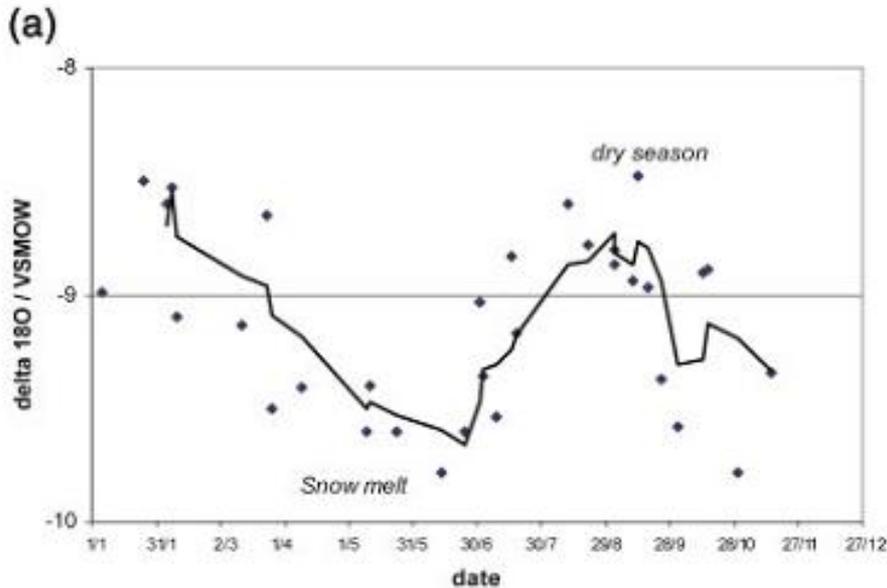
increase of delta values  
from upper to lower parts  
of the basin

influence of **tributaries**  $\Rightarrow$   
different isotopic composition  
 $\Rightarrow$  different source



Ogrinc et al., 2008, JoH

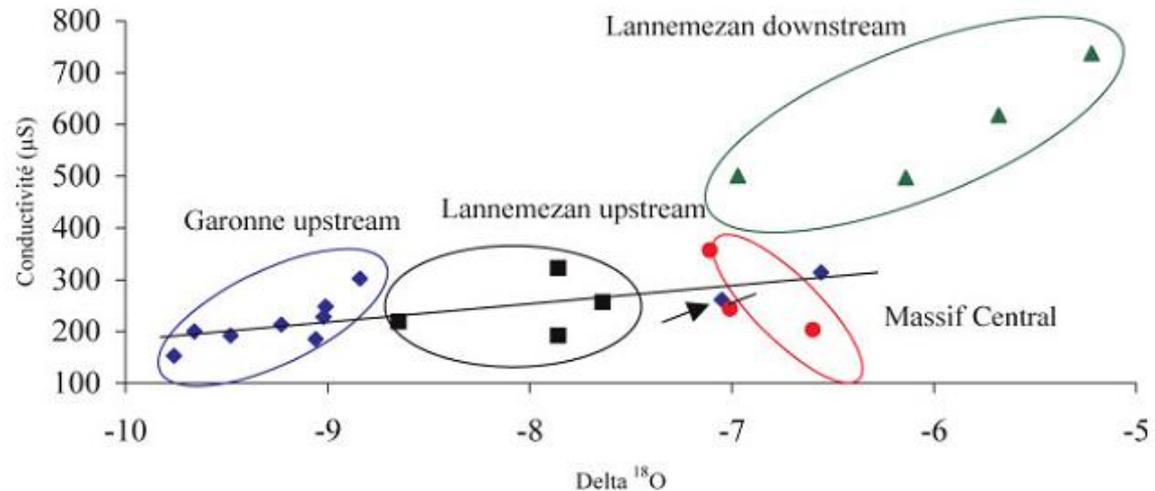
# Other applications...



- spatial and seasonal variability of isotopic content in rivers

Lambs et al., 2009, Rap. Comm. Mass Spectr.

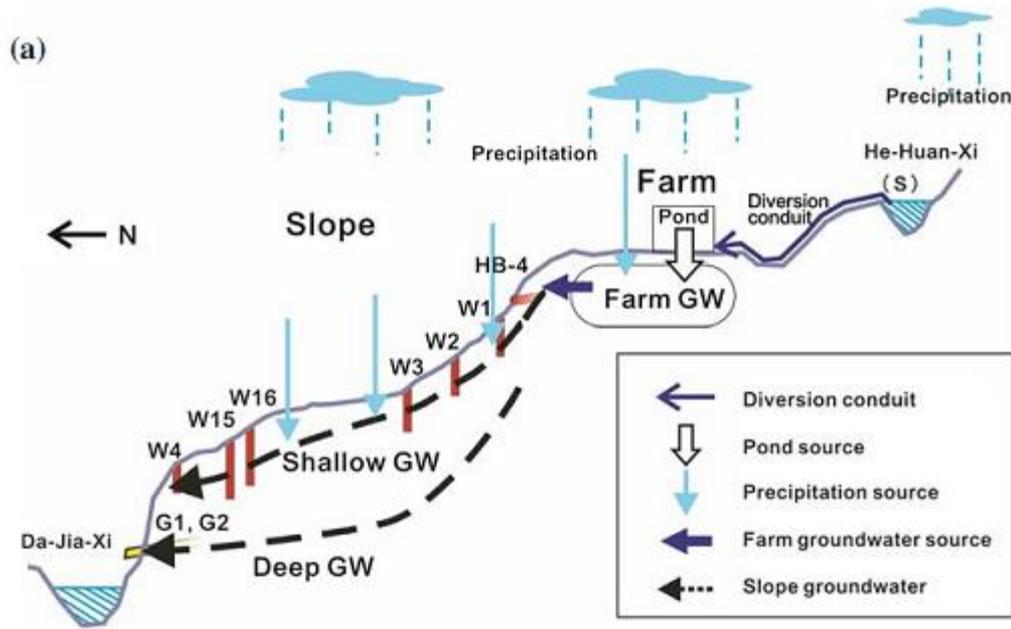
Relationship between conductivity (=solute) - isotopic composition  
→ identification of different "pools"



# Other applications...



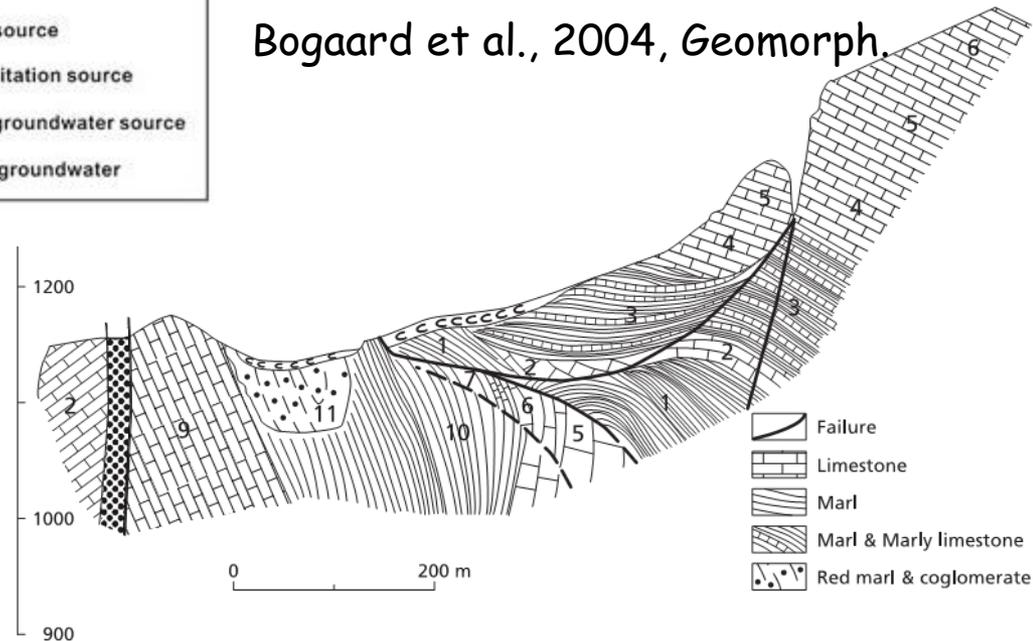
- possible hydrological factors contributing to landslide triggering: influence of different sources of water.



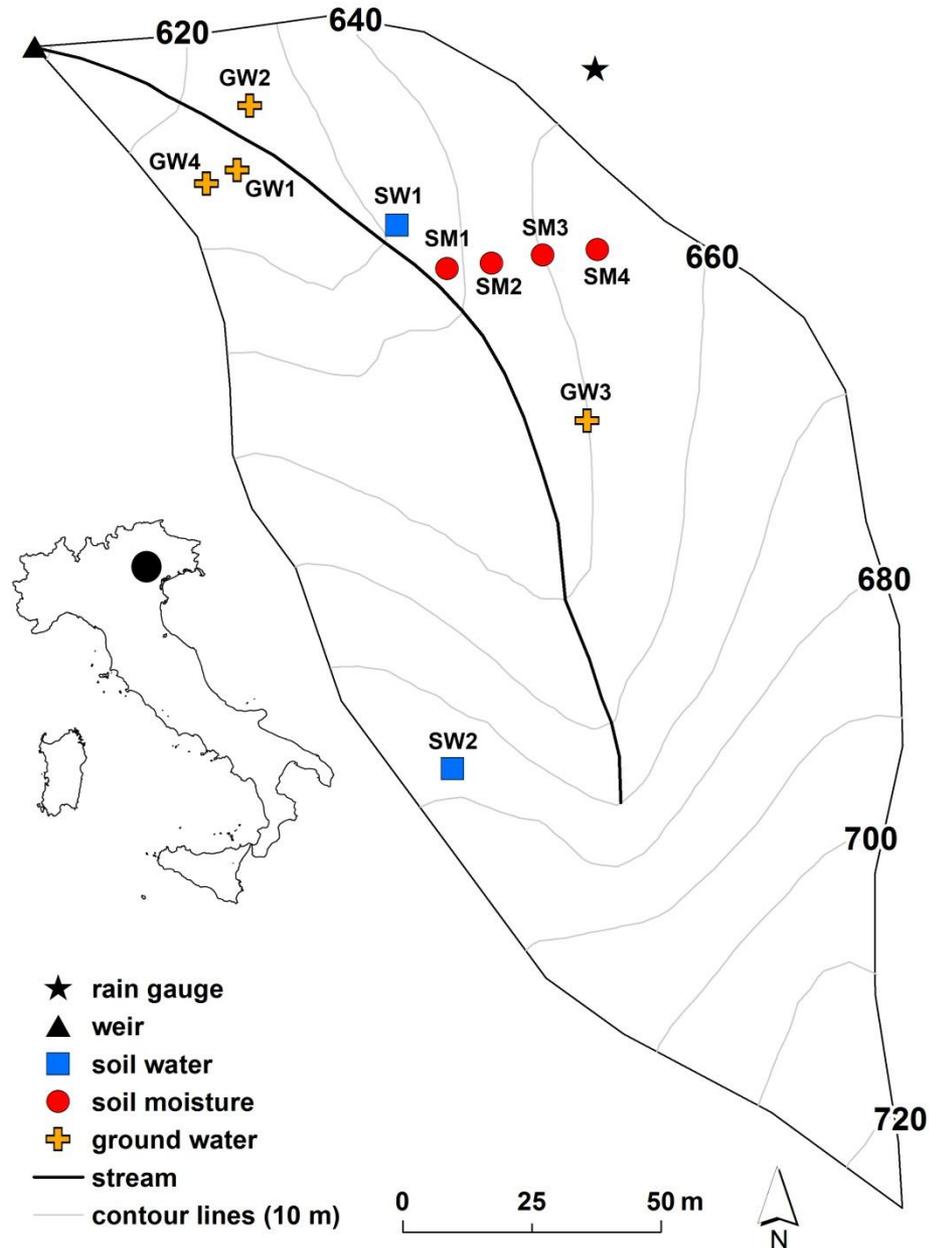
- origin/age of water
- different sources of water
- preferential flowpaths

Bogaard et al., 2004, *Geomorph.*

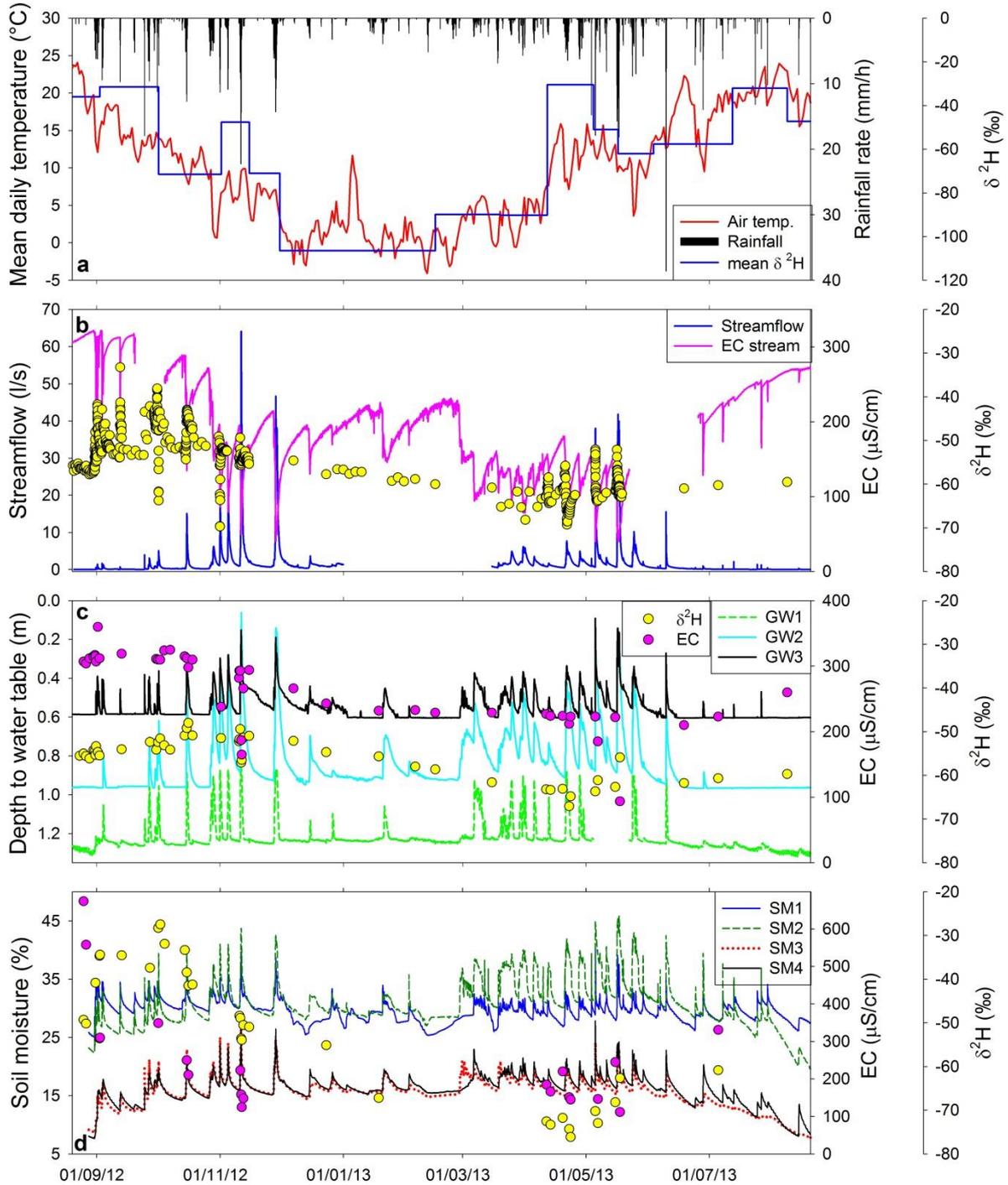
Peng et al., *Environ. Geo.*, 2007



# Examples from Ressi catchment

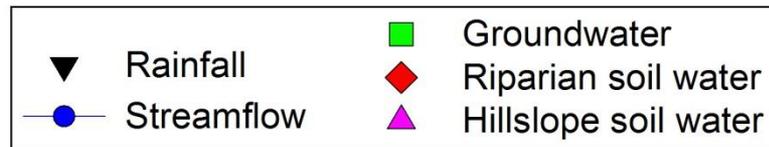
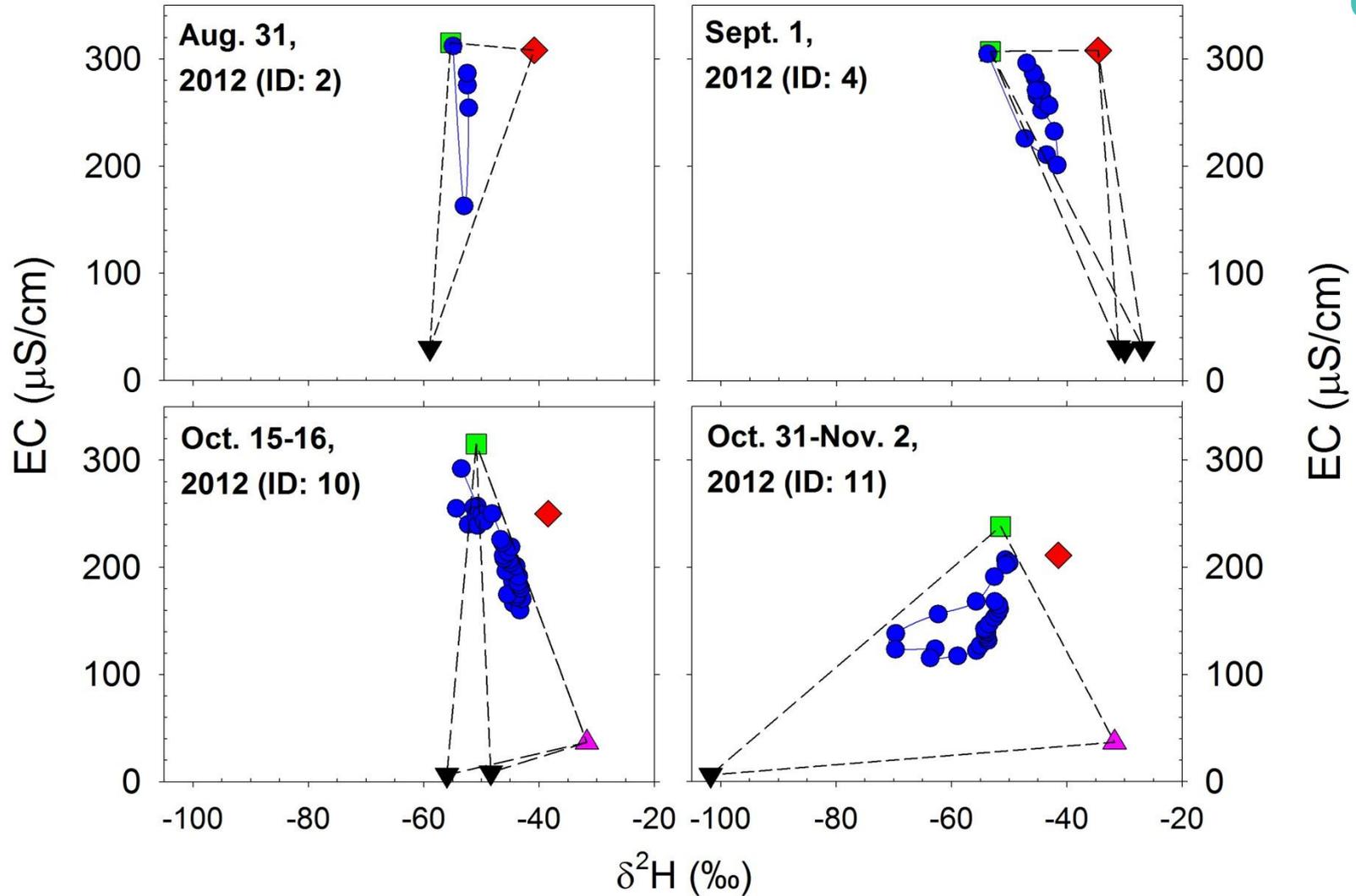


Penna et al., in preparation

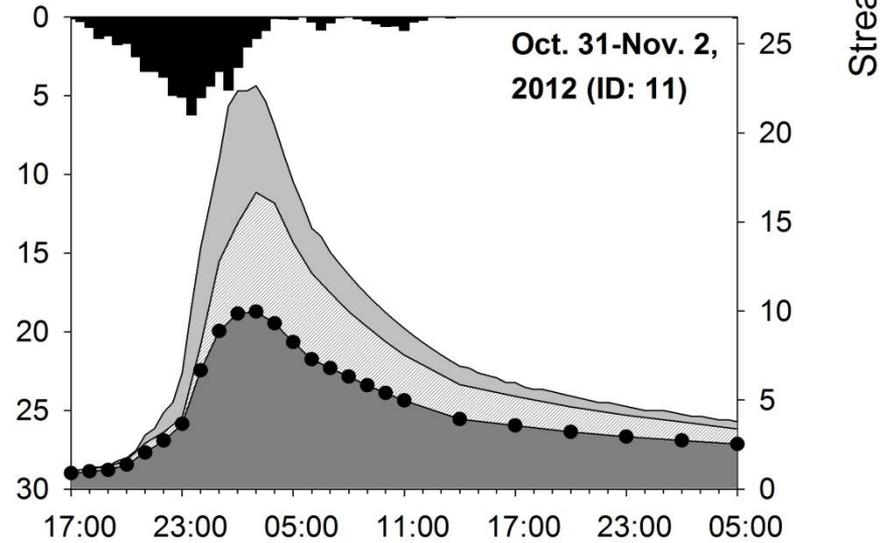
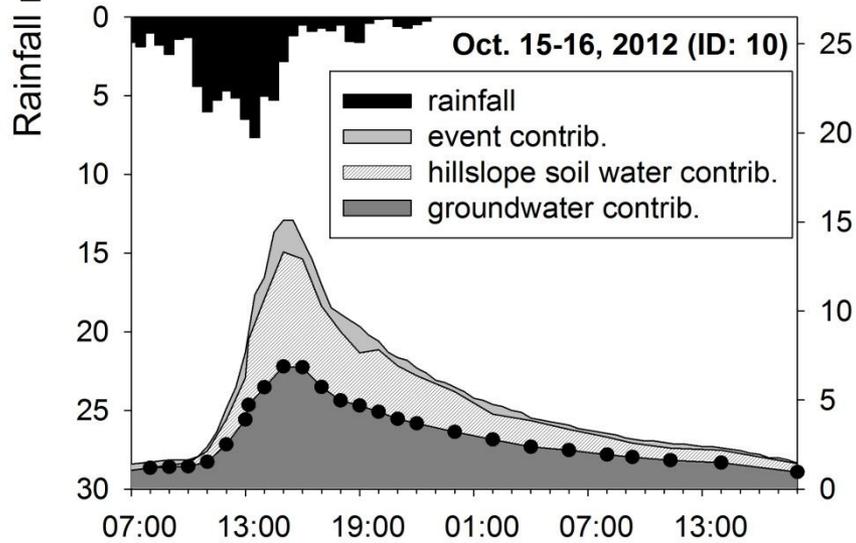
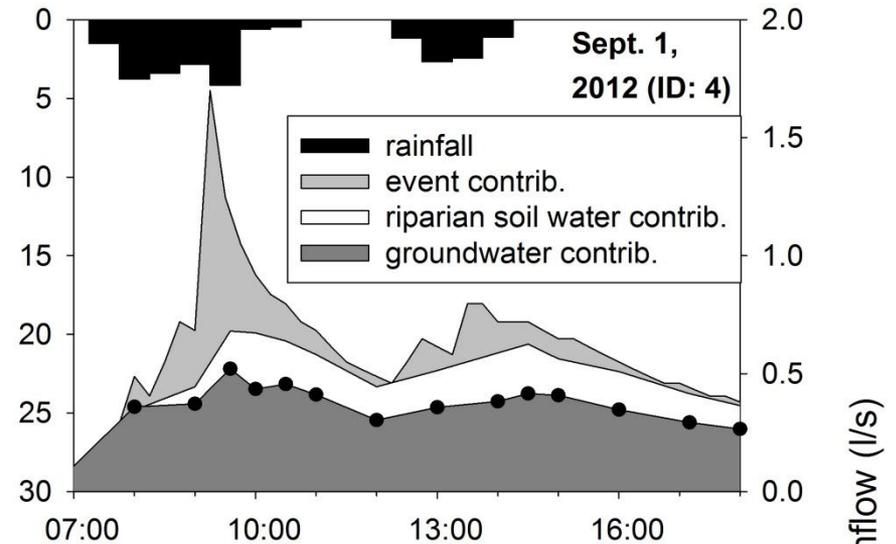
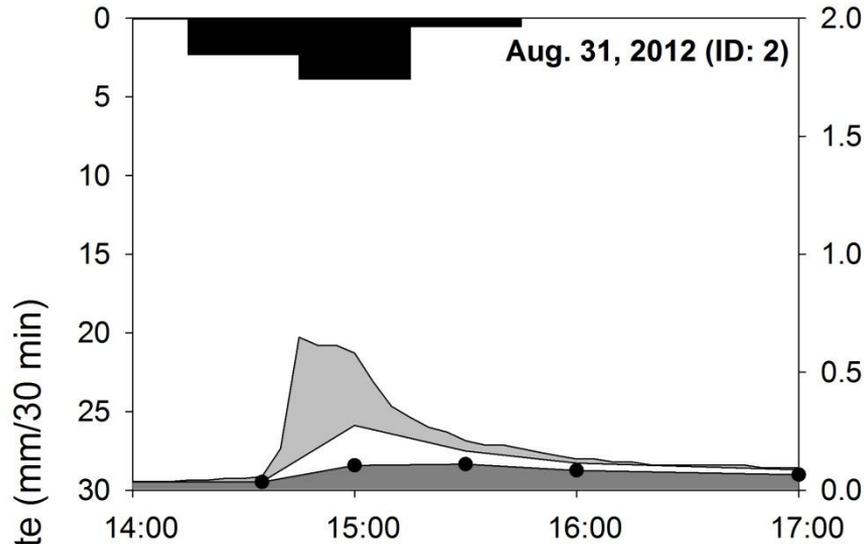


Penna et al., in preparation

# Examples from Ressi catchment



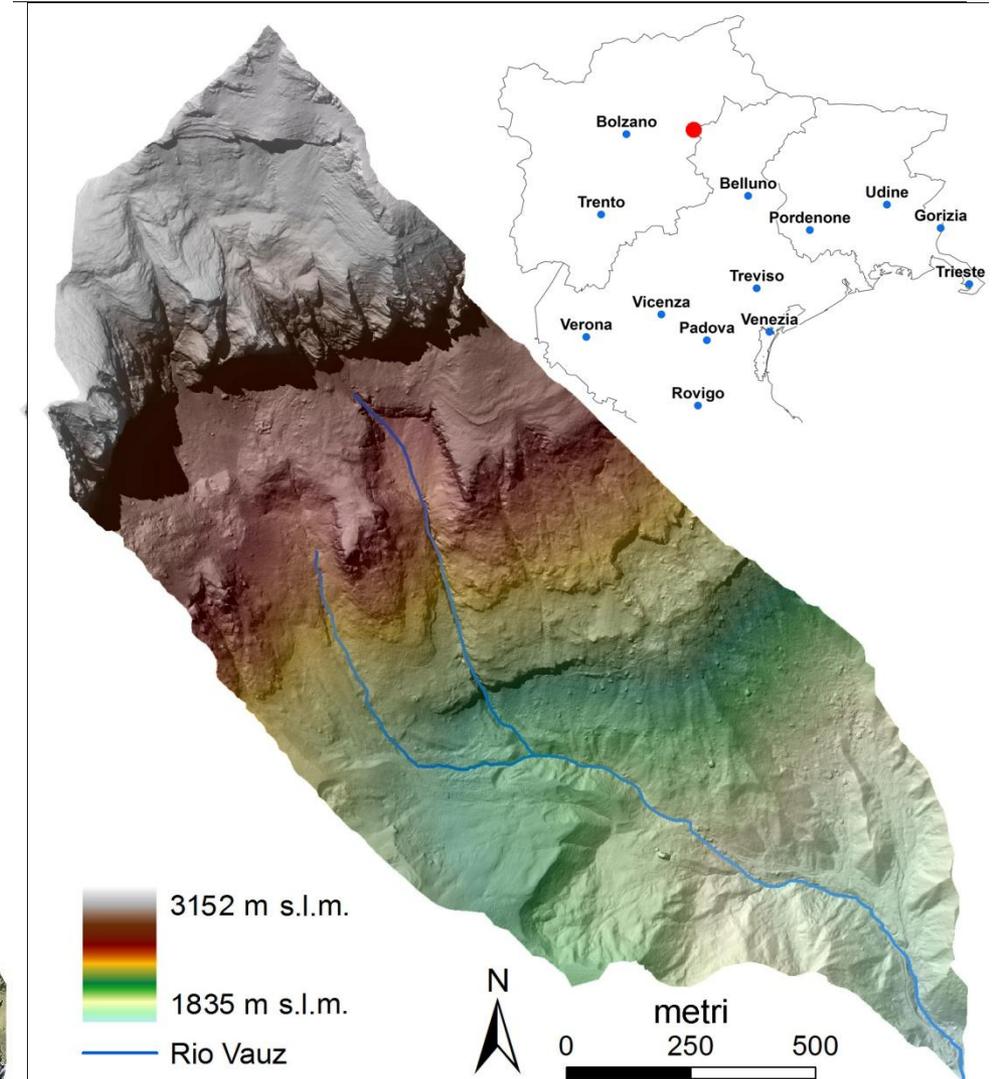
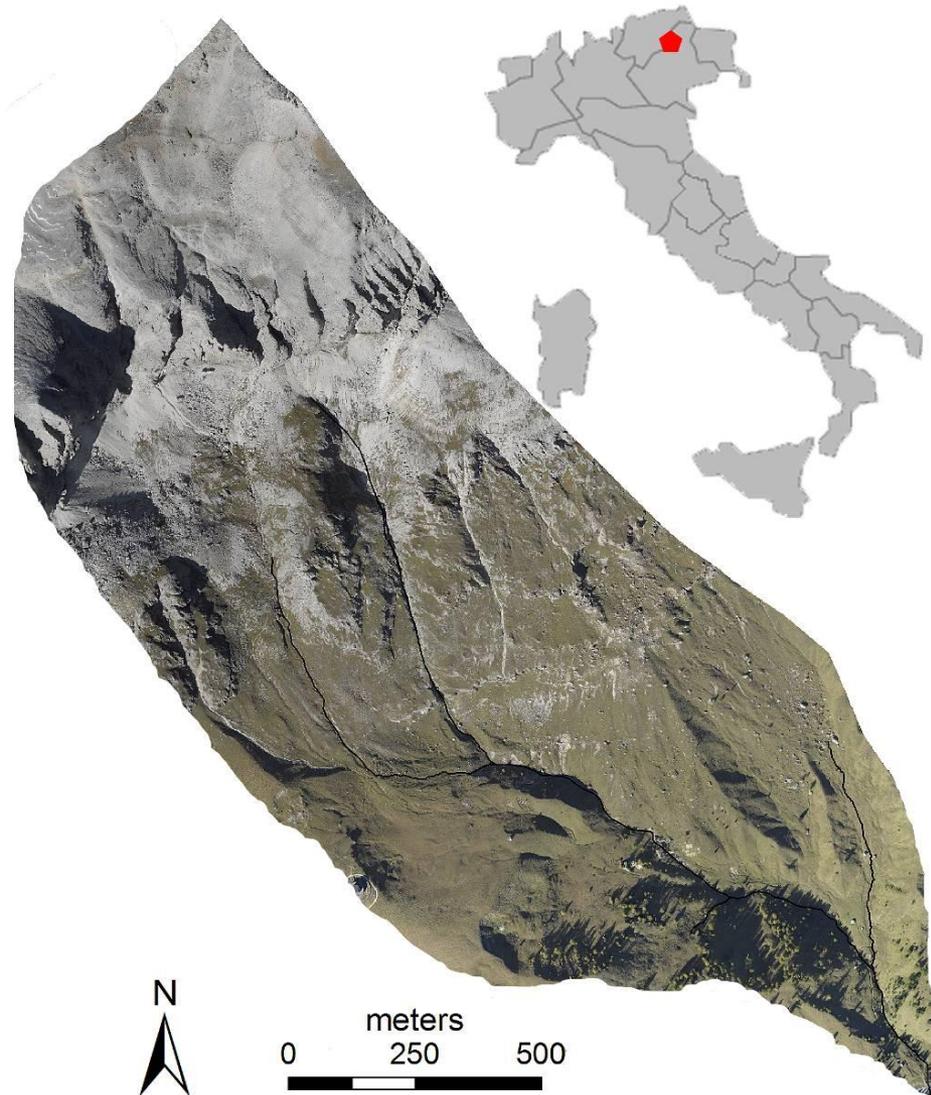
# Examples from Ressi catchment



# Examples from our Dolomiti catchment



## Rio Vauz Basin



# Practical aspects

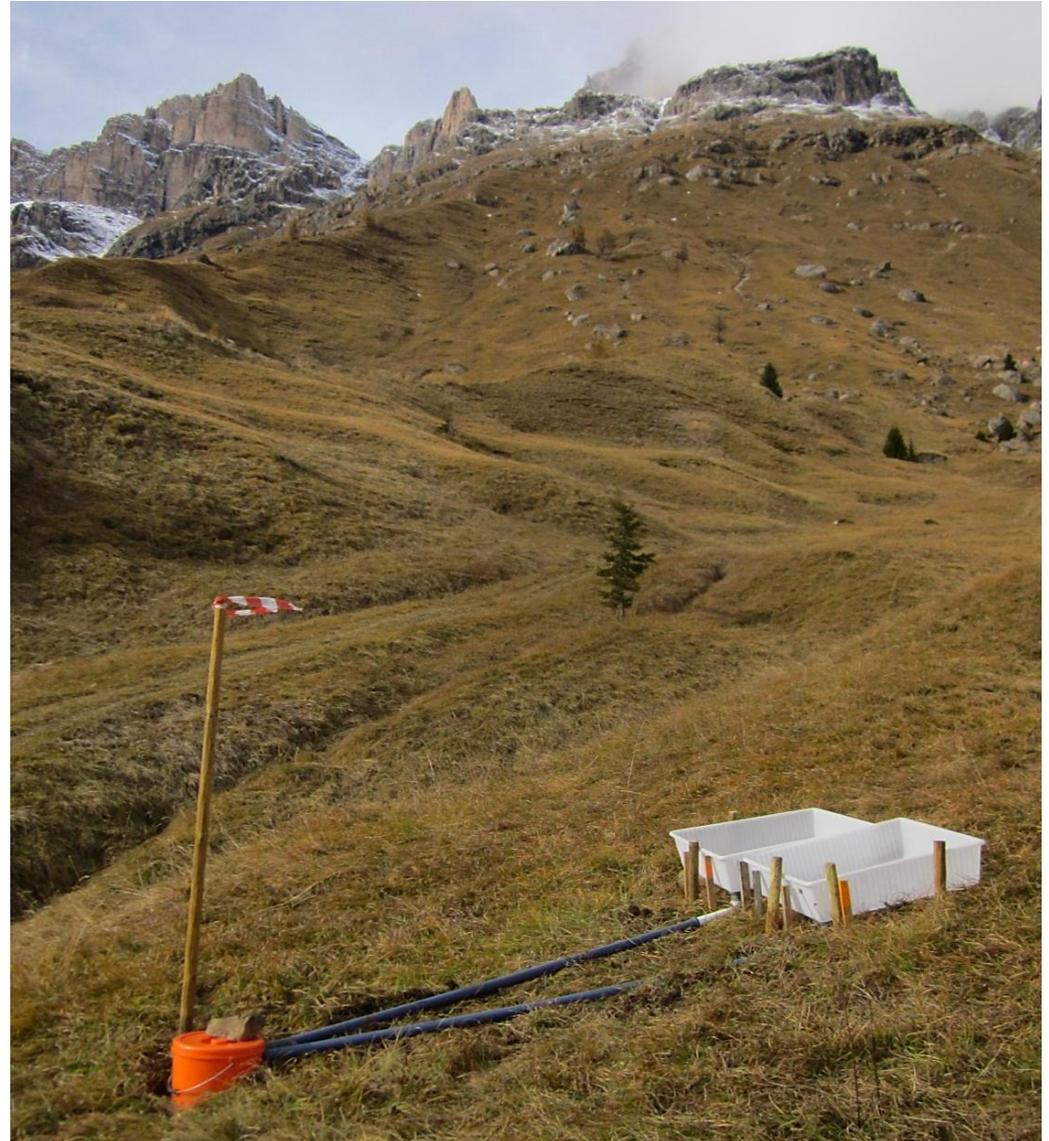
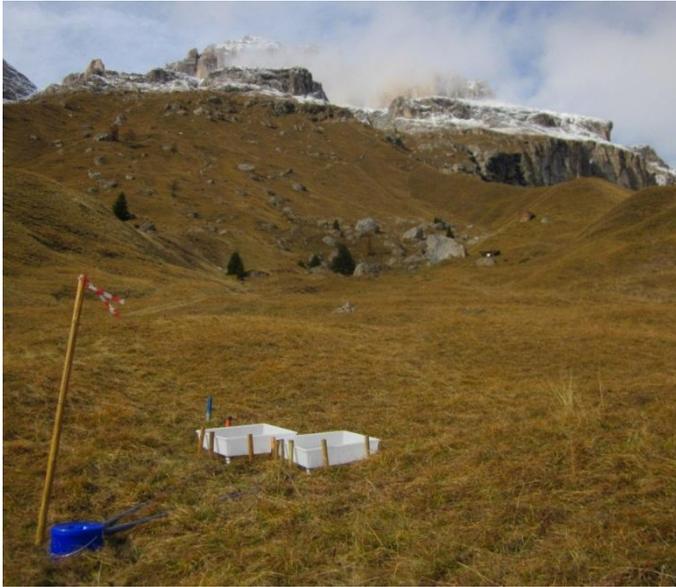


## Sampling snowmelt



# Practical aspects

## Sampling snowmelt



# Practical aspects



isotopic sampling in creek ( $\Rightarrow$  automatic samplers), gw, soil water ( $\Rightarrow$  gutter lysimeter) or suction cup



# Practical aspects



**Attention:** in hydrograph separation applications we have to take into account the temporal variability of isotopic content of precipitation during rainstorm.



TABLE 1. Deuterium Variations for 5 mm Sequentially Collected Glendhu 2 Storm Rainfall, February 23, 1988

Time	$\delta D, \text{‰}$
1040	-94.8
1235	-92.2
1320	-93.8
1400	-77.0
1455	-76.0
1545	-76.9
1645	-68.0
2030	-61.9

McDonnell et al., 1990, WRR

Gatz et al., 1971

Successive sampling of precipitation → incremental mean

# Practical aspects



## Successive sampling of precipitation



courtesy Martin Sanda,  
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Prague

## References - books



- Clark, I., and P. Fritz, *Environmental Isotopes in Hydrogeology*, Lewis Publishers, Boca Raton, 1997.
- Gonfiantini, R, Environmental isotopes in lake studies, in *Handbook of Environmental Isotope Geochemistry*, vol. 2, edited by P. Fritz and J.-Ch. Fontes, pp. 113-168, Elsevier, Amsterdam, 1986.
- Kendall C., McDonnell J.J., 1998. *Isotope Tracers in Catchment Hydrology*. New York, *Elsevier*, 1998.
- James R. Ehleringer, Anthony E. Hall, Graham D. Farquhar (Editors) *Stable Isotopes and Plant Carbon-Water Relations (Physiological Ecology Series)* 1993, Academic Press, ISBN: 0122333802

## References - websites

- <http://www.sahra.arizona.edu/programs/isotopes/index.html>
- [http://www-naweb.iaea.org/napc/ih/IHS\\_science3.html](http://www-naweb.iaea.org/napc/ih/IHS_science3.html)
- <http://wwwrcamnl.wr.usgs.gov/isoig/res/funda.html>