



# Groundwater hydraulics 9

## Natural tracers in hydrology

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**Dept. Landscape Water Conservation**

# Contents

- **Tracers in hydrology**
- **Stable water isotopes in hydrosphere**
- **Laser spectroscopy as analytical tool**
- **Use of stable isotopes**

# Hydrology – water in the environment

## Monitoring of hydrological variables

mostly precipitation, runoff, groundwater, soil moisture

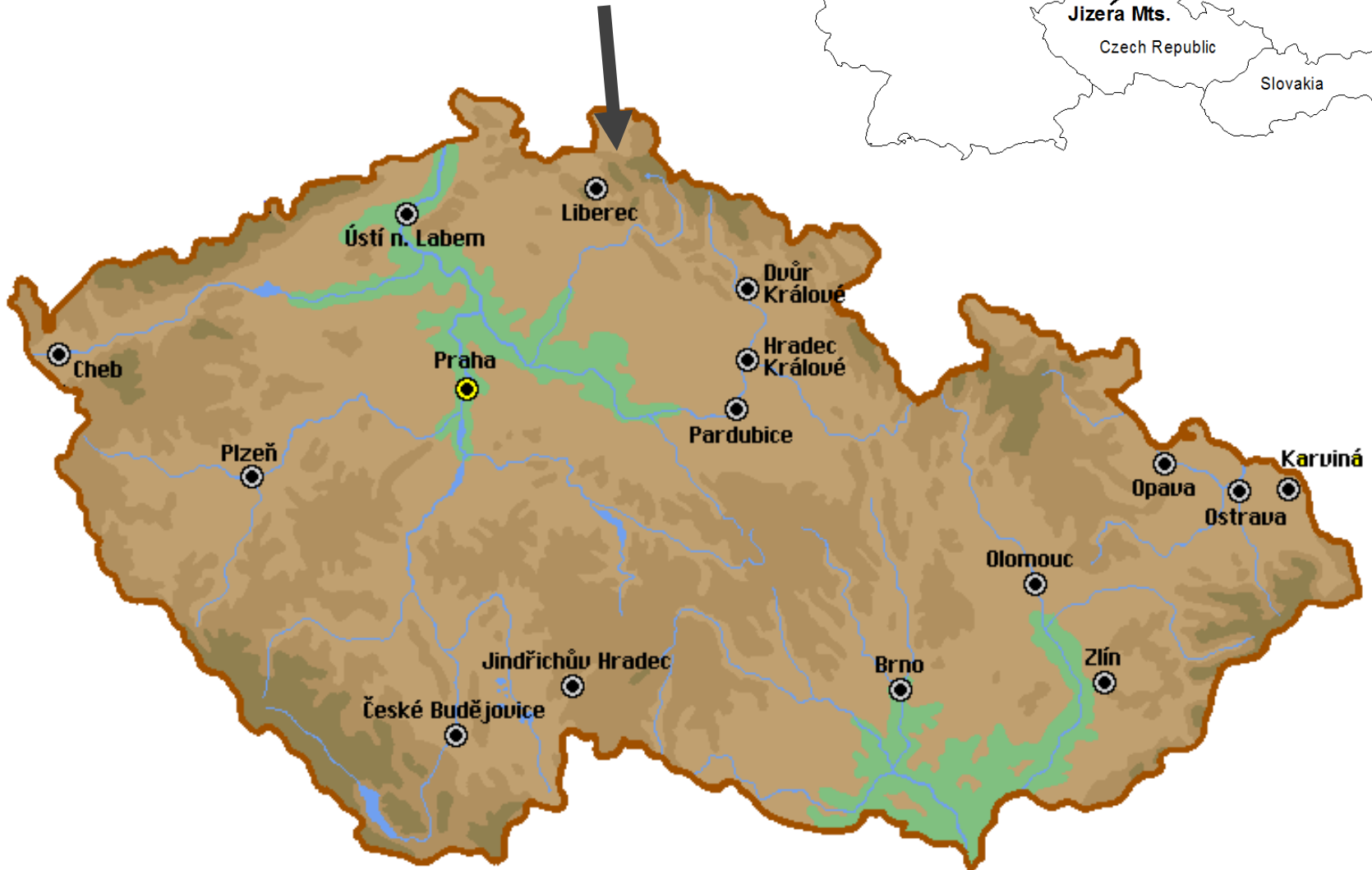
## Site description

Topography, soil science, geology, geophysics

## Tracking water flow

Mostly “natural” compounds in water

# Location of Jizera Mountains



# Small experimental catchment

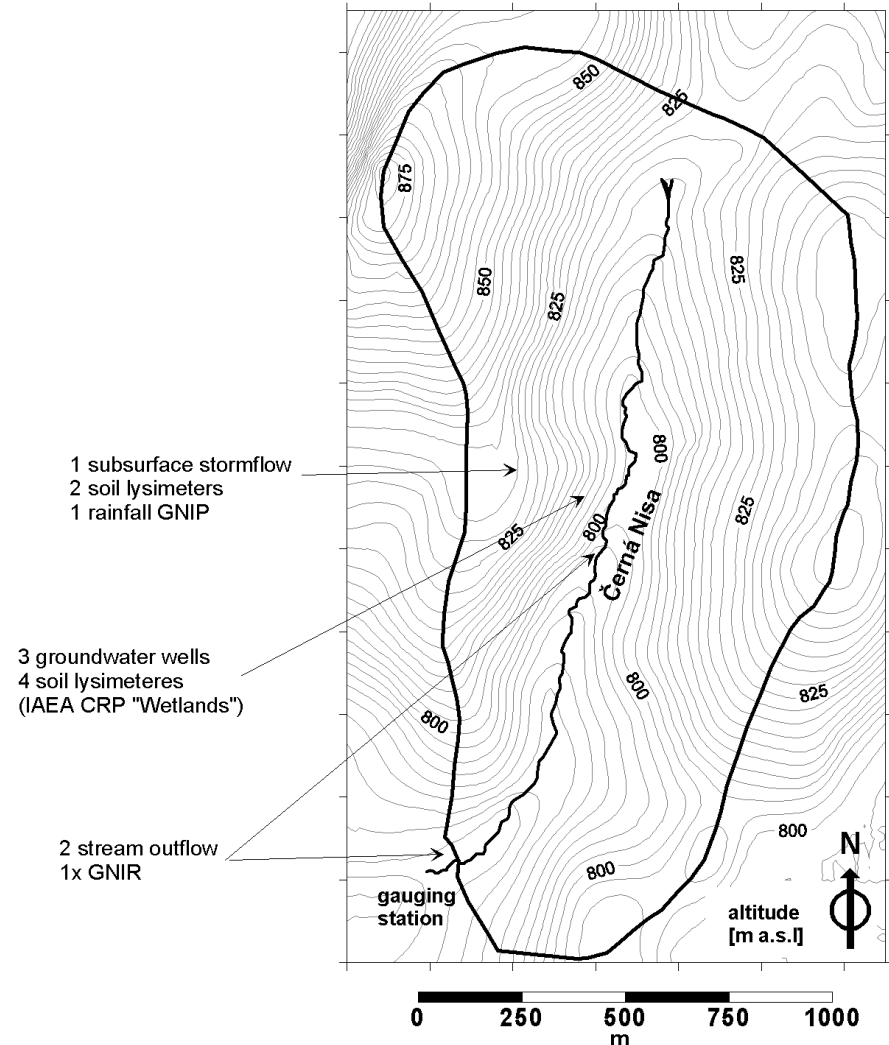
## Uhlířská, Jizera mountains

Uhlířská (1.78 km<sup>2</sup>)  
(700-900 m altitude)

- humid (1200 mm/yr) and cold (5°C)

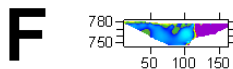
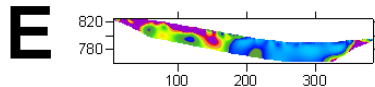
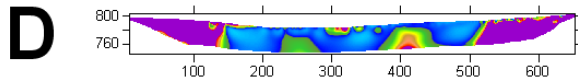
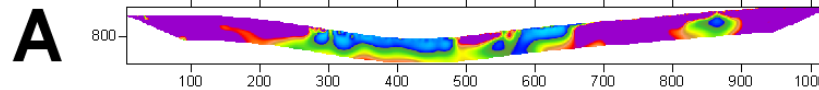
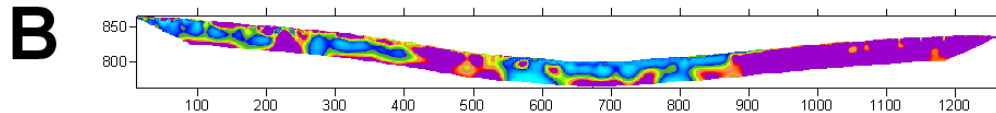
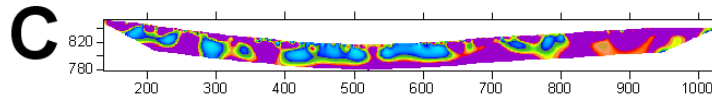
- 10-60 m deep deluviofluvial aquifer

- fractured and fissured granitic bedrock

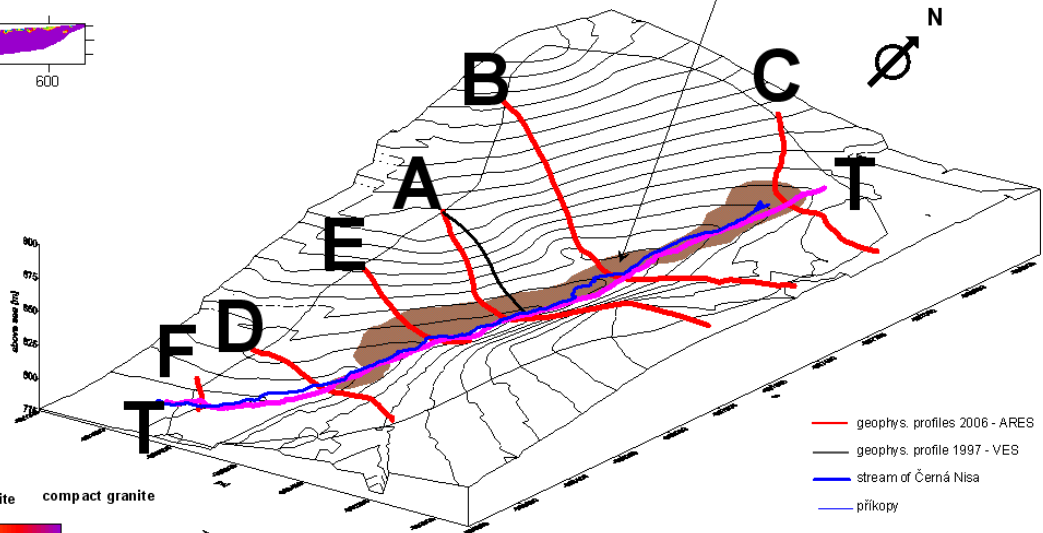


# Electrical resistivity tomography for the detection of large scale formations

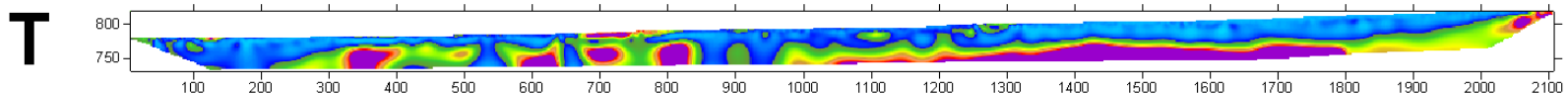
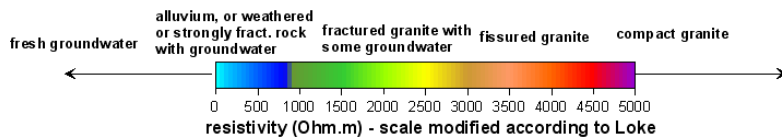
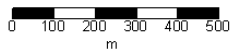
units on graphs:  
meters



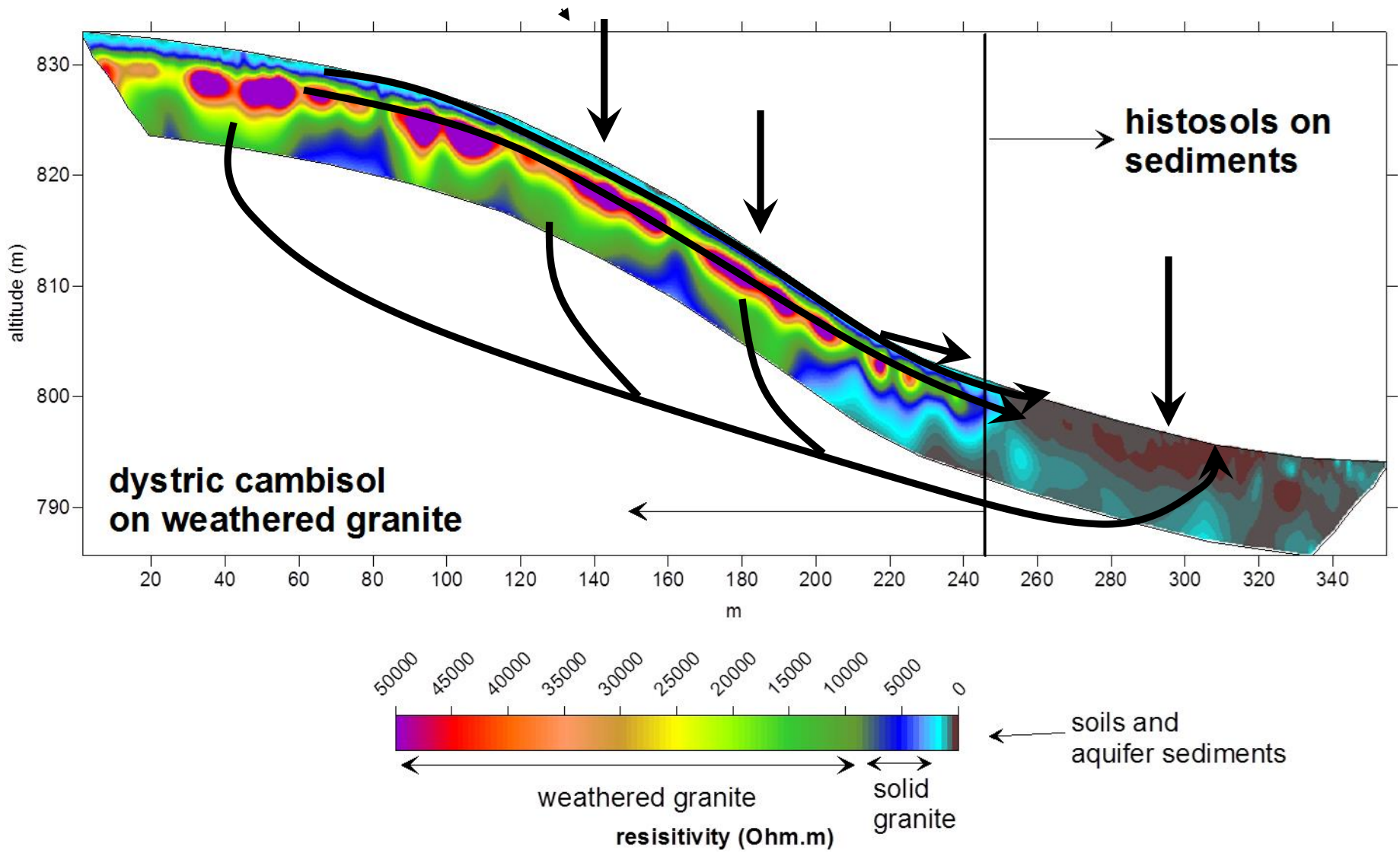
brown designates peat area



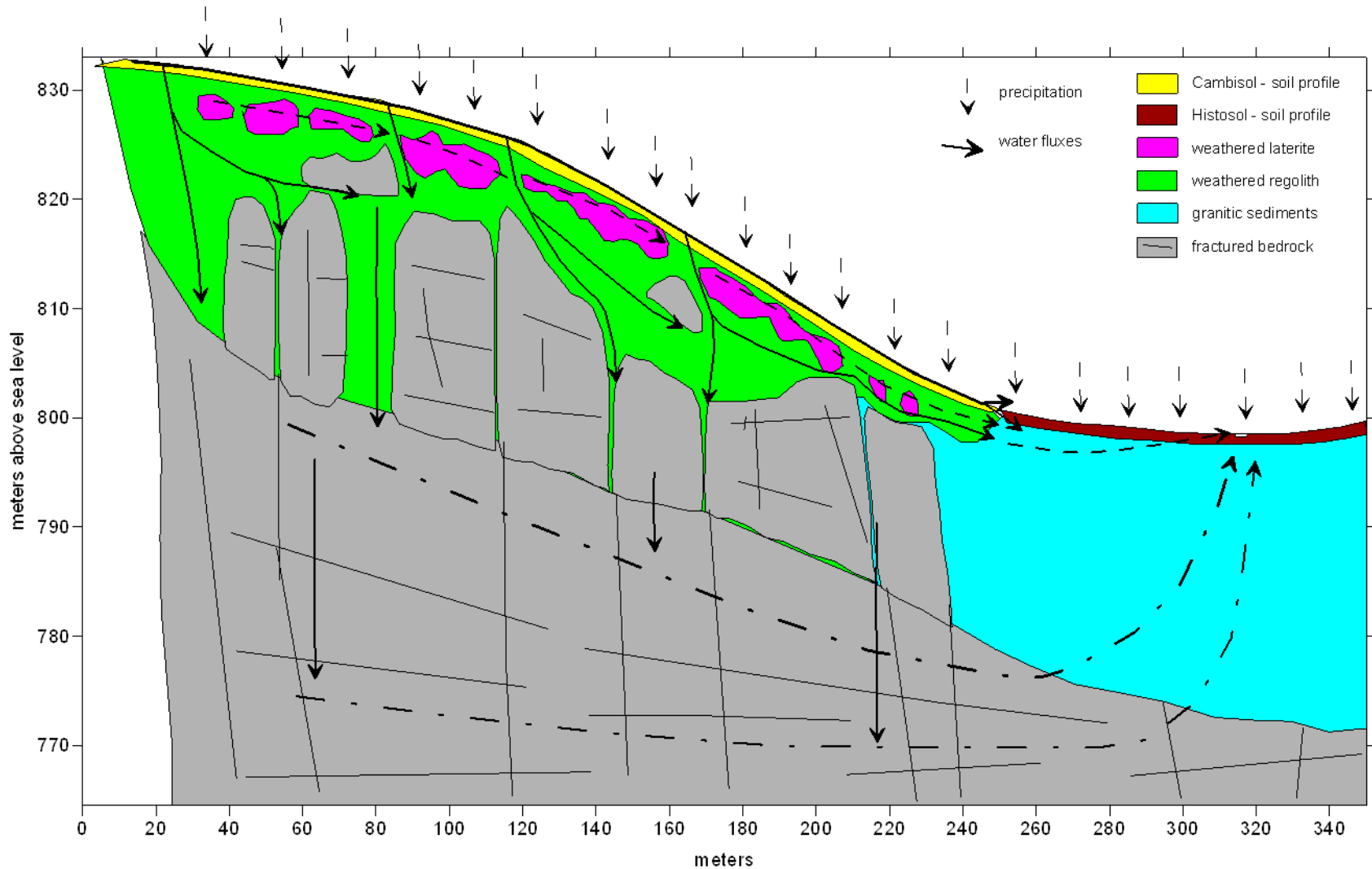
- geophys. profiles 2006 - ARES
- geophys. profile 1997 - VES
- stream of Černá Nisa
- příkopy



# Possible travel paths of water



# Possible travel paths of water





# Soil profile upslope

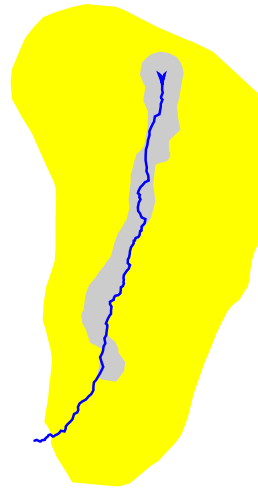
*Cambisols and Podzols*

based on the decayed  
granite bedrock

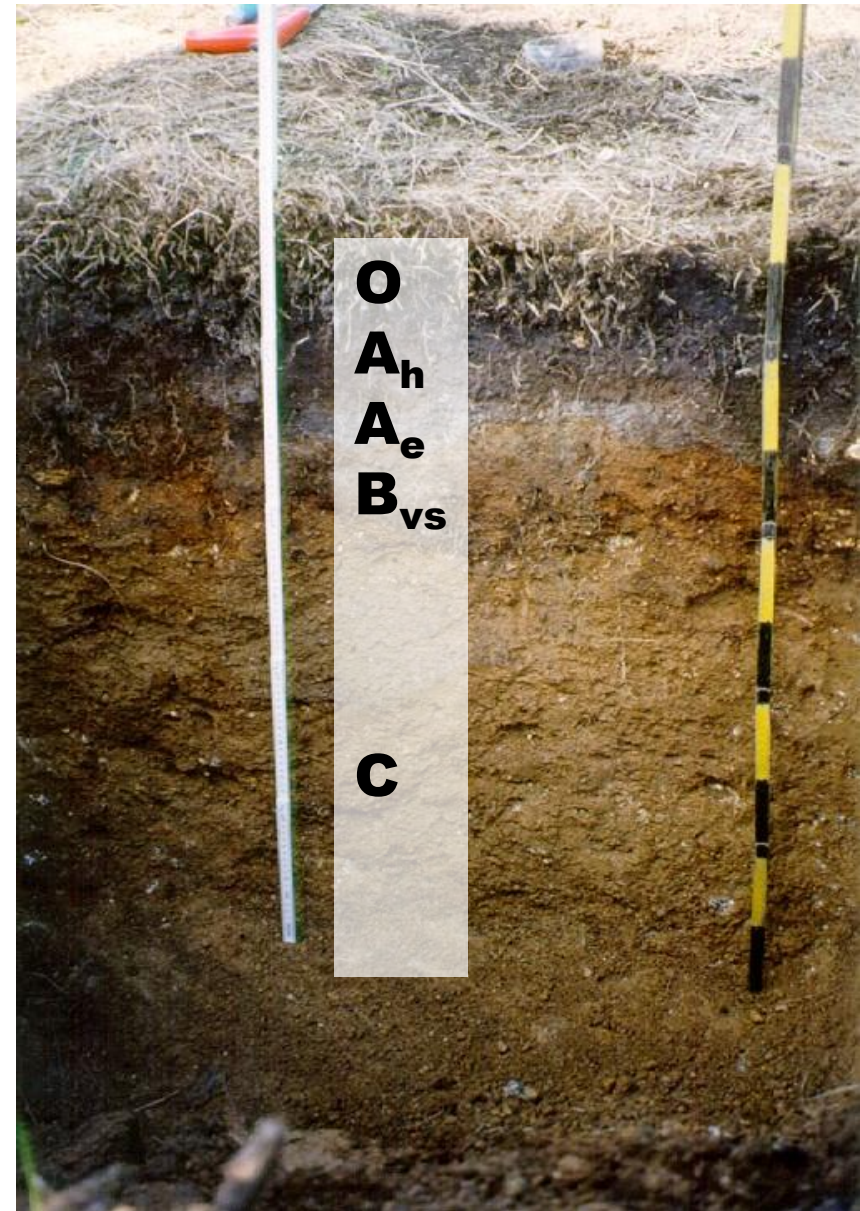
shallow (app. 80 cm)

very heterogeneous

layered due to hydrological,  
and geopedological factors  
(peaty topsoil, stony  
decaying bedrock layer)



90%  
area



# Soil profile downslope

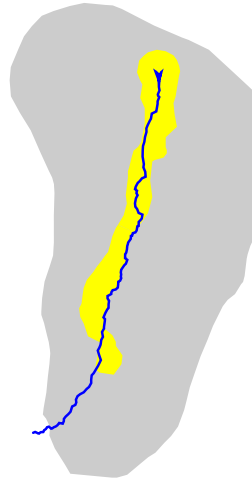
*Histosols*

based on the alluvial  
sediments

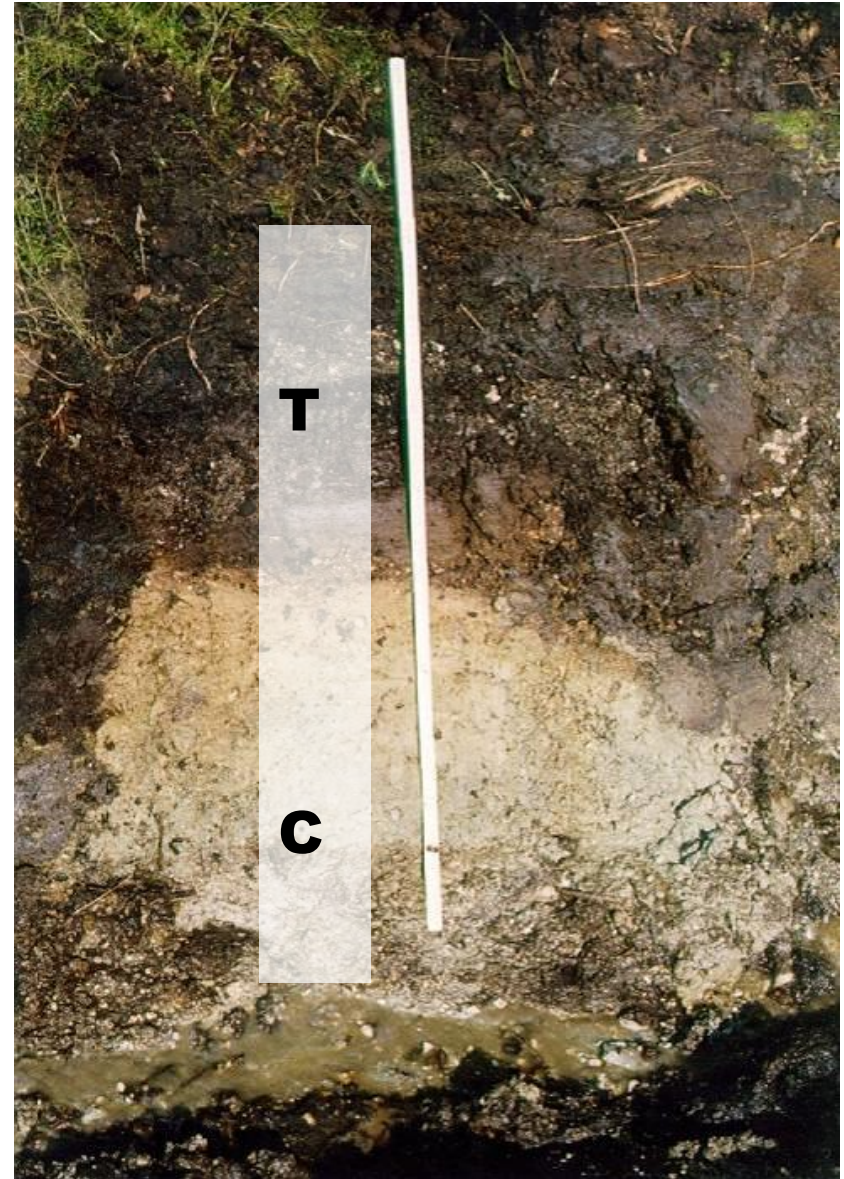
1-3 m in depth of peat  
uneven thickness

thicker (est. 10-60 m) of  
alluvial deposits

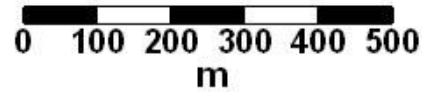
drainage ditches by  
forestry management  
(spruce production)



10%  
area

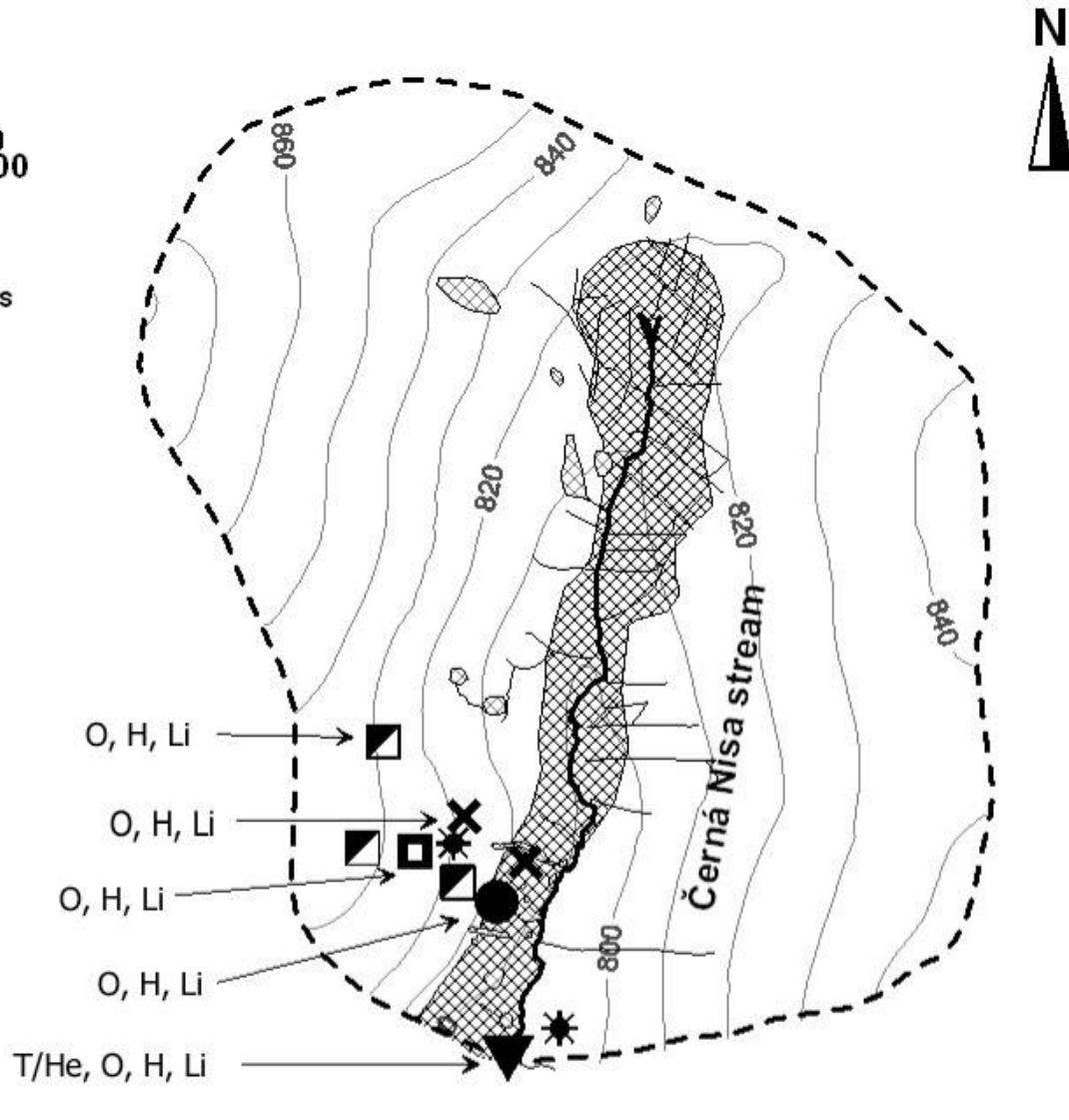


# Subcatchment Porsche (1.18 km<sup>2</sup>) in Uhlířská



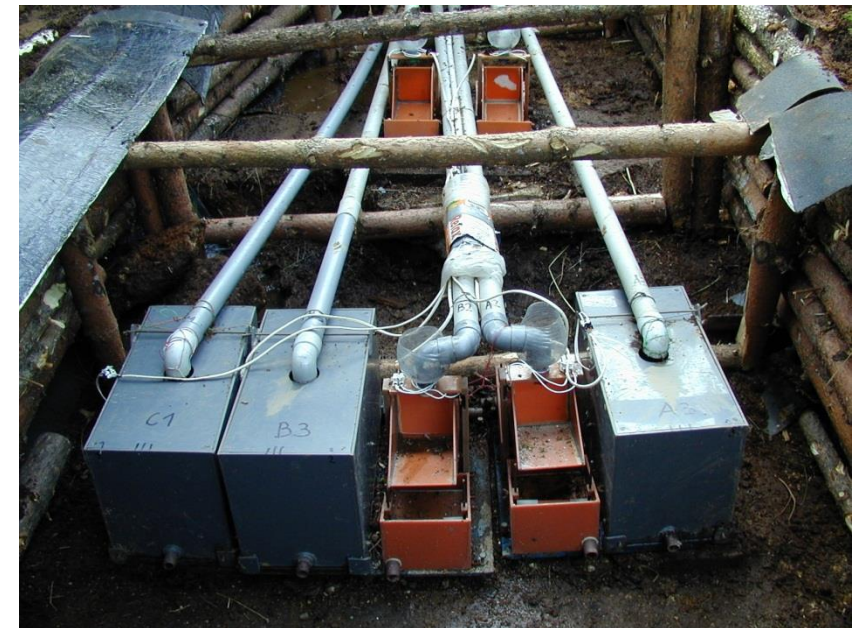
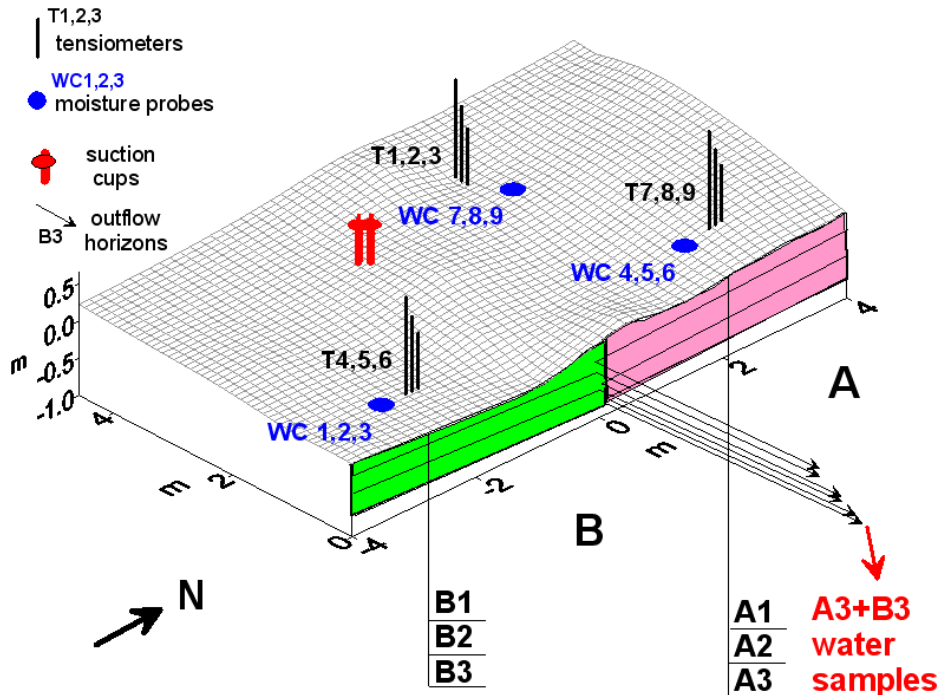
numbers on countour lines  
indicate altitude (m a.s.l)

- Černá Nisa stream
- tributaries
- wetlands
- catchment divide
- raingauge
- cambisol, podzol  
pore water
- precipitation  
samplers
- subsurface  
trench
- groundwater  
peat water
- gauging  
station



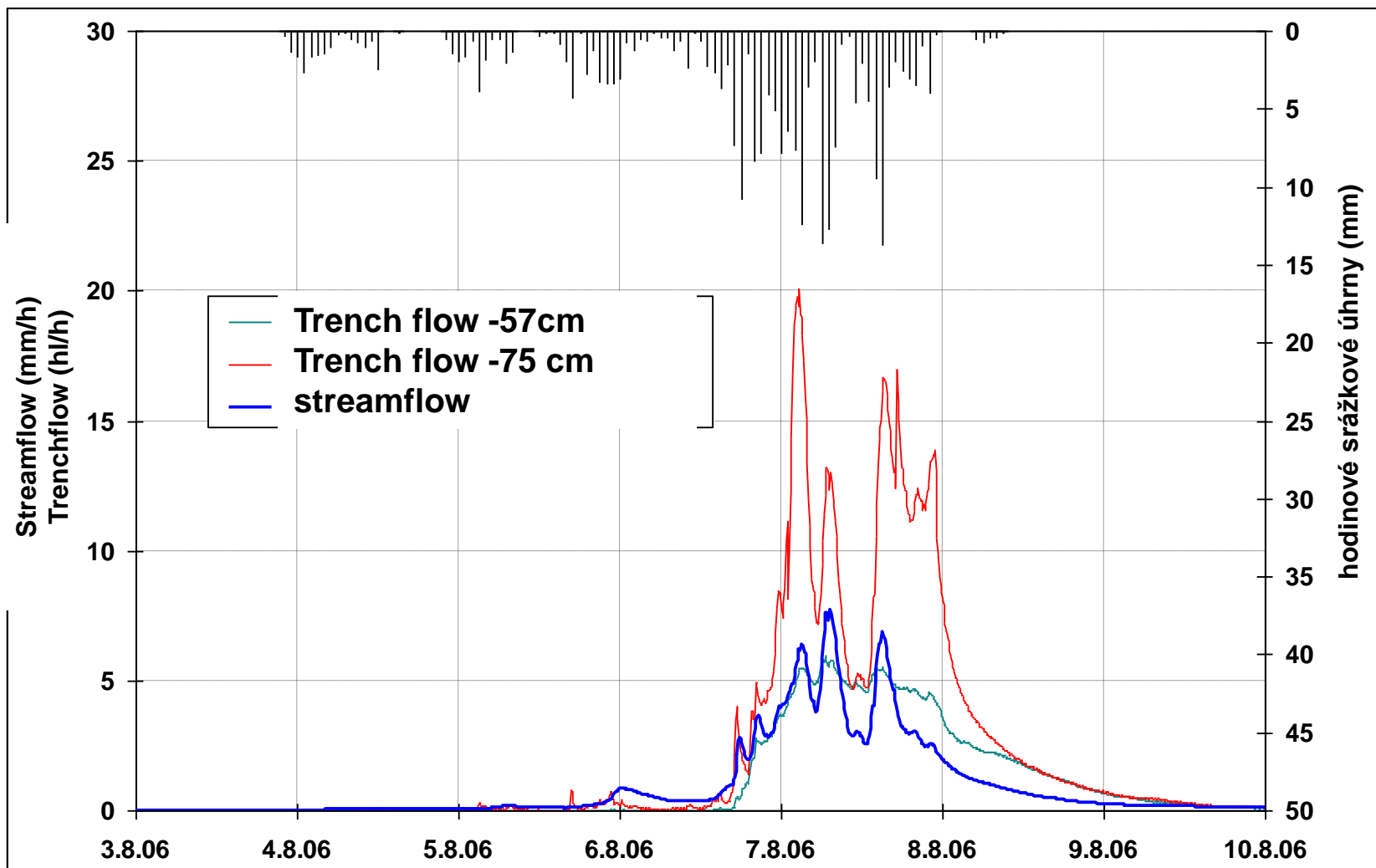
# Subsurface processes on the hillslope

## Subsurface trench with the monitoring system



# Subsurface outflow and streamflow

## Similar dynamics thanks to preferential paths



# Why tracers?

- **tool for the evaluation of runoff formation mechanisms**
- **identification of water motion mostly under surface**
- **mathematical modelling of water cycle**

# Natural tracers in hydrology

**Available ions and compounds, e.g.  $\text{Ca}^{2+}$ ,  $\text{SiO}_2$**

Concentration change in water after contact with soil-rock environment – good for water origin

**Isotopes: mostly stable  $^{18}\text{O}$ ,  $^2\text{H}$**

Variable concentration in precipitation – good for water dynamics

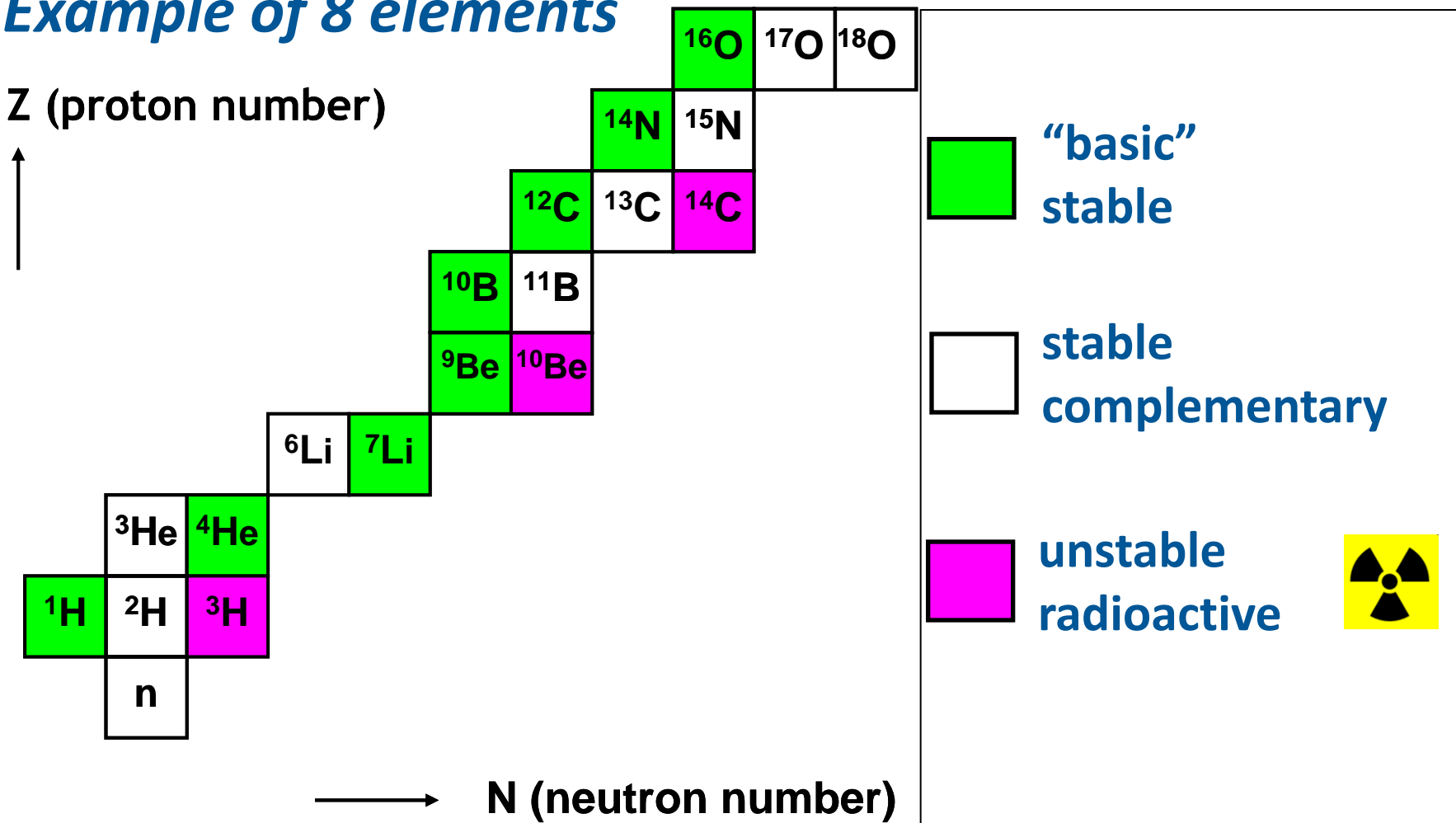
**Globally spread compounds (anthropogenic)**

**e.g.  $^3\text{H}$ - $^3\text{He}$ , freons (CFC)**

Changing concentration source in the atmosphere  
- good for age dating

# Isotopes in natural environment

## Example of 8 elements





# Stable isotopes in water molecule

$^1\text{H}$ ,  $^2\text{H}$ ,  $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ,

- present in hydrological cycle
- variable concentration in precipitation
- molecules themselves are tracers
- easy to handle and analyse

# Heavier stable isotopes in water

## $^2\text{H}$ (Deuterium) molecule

$^2\text{H}/^1\text{H} = 1.5576 \cdot 10^{-4}$  (V-SMOW), approx 1:6400

$$\delta^2\text{H}_{\text{sample}} = \left( \frac{\left( \frac{^2\text{H}}{^1\text{H}} \right)_{\text{sample}}}{\left( \frac{^2\text{H}}{^1\text{H}} \right)_{\text{V-SMOW}}} - 1 \right) * 1000 [\text{‰}]$$

## $^{18}\text{O}$

$^{18}\text{O}/^{16}\text{O} = 2.0052 \cdot 10^{-3}$  (V-SMOW), approx 1:500

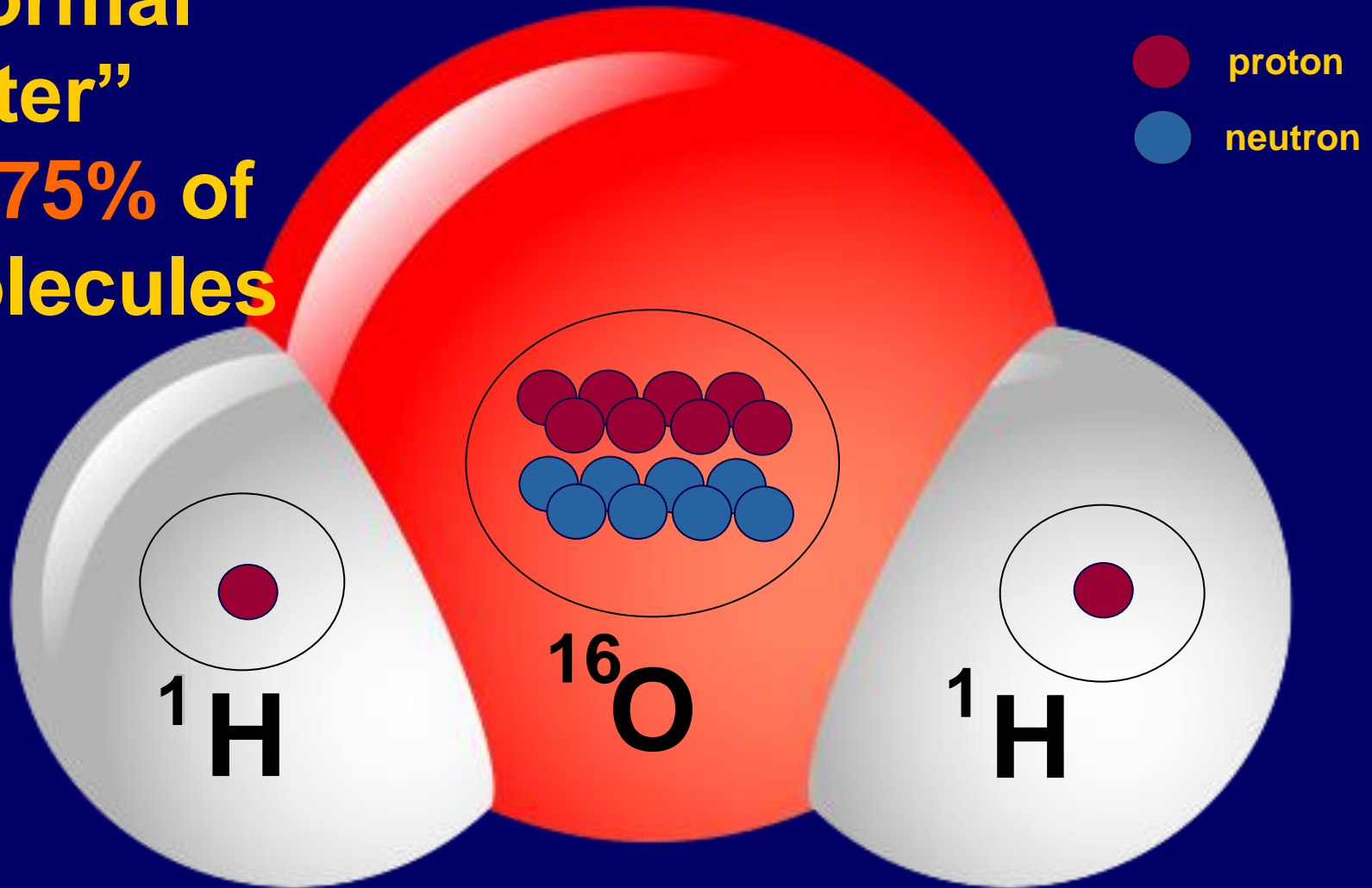
$$\delta^{18}\text{O}_{\text{sample}} = \left( \frac{\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{V-SMOW}}} - 1 \right) * 1000 [\text{‰}]$$

Concentration relative to V-SMOW

(Vienna Standard Mean Ocean Water  $\delta^2\text{H}=0\text{‰}$ ,  $\delta^{18}\text{O}=0\text{‰}$ )

# Stable isotopes of water molecule

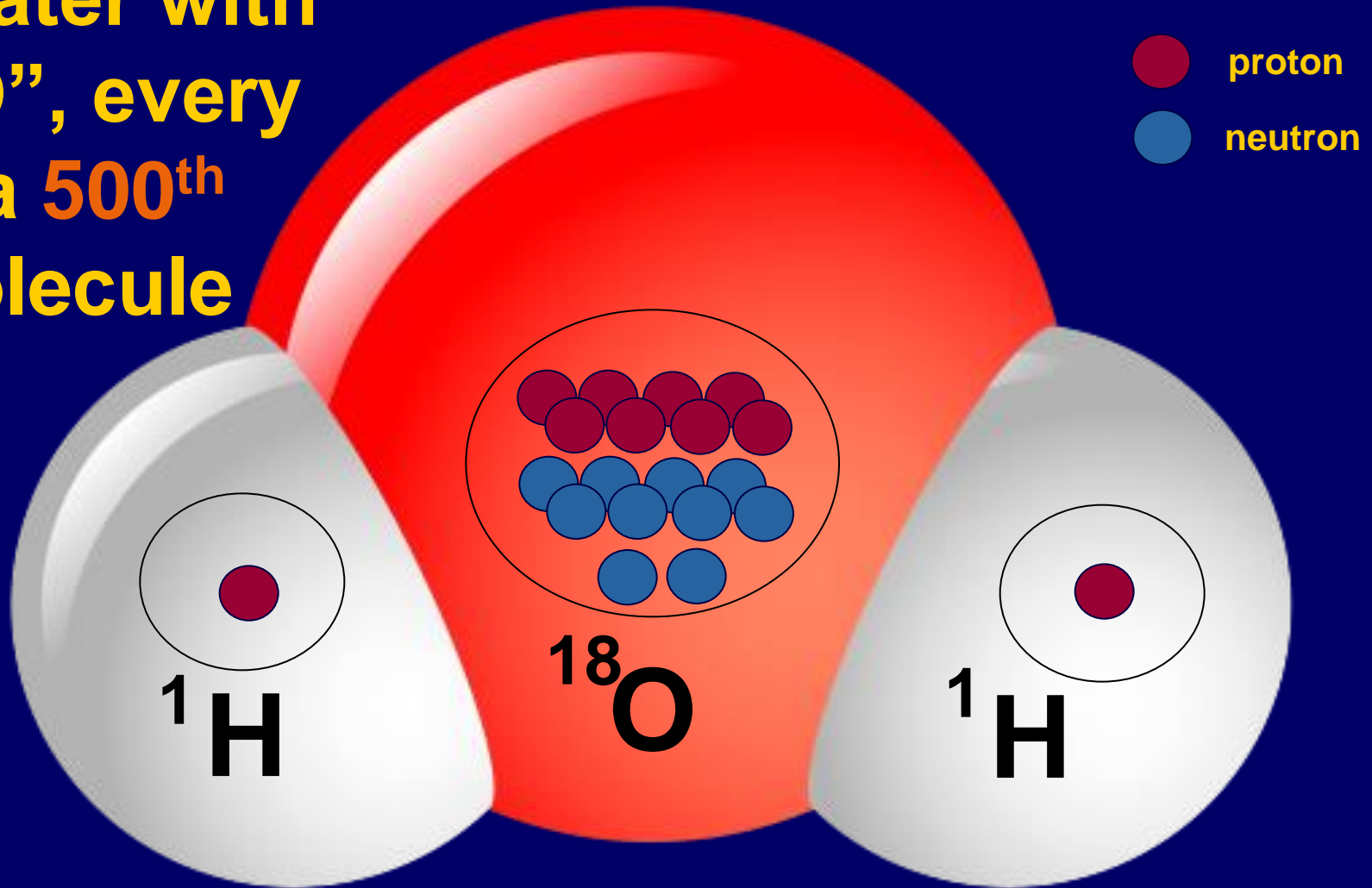
“normal  
water”  
99.75% of  
molecules



Total molecular weight = 18

# Stable isotopes of water molecule

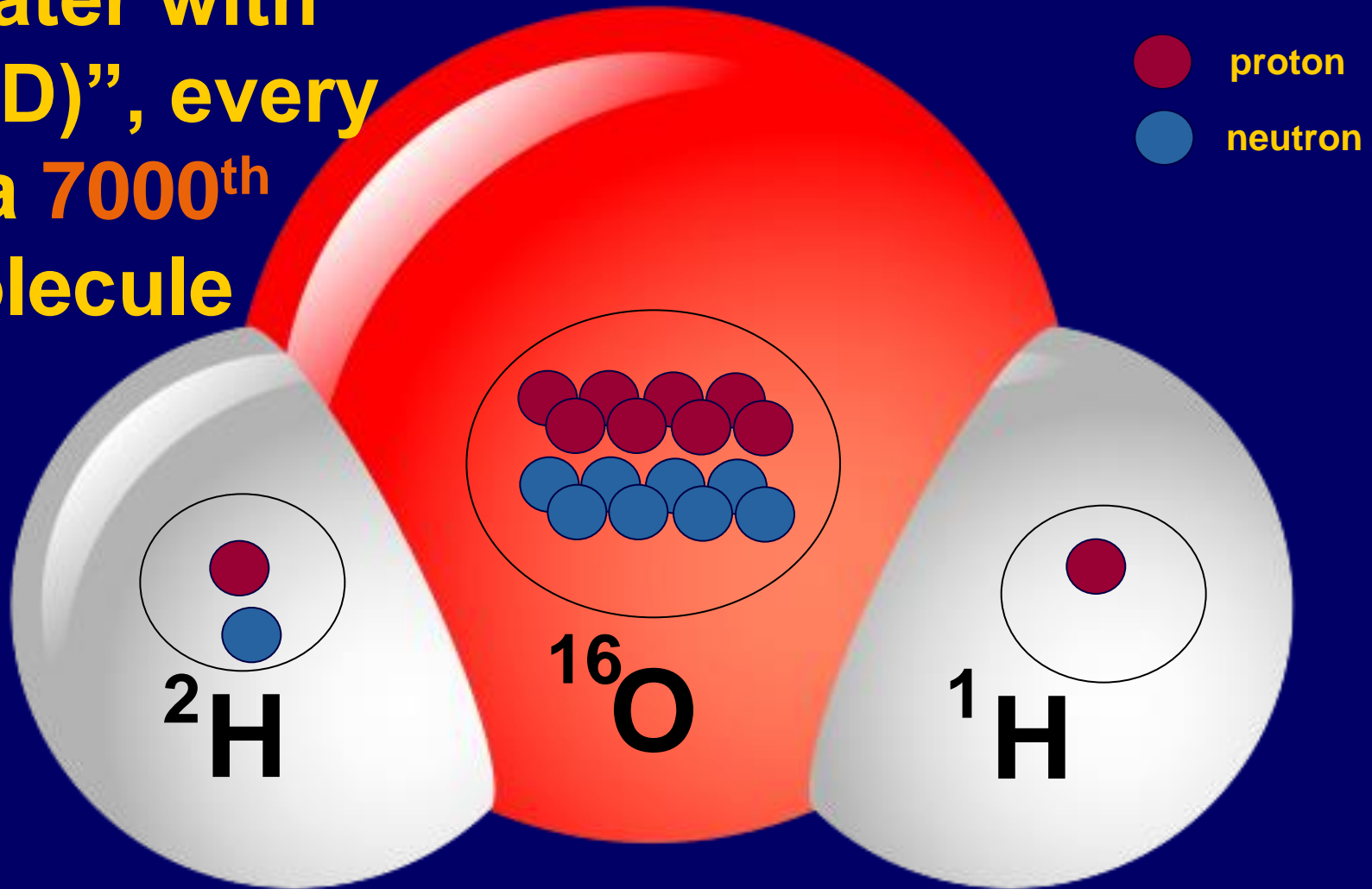
“water with  $^{18}\text{O}$ ”, every cca 500<sup>th</sup> molecule



Total molecular weight = 20

# Stable isotopes of water molecule

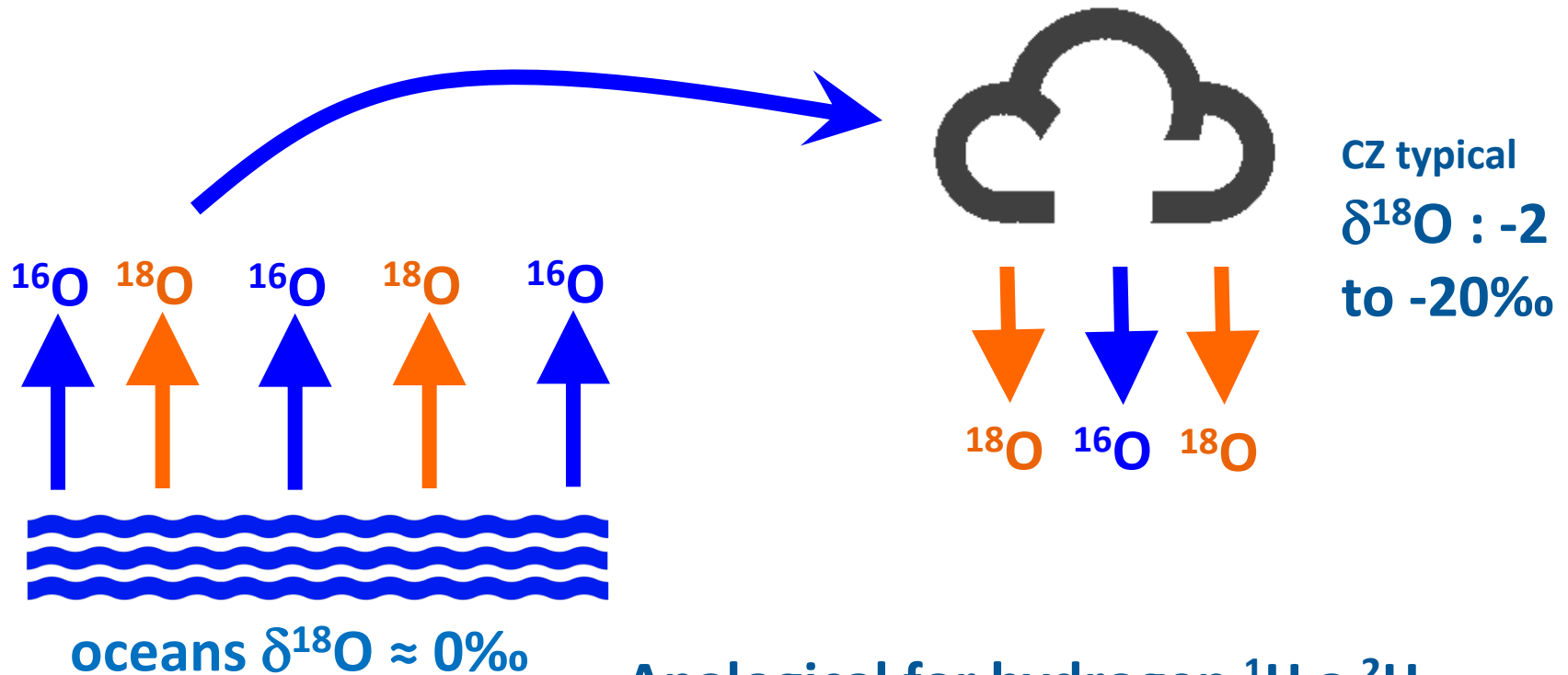
“water with  $^2\text{H}(\text{D})$ ”, every cca 7000<sup>th</sup> molecule



Total molecular weight = 19

# Stable isotopes of water in hydrocycle

- Difficult evaporation of molecule with heavier atoms
- Easier condensation of heavier molecules
- ie. Depletion of water masses in terms of heavier isotopes

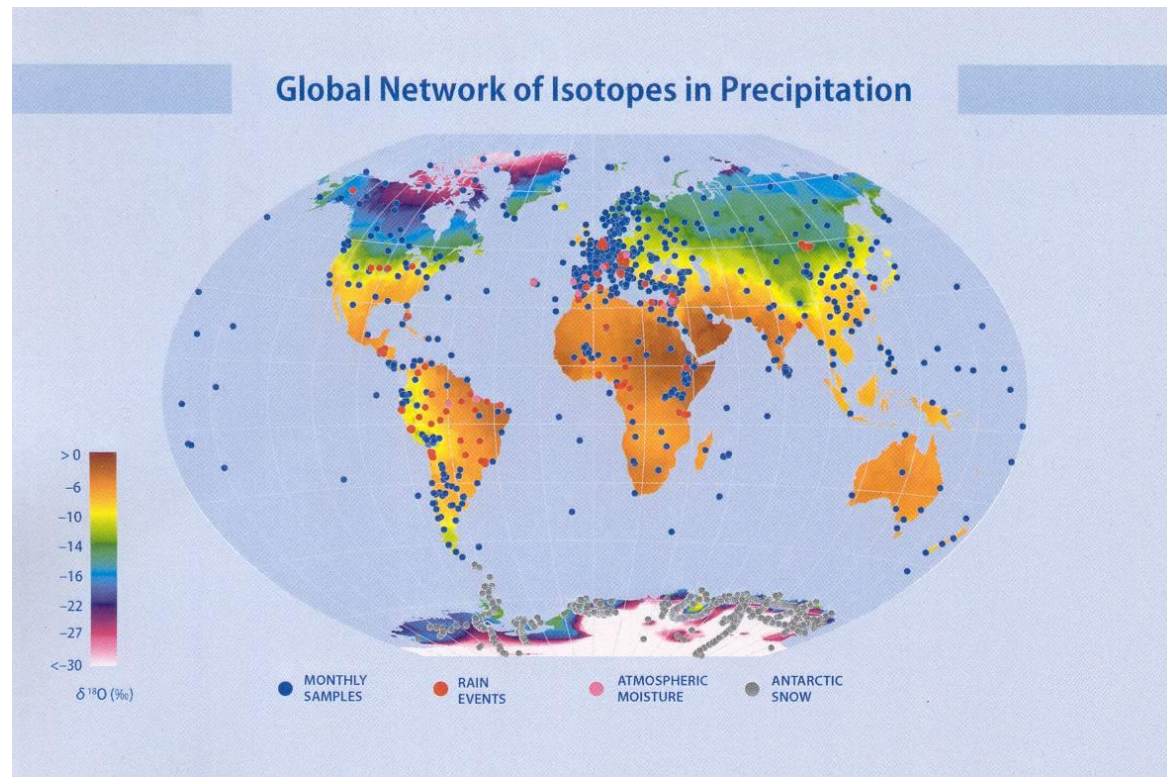


Analogical for hydrogen  $^1\text{H}$  a  $^2\text{H}$   
Occurs for O and H inside water mol.

# Concentration of stable isotopes depends on:

- distance from the ocean
- altitude and geographical latitude
- temperature of the atmosphere forming precipitation (frontal rain, local storm)

**GNIP – Global network of isotopes in precipitation**  
(IAEA, Vienna)



# Determination of isotopic concentrations

## Isotope ratio mass spectrometry (IRMS)

Very precise, for all isotopes, separate O and H measurements, financially demanding, sample preparation is tedious, active since 1950

## Laser spectroscopy (ICOS/CRDS)

Quite precise, for some isotopes/molecules only, quick and simultaneous measurement of O and H, 10x cheaper than IRMS,

Easy sample preparation

Easy operation

Commercially available since about 2007

Lab CTU, FCE, K143

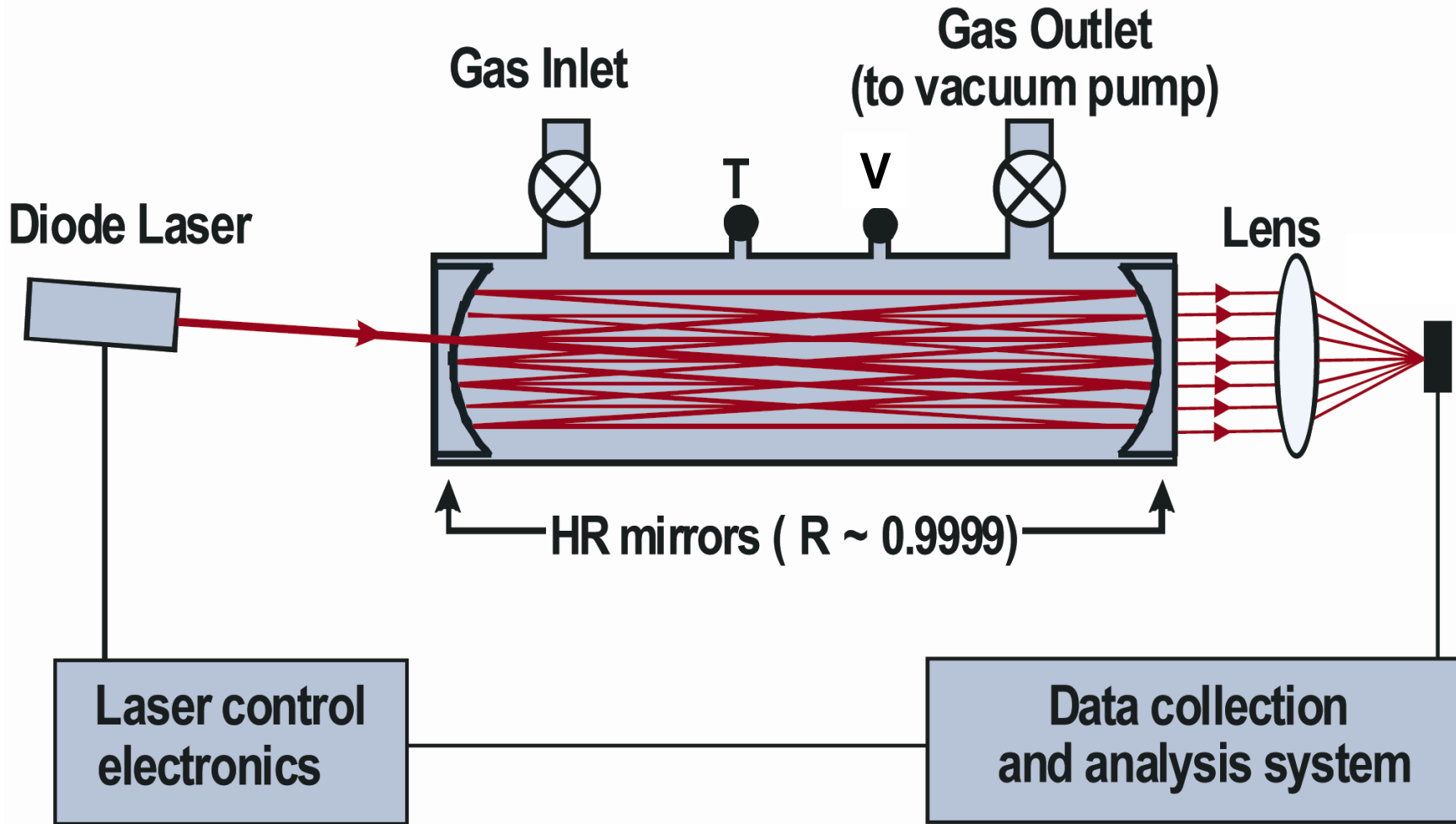




# Scheme of off-axis spectroscope

Integrated Cavity Output Spectroscopy (ICOS)

Cavity Ring Down Spectroscopy (CRDS)

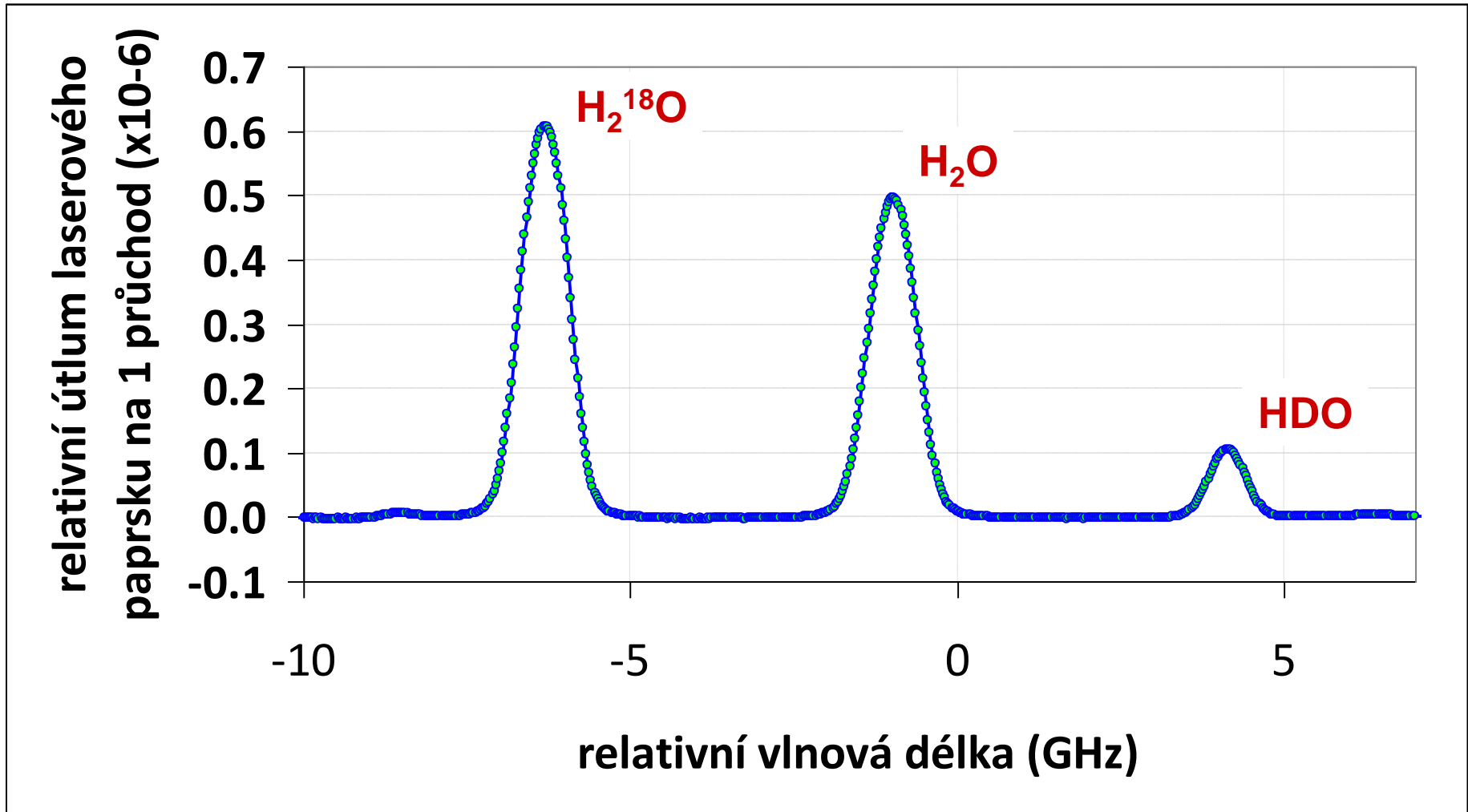


vzorek vody – cca 500 nl je vypařen a převeden do komory laseru  
vodní pára  $3 \times 10^{16}$  molekul/ml, absolutní tlak max. 5 mBar (0.5 kPa)

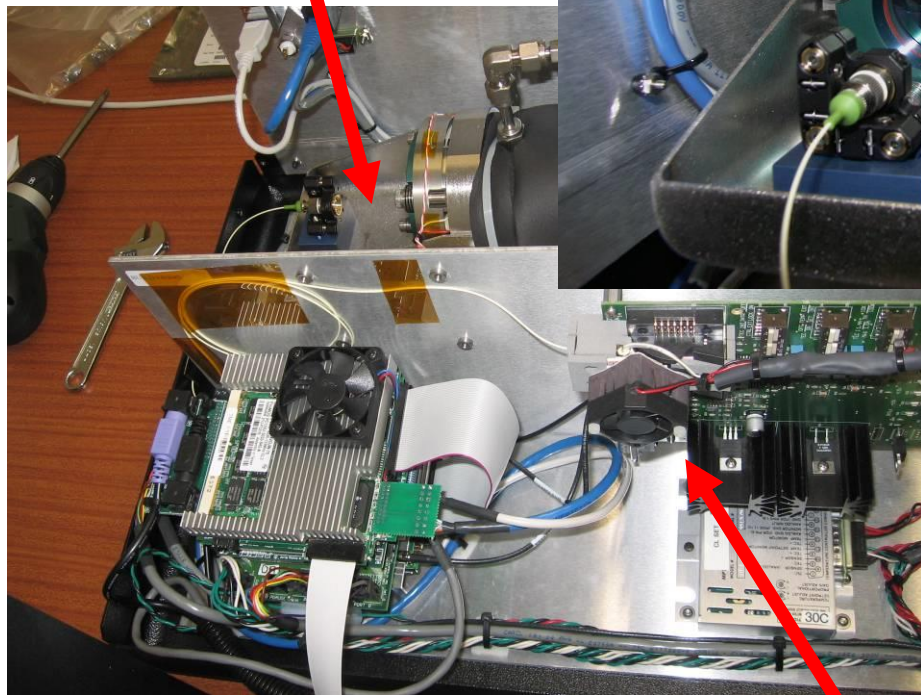
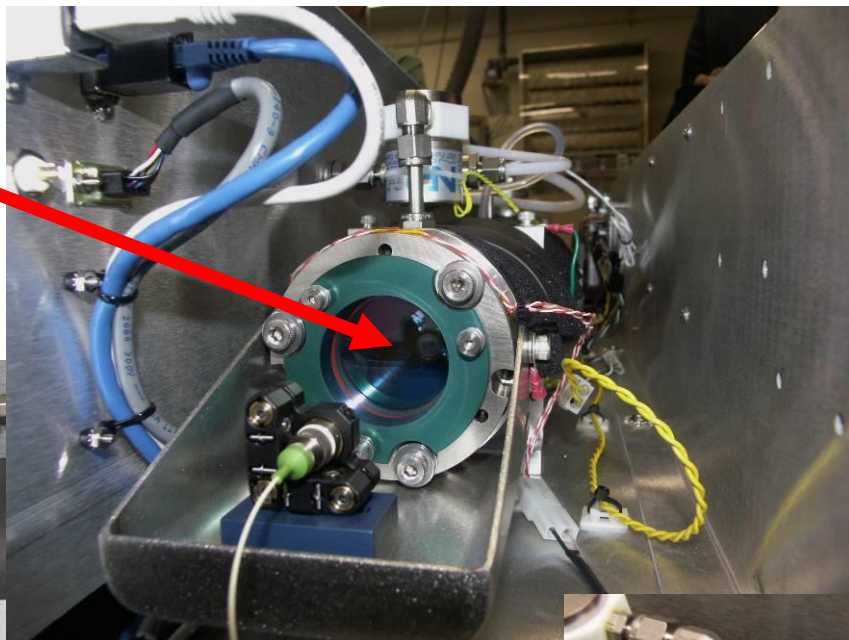
# Beer law of absorption

$$I = I_0 e^{-\mu d}$$

I- output intensity,  $I_0$  – input intensity,  $\mu$  – coef. attenuation – acc. to pressure and isotopic concentration  
d- length of laser beam travel  
spectrogram example

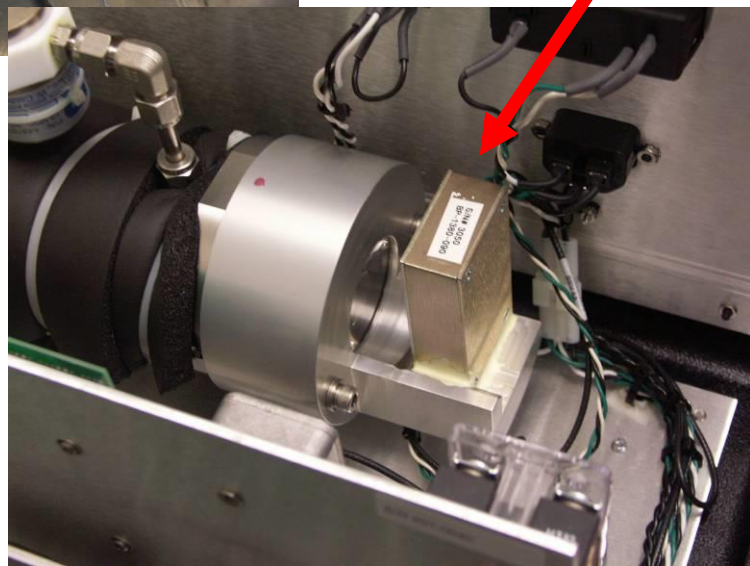


Laser diode entry

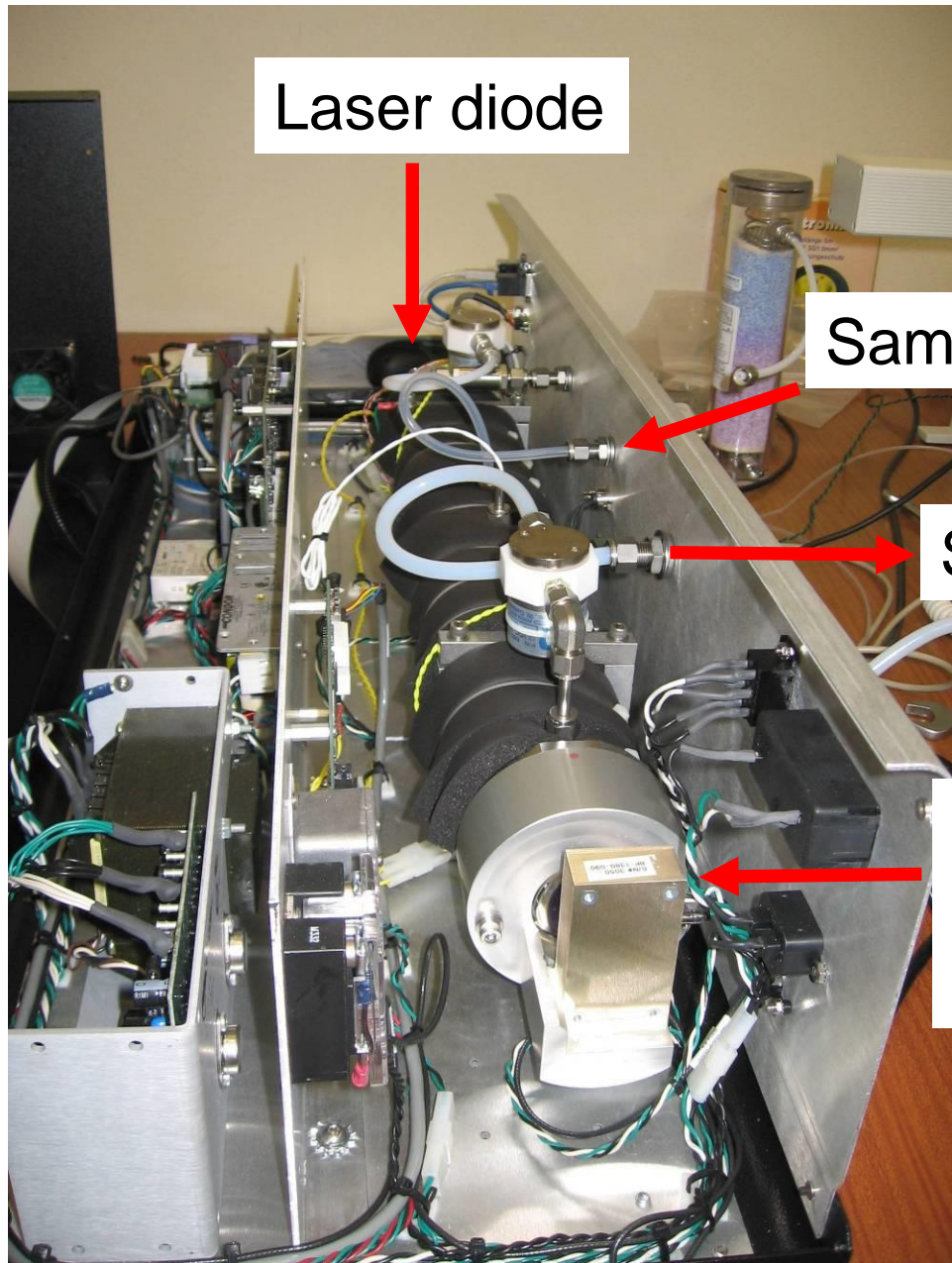


computer

detector



IAEA



Laser diode

Sample inlet

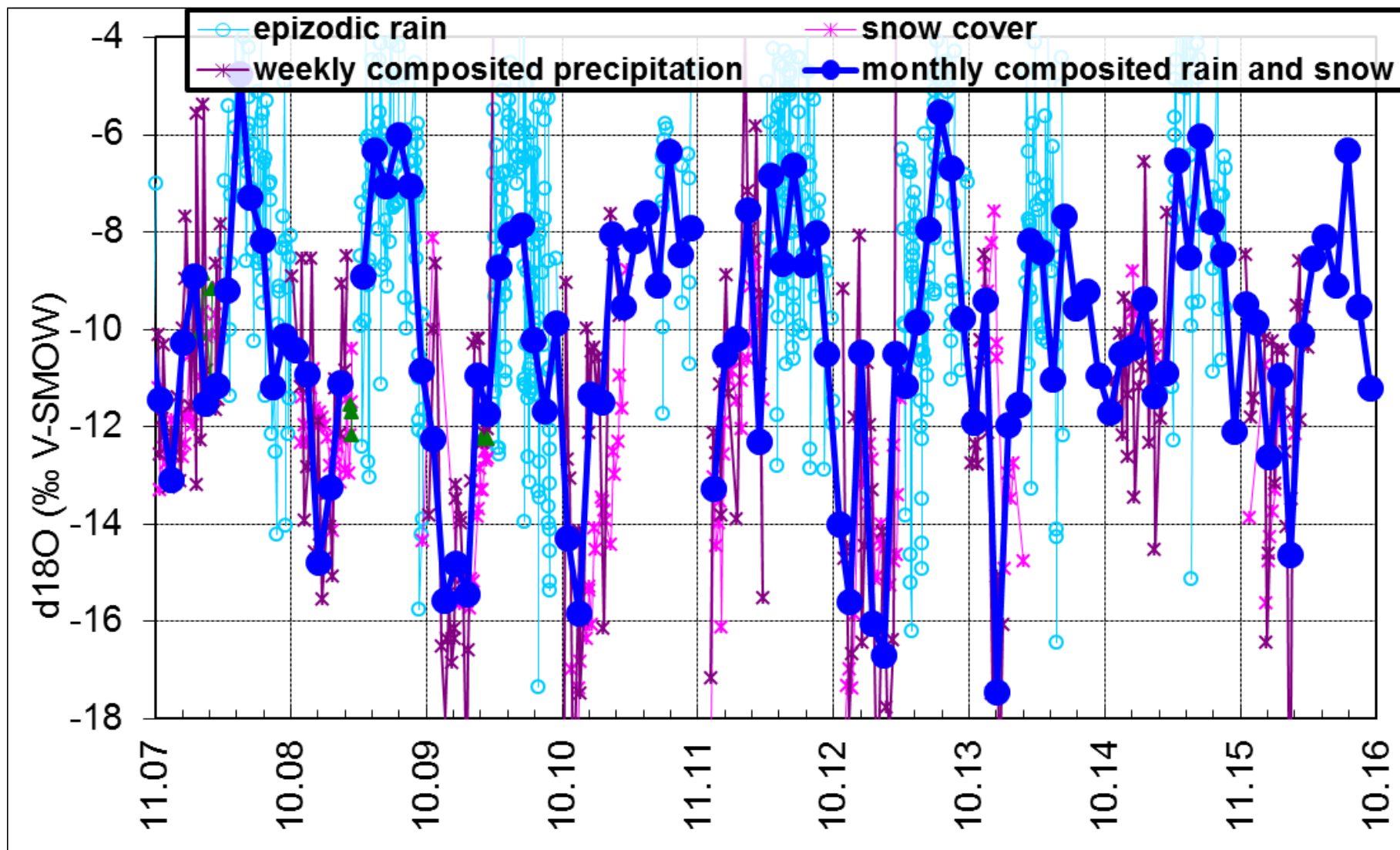
Sample outlet

Detector of the decay and absorption

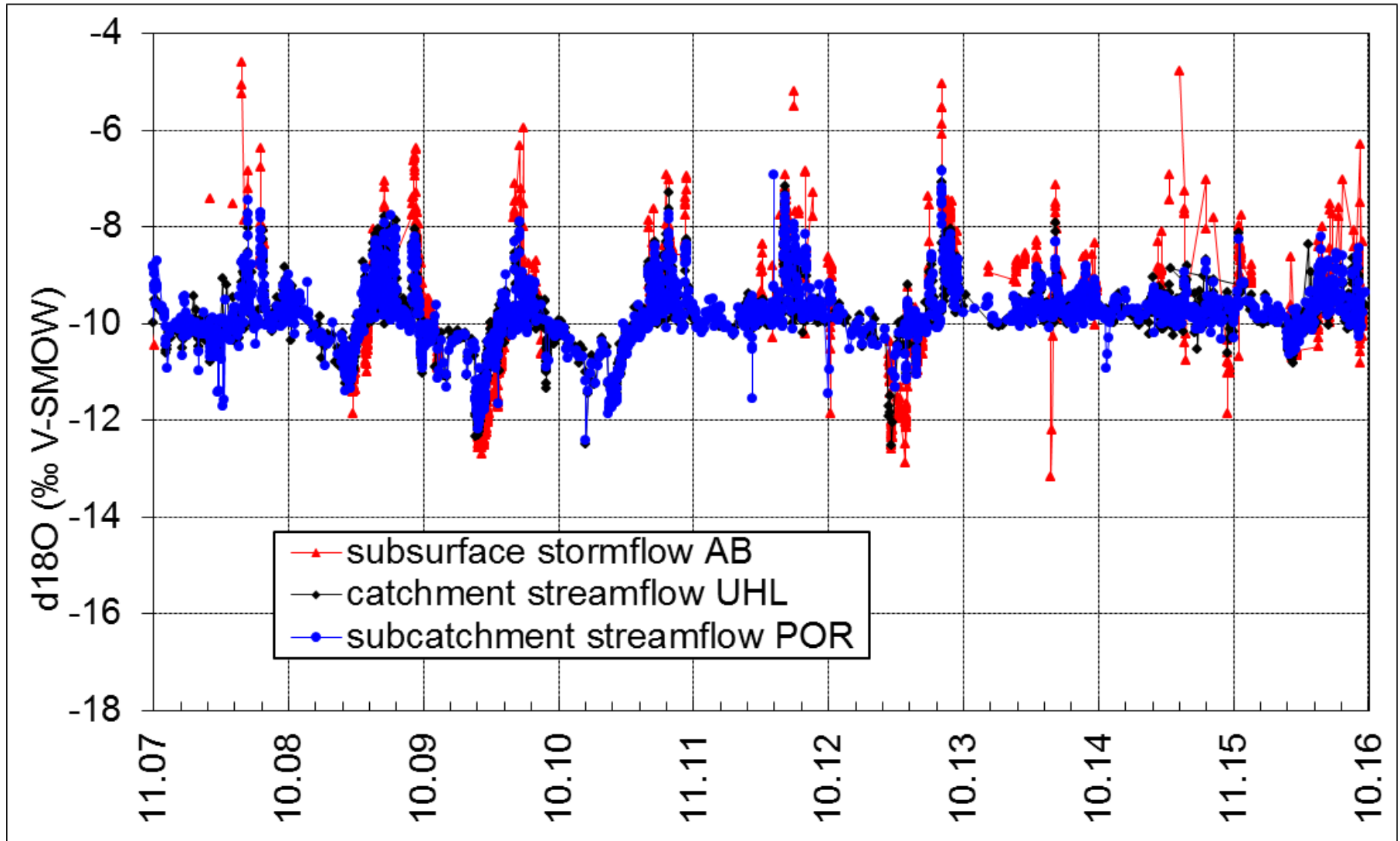
# Stable isotopes use in hydrology

- mean residence time of water in system
- isotopic separation > how much of even and pre-event water is in the stormflow
- flow in soil profile, in groundwater
- detection of sources (dam seepage vs. groundwater; sewage vs. groundwater)
- snowmelt
- evaporation evaluation
- paleohydrology (recent and old water)
- climate change (ice core isotope hydrology)
- total balance

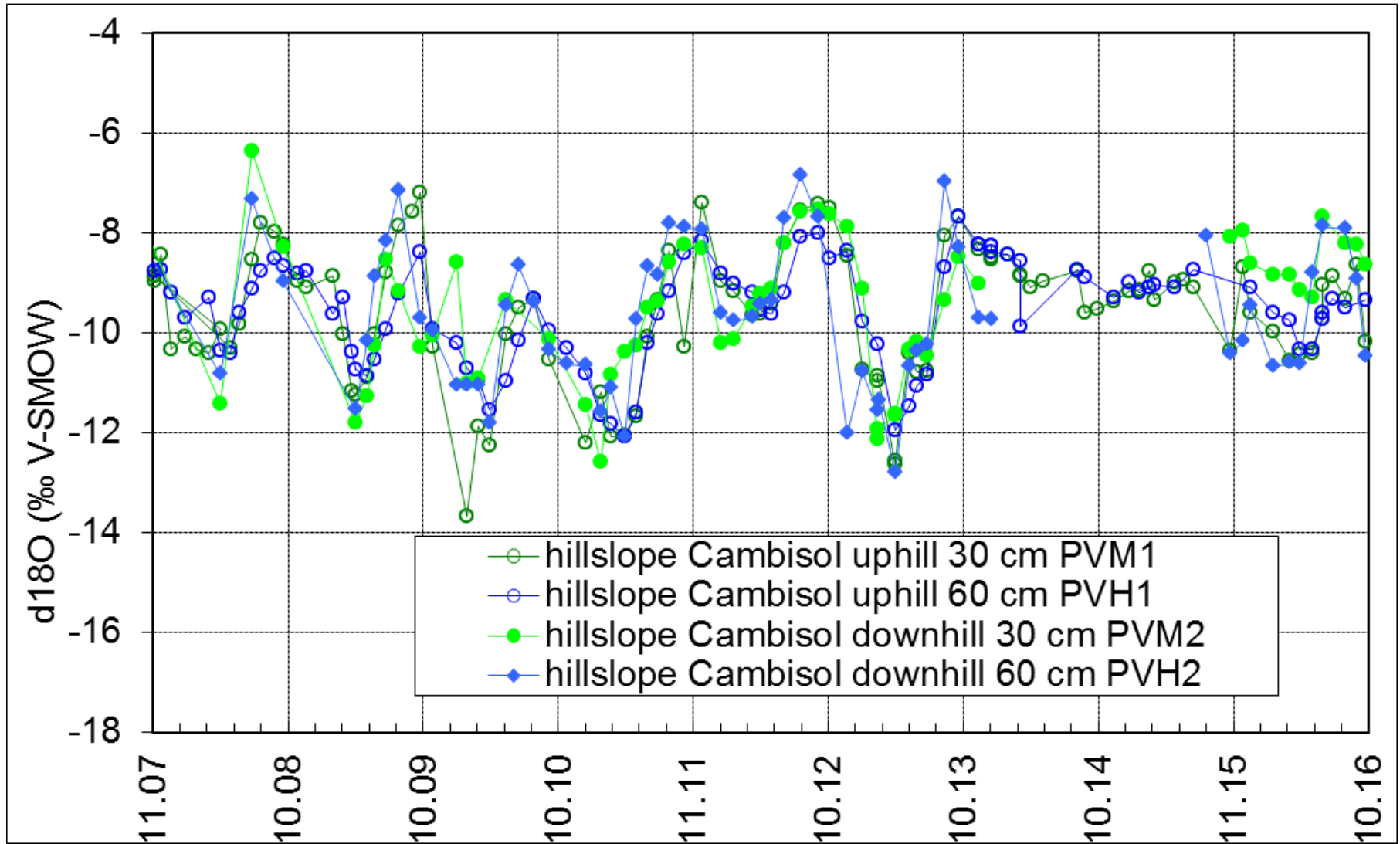
# $^{18}\text{O}$ in precipitation



# $^{18}\text{O}$ in soil runoff and streamflow

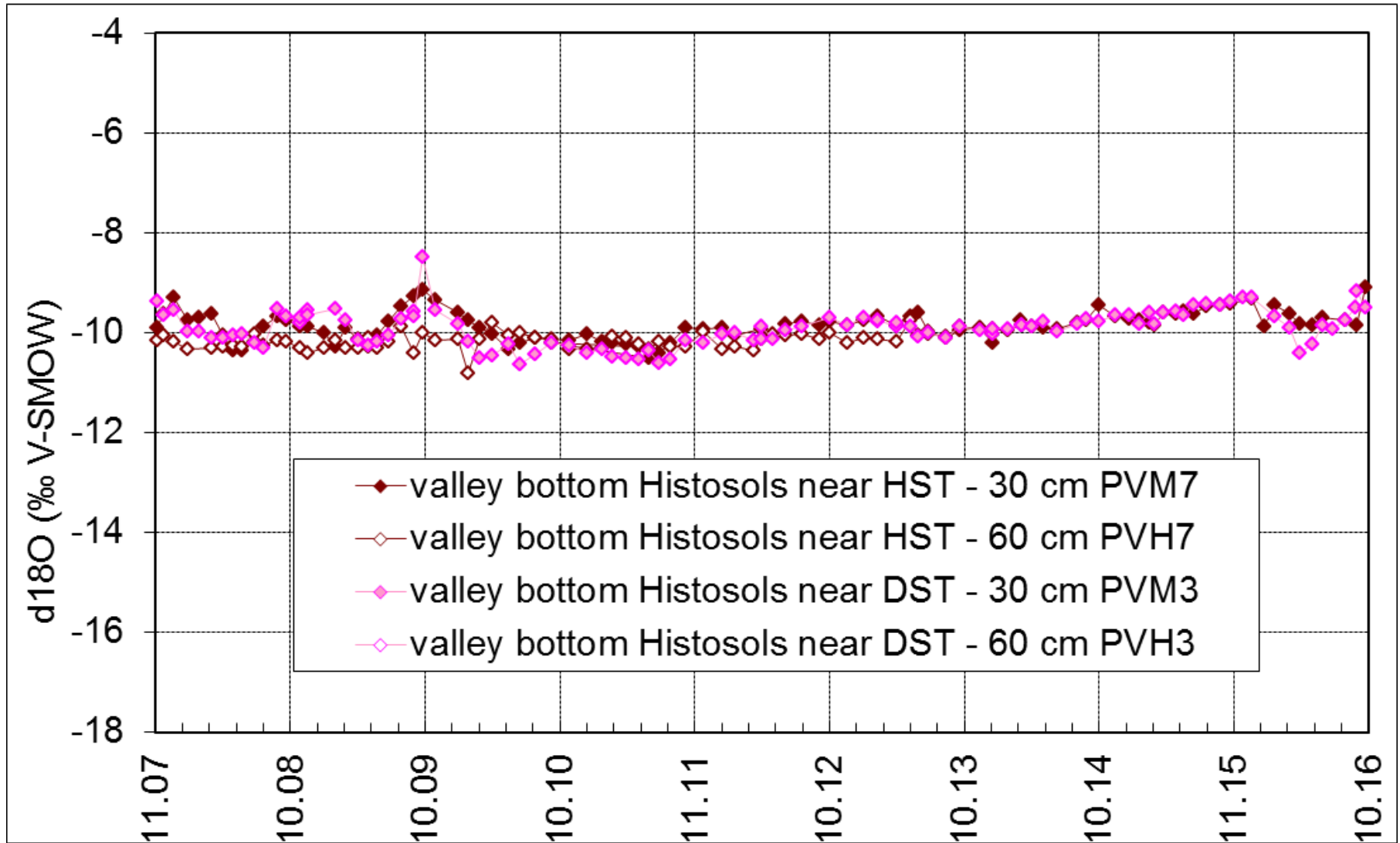


# $^{18}\text{O}$ in Cambisol and Podzols pore water

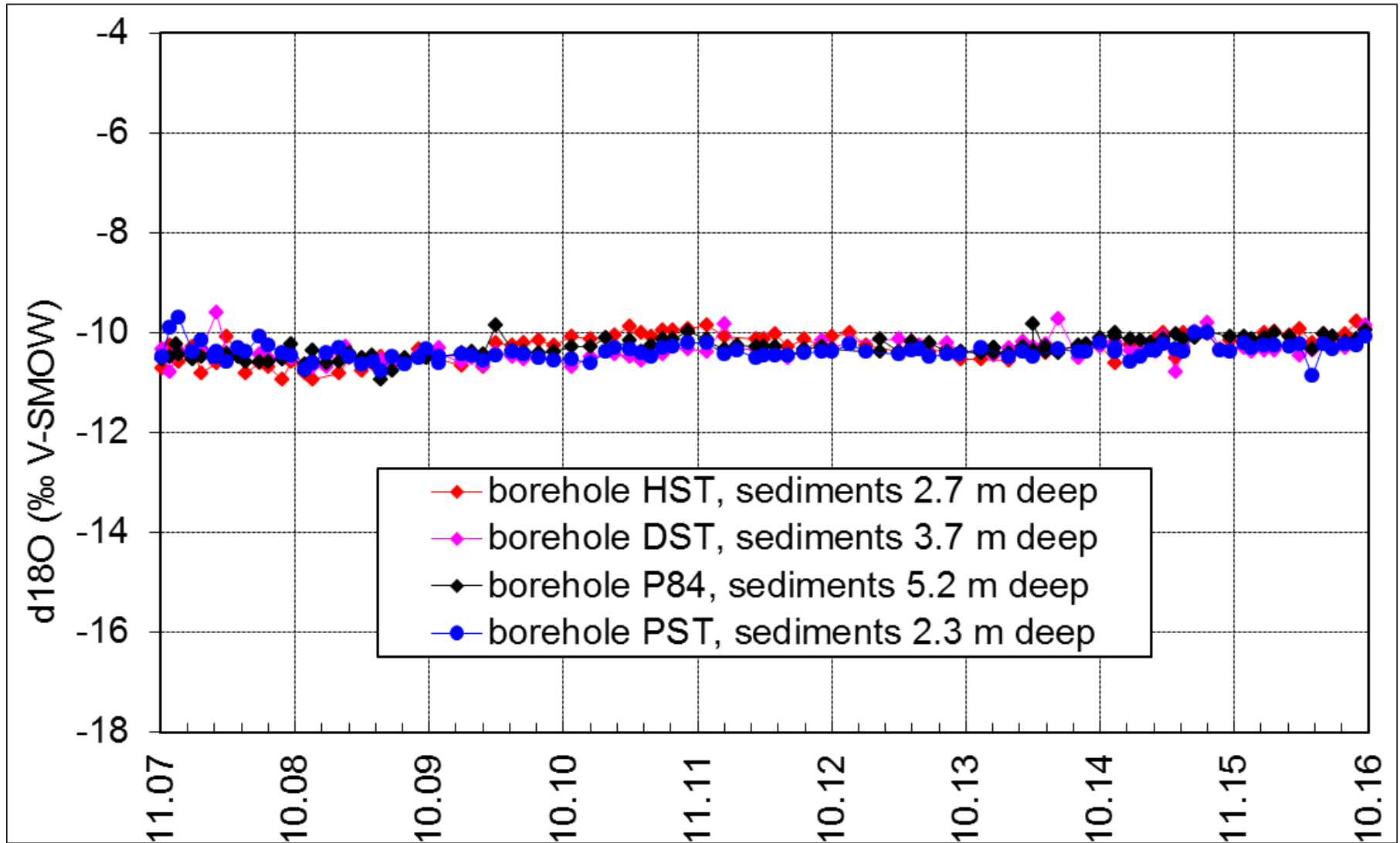




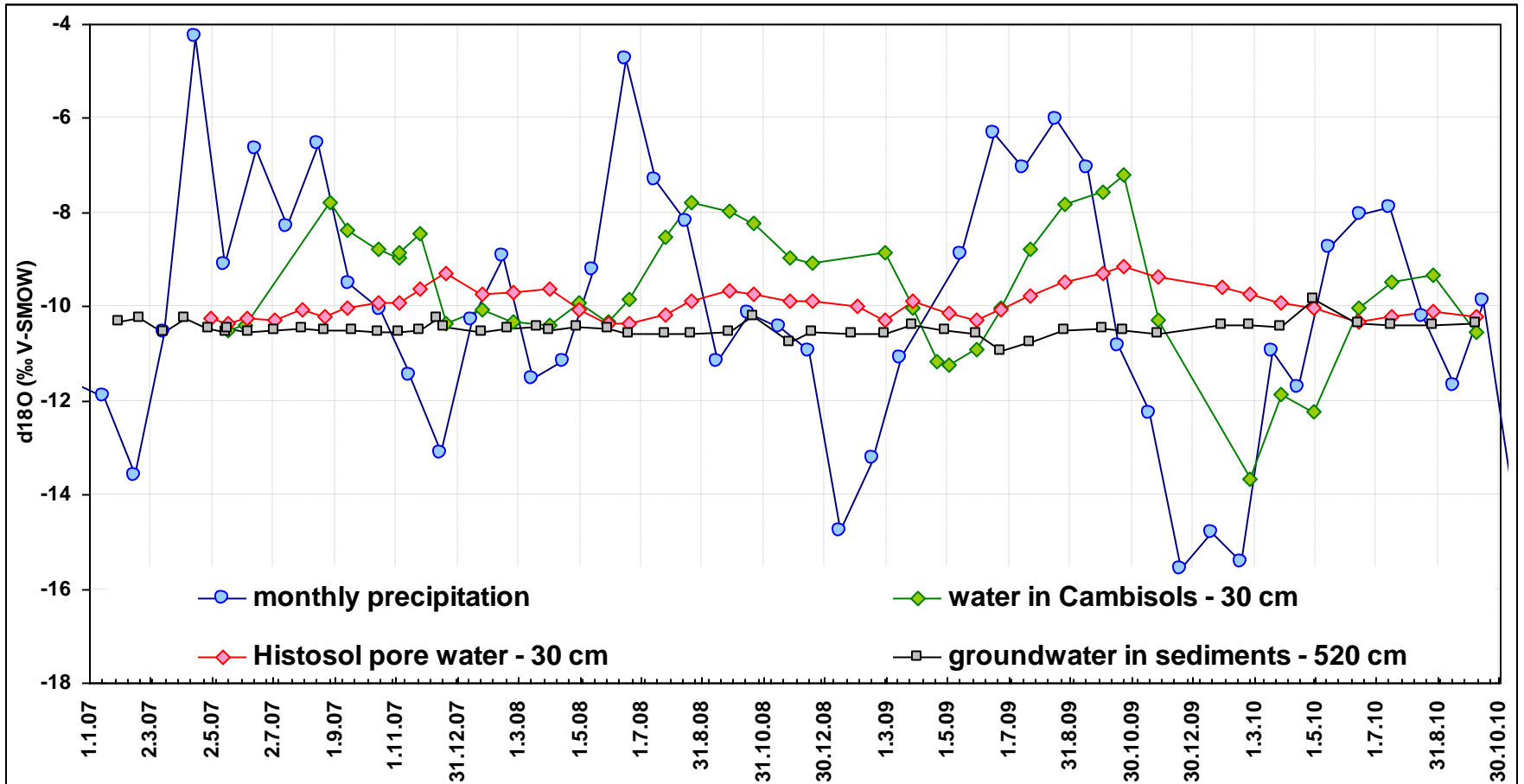
# $^{18}\text{O}$ in Histosol pore water



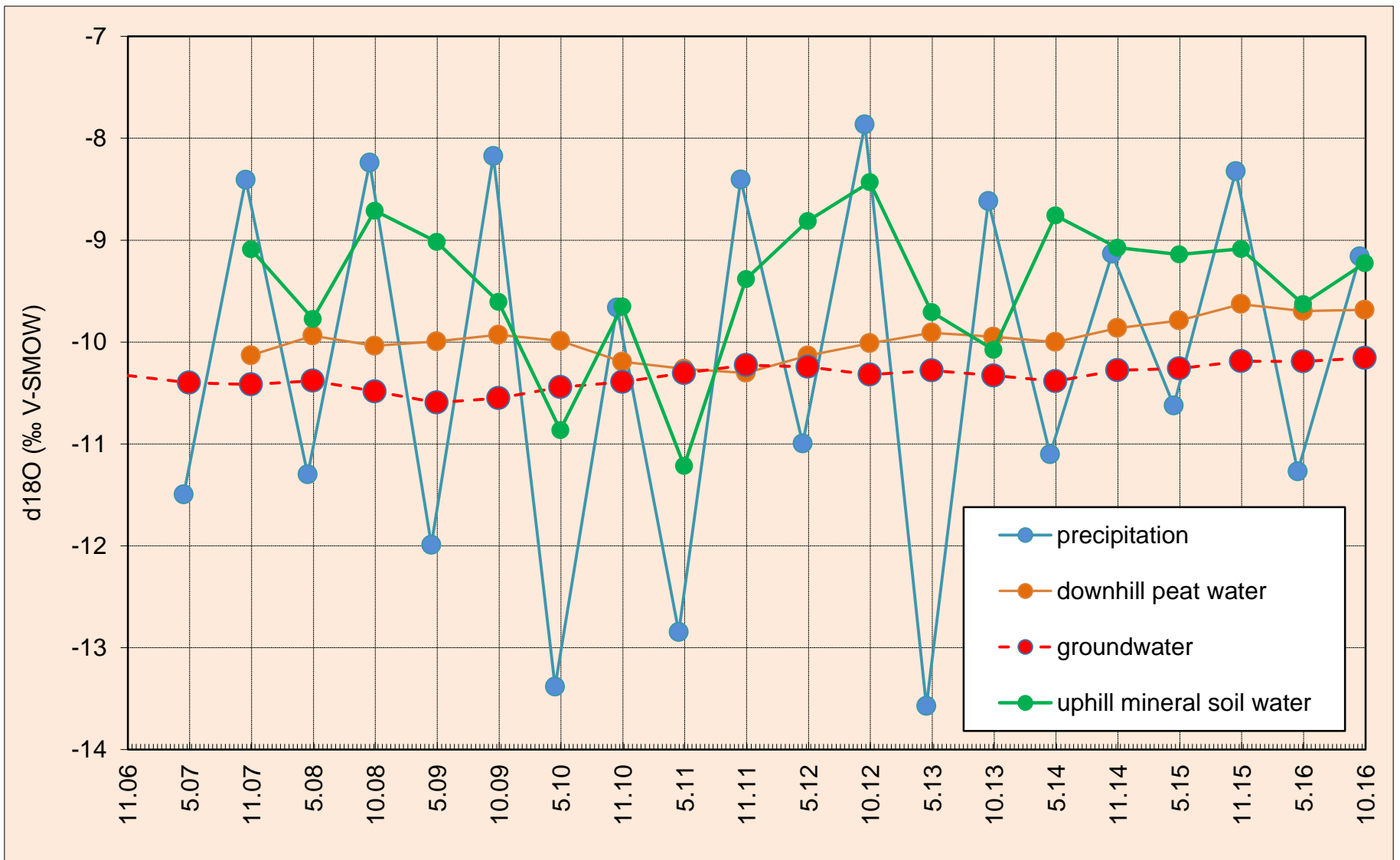
# $^{18}\text{O}$ in groundwater



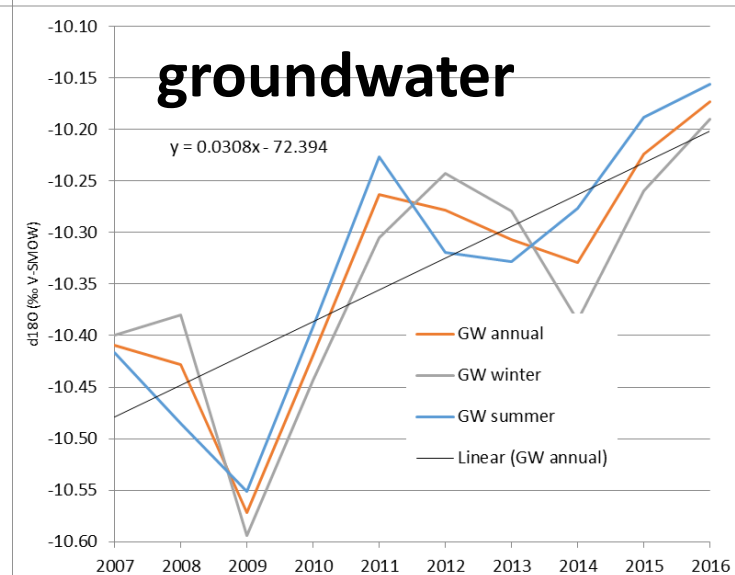
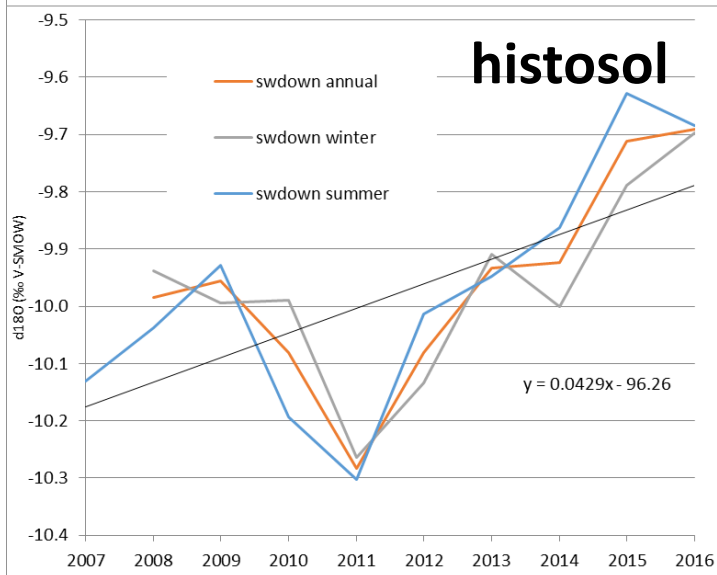
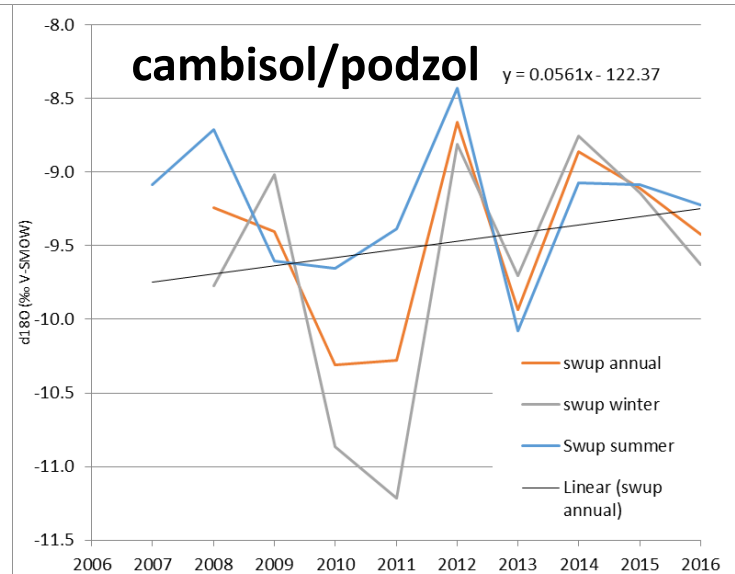
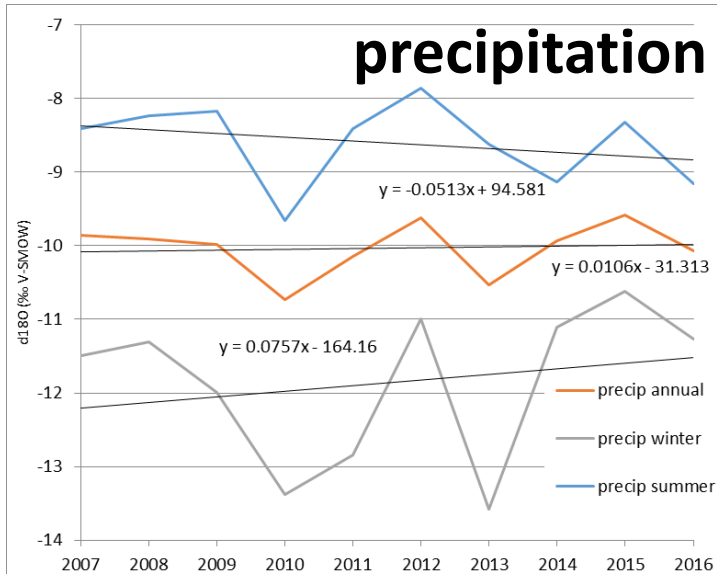
# Seasonal mixing of waters in the soils and groundwater



# Isotope decade 2007-2016



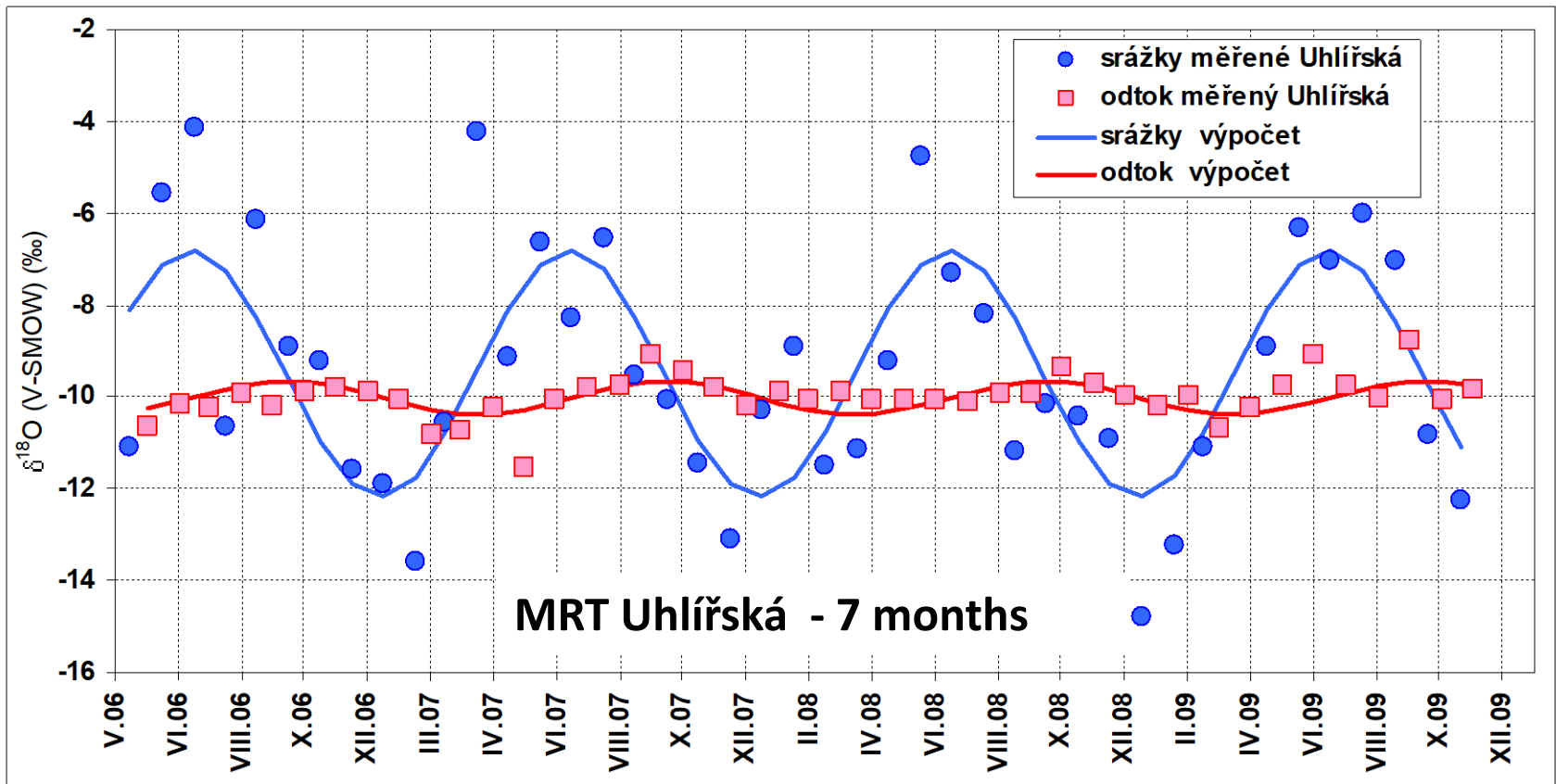
# Isotope decade 2007-2016



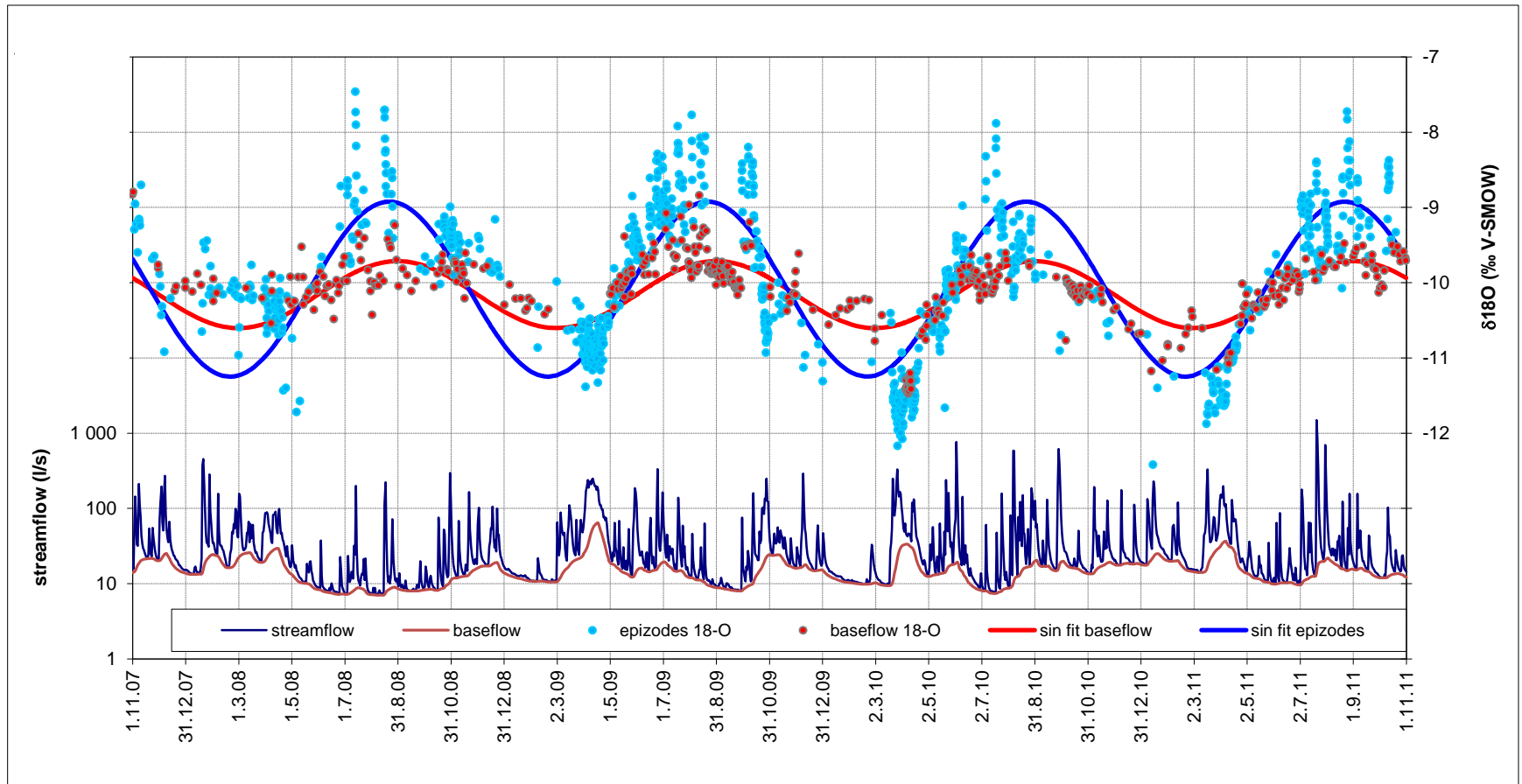
# Use of isotopic data for Mean residence time (MRT) of water in system – linear reservoir model

$$MRT = \left( \frac{1}{b'} \right) \left[ \left( \frac{A_p}{A} \right)^2 - 1 \right]^{0.5}$$

Attenuation of precipitation on runoff  
 Input – (rain  $A_p$ ) a output (runoff  $A$ )  
 conversion  $((1/b') = 6/\pi$  (for months))



# Mean residence time of baseflow and events

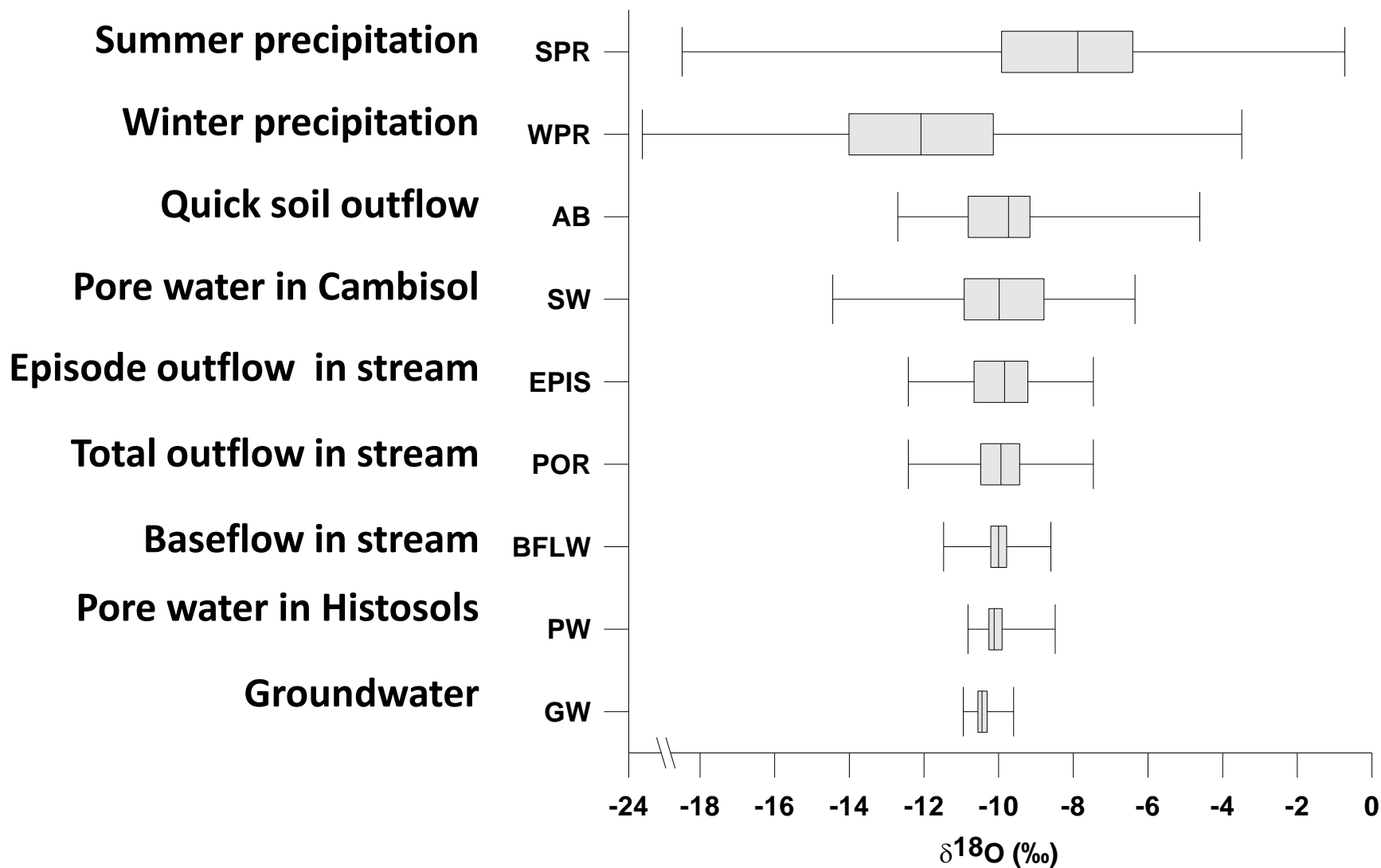


**BFLOW average index of baseflow is 0,673**

**Mean residence time is 12.3 for baseflow, 4.4 months for event flow**

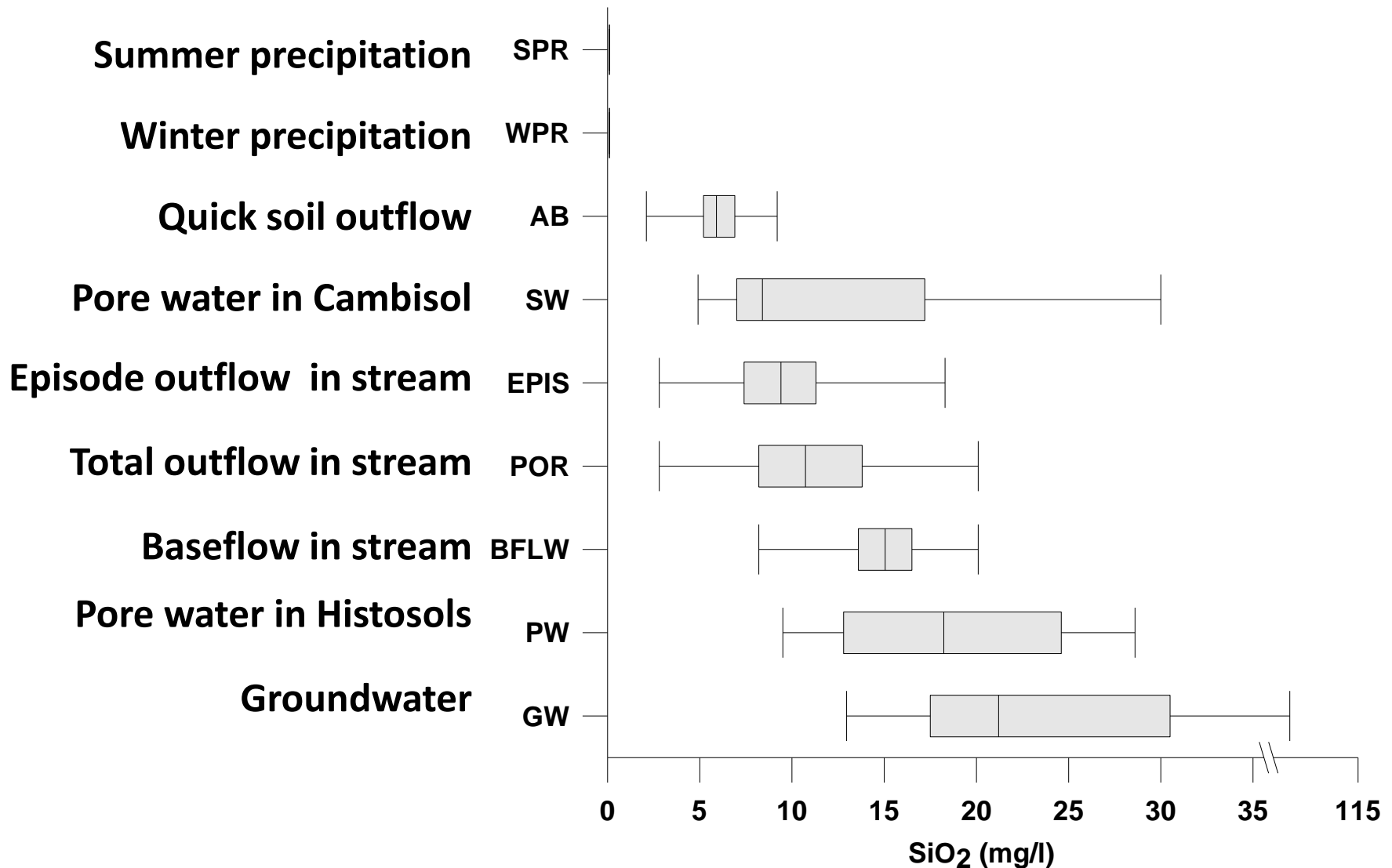
**Groundwater is main component in summer storm flow and snowmelt**

# Gradual attenuation of $^{18}\text{O}$ signal in catchment waters

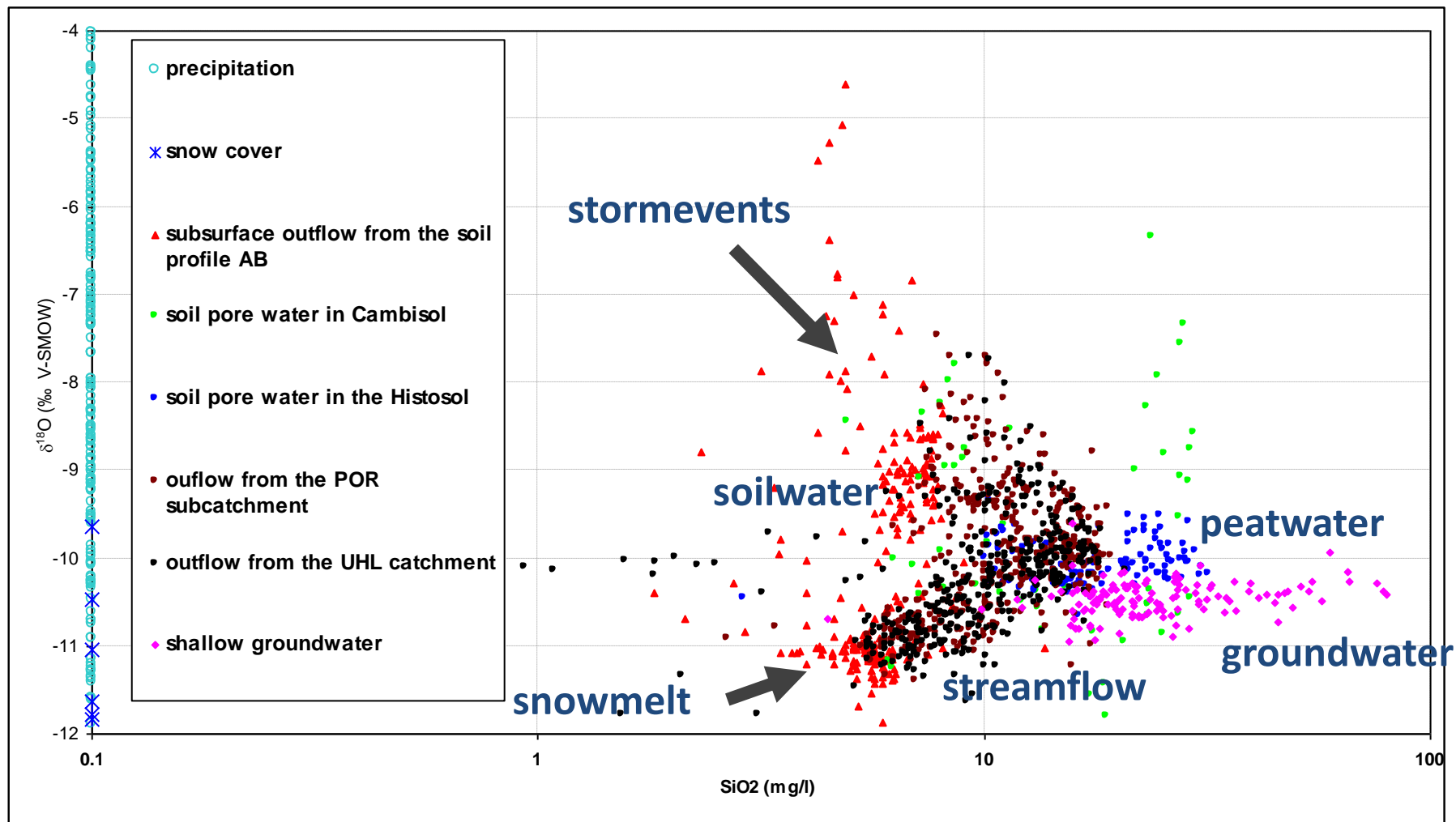




# Gradual increase of SiO<sub>2</sub> in catchment waters

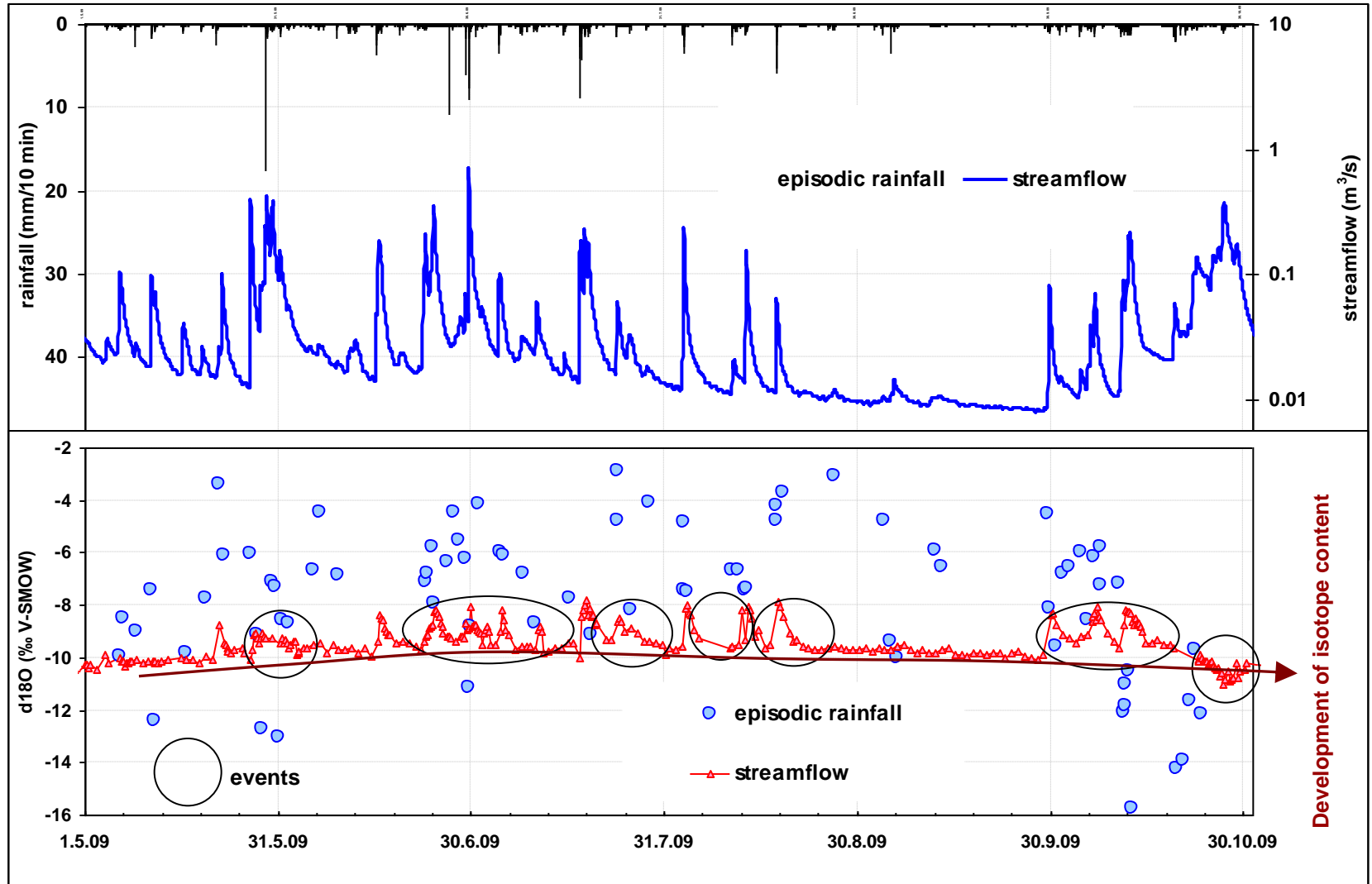


# End members by $^{18}\text{O}$ and $\text{SiO}_2$ in catchment waters

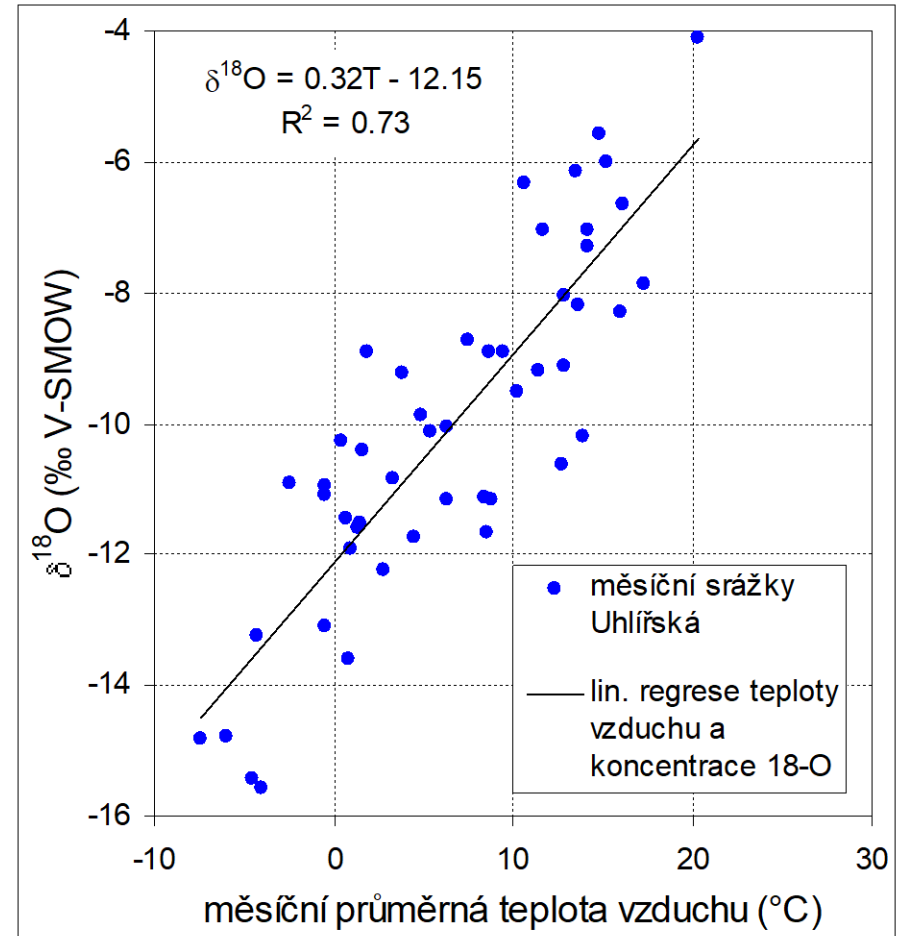
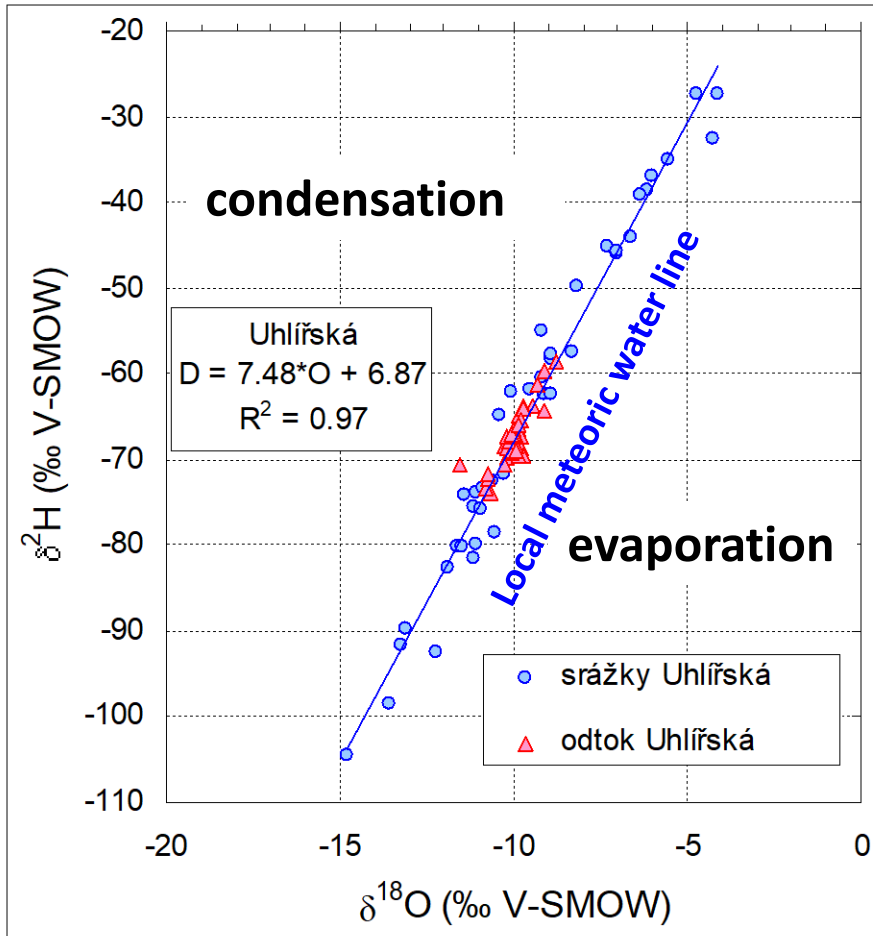


# Response of streamflow to rainfall

Dominant effect of pressure drained groundwater mixed with soil and rain water



# Vztah $\delta^2\text{H}$ a $\delta^{18}\text{O}$ ve srážkové vodě a odtoku a vztah k teplotě prostředí



# Isotopic separation

$$R_s = \frac{Q_s}{Q_t} = \frac{c_t - c_n}{c_s - c_n}$$

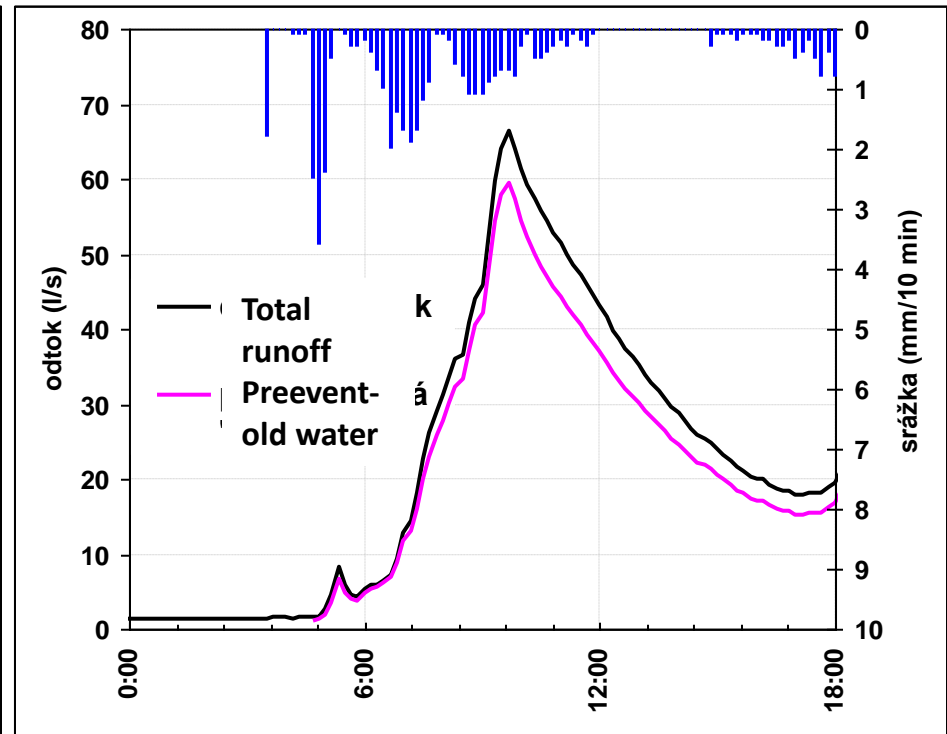
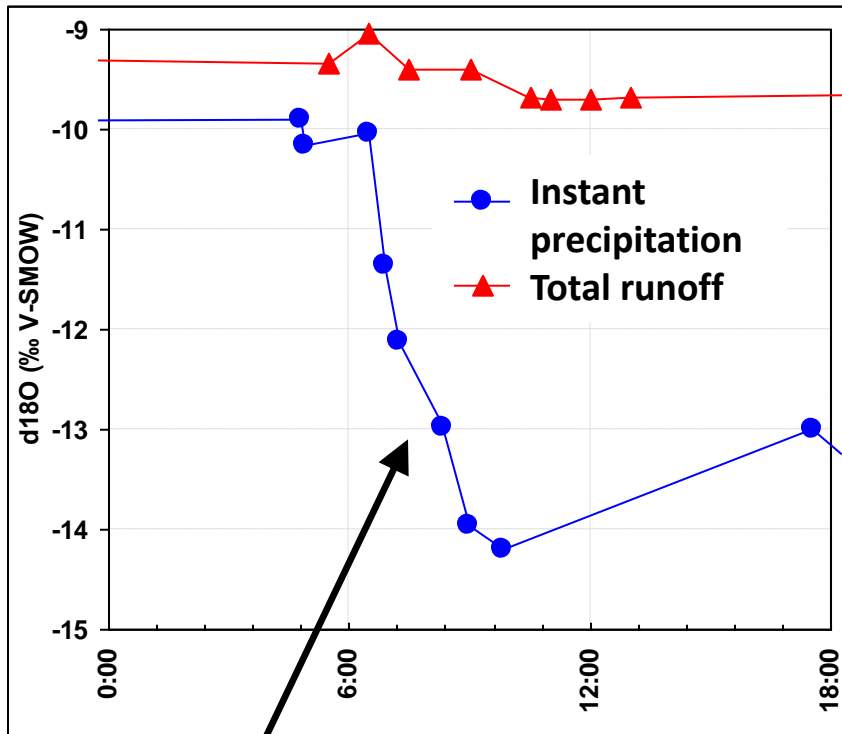
$Q_t$  total runoff,  $Q_s$  runoff of “old” water,  $Q_n$  runoff of “new” water

$c_t$  concentration of isotopes in total runoff

$c_s$  concentration of isotopes in old water – groundwater or baseflow

$c_n$  concentration of isotopes in precipitation

$R_s$  instant ration of old-preevent water in runoff



rainfall-runoff even in drained agricultural catchment,  
7.8.2010

Rainout effect – decrease of concentration of heavier isotopes of O (and H) during frontal rain.

# Deuterium excess in decoding sources of water in the catchment

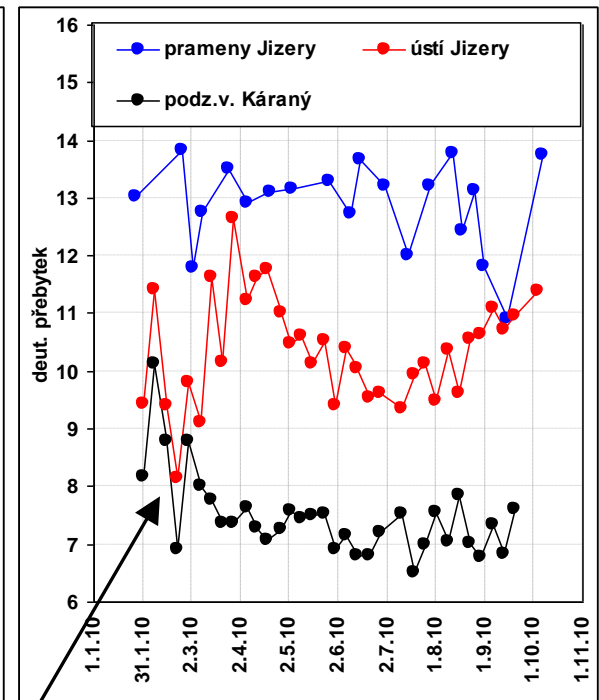
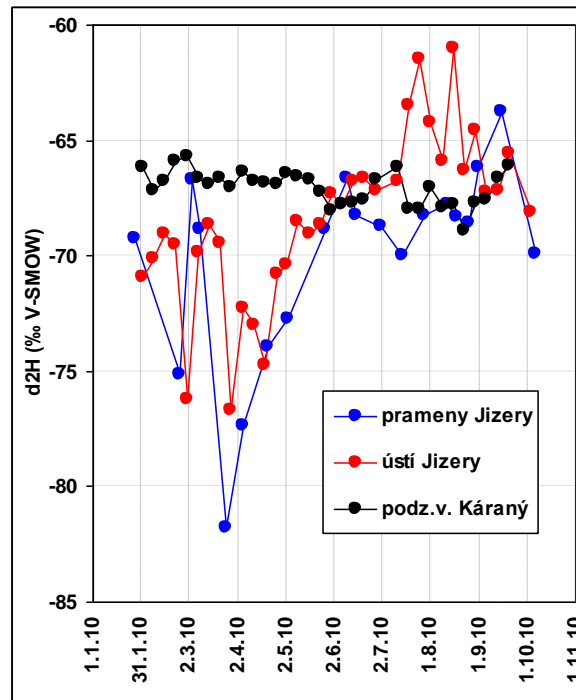
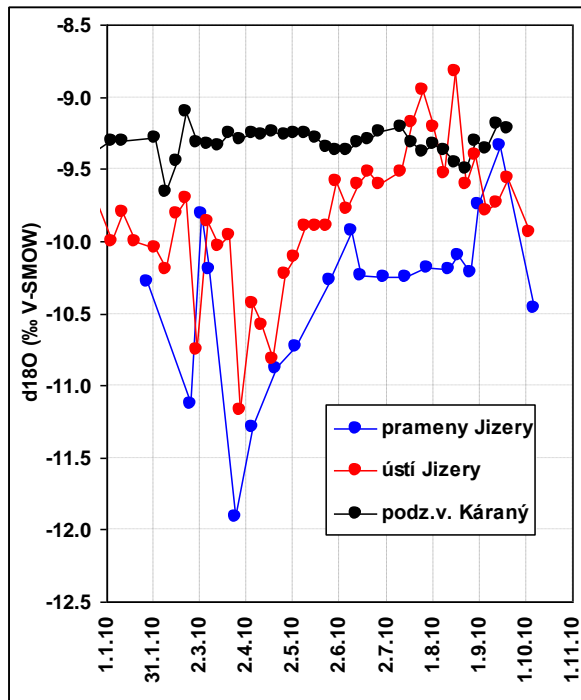
$$d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$$

d .. Deut. excess (-)

$\delta^{18}\text{O}$

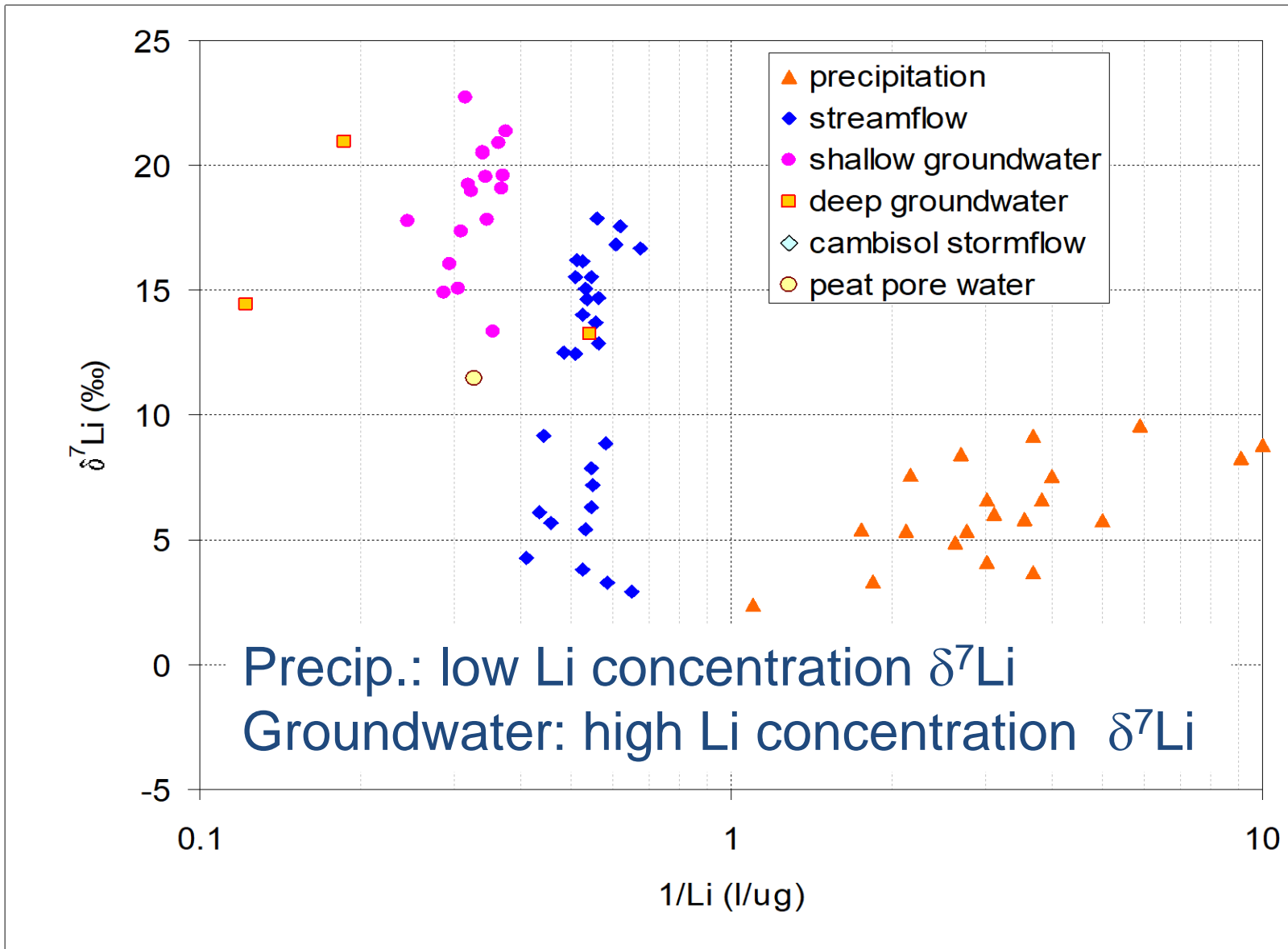
$\delta^2\text{H}$

deut. excess

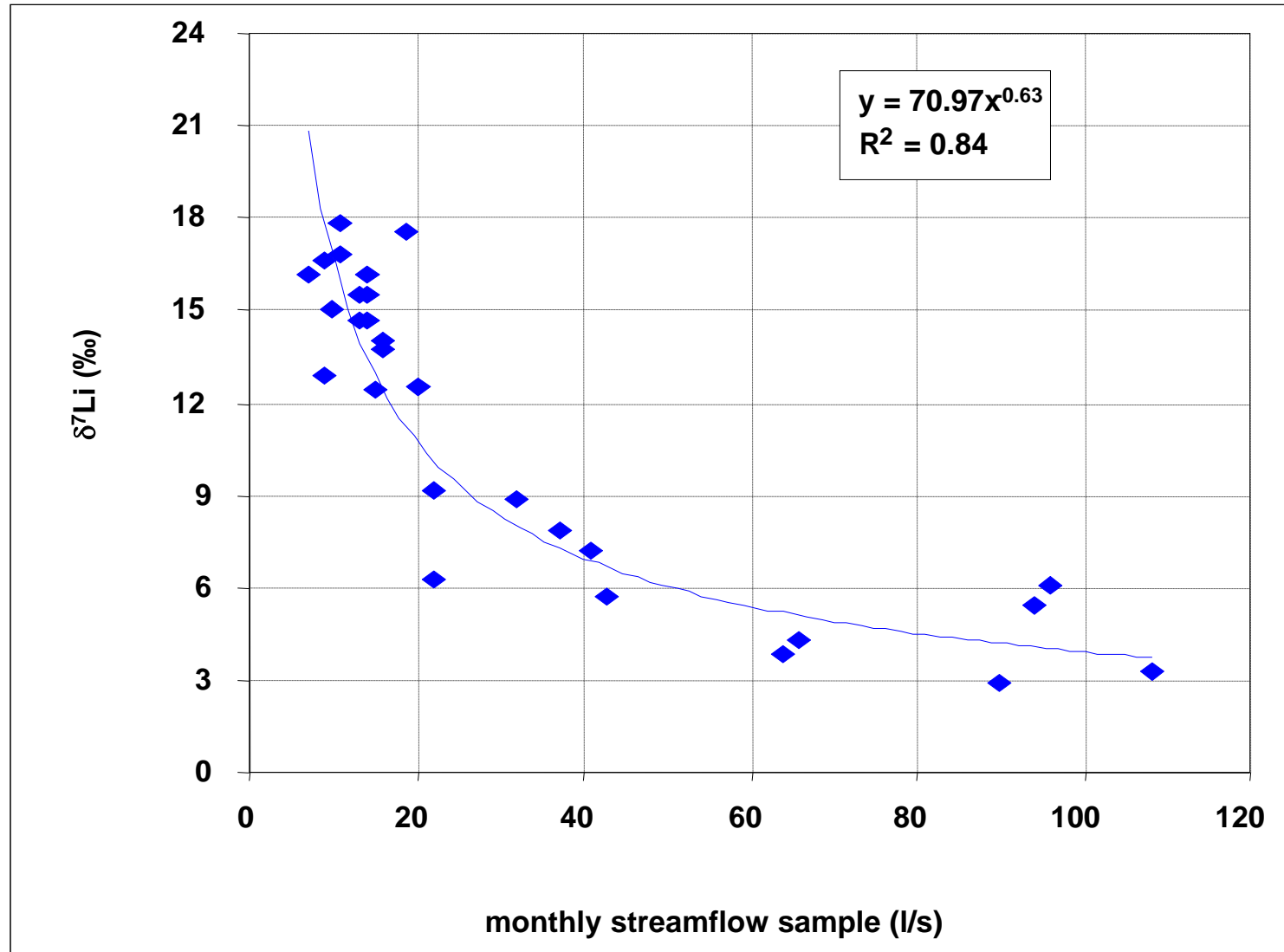


Mixed Jizera river water and local groundwater while pumped

# Li isotopes– causalities – end members

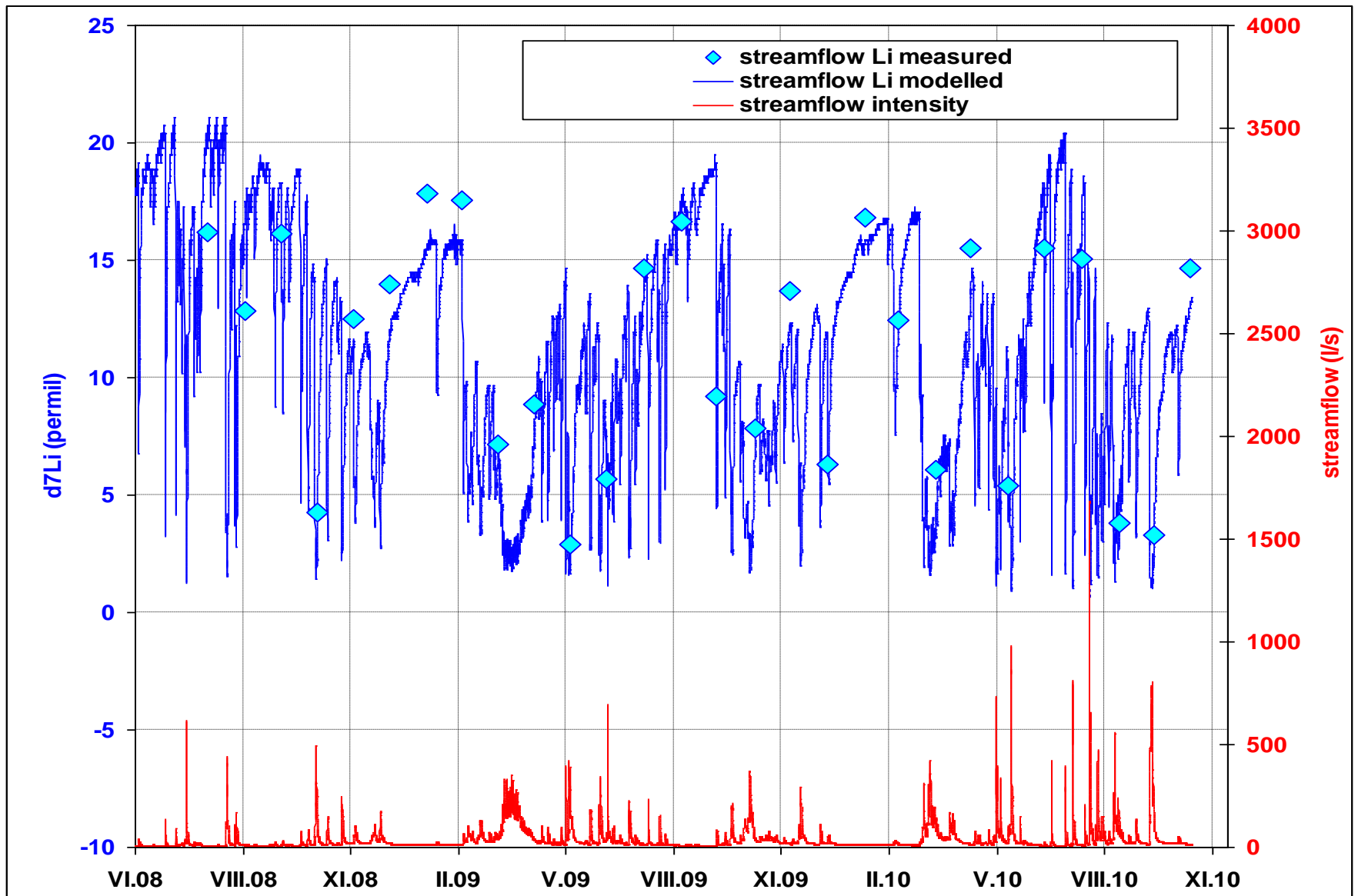


# “Rock” $\delta^7\text{Li}$ is present in baseflow Less present in event flow

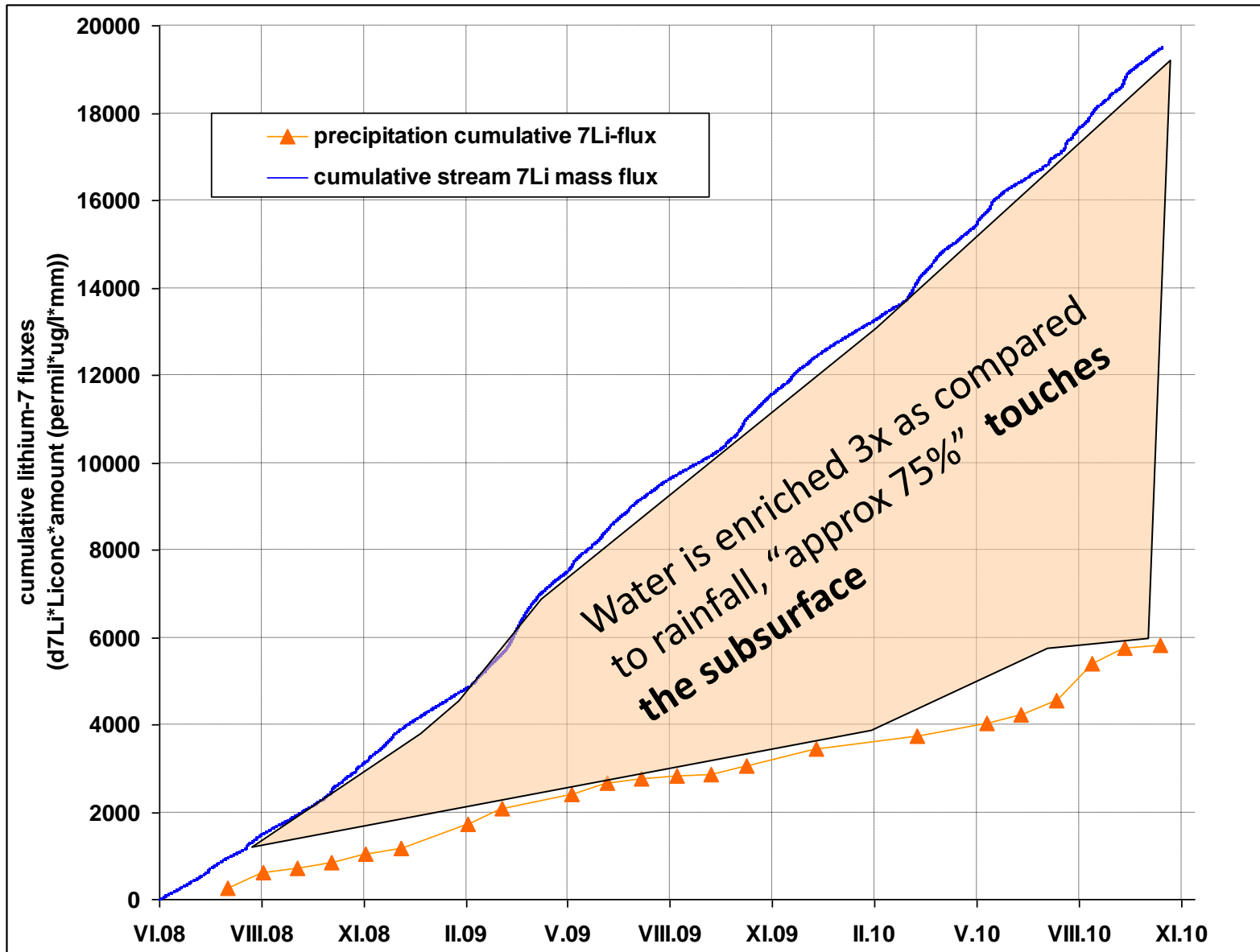




# Outflow and $\delta^7\text{Li}$ content



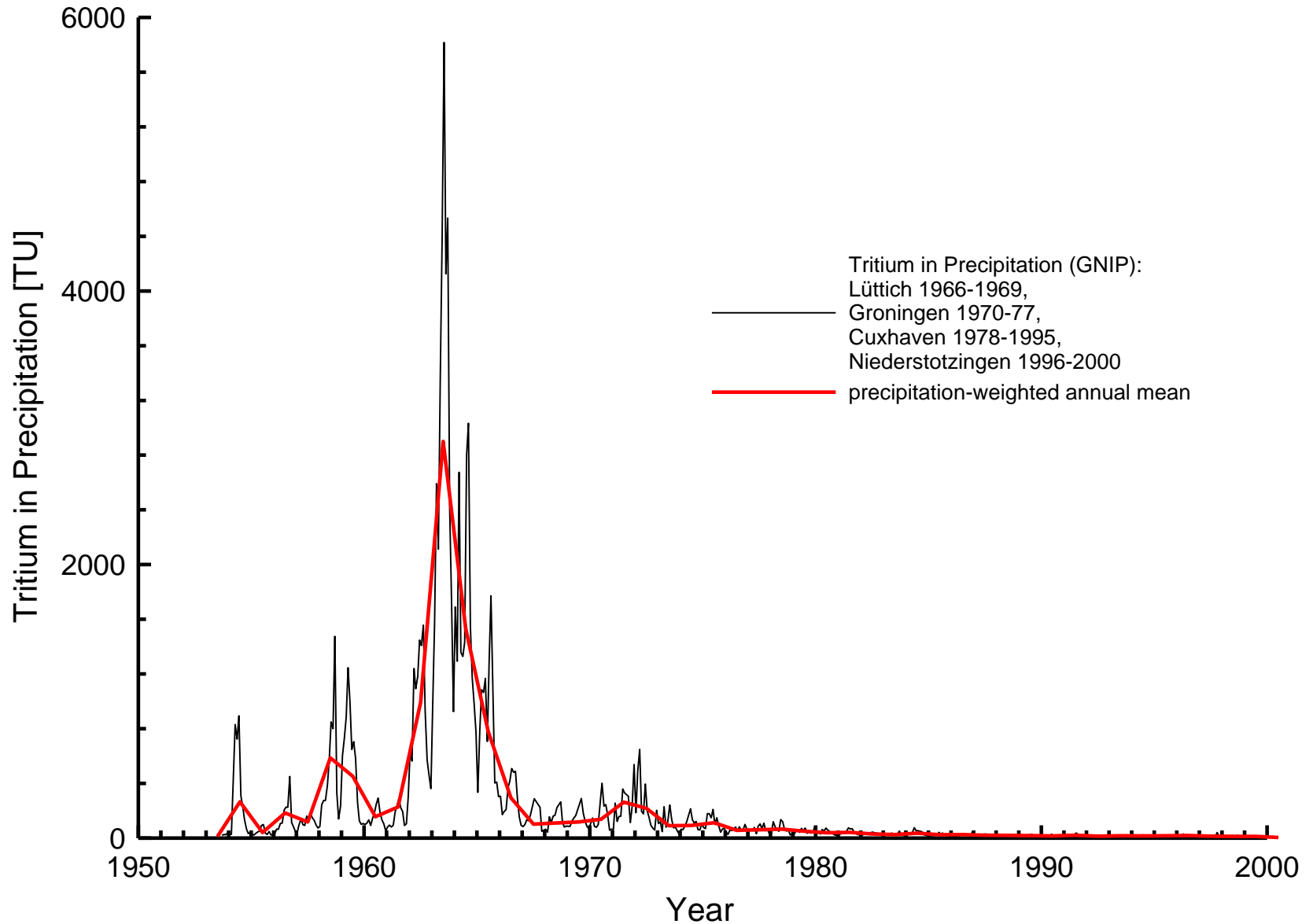
# cumulative mass flux of $\delta^7\text{Li}$



# Tritium / Helium



# Tritium input function

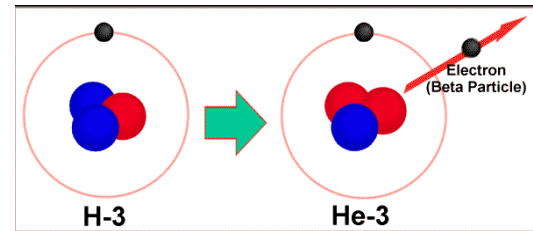


# Groundwater dating by T/He in multiscreen well



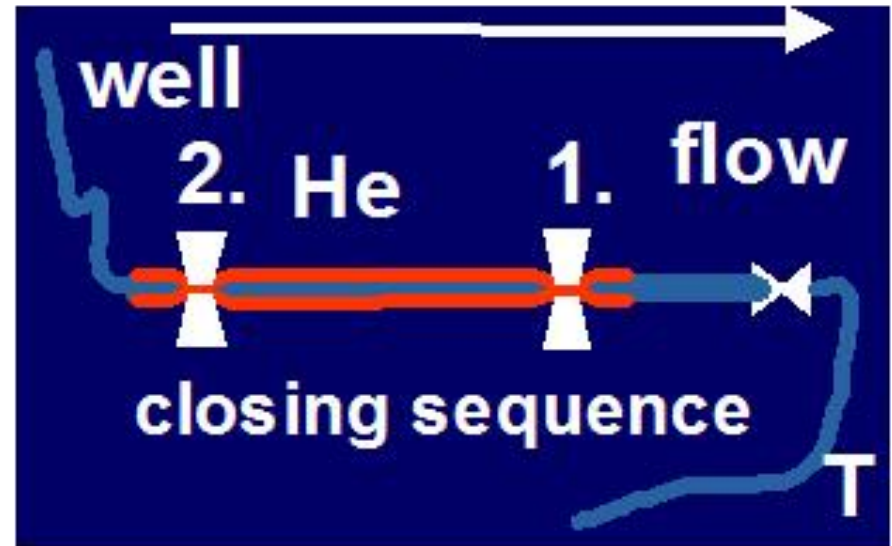
3 adjacent wells at  
the gauging station  
10,20,30 m deep

Tritiu to helium

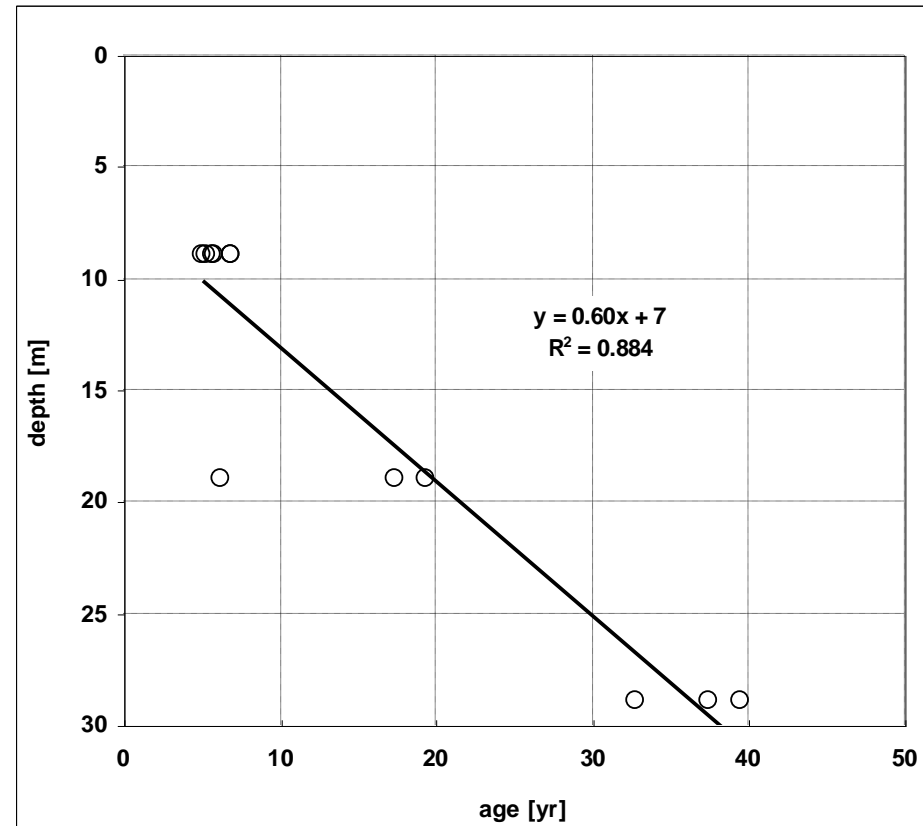
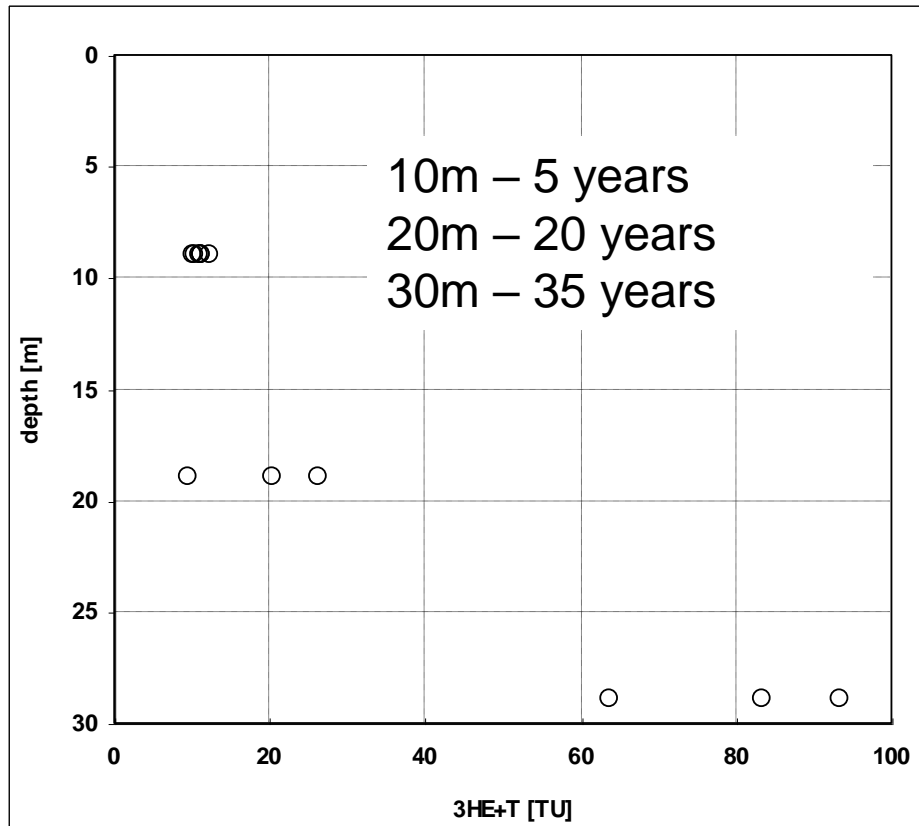


$$t_{1/2} = 12.33 \text{ years}$$

# Isotope sampling – copper tubes

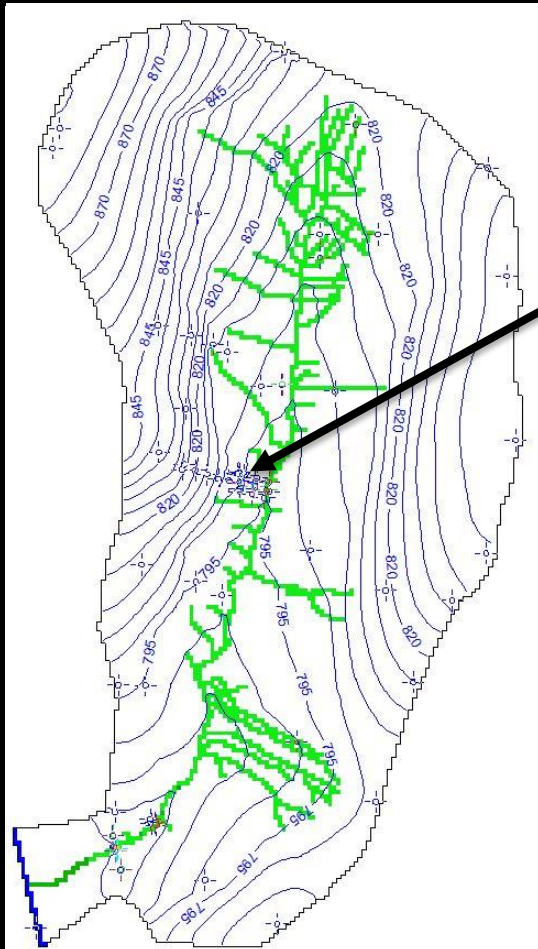


# T/He dating - 3 campaigns of sampling of multiscreen well by std. Cu tubes

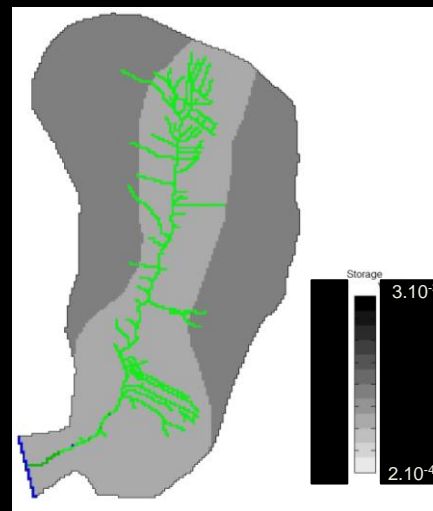
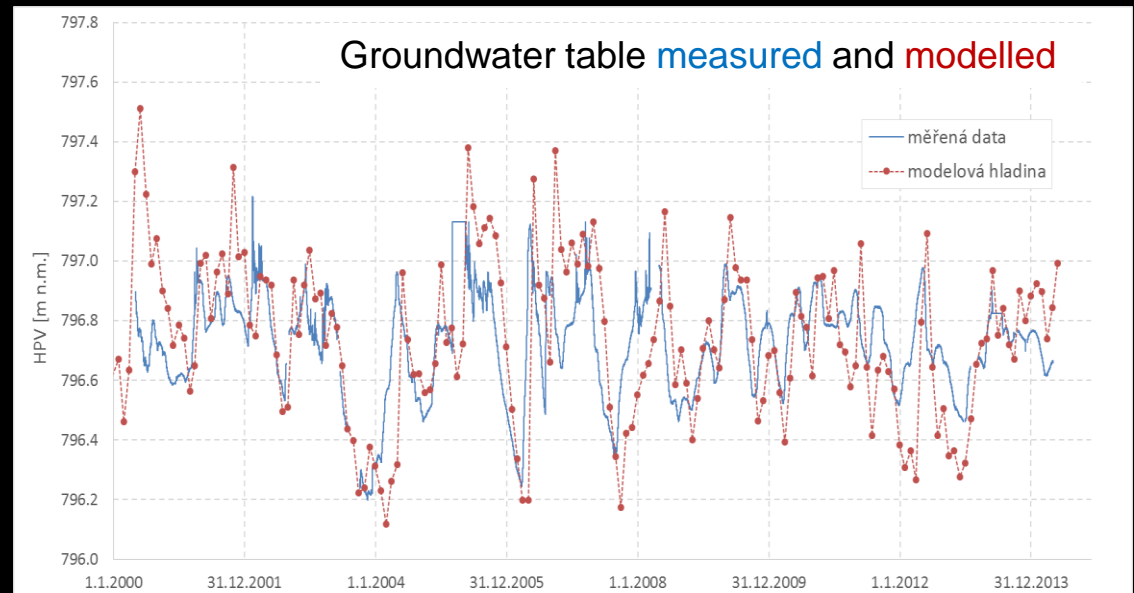


deep percolation of 0.6 m/year, i.e. assuming 20% porosity – 120 mm (10% of precipitation)

# Groundwater modelling using isotopes



Groundwater in calibrated model

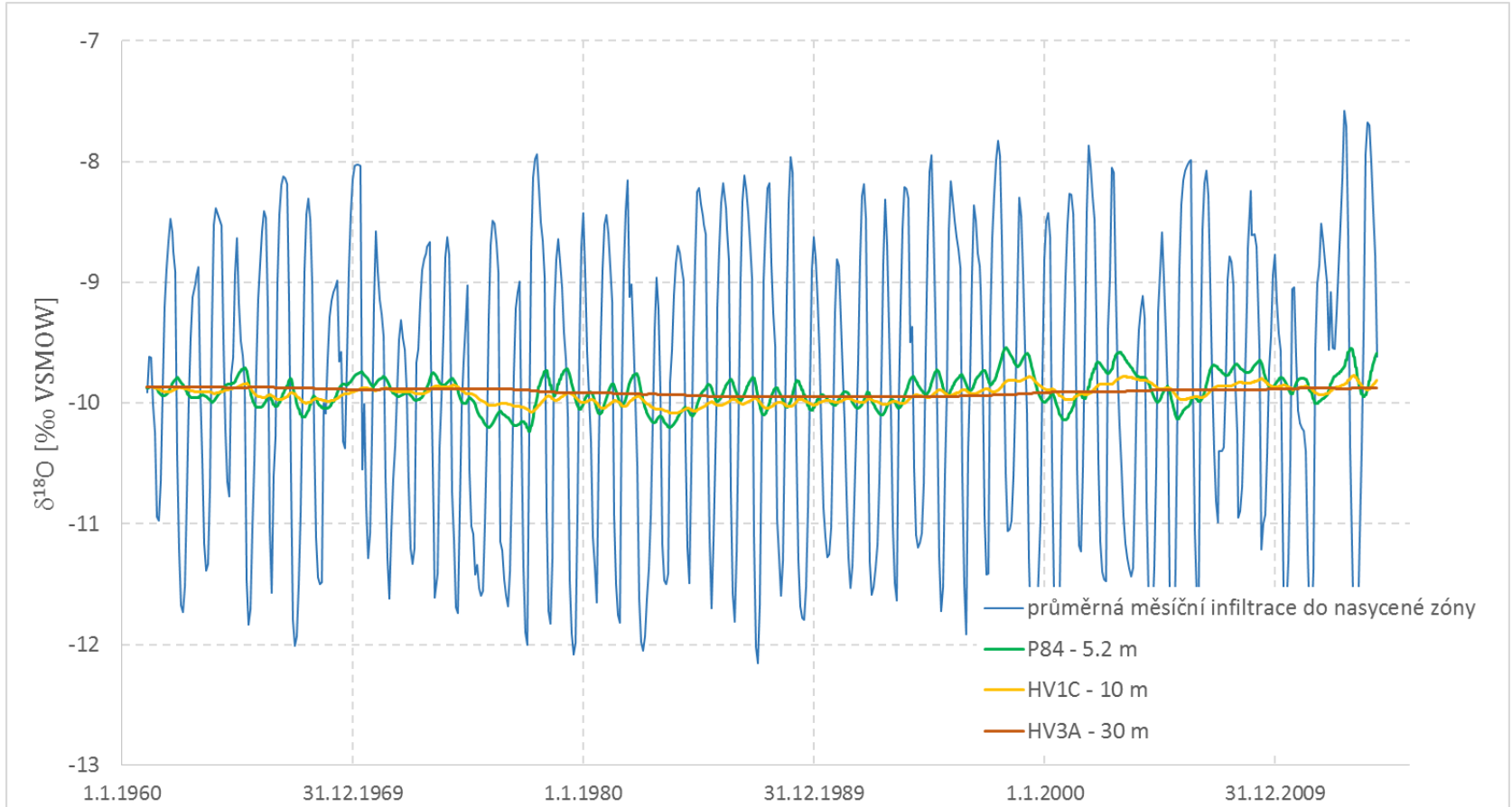


Storativity in first model layer



# Modelling of flow of groundwater and transport of $^{18}\text{O}$

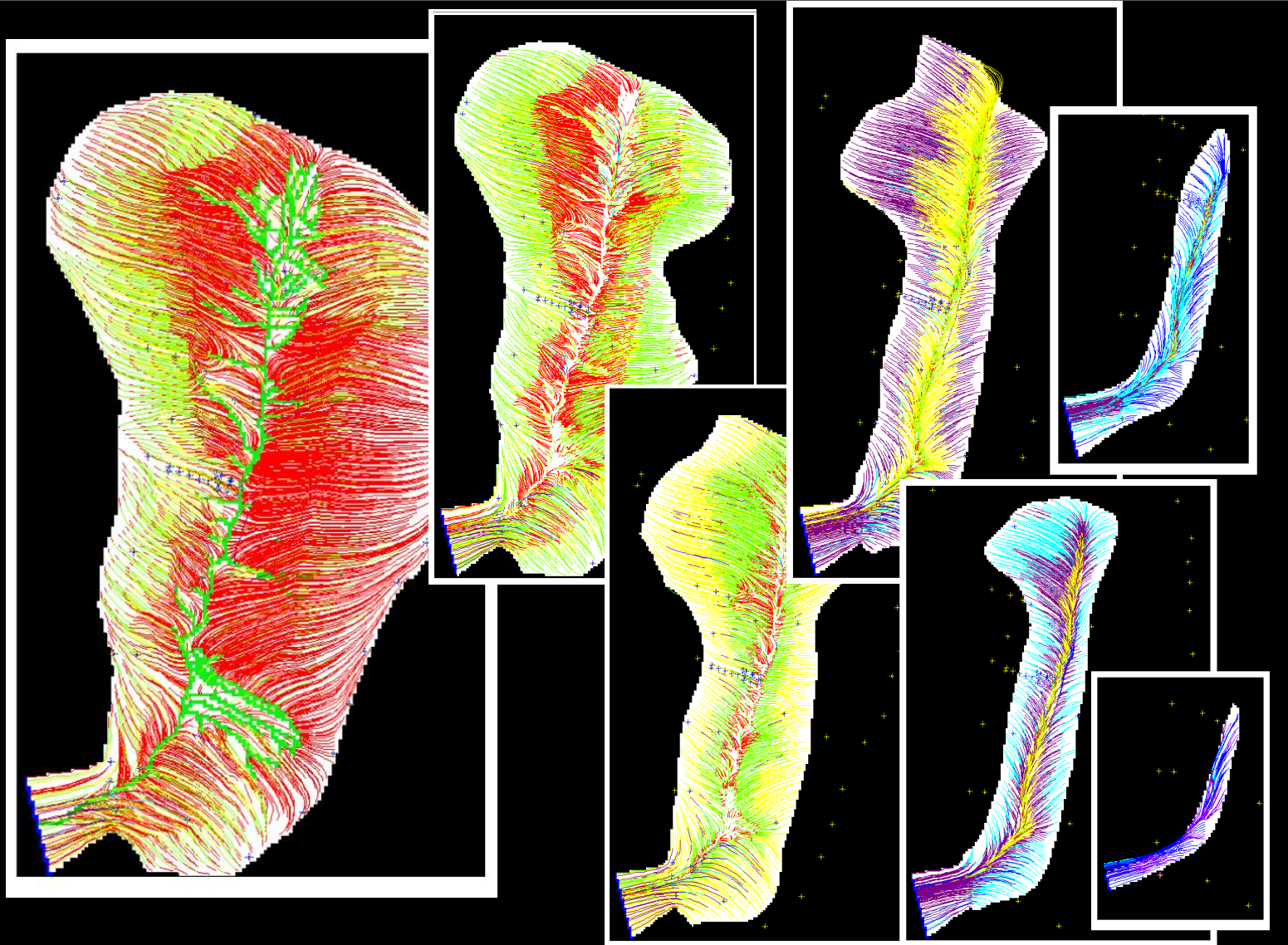
## MODFLOW, MT3D



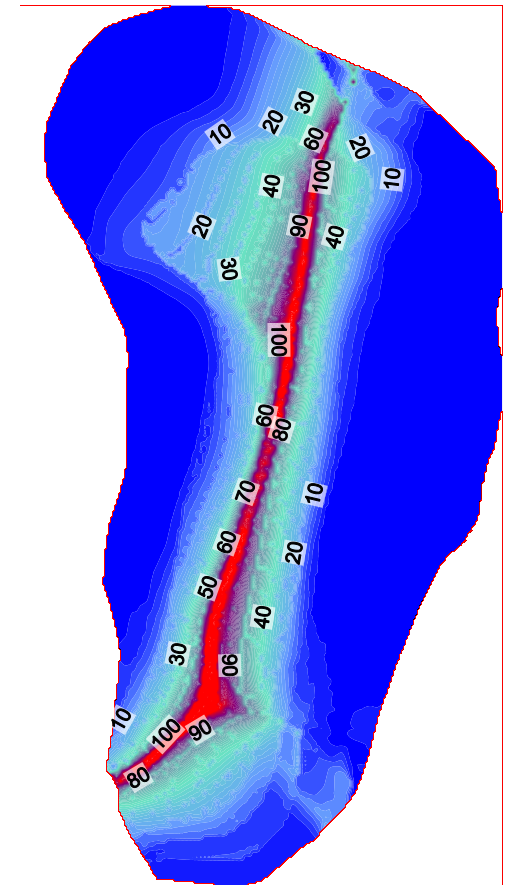
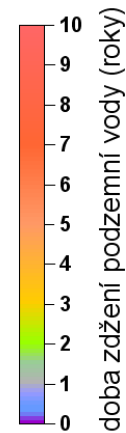
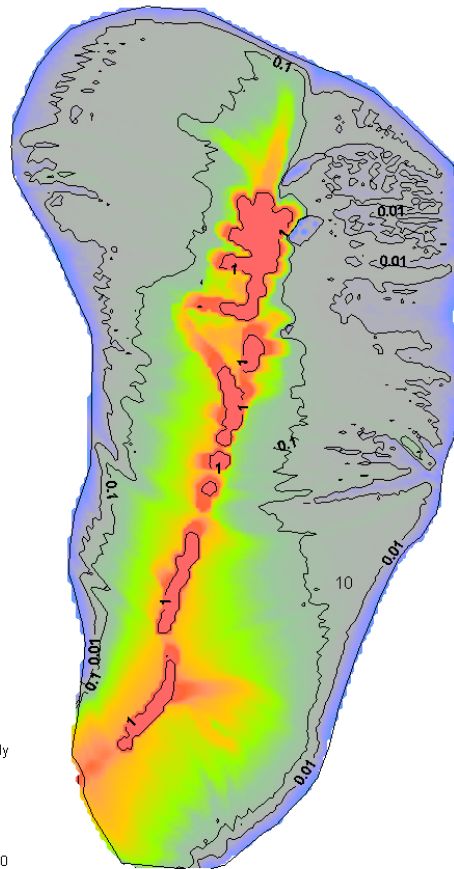
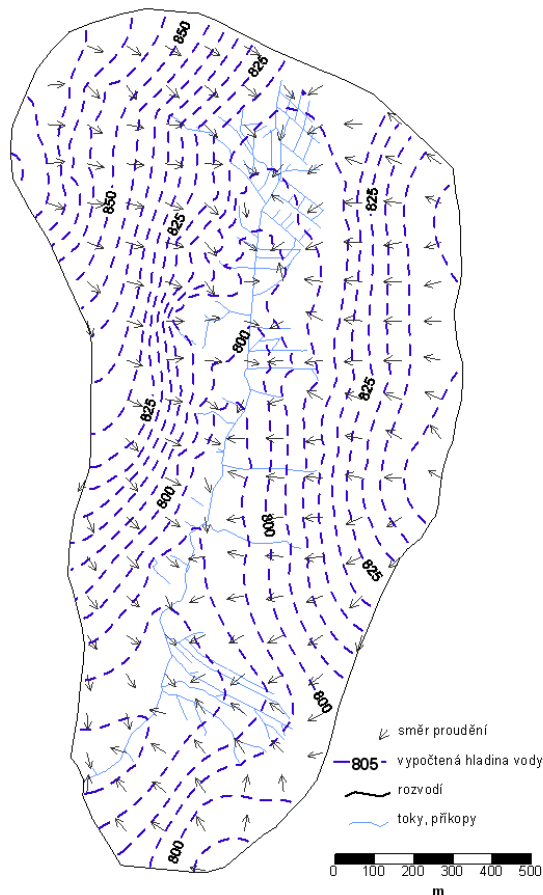
Confirmation of major mixing effect in the aquifer

Groundwater recharge isotopic concentration in blue series

# Particle tracking in MODPATH in all 7 layers

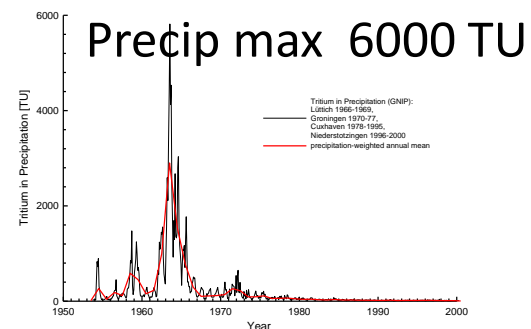


# Simplified version of 1 layer model with variable depth of the aquifer. Steady state (MODFLOW, MODPATH)

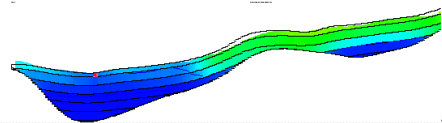


Groundwater table, isochrones (scale in years)

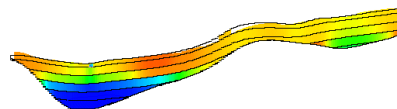
# Flow and tritium+helium transport



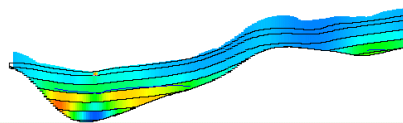
1961



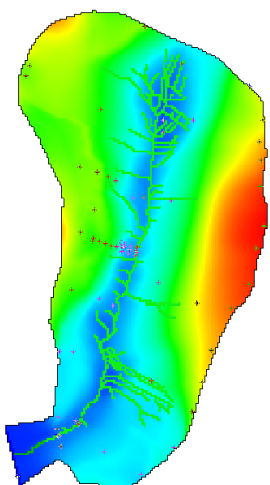
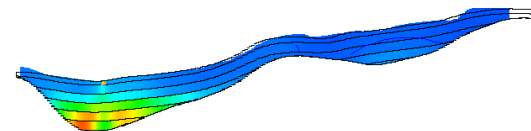
1966



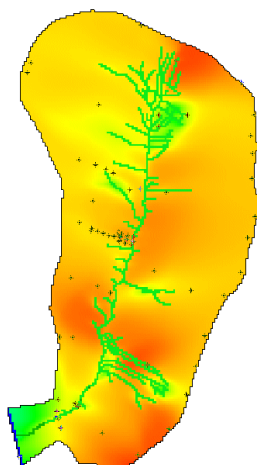
1986



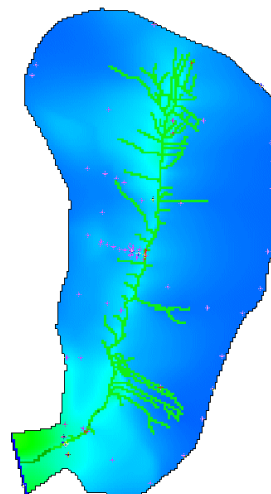
2014



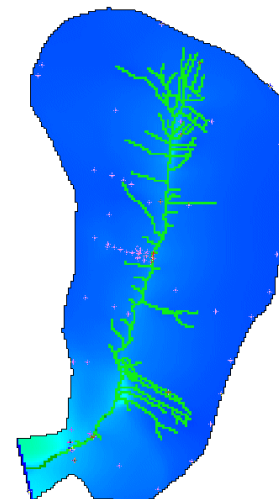
5- 660 TU



5-856 TU



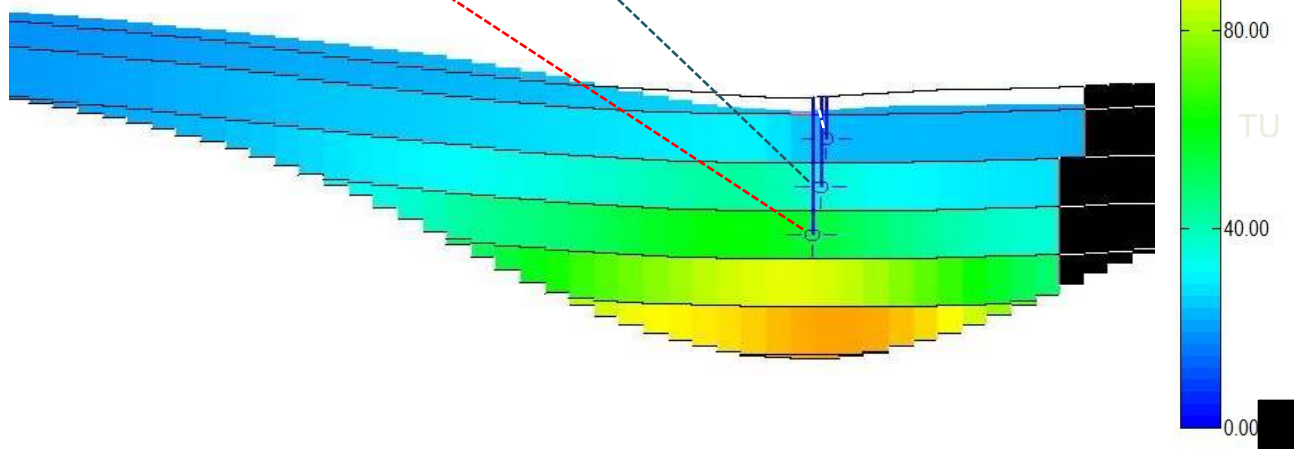
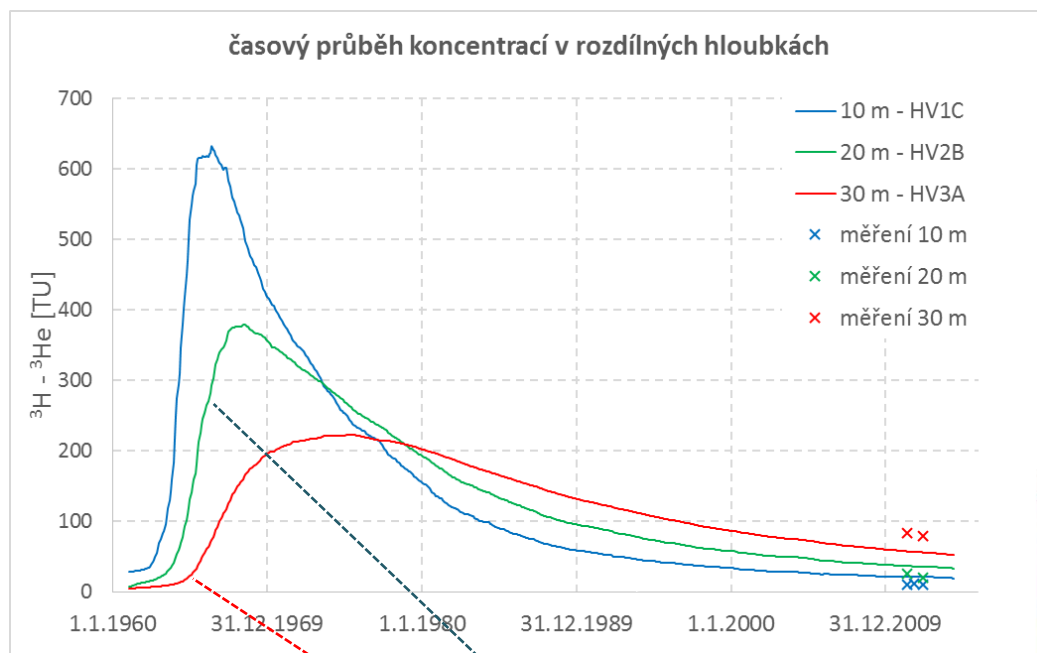
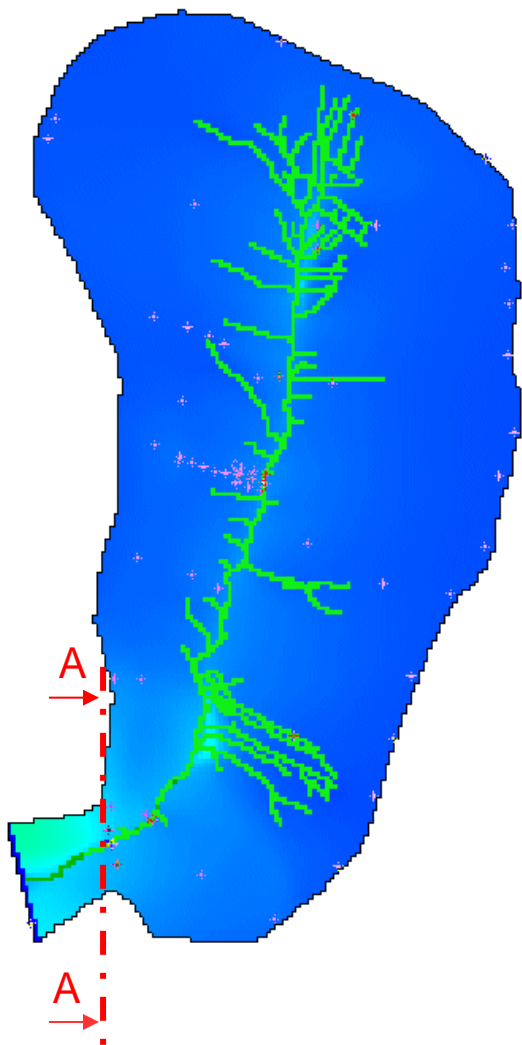
17-750 TU



5-100 TU

# Flow and tritium+helium transport

## Breakthrough in different depths



# Thanks to your attention

