Natural tracers in experimental hydrology

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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 km²)
(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
Possible travel paths of water

- Dystric cambisol on weathered granite
- Histosols on sediments
- Soils and aquifer sediments

Weathered granite
Resistivity (Ohm.m)
Solid granite
Possible travel paths of water
Soil profile upslope

*Cambrisols 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)
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)
Subcatchment Porsche (1.18 km$^2$) in Uhlířská

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

Numbers on contour lines indicate altitude (m a.s.l.)
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. Ca\(^{2+}\), SiO\(_2\)
Concentration change in water after contact with soil-rock environment – good for water origin

Isotopes: mostly stable \(^{18}\)O, \(^2\)H
Variable concentration in precipitation – good for water dynamics

Globally spread compounds (anthropogenic)
e.g. \(^3\)H-\(^3\)He, freons (CFC)
Changing concentration source in the atmosphere - good for age dating
Isotopes in natural environment

Example of 8 elements

Z (proton number)

N (neutron number)

IAEA-Int. Atomic Energy Agency
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 molecule

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

$^2\text{H}/^1\text{H} = 1.5576 \times 10^{-4}$ (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) \times 1000[\%]$  

$^{18}\text{O}$

$^{18}\text{O}/^{16}\text{O} = 2.0052 \times 10^{-3}$ (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) \times 1000[\%]$  

Concentration relative to V-SMOW  
(Vienna Standard Mean Ocean Water $\delta^{^2\text{H}}=0\%$, $\delta^{^{18}\text{O}}=0\%$)
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$^{th}$ molecule

Total molecular weight = 20
Stable isotopes of water molecule

“water with $^2$H(D)”, every cca $7000^{th}$ 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

Oceans $\delta^{18}O \approx 0\%$

Analogical for hydrogen $^1H$ a $^2H$
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
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

detector

computer

IAEA
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

- Epizodic rain
- Snow cover
- Weekly composited precipitation
- Monthly composited rain and snow

$d^{18}\text{O} \, (\%_{\text{VP-SMOW}})$

- 11.07
- 10.08
- 10.09
- 10.10
- 10.11
- 10.12
- 10.13
- 10.14
- 11.15
- 10.16
\( ^{18} \text{O} \) in soil runoff and streamflow

![Graph showing \( ^{18} \text{O} \) values over time](image)

- **Legend**:
  - red triangle: subsurface stormflow AB
  - black triangle: catchment streamflow UHL
  - blue circle: subcatchment streamflow POR

- **Y-axis**: \( ^{18} \text{O} \) (‰ V-SMOW)
- **X-axis**: Dates from 10.07 to 11.16
$^{18}\text{O}$ in Cambisol and Podzols pore water
$^{18}$O in Histosol pore water
$^{18}\text{O}$ in groundwater

- borehole HST, sediments 2.7 m deep
- borehole DST, sediments 3.7 m deep
- borehole P84, sediments 5.2 m deep
- borehole PST, sediments 2.3 m deep
Seasonal mixing of waters in the soils and groundwater

![Graph showing seasonal mixing of waters in the soils and groundwater](image-url)
Isotope decade 2007-2016

- d18O (‰ V-SMOW)

- precipitation
- downhill peat water
- groundwater
- uphill mineral soil water
Isotope decade 2007-2016

**Precipitation**

\[ y = -0.0513x + 94.581 \]

\[ y = 0.0106x - 31.313 \]

\[ y = 0.0757x - 164.16 \]

**Cambisol/Podzol**

\[ y = 0.0561x - 122.37 \]

**Histosol**

\[ y = 0.0429x - 96.26 \]

**Groundwater**

\[ y = 0.0308x - 72.394 \]
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 $^{18}$O signal in catchment waters

- Summer precipitation
- Winter precipitation
- Quick soil outflow
- Pore water in Cambisol
- Episode outflow in stream
- Total outflow in stream
- Baseflow in stream
- Pore water in Histosols
- Groundwater

$\delta^{18}O$ (%)
Gradual increase of SiO$_2$ in catchment waters

- Summer precipitation
- Winter precipitation
- Quick soil outflow
- Pore water in Cambisol
- Episode outflow in stream
- Total outflow in stream
- Baseflow in stream
- Pore water in Histosols
- Groundwater

![Box plot showing SiO$_2$ concentrations in different water sources.](image-url)
End members by $^{18}$O and SiO$_2$ in catchment waters
Response of streamflow to rainfall

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

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

$D = 7.48^*\text{O} + 6.87$

$R^2 = 0.97$

condensation

$měsíční srážky Uhlířská$

$měsíční srážky Uhlířská$

$měsíční průměrná teplota vzduchu (°C)$

$měsíční průměrná teplota vzduchu (°C)$

$\delta^{18}\text{O} = 0.32T - 12.15$

$R^2 = 0.73$
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

\[ d = \delta^2H - 8 \times \delta^{18}O \]

\( \delta^{18}O \) \hspace{1cm} \( \delta^2H \) \hspace{1cm} deut. excess

Mixed Jizera river water and local groundwater while pumped
Li isotopes – causalities – end members

Precip.: low Li concentration $\delta^7$Li
Groundwater: high Li concentration $\delta^7$Li
“Rock” $\delta^7$Li is present in baseflow
Less present in event flow

$y = 70.97x^{0.63}$
$R^2 = 0.84$
Outflow and $\delta^{7}$Li content

![Graph showing outflow and $\delta^{7}$Li content over time with streamflow Li measured, streamflow Li modelled, and streamflow intensity lines.](image-url)
cumulative mass flux of $\delta^7\text{Li}$

Water is enriched 3x as compared to rainfall, “approx 75%” touches the subsurface.
Tritium / Helium
Tritium input function

Tritium in Precipitation (GNIP):
Lüttich 1966-1969,
Groningen 1970-77,
Cuxhaven 1978-1995,
Niederstotzingen 1996-2000
precipitation-weighted annual mean
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

- 10m – 5 years
- 20m – 20 years
- 30m – 35 years

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

Groundwater table measured and modelled

Storativity in first model layer
Modelling of flow of groundwater and transport of $^{18}$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 layear model with variable depth of the aquifer. Steady state (MODFLOW, MODPATH)

Groundwater table, isochrones (scale in years)
Flow and tritium+helium transport

Tritium in Precipitation (GNIP):
- Lüttich 1966-1969,
- Groningen 1970-1977,
- Cuxhaven 1978-1995,

precipitation-weighted annual mean

Year
Tritium in Precipitation [TU]

Precip max 6000 TU


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