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Environmental tracers in experimental hydrology

Пріролені стоповаче в експериментальній гидрології

Summary

Naturally abundant ions, stable or radioactive isotopes and antropogeneous contaminants such as chlorofluorocarbons are useful environmental tracers allowing the hydrologists to precise the concepts of runoff formation. Tracer methods were introduced into hydrological research as complementary tools to conventional hydrologic methods for addressing questions of where water goes when it rains, what pathways it takes to streams and how long water resides in aquifers. They complement hydrological, meteorological, geological and geophysical observations to assess aquifer properties, water transport in soils, vegetation and atmosphere, and geochemical processes, which often cannot be measured in the field. Unlike most of dissolved ions, isotopes in both water and solutes are dominantly conservative (i.e. stable) or radioactive and can reliably trace the complex stream-aquifer or water-soil-rock interactions. The last decades have seen a rapid increase in isotope-based hydrological studies, largely carried out in small well-instrumented experimental catchments, on the order of 0.01 to 100 km² and located typically in headwater areas. In contrast, much potential waits to be realized in terms of how isotope information may be upscaled and test numerical flow, transport and rainfall-runoff models, and aid in the sustainable water resources management at larger scales. This lecture reviews the major applications of isotopes to catchment studies in Czech, Slovak and World context, and addresses a variety of prospective new directions in research and practice.

Key words:

runoff formation, bedrock and soil environment, geochemical indicators, stable isotopes of hydrogen and oxygen, non-stable tracers

Souhrn

Přirozené stopovače, jako např. přírodně dostupné ionty, stabilní nebo radioaktivní izotopy, nebo antropogenní kontaminace formou freonů poskytují hydrologům výjimečnou příležitost při upřesňování konceptů tvorby odtoku, jež často nemohou být vytvořeny na základě jiných terénních měření. Izotopové metody byly zavedeny do hydrologického výzkumu jako doplňkový nástroj ke konvenčním hydrologickým postupům pro zodpovězení otázek jak voda infiltruje pod terén, jakými cestami se ubírá k povrchovému toku a jak dlouho se zdržuje ve zvodních. Tyto metody často doplňují hydrologická, meteorologická, geologická a geofyzikální pozorování při poznávání podporchových geochemických procesů, vlastností zvodní a pohybu vody v půdě, vegetaci a atmosféře. Na rozdíl od většiny rozpuštěných iontů, izotopy ve vodě i pevné fázi jsou převážně konzervativní (t.j. stabilní) nebo radioaktivní a mohou tak důvěryhodně stopovat procesy v komplexu tok-zvodeň nebo voda-půda-hornina. V posledních dekadách byl zaznamenán rapidní nárůst izotopově orientovaných hydrologických studií, často prováděných v malých dobře vybavených experimentálních povodích o velikostech 0.01 až 100 km², zpravidla se nacházejících ve zdrojových oblastech tvorby odtoku. Potenciál izotopových postupů je ovšem zatím méně využit v přenosu informace mezi měřítky, testování numerických modelů proudění a transportu, srážko-odtokových modelů a hodnocení udržitelnosti hospodaření s vodními zdroji ve velkém měřítku. Tato přednáška přináší přehled hlavních aplikací v oblasti izotopové hydrologie v povodích České a Slovenské republiky, jakož i ve světovém kontextu, a dotýká se perspektiv nových směrů ve výzkumu a praxi.

Klíčová slova:

tvorba odtoku, horninové a půdní prostředí, geochemické indikátory, stabilní izotopy vodíku a kyslíku, nestabilní stopovače

Table of contents

1. Introduction	5
2. History of the tracers employment in hydrology	6
3. Stable isotopes in water molecule	8
4. Selected hydrological methods using stable isotopes	10
5. Laser spectroscopy as a modern analytical method for engineers	12
6. Use of isotopes in hydrology of the Czech and Slovak Republic.	12
7. Summary and outlook	18

1. Introduction

Headwater catchments in humid temperate mountainous regions of Central and Northern Euroasia and Northern America are abundant in precipitation and therefore crucial for determination of water quantity and quality of larger urbanized lowland basins. Water from the headwater catchments is often naturally preserved and serves as drinking water resource for communities located in foothills or adjacent territories. Principal factors controlling the rainfall-runoff processes in these catchments are relatively quick transformation of precipitation into streamflow, major role of snowcover and forests, and impact of deforestation and snowmelt. Simulation and prediction of floods, changes in runoff due to deforestation and prediction of snowmelt for operational purposes are therefore among the main objectives of headwater catchment hydrology. Headwater catchments became places of comprehensive hydrological monitoring and numerous rainfall-runoff models have been elaborated, calibrated and validated with monitoring data from headwater catchments.

Supported by the empirical observations, the rapid development of quantitative hydrological approaches largely satisfied the need for good fit in observed and simulated runoff from the catchment caused by precipitation or snowmelt. However, the accurate quantification of catchment runoff is not always accompanied by a relevant physical understanding as to which paths and mechanisms deliver water to the stream. Often the models provide good answers but not for good reasons, since they simplify the rainfall-runoff transformation and cannot properly evaluate the variety of hypotheses about the water travel pathways. Subsurface water flow, mixing and storage, although not directly measured and often underestimated, became therefore essential elements to be conceptually understood and incorporated into the catchment models. Three major environments with an essential impact on mixing and storage and runoff dynamics were identified – hillslope soil profiles, wetlands and fractured or porous bedrock. Their recharge via preferential flowpaths, communication among each other and interactions between the saturated and unsaturated zones are therefore of particular importance for understanding the complex nature of runoff formation in headwater catchments. Cycling of water and nutrients in wetlands is an important

additional key for understanding effects and consequences of acid rain and associated deforestation.

2. History of the tracers employment in hydrology

Since the 1960's, environmental tracers such as abundant ions, stable or radioactive isotopes or antropogeneous chlorofluorocarbons provide a substantial support to modern hydrology for precisising the concepts of runoff formation. The geochemical tracers include ions (e.g. Ca^{2+} , K^+ , Na^+ , Mg^{2+} , HCO_3^- , SO_4^{2-} , NO_3^- , NH_4^+ , Cl^-); metals e.g. Al, Fe; dissolved silica (SiO_2); dissolved organic carbon (DOC) or lumped parameters as temperature, pH or electrolytic conductivity. The most used of them are Cl^- , Ca^{2+} and SiO_2 , only rarely present in the rainwater, however found in the soil profile and bedrocks in abundance. A pioneering study in this context (Kennedy, 1971) describes the dissolution of silica from the soil matrix.

Environmental isotopes are present in molecules of both water itself and dissolved solutes, primarily SO_4^{2-} , NO_3^- and DOC. Whereas the water isotopes (stable ^2H and ^{18}O and radioactive ^3H) are part of water molecule itself and therefore unaffected by decay, reaction or chemical adsorption, isotopes of solutes (primarily ^{15}N , ^{34}S , ^{14}C , ^{13}C) and noble gases (^3He) are nonconservative and in addition less straightforward in sampling and analysis. The application of environmental isotopes in catchment hydrology has been therefore concentrated on the natural oxygen and hydrogen stable isotopes in water molecules.

Introduction of tracer approaches into catchment hydrology in the 1960's caused a major shift in understanding of hydrological processes in catchments. Isotopic (Dinçer et al, 1970) and chemical (Pinder and Jones, 1969) tracers promoted new concepts of the essential subsurface contribution to runoff events, which partly contradicted to the traditional concept of formation of quick surface runoff (Sklash and Farvolden, 1979). Whereas isotopic tracers revealed the portions of current rainfall and previously stored water in the event, hydrochemical tracers (principal cations and anions) proved to be able to identify spatial origin (typically saturated or unsaturated zone, or various geological settings, according to the chemical characteristics of the formations) of the runoff contributions. Solute isotopes such as ^{87}Sr (Stueber et al., 1987), ^{13}C , ^{34}S and ^{15}N (Kohl et al., 1971) have provided important information on biological and geological

sources of solutes delivered to surface water via discharged groundwater. Several other cosmogenic (^7Be , ^{10}Be , ^{24}Na , ^{41}Ca) and lithogenic (^6Li , ^{37}Cl , ^{11}B , ^{143}Nd , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{210}Pb) isotopes have been introduced into catchment hydrology research within the last two decades and many potential applications are yet to be utilized. Isotopic conservative tracers, particularly ^{18}O and ^2H , and principal ions quickly advanced to nearly-standard hydrological monitoring elements, and opened a wide spectrum of new research questions on how to explain the substantial role of subsurface waters even in small headwater catchments where the traditional view would assume a dominant role of near-surface flow. Extended subsurface mixing and relatively long groundwater flow times in catchments became prominent hydrological research objectives, formulated for example in McDonnell (2003): Where water goes when it rains, which pathways it takes and how long it resides in the subsurface.

The first global compilation of stable water isotopes in freshwaters was provided by Craig (1961). In the same year, the International Atomic Energy Agency and the World Meteorological Organization established the Global Network of Isotopes in Precipitation (GNIP) as the repository of isotope data in atmospheric waters (IAEA/WMO, 2006). Systematic measurements of isotope contents of river waters were carried out since the 1980's (e.g., Mook 1982). The adaptation of the lumped-parameter flow models for estimation of water residence times catchments (Małozzewski and Zuber, 1996) offered new insights into the rainfall-runoff response across river basin scales, for example in the Danube basin (Rank et al, 2003), and basins in Switzerland (Schotterer et al, 1993). Recently the IAEA has launched the complementary worldwide database Global Network of Isotope Data in Rivers GNIR (Vitvar et al, 2007). These data serve on one hand for local and regional water studies, on the other hand as global repositories for mapping spatial and temporal variability of isotope contents. A pioneering study on mapping of stable water isotope concentrations in rainfall and streams in the conterminous U.S.A. was performed by Kendall and Coplen (2001) and several approaches have been developed particularly for mapping and interpolation of GNIP data (Bowen and Ravenaugh, 2003). The thorough understanding of global isotope patterns in precipitation has led to efforts in coupling the isotopic balance of the atmosphere with runoff models and simulation of groundwater recharge (Henderson-Sellers et al, 2005). In the last years, isotope maps are being

produced (Bowen et al., 2007), mapping waters isotopically different from local precipitation (tapwater, irrigation return water, crops, etc.) and opening new research perspectives for the use of water isotopes.

3. Stable isotopes in water molecule

Hydrogen can be found as a stable isotope ^2H (D-deuterium) within the pool of more frequent isotope ^1H approximated to $^2\text{H}/^1\text{H}=0.00015$. Oxygen isotopes exist in the form of ^{16}O , ^{17}O and ^{18}O , with an approximate ratio $^{18}\text{O}/^{16}\text{O}=0.00204$ utilized more often than $^{17}\text{O}/^{16}\text{O}$ ratio. Isotopes can form alternative water molecules to the standard ones ($^1\text{H}_2^{16}\text{O}$), where two combinations are most frequent ($^1\text{H}_2^{18}\text{O}$; $^2\text{H}^1\text{H}^{16}\text{O}$). The conversion of the isotopic concentration in water for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ follows the equations (1) and (2)

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

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

where ^{18}O , ^{16}O , ^1H a ^2H are isotopic contents in water molecules and in standard of Vienna-Standard Mean Ocean Water (V-SMOW).

The application of water stable isotopes is based on the fact that the ratio of heavier to lighter isotopes changes on the phase interface. As the heat is applied to liquid water, more energy is required to move a heavier than a lighter atom into the vapour. Hence the isotopic content in precipitation and subsequently in streams and subsurface water depends on the temperature during condensation. Temporal fluctuations of the $\delta^{18}\text{O}$ ($\delta^2\text{H}$) are most pronounced when the temperature of precipitation is either significantly lower or higher than the averaged annual temperature. On contrary to, water masses infiltrated in the subsurface undergo various degrees of mixing. Thus, soil pore water and groundwater exhibit narrower amplitude of fluctuation closer to averaged isotopic content, because water masses of

different isotopic signatures contribute to a mixed pool of water with residence time of several years. This concept allowed that in the late 1960's and early 1970s, stable water isotopes and related hydrochemical tracers became a new tool to quantify the portion of streamflow discharged from aquifers (also referred as to groundwater runoff or baseflow) during stormflow events (Pinder and Jones, 1969; Dinger et al, 1970). The calculated substantial subsurface contribution to runoff events essentially contradicted to the traditional view of formation of quick surface runoff and caused a shift in understanding of the stream-aquifer interactions in headwater catchments. Based on the analyses of the content of stable water isotopes (^{18}O or ^2H), water already present in the small catchment prior to the rainfall (commonly referred to "old or "pre-event" water) is discharged to the stream and at the same time replaced by event water throughout the porous space. The mechanistic process is not understood completely. Secondly, using the isotopic content in rain, pre-event outflow or groundwater to determinate ratio of "old" and "new" water fractions in the streamflow, a contradiction is found when confronted with the same approach using basic elements such as silica or calcium. Kirchner (2003) proposes that there are several pools (or a continuum of stores) of pre-event water within the catchment, mobilized under different conditions.

The conceptualisation of subsurface mixing and storage in catchments is closely related to the isotopic assessment of water residence times or transit times through the subsurface from the point of infiltration to the exfiltration in streams, springs or captured wells. Although these applications traditionally contain a wide portfolio of approaches (^3H , ^3He , ^{14}C), the hydrology of small headwater catchments often focused only on stable isotopes of oxygen and hydrogen in water. This can be certainly justified by the consensus that the principal fluxes in headwater catchments are shorter than 4-5 years and therefore may be dominantly assessed by the isotopes of oxygen and hydrogen. On the other hand, the new findings on the substantial role of subsurface mixing and storage in catchments require application of approaches which can describe recharge, fluxes and discharge of very short to very long travel times. The modern experimental hydrology therefore tends to the use of multi-tracer approaches, where the hydrochemical and isotopic tracers complement each other and conceptualise more realistically the rainfall-runoff process.

4. Selected hydrological methods using stable isotopes

The amount of ^{18}O and ^2H entering the catchment in form of precipitation is proportional to several climatic and geographical factors (e.g., Gat, 2009) in particular the amount and intensity of precipitation and the temperature during the rainout. The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is called „deuterium excess“

$$d = \delta^2\text{H} - 8 * \delta^{18}\text{O} \quad (3)$$

Where d is deuterium excess, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are isotopic concentrations.

This parameter characterizes the intensity of atmospheric recycling of the repeatedly evaporated and precipitated water before the contact of water with the surface. It enables to evaluate, on regional and larger scales, origin and thermal conditions of air masses causing the precipitation. Deuterium excess is also important quantitative measure for the evaporation from open water bodies (Gat, 2009).

The concept of climate-based fluctuations of ^{18}O and ^2H in precipitation and consequently in surface and subsurface waters provides the methodological base of the two essential approaches in the catchment isotope hydrology mentioned above – first, the quantification of the groundwater contribution to runoff, and second, the estimation of water residence times in streams and aquifers.

The calculation of the groundwater contribution to stream runoff is based on the assumption that during runoff events ^{18}O or ^2H have significantly different concentrations in stream and the falling precipitation (Sklash and Farvolden, 1979). High frequency isotope data are employed in the following set of equations:

$$Q_t = Q_s + Q_n \quad (4)$$

$$c_t Q_t = c_s Q_s + c_n Q_n \quad (5)$$

$$R_s = \frac{Q_s}{Q_t} = \frac{c_t - c_n}{c_s - c_n} \quad (6)$$

where: Q_t is total outflow, Q_s is the amount of pre-event water in the outflow, Q_n is the amount of the event water in the outflow, c_s is the concentration of tracer (e.g. $\delta^{18}\text{O}$) in the streamwater prior to the event, c_n is the

concentration of tracer in the streamwater during the event, R_s is the instantaneous fraction of pre-event water in the outflow during the event (-). This concept highlights the dominant role of subsurface runoff during rainfall-runoff episodes and caused in the 1960's the reevaluation of original concepts where surface flow was the prevailing component of stream runoff. In recent decades there is a growing effort to employ the results of isotopic runoff component separation as meaningful parameters of rainfall-runoff models (Seibert and McDonnell, 2002).

Second dominant isotope hydrology approach is the estimation of the subsurface water mean residence time, i.e. the time which elapses between infiltration and discharge of water in catchments. This method is based on the fact that the annual fluctuation of ^{18}O and ^2H in precipitation has a nearly sinusoidal form. Water infiltrating into the subsurface typically undergoes mixing with water already present in the catchment, thus attenuating the input amplitude of isotopes in precipitation. This concept of muted isotope records has been elaborated by Małozewski and Zuber (1996) and employed in many catchments (e.g. Soulsby et al, 2000).

Seasonal function of $\delta^{18}\text{O}$ or $\delta^2\text{H}$ fluctuation in monthly rainfall is fitted by a sine function. Mean Residence Time is derived according to the equation (7) expressing decrease of the input amplitude (A_p) and output amplitude (e.g. in runoff A) in the linear reservoir. $((1/b') = 6/2\pi)$ is conversion factor for time unit in months).

$$MRT = \left(\frac{1}{b'}\right) \left[\left(\frac{A_p}{A}\right)^2 - 1 \right]^{0.5} \quad (7)$$

This approach has been applied in several catchments (Soulsby et al., 2000; Holko et al., 2008).

Fluctuations of ^{18}O and ^2H in temperate climate rainfall typically attenuate completely in the aquifer within 4-5 years, due to consecutive mixing from several seasons. Therefore larger catchments and deeper aquifers must be examined by other methods, such as isotopes ^3H or ^3He , dating waters present in catchments for between 5 years and several decades (Michel, 2004). The time factor in rainfall-runoff relation is also instrumental for the

assessment of groundwater vulnerability, groundwater recharge and possible cleanup of infiltrated contamination.

5. Laser spectroscopy as a modern analytical method for engineers

The recently developed laser spectroscopic apparatus for water isotope analyses provides accuracy and precision required (Penna et al., 2010) in hydrological measurements to complement the traditional isotope ratio mass spectrometry (IRMS) technique in the field of analytical isotopic detection (IAEA, 2007). This new less laborious, yet acceptably precise approach, gives to the hydrological community a new powerful tool for enhanced hydrological monitoring in space and time. Until present, the use of water isotopes in hydrology was usually limited to monthly averaged or sampled components of the hydrological cycle in catchment. Due to high analytical costs of the mass spectrometer, only a limited number of studies provided detailed data of ^{18}O or ^2H on the daily or hourly basis or even shorter time step. Since the laser spectroscopic technique is applicable almost as daily routine and can be linked to IRMS as calibration procedure, an extended sampling of the water cycle components (rainfall, soil water, groundwater and stream outflow) may quickly become a standard for hydrological studies in catchments. These isotopic datasets with high degree of spatial and temporal resolution can support building of innovative concepts and hypotheses about runoff formation and related hydrological processes in catchments.

6. Use of isotopes in hydrology of the Czech and Slovak Republic

First use of isotopes in the catchment hydrology in former Czechoslovakia is known from Dinçer et al. (1970) and his original method of runoff components separation during the period of snowmelt in Modrý potok, Krkonoše Mts. Further isotopic studies in the Czech and Slovak republic were presented in Bůzek et al. (1995) and Kantor et al. (1987). Isotope methods applied in the last decades in the Czech Geological Survey include hydrology (Bůzek et al., 1995; Bůzek et al., 2009), and biogeochemistry (Hruška and Krám, 2003) where isotopes of sulphur (Novák et al., 2005) and nitrogen (Oulehle et al., 2008) detect origin and cycling of elements in catchments. Measurements and interpretation of radioactive isotopes of hydrogen (^3H) and carbon (^{14}C) at the Faculty of Science, Charles university (Šilar, 2003; Vysoká et al., 2008; Jiráková et al., 2010) complemented the

work of the Czech Geological Survey. First longterm isotope hydrological observation was introduced by CTU in Prague, Faculty of Civil Engineering in 2006 at the experimental catchments of Jizera Mts., namely Uhlířská (Šanda et al., 2010). At present, this institution is a regional center for isotopic analysis of stable oxygen and stable hydrogen by means of laser spectroscopy. High throughput of samples also enables application of stable water isotopes in the field of modelling flow and transport in porous media (Vogel et al., 2010).

The catchment of Jalovecký creek, Slovakia, has been monitored for stable water isotopes since 1990 (Holko and Kostka, 2006). Analytical support of Geological institute of Dionýz Štúr also enables isotope applications in other parts of the country, such as karst formations (Malík et al., 1993). Catchments of Uhlířská and Jalovecký creek are national representatives in the networks GNIP and GNIR (IAEA/WMO, 2006; Vitvar et al., 2007).

The headwater catchments in the Jizera Mts. became a leading research facility of regional and continental importance in the last 10 years. Their geographical and ecological settings present a typical Central European temperate boreal zone with large amount of precipitation, humid climate, relatively preserved nature and a recent history of deforestation due to acid rain impact in the 1980-1990's. First hydrological data were collected in 1982 and the catchments were subsequently equipped with monitoring and sampling network. Synthetical works covering the first phase of monitoring (Kulasová et al., 2006) revealed, for example, that deforestation caused by acid rain did not result in any significant increase of streamflow, indicating that there must be a major groundwater storage of buffering effect on runoff. Further studies (Dragomir, 2007) showed that the stream carries a relatively high portion of subsurface baseflow, accounted later by Šanda et al. (2009) to preferential recharge on the boundary between soil and fractured bedrock. Hrněří et al. (2010) evaluated the factors controlling the frequency and magnitude of runoff events and highlighted the antecedent soil wetness as particular impact.

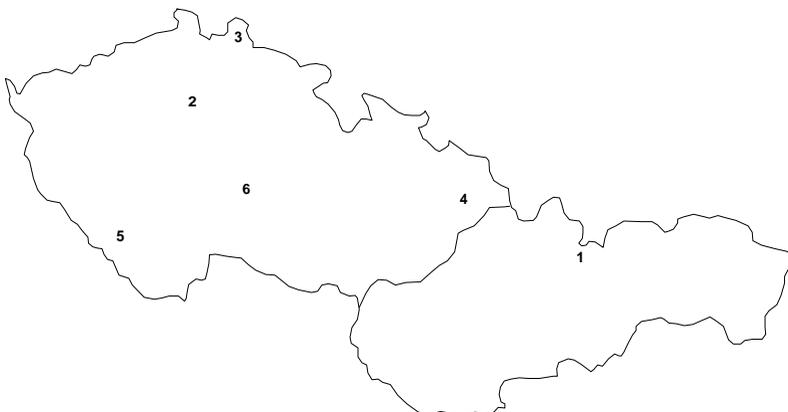


Figure. 1: Permanently monitored sites for oxygen and hydrogen isotopic content in water in Central European region (ordered by duration of sampling) 1. Jalovecký creek in Western Tatras, 2. lower Jizera at its outlet, 3. Jizera Mts. (Uhlířská, Jezdecká, Smědava I, Velká jizerská louka catchments), 4. Červík in Beskydy Mts., 5. Liz in Šumava Mts., 6. Kopaninský creek at Bohemo-Moravian highland

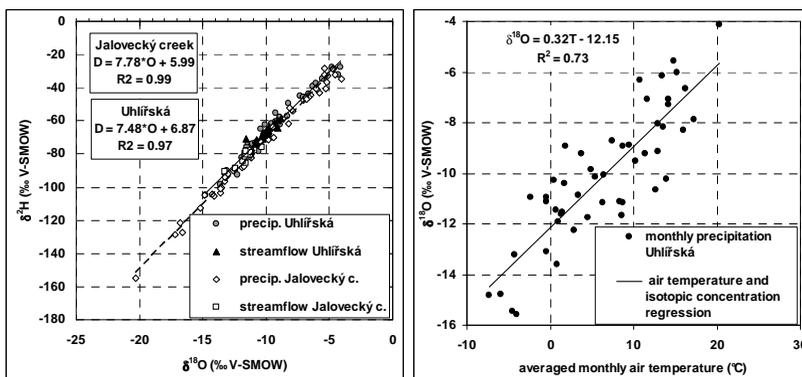


Fig. 2: Relation of ^{18}O and ^2H in precipitation and stream outflow at Uhlířská and Jalovecký creek (left) and linear regression of ^{18}O and averaged monthly air temperature at Uhlířská (right).

Samples of liquid and solid precipitation and streamwater are typically collected in monthly, weekly, daily or event based step. They are complemented by samples of soil pore water, groundwater, subsurface stormflow, snowmelt or snow profile at selected locations.

Fig. 2 (left) presents relationship of ^{18}O and ^2H isotopes in precipitation and stream outflow at Uhlířská and Jalovecký creek catchments. Because the measured values follow the Local Meteoric Water Line (LMWL), it is obvious that surface waters originate in local precipitation with limited to none evaporation. Fig. 2 (right) demonstrates that increasing air temperature (here for Uhlířská catchment) is one of key factors of higher concentration of heavier isotopes.

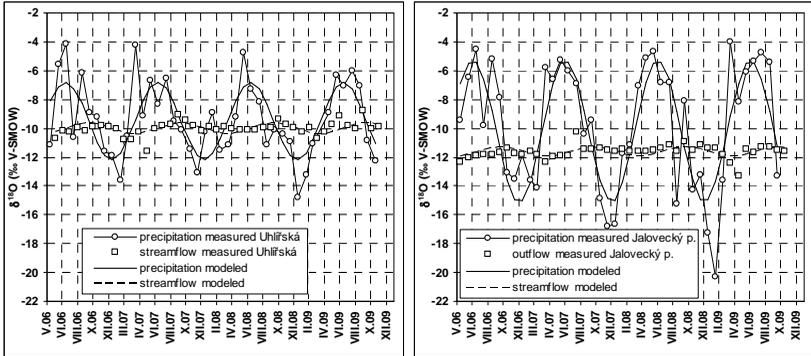


Fig. 3: Concentration of ^{18}O in precipitation and streamflow at Uhlířská (left) and Jalovecký creek (right)

Fig. 3 presents the comparison of ^{18}O concentration record in precipitation and stream flow over 3 years. Relatively regular record of isotopic concentration in precipitation according to the averaged monthly temperature in sinusoidal cycles is fitted by the least square regression. Mixing of water in the subsurface causes an attenuation of the amplitudes of ^{18}O concentration from precipitation to outflow. This transformation is quantified by eq. 7 and depends on the average period for which water is residing in the catchment, so called mean residence time (MRT). The Uhlířská catchment shows MRT approximately of 7 months and Jalovecký creek MRT is in the range of 14 months. Longer MRT for Jalovecký creek can be explained with the retardation effect of fissure flow in groundwater system with high capacity to retain sparse summer infiltration, and major effect of infiltration during snowmelt. This effect is less pronounced at Uhlířská, due to quick communication of soil profile, weathered granitic mantle and crystalline bedrock.

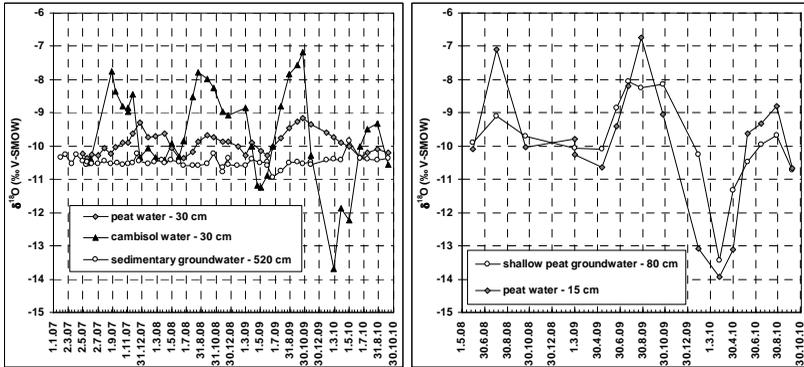


Fig. 4: Isotopic content of ^{18}O in peat and groundwater: Uhlířská fens (left) Mires of Jizera bogs (right).

Fig. 4 shows differences in ^{18}O concentration records in peat and groundwater at Uhlířská and Mires of Jizera (Big Jizera Meadow). At Uhlířská fens (left), waters in peat are well mixed due to discharge of very well mixed groundwater. In contrary to Mires of Jizera bogs do not contribute to the groundwater discharge, facilitating instead a vertical infiltration of precipitation.

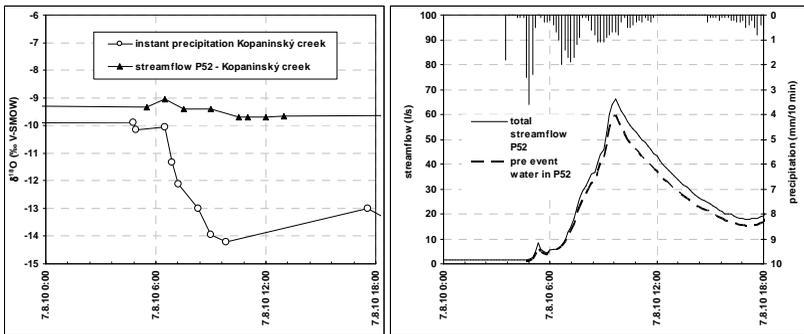


Fig. 5: Isotopic separation of a significant summer storm at Kopaninský tok (Bohemo-Moravian highlands)

Fig. 5 demonstrates an example of isotopic separation of a significant summer storm event in tiled agricultural catchment with depletion of heavier oxygen isotope during the event. Despite the pronounced decrease of the ^{18}O concentration in the precipitation, only a slight decrease of the

^{18}O concentration in the outflow (left) reveals that the essential amount of water forming the flood originates from soil and groundwater (right).

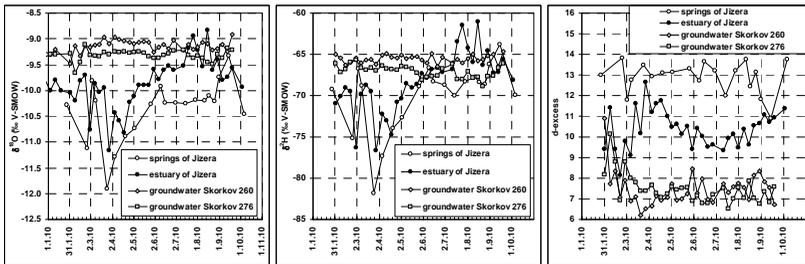


Fig. 6: Isotopic composition of upper and lower Jizera flow and groundwater for ^{18}O (left), ^2H (middle), deuterium excess (right).

Fig. 6 elucidates the synthetical interpretation of ^{18}O and ^2H isotopes in deuterium excess values. Concentrations of individual isotopes ^{18}O and ^2H (left and middle) highlight the impact of mountainous snowmelt on the Jizera stream and, in contrary, a relatively constant isotopic concentration of local groundwater at lower Jizera basin. The deuterium excess, however, continuously distinguishes the impact of these end-members on the interaction of the Jizera river with the local aquifers, in particular during spring and autumn when the end-members have very similar isotopic concentrations. Higher altitudes of springs of Jizera show higher deuterium excess values, the outlet of Jizera to Labe at Předměrice is a mixture of waters including regional averaged precipitation over the entire catchment, and local groundwater at the Jizera outlet is a product of local rainfall in the lowest Jizera location. Fig. 6 (right) shows therefore a relatively high deuterium excess for the lower Jizera river, indicating that a significant portion of water comes from the upland region and only a small portion is from exfiltrated groundwater along the lower reaches. Overlapping values of deuterium excess for the local groundwater and the low Jizera river show the forced river bank filtration to the wells as a result of drinking water production for the Central Bohemia.

7. Summary and outlook

This lecture summarizes the use of environmental tracers in catchment hydrology with emphasis on the stable isotopes of hydrogen and oxygen in water. Their main contribution lies in the improvement of runoff formation concepts, particularly in terms of origin and velocity of subsurface flow. In order to provide complex picture of the catchment functionality on both small and large scale, multi-tracer methods must be applied, complementing the hydrological, hydrochemical and geophysical approaches. Much potential is available in development of isotope analytical techniques, which can on one hand further promote highly resolved monitoring of stable water isotopes (e.g., through the laser spectroscopy), on the other hand facilitate the use of radioactive and non-conservative isotopes for the assessment of groundwater recharge and flow in larger catchments and aquifers. Isotopes of ^3H (tritium) decaying into ^3He , or selected chlorofluorocarbons, are good examples of how precised analytical techniques may promote innovative complementary applications.

Another perspective field of isotope approaches is the assessment of carbon sequestrations and other environmental liquid and gaseous fluxes during the climate change. These approaches combine chemical monitoring with isotope analysis of water, gases and nutrients (such as CO_2 , CH_4 or NO_x) and may be supported by recent progress in laser spectrometry measurements of stable isotopes ^{13}C or ^{15}N .

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