

Isotopic study of nitrates and bicarbonates in mineral waters of the Southeast Poland

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The territory of Southeast Poland, and especially its southern part, is rich in various mineral and therapeutic waters of high quality. The balneological resources of the region and in particular its mineral and therapeutic waters of Iwonicz Spa, Lubatówka and Horyniec Spa are exceptionally precious.

Isotope studies of $\delta^{13}\text{C}$ in bicarbonate ions were conducted, and they were used to prove the hypothesis about the origin of the Iwonicz Spa and Lubatówka water. The observed variation of $\delta^{13}\text{C}$ in bicarbonate ion ranges from -5.0 to $+24.0$ per mill PDB.

On the other hand, isotope methods with double markers, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- ions were used to identify the origin of nitrates in Iwonicz Spa and Horyniec Spa waters. Because nitrates from different sources have different isotope compositions, it is possible to test the quality of water and identify alteration processes of nitrate compounds in the aquifer. For these purposes the studies of nitrates isotope composition were conducted for the first time in the selected waters of the investigated region. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in the NO_3^- ions prove that these nitrates are derived from soil organic compounds. It is not possible to estimate the advancement of the alteration processes of nitrogen compounds (mainly nitrification) at this stage of studies.

The author has also identified reducing-oxidizing conditions in the aquifer because they influence hydro-geochemical processes and migration of elements.

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Error in variables regression model for meteoric water line determination

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Since the very beginning of the stable isotope investigations it was established that $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are interrelated and their relation reflects certain processes which can help to track the history of water path through the hydrological cycle. It was Craig (1961) who first discovered a global relation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ and illustrated its relative stability. This relation can be described as the global meteoritic water line with relation $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$. Several authors have studied distribution of local characteristics of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation as well as in various water bodies. It was determined that relation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ can depend on locality and these relations are defined as local meteoritic water lines.

In isotope hydrology the relation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ variables is usually estimated by orthogonal regression. The application of this regression analysis is a mutual agreement among isotope hydrologists. However, detailed inspection of statistical principles of the regression analyses when both variables in the model are subject to error, as it is the case of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ variables, shows that orthogonal regression can be questionable.

The paper discusses determination and illustrates the application of error in variables regression model in relation to the meteoritic water line. Errors in variables regression model are mathematically and statistically more correct than other regression models, however it poses several problems in its application to stable isotope hydrology. The model is compared and discussed in comparison with other "unsuitable" regression models frequently applied in the isotope hydrology literature.

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Stable isotope feature of groundwaters from Graciosa volcanic Island (Azores) – preliminary results

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The Azores archipelago is made of nine islands all of volcanic origin and a few islets located in the North Atlantic Ocean, about 1800 km west of Portuguese mainland at the triple junction of the Eurasian, North American and Nubian plates (Azores Triple Junction = ATJ). Graciosa Island is part of the Central Group of Azores archipelago and is located on the Terceira Rift, a major tectonic feature of the ATJ. The main hydrothermal manifestations at Graciosa Island occur in the Caldeira volcano (SE part of the island), and particularly inside the huge (150 m wide, 80 m high) Furna do Enxofre lava cave located in the Caldeira, where a bubbling mud pool releases steam and gases, leading to the accumulation of CO₂ at the bottom of the cave, filled by a coldwater subterranean lake. Three field work campaigns were carried out at Graciosa Island and 14 water samples have been collected, from boreholes, springs and the subterranean lake for isotopic (¹⁸O, ²H and ³H) and chemical analysis. The groundwater samples were plotted along the GMWL, and two water groups were identified in the δ¹⁸O vs. δ²H diagram. The splitting up of the samples is even more visible when the O-18 content is plotted as a function of the temperature or as a function of the electrical conductivity. Besides the differences in mineralization and temperature observed in the groundwater samples from Graciosa Island, an isotopic shift towards more enriched values is also observed. The salinity and isotopic content seems to indicate not a simple mixture between two end-members, i.e. seawater – fresh water: another process of mineralization and isotope enrichment must be considered in this active volcanic environment. A hypothesis to be formulated is that the source of salts could be associated to mixing with boiling seawater, that by evaporation will be able to: i) increase groundwater salinity, ii) strongly change the ²H content to more enriched values, and iii) absent or limited variation in δ¹⁸O content.

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Determining forest turbulent transport and evapotranspiration partition with the help of a new soil water isotope model

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We determine the profile of turbulent transport and evapotranspiration ET partition in an Eucalypt forest for a two-week period. We therefore optimise agreement between modelled and measured vertical profiles of temperature T , water vapour H_2O , carbon dioxide CO_2 , and deuterium content of water vapour HDO . Modelling was done by a Soil Vegetation Atmosphere Transfer (SVAT) model, enhanced by a new scheme for coupled transport of heat, water and stable isotopes in soil and litter.

We first present the new water isotope model Soil-Litter-Iso. Deuterium contents (δD) of soil evaporation and vertically-resolved transpiration are then derived using the SVAT model as prior estimates for the optimisation. An advection-diffusion description is used in the SVAT model for the isotopic composition of transpiration, and Soil-Litter-Iso is used for isotopes in soil evaporate.

Predictions of δD in soil evaporate were validated using soil chamber measurements, while the transpirates were validated using isotopic analyses of leaf and xylem water, combined with leaf-level gas exchange measurements. Hence, modelled energy, water and trace gas concentration profiles are generated using Lagrangian dispersion theory combined with source/sink coming from the SVAT model. Optimisation of turbulent transport and ET partition was then performed twice, once with and once without profiles of δD of water vapour. The modelled concentration profiles resulting from inclusion of δD demonstrate our ability to make consistent estimates of both the source distributions and δD of the water vapour sources. However, introducing measurements of δD in water vapour does not significantly alter resulting estimates of turbulent transport and the ET partition, suggesting that the additional data and modelling required to use deuterium are not warranted for the purpose of partitioning ET using the framework presented here.

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Stable isotope composition of carbon dioxide and TDIC reservoir associated with mineral waters of the Polish Flysch Carpathians

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Mineral waters widely occurring in the Polish Flysch Carpathians owe their high mineralization to the presence of geogenic carbon dioxide. For several decades origin of gaseous CO₂ in this area has been a subject of many controversies. Early hypotheses pointed to mantle origin of CO₂. Results of ³He-²⁰Ne analyses performed at the end of the last century suggest that the mantle component in the total geogenic flux of CO₂ is in the order of several per cent. Between 1997 and 2004, 20 samples of TDIC and 41 samples of gaseous CO₂ from 36 sources representing boreholes, springs and "dry exhalations" have been analysed. Measured δ¹³C values of gaseous carbon dioxide are within the range between -5.8 to -1.0‰, pointing to thermal decomposition of crustal carbonate rocks as the primary source. The carbon isotope composition of TDIC reservoirs (δ¹³C) calculated from molalities of individual carbon species in waters are out of isotopic equilibrium with gaseous CO₂ present in the area. Oxygen isotope composition of gaseous CO₂ is also out of equilibrium with mineral waters at the measured temperatures, although distinct trend towards equilibrium is observed for number of waters with different isotopic composition.

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Assessing the impacts of anthropogenic activities on groundwater quality using nitrogen isotopes – Alter do Chão-Monforte (Portugal)

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The Alter do Chão-Monforte aquifer is composed by Cambrian carbonate formations and Pre-Variscan basic igneous complex. The groundwater flow in the Alter do Chão-Monforte aquifer (Alentejo, Portugal) is quite influenced by the lithology and structural features. The aquifers are unconfined with a mixed karstic-fissured circulation. Direct recharge is important and natural discharge is from springs located in the contact of limestones with the fissured rocks. This aquifer system represents one of the main water resources of this region, located in an area of intensive agriculture and cattle breeding, generating growing nitrate pollution problems.

The use of isotope techniques is an important tool to evaluate aquifers contamination origin, so 14 groundwater samples were collected from wells, drilled wells and springs for chemical and isotopic analysis ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ of NO_3 and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of H_2O).

The major sources of nitrate, responsible for the water resources degradation present isotopically distinct $\delta^{15}\text{N}$ values. Using these features, stable nitrogen isotopes can offer a direct way of source identification. The relative contribution of the different sources to groundwater or surface water can be estimated by mass balance. However, in some situations, such as soil-derived nitrate and fertilizer, nitrate shows overlapping $\delta^{15}\text{N}$ values, preventing their separation using $\delta^{15}\text{N}$ alone. Thus, the analysis of $\delta^{18}\text{O}$ of nitrate in conjunction with $\delta^{15}\text{N}$ is fundamental to improve the ability to trace nitrate origins. From the dual isotope study of groundwater nitrate conducted in Alter do Chão-Monforte region, proved to be useful in source identification allowing for establishing the manure and septic waste and N soil as the main nitrate sources in the analysed waters. The samples with nitrates derived from manure and septic waste are mainly located near cattle breeding activities. This study allowed identifying nitrogen sources and assessing agriculture, cattle breeding, urban and industrial contributions to nitrogen cycle in Alter do Chão-Monforte groundwater ecosystem, based on the fact that the main sources of nitrate in the area have distinct $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values.

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$\delta^{18}\text{O}$ spatial distribution of precipitation in Croatia

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The precipitation as the input into the water system and its stable isotope composition is a basic part whose knowledge is required for proper use and management of water resources. The geomorphology of Croatia (e.g. high mountains next to the sea) can cause specific local conditions. We have monitored the stable isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of precipitation in more than 25 stations in various locations at different altitudes. For the work reported here, only those data sets are used that span at least one year, altogether 22 stations. The $\delta^{18}\text{O}$, $\delta^2\text{H}$ and d-excess altitude effects have been extracted from the measured data base of precipitation isotope ratios. This data base has been used to produce a gridded map of $\delta^{18}\text{O}$ for Croatia.

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The effect of the mutual interaction between climate change and the land-use pattern on the hydrologic regime under dry-land conditions

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Under a given land-use pattern the response of the hydrological regime to climate change, and in particular to changes in precipitation and temperature, is well documented for different climate regions and can be monitored by the response of the ITF (the Isotope Transfer Function) to the transition from precipitation to either surface runoff or groundwater recharge.

Changes in the land-use pattern (be it deforestation, agricultural activity or urbanization) similarly affect the hydrological regime and its isotopic signature, in particular the partitioning of the incoming precipitation into evapotranspiration, surface runoff or groundwater recharge fluxes, respectively. An additional anthropogenic factor of great relevance under dry-land conditions is provided by the introduction of extraneous water resources via irrigation practices, canalization or the use of recycled or desalinized water sources, thus profoundly affecting the isotopic signature of the water resources.

The inter-dependence between the changes in land-use pattern and the climate regime has also to be recognized when considering the isotopic response of the hydrologic systems. The most dramatic effect is to be expected under semi-arid conditions as these can then be converted to more moist or dry-land conditions, respectively, as a result of changes of the climate pattern.

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Hydrogeochemistry of Alpine springs from North Slovenia: insights from stable isotopes

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Hydrochemistry and stable isotope compositions of karst spring waters provide critical information regarding sources of groundwater recharge and water-rock interaction along flow paths.

The investigated Alpine springs in Slovenia represent waters strongly influenced by chemical weathering of Mesozoic limestone and dolomite, only one spring was located in Permo-Carbonian shales. The carbon isotopic composition of dissolved inorganic carbon (DIC) and suspended organic carbon (POC) as well as major solute concentrations yielded insights into the origin of carbon in Alpine spring waters. The major solute composition was dominated by carbonic acid dissolution of calcite. Waters were generally close to saturation with respect to calcite, and dissolved CO₂ was up to fortyfold supersaturated relative to the atmosphere. The $\delta^{13}\text{C}$ of DIC ranged from -15.8‰ to -1.5‰ and indicated less and more vulnerable aquifers. Mass balances for spring waters draining carbonate rocks suggest that carbonate dissolution contributes from about 49% to 86% and degradation of organic matter from 13.7% to 51.4%, depending on spring and its relation with geological composition. Isotopic composition of oxygen ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$), and tritium values range from -12.2 to -9.3‰ , and from 6.4 to 9.8 TU, indicate recharge from precipitation. Residence time and age of spring water are related to distance of flow path of groundwater and mixing with older water retained in Alpine slopes from recharge to emerge.

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Estimation of groundwater transit time by lumped parameter model using $\delta^{18}\text{O}$ on Szentendre Island, Hungary

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The drinking water of Budapest is mainly supplied from the good quality riverbank filtration system of the Szentendre Island. It is important to know the transit time and dispersion of the water from the Danube to the production wells and the dilution of a potential pollution for the safe operation of the system.

In this paper we examined a multiple collector well on the Szentendre Island. Water samples were taken from the collector well as well as the Danube River (near the well) 4–5 times a week between 24 February and 31 May 2011 for oxygen isotopic measurements. We also measured the background water of the island which could mix to the water of the collector well. The measured $\delta^{18}\text{O}$ value of the well was compared with the expected composition of the well by a lumped parameter model. The lumped parameter model is the most widely used method for the interpretation of stable isotopic data.

Although in the sampled period the oxygen isotopic composition of the Danube water (between -10.40‰ and -11.1‰) and the background water (-10.40‰) were close to each other, certainly the portion of the Danube water was dominant ($> 93\%$) in the collector well. The oxygen isotopic composition of the collector well water changed between -10.48‰ and -10.93‰ . The transit time of the water from the Danube to the collector well is 17–18 days by the lumped parameter model, which is realistic, considering other case studies. The dispersion of the geological settings is $P_D=0.8$. The water level of the Danube was stagnant in the measured period. Refining the results it would be important to use other input parameters (tritium, chemistry, temperature, etc.) and compare the results with other models.

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Isotopic investigations on some mineral waters from Corund, Harghita County, Romania

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Corund village is located on the eastern side of the Transylvanian Basin, southwest of the volcanic plateau of Gurghiu Mts., in the catchment of Corund River, at an elevation of 590 m. From a geological point of view, the study area consists of three major types of rocks: Middle Miocene (Badenian) salt deposits of the Transylvanian Basin, Pannonian sediments mainly represented by marls, salty and carbonated clays and sandstones, and the products of the Neogene volcanic activity of the Gurghiu Mts. aged 9.4–5.4 Ma. Along the valleys, Quaternary alluvial deposits are also present. At the southern part of the area, mineral water springs are carbonated-ferrous and fizzy with mineralizations between 379–1800 mg/l. On the northern part, the springs are carbonated-salty and fizzy with high mineralizations (134,000–142,000 mg/l). Significant CO₂ contents can be measured at each source (704–1,760 mg/l), with pH ranging between slightly acidic to neutral (5.2–6.8) values.

We sampled the Corund River and 8 springs on 11 March 2011. The oxygen vs. hydrogen isotopic compositions of the Corund River and the Dióvápai spring, Árcsó spring-1, Árcsó spring-2 and Cseredombi spring were lying on the GMWL. The $\delta^{18}\text{O}$ and δD values varied from -10.6 to -9.2‰ , and from -76 to -67‰ , respectively. It means that the river and these springs originate from local precipitation. The high conductivity could be due to the leakage through the volcanic tuffs and subordinately limestones. These springs are on the southern part of the area. Szőlő-máli spring is a large open hole, thus its isotopic composition indicates evaporation effect. The stable isotopic compositions of the Unnamed Spring, Csigadomb spring and Salty fountain are very peculiar: their $\delta^{18}\text{O}$ values vary from $+7.4$ to $+8.6\text{‰}$, while their δD values are the same (cca. -21‰) within the analytical uncertainty. These springs may have been affected by fractionation during the dissolution of salt, largely changing the isotopic composition, or alternatively, these springs may be fossil evaporated seawater. These springs are on the northern part of the area.

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Quantitative assessment of lake water balance components: new calculation approach

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The study aimed at the application of oxygen and hydrogen stable isotopic analyses of lake waters, groundwaters and precipitation waters to quantitatively assess the magnitude of lake water balance components, i.e. amount of water supply, evaporation and outflow to groundwater aquifers. The field studies were carried out within the mining area of Lignite Mine Konin and on the neighbouring Powidzkie Lakes, central Poland, from October 2007 to April 2009. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation waters vary from -140 to $+13\text{‰}$ and from -19.3 to 7.6‰ , for lake waters from -44 to -21‰ and from -5.2‰ to -1.7‰ , and for groundwaters from -10.2 to -6.5‰ and from -75 to -42‰ , respectively.

The isotopic data obtained have been applied to calculate the lakes' water balance using the Craig-Gordon model and isotopic mass balance. The equations of isotopic mass balance have been modified to construct an original calculating method, based on the coupled usage of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. Applying this new calculating approach allowed to obtain more precise and lake-specific water balance components, when compared to the commonly used calculation approach based on separate usage of 2 equations (distinct for H and O isotopes). Moreover, the proposed method enable the simultaneous calculation of 3 unknown lake water balance components (i.e. evaporation, input and outflow amount) based entirely on isotopic signatures of lake waters and precipitation. The isotopic signature of groundwaters reinforced the conclusions driven from lake water balance calculations concerning the amount of lake waters outflow (from the particular lake) to groundwater aquifers.

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Strontium isotopic ($^{87}\text{Sr}/^{86}\text{Sr}$) and geochemical signatures of CO_2 -rich thermal and mineral waters (N-Portugal)

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The main objective of this study was to use Sr isotopic and geochemical signatures to improve knowledge on the relation between hot (Chaves – 76 °C) and cold (Vilarelho da Raia, Vidago and Pedras Salgadas – 17 °C) CO_2 -rich mineral waters discharging at the northern part of Portuguese mainland. The regional geology is dominated by Hercynian granites (syn-tectonic–310 Ma and post-tectonic–290 Ma) and Silurian metasediments (quartzites, phyllites and carbonaceous slates). The thermomineral waters have $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios between 0.716713 and 0.728035. The plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ for the hot and cold mineral waters shows a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ values from the north to the south due to the interaction with young granitic rocks having lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In such diagrams, the scattering of the Sr data can be understood through the existence of three end-members (Vilarelho da Raia/Chaves, Vidago and Pedras Salgadas) of a concentration trend, from the rain waters towards the CO_2 -rich thermal and mineral waters, suggesting different underground flow paths. In fact, the plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $(\text{Ca}+\text{Mg})/\text{HCO}_3$ shows the same three end-members, being the Vidago and Pedras Salgadas CO_2 -rich mineral waters characterized by higher $(\text{Ca}+\text{Mg})/\text{HCO}_3$ ratios and lower $^{87}\text{Sr}/^{86}\text{Sr}$ values. This trend could be ascribed to: i) the fact that in CO_2 -rich hydromineral systems, low temperatures enhance water-rock interaction (with a special emphasis on Ca and Mg increasing in waters), and ii) the fact that in the case of Vidago and Pedras Salgadas CO_2 -rich mineral waters, the recharge areas are characterised by the presence of highly fractured quartzites with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios around 0.726642, while in Vilarelho da Raia / Chaves the recharge areas are within granitic rocks with much higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (from 0.743689 up to 0.789683). These values also indicate that no equilibrium was reached between the CO_2 -rich thermal and mineral waters and the granitic rocks. In fact, the mean Sr isotopic ratio of the thermal and mineral waters ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{mean}} = 0.722419$) is similar to the Sr isotopic ratios of the plagioclases of the granitic rocks (from 0.71261 to 0.72087).

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Application of isotopes for assessment of pollution probability of drinking water resources in Georgia

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The Tbilisi-Baku-Ceyhan crude oil pipeline has been laid over several groundwater recharge areas in Georgia. Since the time of planning, and even after its opening, there are intensive discussions on the possibility of ecological catastrophe in the case of its damage (spilling) at some areas. One of such most complicated and extremely responsible sections lies within the geomorphologically dangerous Borjomi area, where the problem is connected to possible pollution of drinking groundwater source from lava layer at Bakuriani-Tsikhisjvari area by oil-products. In order to study the possibility of spoiling of drinking water in Borjomi area a conceptual model of water flows has been developed with special focus on 1) the interactions of the rivers and mineral springs with the surrounding aquifers; 2) use of nuclear techniques (natural isotopes) and geophysical prospecting in selected areas for investigation of the recharge and discharge areas of the groundwater and possible propagation directions of pollution; 3) compile numerical hydrogeological model of catchment and organize the control system against possible drinking water pollution.

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Relationship between atmospheric circulation and stable isotope composition of Belgrade daily precipitation

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Factors that control stable isotopic compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of meteoric precipitation involve fractionation processes associated with the evaporation and condensation history of the precipitating water vapour.

Daily precipitation were collected in the period from May to December 2010 as well as the corresponding meteorological data (air temperature, humidity, amount of precipitation) in Vinča Institute of Nuclear Sciences (44°45'33" N, 20°35'57" E), Belgrade, Serbia. Our goal was to collect the sample representing the precipitation that had fallen over the previous 24-hour in the order to understand the relationship between atmospheric circulation and stable isotope content of individual precipitation events. However, during weekends and holidays precipitation was collected as a composite sample. The highest daily $\delta^{18}\text{O}$ and ^2H values were measured on 9 December (-1.3‰ and -8.7‰), respectively, whereas the lowest values were measured on 28 December (-143.2‰ and -19.3‰), respectively. Circulation back trajectories, weather maps, and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for 69 precipitation samples were examined to determine the circulation type for each event.

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Hydrogeochemical and isotopic assessment of seawater intrusion into alluvial aquifers in the Western Algiers coastal area (Tipasa, Algeria)

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Western Algiers coastal region that extends up to the city of Tipasa is known for both tourists and agricultural vocations. It is composed of three alluvial valleys, namely Wadi El-Hachem, Wadi Mazafran and Wadi Nador. These three small catchments being exorheic, the alluvial aquifers that they host are thus very likely to be subjected to a saline hazard through seawater encroachment. Besides industrial and agricultural developments, unrestrained demographic growth has induced important needs for freshwater. Unfavourable climatic conditions causing long period droughts have predictably led to a contamination of coastal groundwaters along the Mediterranean by ingressive seawater. Intensive pumping practices in use for the sake of securing water allocation for both populations and agriculture have drastically affected the groundwater reserves through overexploitation of the resource creating a consequent drawdown in the water table. During the dry season, the mobile fresh/sea water interface moves forward farther inland contaminating wells and boreholes. Two out of the three valleys that are present in the investigated sector were targeted by the present study. Two approaches making use of both hydrochemical and isotopic tools were applied to assess the extent of seawater intrusion. For Wadi Nador, the Br vs. Cl plot showed that the points align in a parallel way to seawater dilution line confirming thus a marine origin for those elements. Na/Cl ratio vs. Cl plot brings to the fore two poles of points: one composed of shallow unaffected groundwater and a second one composed of deeper boreholes and wells for which seawater is present to different extents. This is further confirmed by isotopes which exhibited a wide range of values mirroring the affected and unaffected areas as well as those points submitted to intermingling between different end-members.

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Isotopic composition of sulphates dissolved in waters of deep aquifers associated with copper ore deposits: implications for sulphate source and water-rock interaction

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In Europe the largest resources of copper ore occur in SW Poland in the area of Foresudetic Monocline. The main copper-rich sediments constitute the lowermost part of the Zechstein sedimentary formation of Permian age. As much as seven water-bearing horizons are drained in the mines. They constitute multiaquifer systems of Paleogene-Neogene, Triassic and Permian (Rotliegend and Zechstein). Geochemical studies of drainage waters shows that water-bearing horizons remain in hydraulic connections. Sulphur and oxygen isotope analyses of dissolved sulphates were used to determine the sources of sulphate mineralization and processes affecting the distribution of sulphate concentration in drainage waters. Chemical and isotopic (O and H) composition of drainage waters revealed that all of them form two distinct groups. Brackish waters of $\text{SO}_4\text{-HCO}_3\text{-Ca-Na}$ and $\text{SO}_4\text{-Cl-Ca-Na}$ type and isotopic composition very close to the water of modern hydrological cycle form the first group. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of dissolved sulphates are in the range of 12.05–15.94‰ and 11.07–16.57‰, respectively, are almost identical with S and O isotopic composition of Zechstein anhydrites indicating that their dissolution is the main source of sulphates. Saline waters and brines (TDS in the range 57.9–262.2 g/dm³) of Na-Cl type form the second group of drainage waters. Their ^{18}O and ^2H content locates them in the upper parts of GMWL strongly suggesting their palaeo-infiltration origin. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of dissolved sulphates show large variability, from 3.34 to 13.03‰ and from 5.87 to 15.29‰, respectively. This suggests multiple origin of sulphates mineralization. Some of the brines studied gained their sulphate mineralization from dissolution of anhydrites or gypsum. The presence of recrystallization processes connected with dissolution of anhydrites and secondary precipitation of gypsum are also likely. Much lower $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of sulphates in some brine with respect to that of anhydrites suggest that such waters associate with zones of sulphide (mainly pyrite) oxidation.

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Badenian salinity crisis in Carpathian foredeep: new insights from stable isotope composition of fluid inclusions in halite deposits of Wieliczka and Bochnia, southern Poland

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Halite deposits located in the southern Poland, near Kraków, are famous mostly due to presence of medieval salt mine located in Wieliczka. They were deposited ca. 15 Ma ago and form distinct beds, extending from west to east, on the area of ca. 10 km², with several types of salt identified. Stable isotope composition of fluid inclusions trapped in halite crystals originating from Wieliczka and Bochnia salt mines was investigated. Three distinct groups of samples were analysed: (i) samples derived from so-called "green salt" beds forming extensive horizontal structures, (ii) samples derived from so-called zuber-type salt, and (iii) large monocrystals of halite collected in two crystal caves existing in the mine. The stable isotope data of fluid inclusions form two distinct clusters in the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ space, representing crystal caves and green- and zuber-type salts, respectively. The cluster representing green- and zuber-type salt deposit is shifted to the right-hand side of the Local Meteoric Water Line (LMWL), towards more positive $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, pointing to evaporative conditions during formation of these deposits. The modelling of isotope data suggest that the green- and zuber-type salt deposits might have been formed in a lagoon-type environment, from mixture of sea water and water of continental origin. Although the evaporation trajectories for the Miocene sea water suggest that fluid inclusions might represent remnants of original solution, this notion has to be excluded due to the fact that only halite is present in the deposits. Other salts are present locally only in trace amounts. The data points representing monocrystals of halite collected in the crystal caves lie close to the LMWL and cover the range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values typical for glacial/interglacial infiltration waters. This provide the proof that large monocrystals of halite in the crystal caves are of secondary origin and were formed with participation of infiltration water, most probably during the Quaternary.

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Oxygen isotope variations in shallow lake water and bivalve shells: application of the isotope mass balance model

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Stable oxygen isotope compositions of accretionary biogenic carbonates (e.g. bivalve $\delta^{18}\text{O}_{\text{shell}}$) can potentially record environmental variability of shallow lakes; therefore have been extensively used to evaluate climate and environmental conditions. As $\delta^{18}\text{O}_{\text{shell}}$ reflects the water temperature and the oxygen isotope composition of host water ($\delta^{18}\text{O}_{\text{L}}$), it is required to interpret which climatic parameters and how influence $\delta^{18}\text{O}_{\text{L}}$. Using the known isotope mass balance model ($\delta_2 = [D_1\delta_1 + P\delta_p + I\delta_i - E\delta_e] / D_2$), we tested the hypothesis that $\delta^{18}\text{O}_{\text{L}}$ variability of lake Balaton (Hungary) can be described as a result of combined effects of three climatic parameters such as river runoff, precipitation and evaporation. We calculated $\delta^{18}\text{O}_{\text{L}}$ time series for the period 1998–2008 for whole water body at Siófok (eastern part of Lake Balaton) based on measured precipitation, inflow and evaporation amount and measured precipitation, inflow and calculated vapor $\delta^{18}\text{O}$ data.

Based on the comparison of modelled (for whole water body) and measured surface $\delta^{18}\text{O}_{\text{L}}$ data, the results showed that Balaton is highly sensitive for variation of climatic parameters at the surface, while the whole water body is less sensitive, assuming different stable isotope hydrologic conditions.

High-resolution sampling was made in two *Unio* shells from Siófok covering the period of 2001–2008 and the carbonate samples were analyzed for oxygen isotope composition. On the other hand, $\delta^{18}\text{O}_{\text{shell}}$ values were calculated on the base of model (for whole water body) and measured (surface) $\delta^{18}\text{O}_{\text{L}}$ data using water temperature data, and both predictions were compared to measured shell $\delta^{18}\text{O}$ records.

The prediction based on model data for whole water body fits better the measured shell $\delta^{18}\text{O}$ values, assuming that the whole water body describes the isotope variability of shell more accurately. In addition, we presented the effect of precipitation and evaporation on the $\delta^{18}\text{O}_{\text{shell}}$ values. The relationship between intra-shell amplitude and precipitation/evaporation ratio were determined in order to precisely quantify the meteorological parameters affecting $\delta^{18}\text{O}_{\text{shell}}$ values.

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Sulphate reduction in deep groundwater

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Groundwater in arid to semi-arid regions is mostly recharged hundreds and thousands of years ago. Its abstraction is otherwise managed for agricultural, urban and industrial purposes because of a vital source for social welfare in arid countries. The Dhofar region in the south of Oman is a plain area along the Arabian Sea, but most of the region is covered by a desert landscape, called Najd. Here, extended Tertiary limestone and gypsum/clayish layers form four main aquifer systems A to D which are the source of paleo-groundwater, but also are filled by recent recharge processes.

The water quality is controlled by the aquifer matrices, dissolution and reaction processes. Water type is characterized by Ca-Mg-SO₄-Cl to Na-Ca-Cl-SO₄-HCO₃ composition. Organic rich inclusions are detected in the aquifers B to D.

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ cover a range between -8‰ to $+2\text{‰}$ and -50‰ to $+7\text{‰}$ (vs. VSMOW), respectively. However, the linear relationship detected between the water isotopes is close to the GMWL. No obvious evaporation processes are detected, but the annual monsoon is a clear signal for recent precipitation.

Strong enrichment in ^{34}S and ^{18}O was observed in different parts of the aquifer systems. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ ranges from $+10\text{‰}$ up to $+101\text{‰}$, and from $+2\text{‰}$ to $+18\text{‰}$ respectively. A strong enrichment in ^{34}S due to sulphate reduction processes is not unusual for groundwater. However, the $\delta^{34}\text{S}$ range detected in the Najd groundwater points to bacterial sulphate reduction (BSR) under compound limiting conditions. The sulphate reduction follows different steps depending on the sulphate concentration and the exchange with groundwater. These steps are observed in the groundwater of the Najd. Moreover, sulphate reduction also influences the dissolved organic/inorganic carbon system and affects thus the ^{14}C age dating of the groundwater. Insofar, the knowledge of the occurrence and extension of BSR is important for the evaluation of the groundwater quality, its origin, and dating.

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Radiocarbon age study of Slovenian–Hungarian transboundary groundwater

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A hydrogeochemical evaluation of thermal and cold groundwaters was carried out within the framework of the T-JAM project under a Slovenian–Hungarian Operational Programme. The survey, based on common methodologies by the Geological Institute of Hungary and the Geological Survey of Slovenia, was carried out in SW Hungary and NE Slovenia in the Mura–Zala basin. A uniform hydrogeochemical methodology could be applied for the identification and evaluation of the potential transboundary geothermal aquifers.

Chemical and isotope analyses of 24 cold and thermal groundwater samples were performed.

Main component and trace element analyses confirm the vertical stratification of geothermal aquifers, already suggested in previous studies, and also indicate the presence of transboundary flow systems. Hydrogeological connections are proposed, and groundwater ages are calculated, based on stable ($\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$) and radioactive isotope (^{14}C), and noble gas analyses.

Radiocarbon groundwater age determinations are common in hydrogeology, but the interpretations raise many questions. Different age calculation methods (simple carbon-14 decay, carbon-13 correction, chemical correction with CO_2 content) were made in this study. When the $\delta^{13}\text{C}$ values are shifted significantly towards very positive values they cannot be used for radiocarbon age corrections. Age calculations using the ^{14}C decay or using chemical correction with CO_2 content gave very similar results. The radiocarbon ages vary from fresh water up to 33 500 years.

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Preliminary geochemical and isotope results in a hydrogeologic complex volcanic system aquifer in Tumbaco – Cumbayá region (Ecuador)

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The study zone is located 15 km from Quito (2200 m) including Ilaló, an active volcano in the southern part. The hydrogeologic system is complex, from top to bottom; an aquitard (Cangahua Formation, composed of ashes – max. 60 m thickness) overhanging two volcanic sedimentary series, Chiche (max 120 m depth) and Guayllabamba, which present high hydraulic capacities (for instance there is no hydrogeological information about the Guayabamba series). Another local aquifer (Ilaló) is situated on the side of volcano, composed of volcanic material and overhanging down side the Chiche formation. The aquifer zone is limited by natural barriers, in the North, East and West with rivers San Pedro, Machangara and Chiche. In the southern part we can suppose a hydraulic continuity on either side of Ilaló volcano. Some chemical and isotope results were obtained in the 1980s in the southern part of the aquifer system, and completed in the northern part in 2010. Hydrothermal and overpressured waters are locally present in Ilaló aquifer. The chemical results show no differences between the Ilaló and Chiche aquifers ($\text{HCO}_3\text{-Na}$ to $\text{HCO}_3\text{-Mg}$) but the conductivity range is moderate for Chiche ($400\text{--}600 \mu\text{S}\cdot\text{cm}^{-1}$) and higher ($1000\text{--}3000 \mu\text{S}\cdot\text{cm}^{-1}$) for Ilaló aquifer. Water stable isotopes also show different behaviours for the two aquifers, with an altitudinal recharge zone lower in Chiche (local recharge) despite the Cangahua formation assumed as impermeable. Finally tritium and Carbon-14 show different residence times (actual to 5000 years – Chiche, and older – Ilaló). These first results have allowed improving the knowledge on the hydrodynamic and chemical evolution processes in this complex system (recharge zone, flux direction; residence time, chemical evolution) and the relationship between the two aquifers.

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Tritium level in several European surface waters

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Tritium isotope (radioactive hydrogen) is produced in the upper layer of the atmosphere by the interaction of cosmic rays with the atmospheric nitrogen. It finds its way to environment especially as HTO, entering in hydrological cycle. The atmospheric testing of nuclear weapons increased the inventory of tritium on the Earth's surface, in the early '60s, with more than two orders of magnitude. Since then, the ^3H content in precipitation has decreased continuously, approximating natural levels in our days. Other tritium sources, apart from the natural production, are the anthropogenic activities as: nuclear power plants, watch industry, consumer products and medical wastes.

A review of tritium level and its evolution in surface water from France, Germany, Suisse, Great Britain, Belgium, and Romania has been given in this paper. The values of tritium concentration are studied comparatively for two periods 1993–1994 and 2007–2008, these values being obtained from different monitoring reports of environmental radioactivity.

Applying the "Global Network of Isotope in Precipitation" model, International Atomic Energy Agency developed the "Global Network of Isotopes in Rivers", where one of the monitored isotopes is tritium. The recorded values over 39 years in Vienna location decrease from 544.3 \pm 5 TU (mean of 1966) to 15.8 \pm 2.2 TU (mean of 2005). The nuclear activity developed along the Danube is present in the recorded values by the maximum values of 66.7 \pm 0.5 TU (December 2002), or 129 \pm 0.5 TU (July 2004). Tritium concentration in the Danube water has decreased in the latest years despite numerous nuclear power plants settled on its basin.

Most cases of environmental ^3H contamination are harmless, from the standpoint of radiation protection. The measured concentrations are far below the permissible value of 100 Bq/l (= 840 TU) tritium concentration for drinking water. However, the contamination does cause an increase in environmental ^3H concentrations, which are several orders of magnitude more than normal values, and which must be considered in isotopes hydrology.

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A 9-year record of stable isotope ratios of precipitation in Eastern Hungary: implications on isotope hydrology and regional palaeoclimatology

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The stable isotopic composition of hydrogen and oxygen of precipitation from Debrecen, Eastern Hungary was analysed in event based samples collected from the beginning of 2001 to the end of 2009.

During the monitoring period, the $\delta^{18}\text{O}$ values varied between -22.3‰ and 6.64‰ and the δD values between -176.8‰ and 10.7‰ . The LMWL for the monthly based data ($\delta^2\text{H} = (6.55 \pm 0.22)\delta^{18}\text{O} - 7.74 \pm 1.97$) is close to the GMWL, but shows the effect of secondary evaporation of falling raindrops with lower intercept and slope. LMWL of each year shows highly different parameters due to differences in precipitation amount and summer temperatures, especially in the extreme years of 2002 and 2003. On the basis of our data, deuterium-excess is considered to be the best parameter to reveal the extremities of dry and warm periods. Deuterium excess also proved to be a useful tool to show the different formation histories of certain precipitation events. Good correlation of $\delta^{18}\text{O}$ with temperature was obtained for the samples. The slope of the $\delta^{18}\text{O} - T$ functions for the whole sampling period was $0.32 \pm 0.03\text{‰}/^\circ\text{C}$ for the monthly samples; however, a slope of $0.37 \pm 0.03\text{‰}/^\circ\text{C}$ was obtained if monthly mean temperatures were replaced with the monthly mean temperatures of the rainy days. Considering the temperature dependency of the $\delta^{18}\text{O}$ values in the past, it can be concluded that $\Delta\delta^{18}\text{O}/\Delta T$ relationship using monthly mean temperatures of the rainy days might be a better approach than monthly mean temperatures.

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Detailed isotopic mapping of the karstic Savica River, NW Slovenia

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Savica River is a natural phenomenon with wide spectrum of different high Alpine karstic features in the recharge area interesting for thorough and precise hydrogeological and geochemical study. It flows out from a 300 m long flooded cave, represents one of the largest Slovenian karstic springs and is the main tributary to the biggest Slovene natural lake, Lake Bohinj. The discharge of Savica River is in the interval between 0.03 m³/s to 132 m³/s. The discharge of Savica River is typical of snow-rain regime. The hydrograph consist of two parts, the first part belongs to long spring thawing period that lasts up to 4 months, and the other part is typical for the drainage of karstic aquifer with fast rainfall infiltration rate. High Q_{\max}/Q_{\min} ratio indicates highly developed karstic channel network inside of the Dachstein carbonate rocks. In the major part of recharge area average annual precipitation is up to 3200 mm/year with evapotranspiration well below 550 mm/year. Average annual number of days with the air temperature below frost point is estimated between 70 to 100 days and average fresh snow thickness for the period between 1961 and 1990 was over 4.2 m. In the Savica River hinterland typical weather situation is represented by incoming wet and relatively warm southwest air masses.

However, despite its importance, Savica River was studied only occasionally by chemical and isotopic tracers until now. Therefore, a detailed mapping was performed in August 2010 and February 2011. Approximately every 100 m along the river temperature and conductivity were measured, and discharge was estimated. In addition, samples for isotopic composition of oxygen were collected. The results will enable to 1) investigate the homogeneity of the water body along the Savica River, 2) determine the spatial and temporal trends in isotopic composition along the Savica River, and 3) determine the recharge area.

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