Data Article

Monthly data of stable isotopic composition (δ^{18}O, δ^2H) and tritium activity in precipitation from 2004 to 2017 in the Mecsek Hills, Hungary

István Fórizs [a,*], Zoltán Kern [a,*], József Csicsák [b], Gergely Csurgó [b], Gábor Földing [b], Zoltán Máthé [b], János Ország [c], Géza Szreda [b], Roland Vendégh [b]

[a] Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences
[b] MECSEKÉRC Zrt. Esztergár Lajos u. 19. H-7633 Pécs, Hungary
[c] Public Limited Company for Radioactive Waste Management (PURAM), H-7031 Pf. 12. Paks, Hungary

ARTICLE INFO

ABSTRACT

The stable isotopic composition (δ^{18}O, δ^2H) and tritium activity of monthly aggregated precipitation samples were collected between April 2004 and December 2017 at six sites representing the first published precipitation isotope dataset from the Mecsek Hills (Hungary). The dataset includes 697 stable isotopic and 653 tritium activity concentration data of monthly precipitation samples collected across the Mecsek Hills. At the beginning of the monitoring period, the isotopic composition values suggest an insufficient protection against evaporation and this issue has occasionally reappeared later only in limited periods. These data are presented in brackets in the Supplementary Table and should be disregarded from further analysis until additional verification. This dataset provides isotope hydrological benchmark in comparison with other local and regional datasets of stable isotopes and tritium activities in surface water and groundwater not only in the Mecsek Hills but also in the surroundings. It can support water resource management, and paleoclimatological research. Isotope hydrological evaluation and further discussion

* Corresponding author.
  E-mail addresses: forizs@geochem.hu (I. Fórizs), zoltan.kern@gmail.com (Z. Kern).

on the seasonal trends in the precipitation isotopic characteristics are in progress and the tritium data were used in the derivation of a gridded database (1×1 km) of amount-weighted annual mean precipitation tritium activity for the Adriatic-Pannonian Region (AP^{3}H_v1, [1]).

Specifications Table

| Subject	Earth and Planetary Sciences
Specific subject area	isotope hydrology
Type of data	Table
	Figure
How data were acquired	Aggregated monthly precipitation samples were collected. Stable oxygen and hydrogen isotope composition of monthly precipitation samples were measured by isotope ratio mass spectrometry from 2004 to 2010, and by laser spectrometry (with cavity enhanced absorption technique) from 2011 to 2017. Tritium activities have been analyzed by low-level liquid scintillation counting following electrolytic enrichment.
Data format	Raw data are provided in Excel files as supplementary material.
Parameters for data collection	No pretreatment was required before the stable isotope analysis. Electrolytic enrichment was applied before the analysis of the tritium activities.
Description of data collection	Stable oxygen and hydrogen isotopic compositions were measured by isotope ratio mass spectrometry using a dual inlet Finnigan MAT Delta S, and Finnigan Delta^{plus}XP mass spectrometer in continuous-flow mode until the end of 2010, and by laser spectrometry using a Liquid Water Isotope Analyser (LWIA-24d, Los Gatos Research) thereafter. Tritium activities have been analyzed by low-level liquid scintillation counting following electrolytic enrichment.
Data source location	Six sites in the Mecsek Hills, Hungary
	Z 46.03744°N 18.12443°E 117 m a.s.l.
	B 46.06854°N 18.11269°E 172 m a.s.l.
	V 46.12153°N 18.09230°E 330 m a.s.l.
	II 46.09927°N 18.09149°E 332 m a.s.l.
	Boda 46.08668°N 18.04671°E 233 m a.s.l.
	Het 46.12524°N 18.04776°E 165 m a.s.l.
Data accessibility	With the article

Value of the Data

- The dataset provides benchmark data for isotope hydrological evaluation of the surface water and groundwater in the Mecsek region (e.g. estimating the mean residence time of streamwater and karstic reservoirs).
- The data are especially important because they provide necessary basic isotope hydrological background data for the environmental monitoring of the planned high activity radioactive waste repository.
- Regional paleoclimatological research could also benefit from these data because the isotopic 'temperature' effect in modern precipitation in the Mecsek region can be inferred, which can be a crucial parameter in paleoclimatological applications.
- The dataset provides reference data for (i) authenticity and traceability of agricultural products from this region e.g. for local wines, and (ii) archaeological research of migration of peoples, animals and objects made of organic material.

1. Data Description

The study of the isotopic composition of surface and groundwater started in 2004 (Fig. 1) in the Mecsek region (South Hungary) in order to provide field data to hydrogeological modeling for the geological research programme of Boda Claystone Formation (BCF) within the site selection of a planned high activity radioactive waste repository. The research programme is managed by the Public Limited Company for Radioactive Waste Management. Precipitation samples were collected by the MECSEKÉRC Zrt, stable isotope analysis was performed by the Institute for
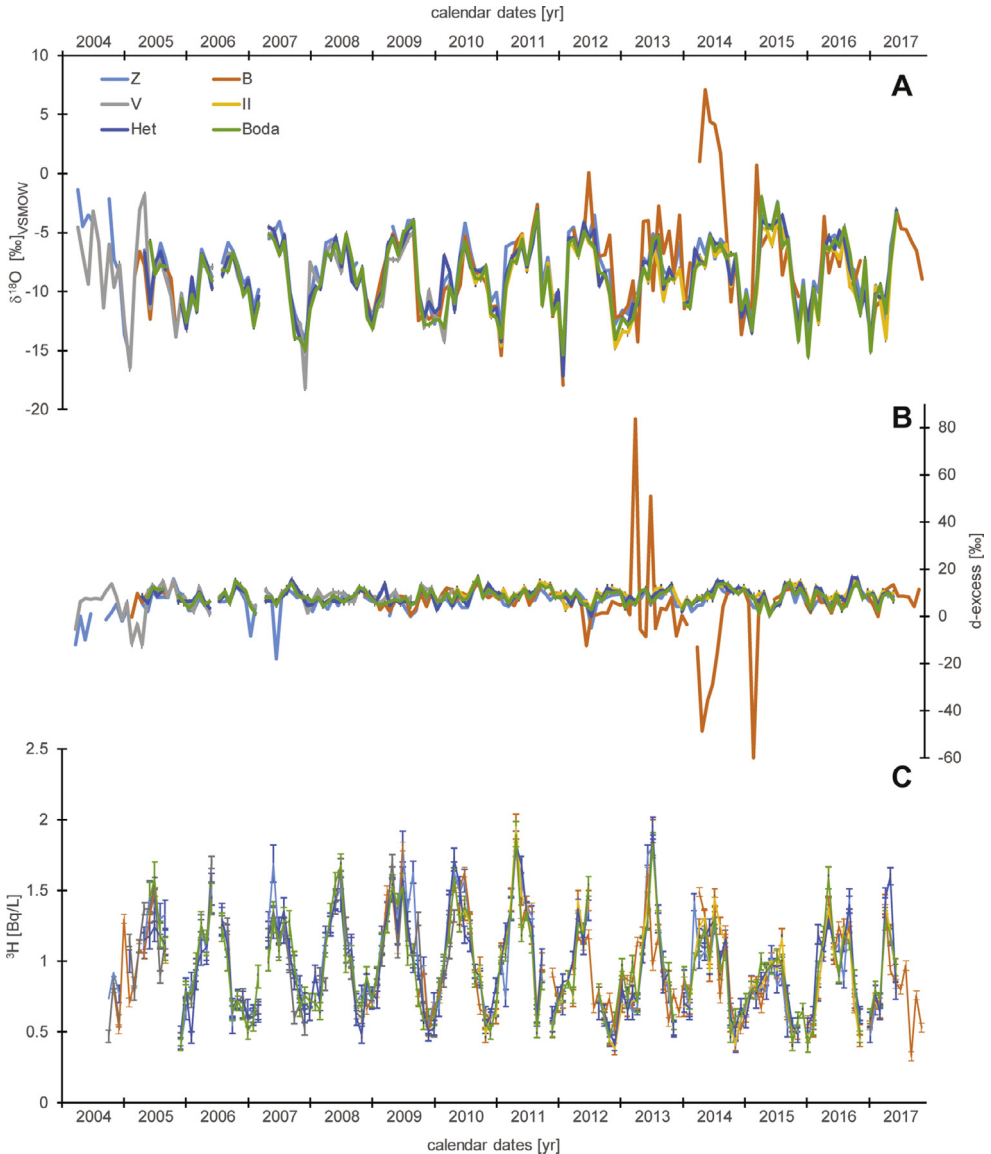
Fig. 1. Isotopic characteristics of monthly precipitation collected in the Mecsek Hills (Hungary) between April 2004 and November 2017. Stable oxygen isotopic composition (A), d-excess (B), and tritium activity concentration (C).
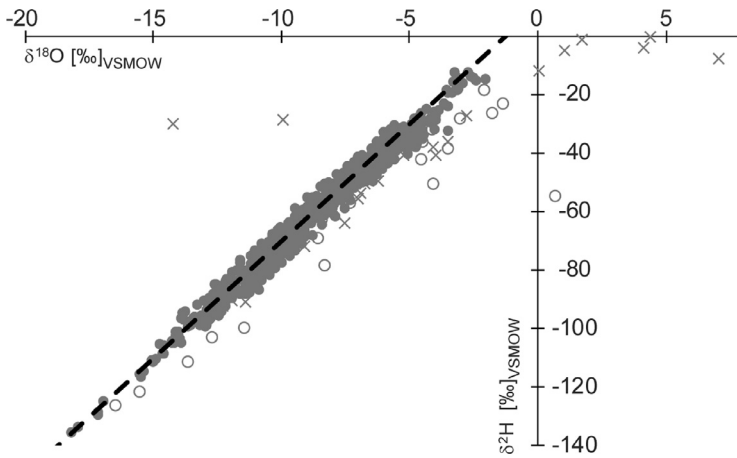
Fig. 2. Distribution of monthly averaged $\delta^2H-\delta^{18}O$ for precipitation in the Mecsek Hills between 2004 and 2017. The dashed black line shows the Global Meteoric Waterline [3]. Data obtained from samples before May 2005 are marked by open circles and the extreme outliers in the dataset of station B (from July 2012 to August 2014 and also in March 2015) are marked by crosses.

Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences and its predecessor (Institute for Geological and Geochemical Research, Hungarian Academy of Sciences), and tritium activity of the water samples were analyzed by the HYDROSYS Labor Ltd.

A unique month in the dataset is April 2007 when there was no precipitation at any station of the network, however November 2011, December 2013, and December 2016 were also rather dry months when some of the stations did not record precipitation. In addition, in months with low precipitation amount it was a quite frequent situation that the collected precipitation was sufficient only for stable isotope analysis and there was not enough material for tritium activity measurements. In one case, October 2010 the sample submitted for stable isotope analysis has been lost. Altogether, stable oxygen and hydrogen isotopic compositions are presented for 697 samples and Tritium activity is available for 653 samples (Supplementary Table).

The time series of the primary isotopic parameters of monthly precipitation data show a high degree of coherency (Fig. 1). There are two remarkable periods when the coherency in the stable isotope data is weaker. Especially d-excess [2] indicates the problematic data in these periods because d-excess values obviously stand out from the typical range of distribution of this parameter. The first period is from the beginning of the record to May 2005 and the second one is between July 2012 and March 2015. In the first period unusually low d-excess values were observed at stations Z and V suggesting evaporation effect until the collector vessel was buried. Failure in evaporation protection can be assumed for samples collected in February and July of 2007 at station Z. There is no deviation in the metadata of station B which could explain the extremely anomalous values seen in the record from July 2012 to August 2014 and also in March 2015.

For the sake of completeness these potentially problematic data are also reported in the dataset, however presented in brackets and it is recommended disregarding these isotopic data in isotope hydrological characterization of the modern precipitation in the Mecsek Hills. Tritium activity data do not seem to reflect these disturbances (Fig. 1c). The point cloud in the dual-isotope space defined by the vast majority of the data (Fig. 2) fits nicely to the Global Meteoric Water Line, describing the global relation of these parameters [3]. Hence these data will be suitable input data for further isotope hydrological modelling and provide a robust modern reference for paleoclimate studies. We point out again that problematic data, presented in brackets in the Supplementary Table, should not be considered until additional verification.

2. Experimental Design, Materials and Methods

2.1. Sample collection

The collection of precipitation samples for isotope hydrological monitoring started in April 2004 at two stations (Z and V) and for a short period (from Nov 2004 to Nov 2005) at station B. Daily precipitation samples were collected in each morning and aggregated in a 5 L plastic (HDPE) container on a monthly basis. Winter precipitation was collected by the same instrumentation as (so no heated funnel was used) if snow had accumulated in the collector when the sample was harvested, it was added to the collection vessel by melting. Special precautions for evaporation prevention was not applied when melting the snow. The network was expanded with two additional stations from May 2005. From then on, the sample collecting vessels were placed in ground cavity, primarily to prevent summer evaporation and winter freezing. This is an approved option for collector configuration for precipitation isotope analysis ('Buried collector': [4]). Monitoring ceased at station V by May of 2010 and the collection place was moved to ~4 km southward (station II) by June 2011. The sample collectors were installed in the recommended safety distance from potential physical barriers [4]. The water samples were transferred to leak-proof plastic bottle and shipped to laboratories. Samples were kept in glass vials closed with plastic caps with conical interior in refrigerator.

2.2. Analytical methods

Stable isotope ratios in water were analyzed in the different periods of time by the following methods and analytical instruments:

2.2.1. From 2004 to 2005
- the δ^{18}O value of water was determined by Finnigan MAT delta S mass spectrometer using CO_2 gas equilibrated with H_2O at 20°C temperature during overnight, where sample containing vessels were shaken. The details of the sample preparation set up is described by Roether [5], the original principle is the one described by Epstein & Mayeda [6].
- the δ^2H value of water was determined by Finnigan MAT delta S mass spectrometer using H_2 gas liberated from 3 μL water by reacting with 100 mg special zinc alloy [7] in a sealed vacuum glass tube at 500°C during 30 min [8,9].

The applied laboratory standard was the BTW (Budapest Tap Water) calibrated against SMOW and SLAP. The normalization factors [10] for both H and O, which were found to be rather stable, were determined circa monthly by applying reference materials W-63333 assigned δ^2H$_{VSMOW-SLAP}$ and δ^{18}O$_{VSMOW-SLAP}$ values of -399.8 and –52.28‰, and W-39500 assigned δ^2H$_{VSMOW-SLAP}$ and δ^{18}O$_{VSMOW-SLAP}$ values of -1.5 and -1.52‰, respectively [11,12,13]. These reference materials were kindly provided by Tyler B. Coplen, the Reston Stable Isotope Laboratory (RSIL), of U.S. Geological Survey (USGS).

The reproducibility was around ±0.06–0.07 ‰ for oxygen. When the difference between the duplicates exceeded 0.2‰ (for oxygen) then we did a third analysis (or a fourth one if it was recommended) for the sake of keeping the reproducibility below ±0.1‰. Occasionally we reanalyzed some samples after several months and the remeasured delta values were always within the ±0.1‰ range to the originally determined one. Therefore we state that the overall estimated (sample storage + sample preparation + analysis) uncertainty was ±0.1‰ for oxygen and ±1‰ for hydrogen.

2.2.2. From 2006 to 2010
- the δ^{18}O value of water was determined by Finnigan Delta^{plus}XP mass spectrometer in continuous-flow mode. The sample preparing process before the mass spectrometric measurement was the following: 1 mL water from each sample (unknown and standard) was

pipetted into a 10 mL vial closed by septum+cap. Each vial was flushed by He gas containing 0.3 v/v% CO_2 during 6 minutes, and the whole set was kept in a heating block at 32°C for minimum 18 hours for getting the isotopic equilibrium in the CO_2-H_2O system.

- the δ^2H value of water was determined by Finnigan Delta^{plus}XP mass spectrometer in continuous-flow mode. The sample preparing process before the mass spectrometric measurement was the following: platinized catalyzer was inserted and 1 mL water from each sample (unknown and standard) was pipetted into a 10 mL vial closed by septum+cap. Each vial was flushed by He gas containing 2.1 v/v% H_2 during 6 min, and the whole set was kept in a heating block at 32°C for minimum 40 min for getting the isotopic equilibrium in the H_2-H_2O system [14].

The applied laboratory standard was the BTW (Budapest Tap Water) calibrated against SMOW and SLAP. The normalization factors [10] for both H and O, which were found to be very close to 1.0, were determined circa weekly by applying reference materials W-63333 assigned $\delta^2H_{VSMOW-SLAP}$ and $\delta^{18}O_{VSMOW-SLAP}$ values of -399.8 and –52.28‰, and W-39500 assigned $\delta^2H_{VSMOW-SLAP}$ and $\delta^{18}O_{VSMOW-SLAP}$ values of -1.5 and -1.52‰, respectively [11,12,13]. The overall estimated (sample storage + sample preparation + analysis) uncertainty was ±0.2‰ for oxygen and ±2‰ for hydrogen.

2.2.3. Since 2011

Both δ^2H and $\delta^{18}O$ values of water were determined by a Liquid Water Isotope Analyser (LWIA-24d, Los Gatos Research). The sample preparing and measurement process was the following: 1 mL water was pipetted into each 2 mL vial closed with septum+cap. The vials were arranged on the tray in the following way: 3 lab standards – 5 unknown samples – 3 lab standards, etc. in the sake to prevent the effect of ambient temperature variation [15]. An autosampler (CTC Analytics GC PAL) using a Hamilton syringe took 1 μL water from the 2 mL vial and injected it through a preformed septum into the vaporizer of the laser analyzer where the water was evaporated at 80°C in low vacuum into the cavity of the analyzer. From each vial 6 injections were carried out, but because of memory effect only the data of the latest 4 injections were taken into account. The overall estimated uncertainty was ±0.2‰ for oxygen and ±1‰ for hydrogen. The applied laboratory standards were the following ones with the assigned δ^2H and $\delta^{18}O$ values in brackets: BWS1 (-9.0; -0.53), BWS2 (-74.9; -10.41), BWS3 (-147.7; -19.95) [16].

Each sample during both the mass spectrometric and laser instrumental analysis was measured in duplicate and the mean values are here presented. All stable isotope measurements were carried out in the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences (Budapest, Hungary) and its predecessors.

The results are expressed in the standard δ-notation [17] relative to Vienna Standard Mean Ocean Water:

$$\delta(\text{‰}) = (R - R_{std}) / R_{std} * 1000 \, [\text{‰}]_{VSMOW},$$

where R and R_{std} are $^{18}O/^{16}O$ or $^2H/^1H$ ratios in the sample and in the standard (Vienna Standard Mean Ocean Water - VSMOW), respectively [18].

During the transition from mass spectrometric to laser spectroscopic analyses several sets of samples were measured by both techniques, and it was found that the measured delta values were the same within the analytical uncertainties. The laboratory – using both mass spectrometers (Finnigan MAT Delta S, and Finnigan Delta^{plus}XP) and the Liquid Water Isotope Analyser – has successfully participated in the water isotope laboratory proficiency tests [19].

A secondary isotopic parameter of natural waters, d-excess [2], has been calculated as d = δ^2H - 8 × $\delta^{18}O$.

Tritium activities have been analyzed by low level liquid scintillation counting following electrolytic enrichment at HYDROSYS Labor Ltd, Budapest. Tritiated water, SRM 4361C H-3 (NIST), was used as standard reference material. Activity concentration of the samples is expressed in Bq/L.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

Acknowledgments

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.dib.2020.106206.

References

[1] Z. Kern, D. Erdélyi, P. Vreča, I. Krajcar Bronić, T. Kanduč, M. Štrok, I. Fórizs, L. Palcsu, M. Süveges, G. Czuppon, B. Kohán, I.G. Hatvani, Isoscape of amount-weighted annual mean precipitation tritium (^{3}H) activity from 1976 to 2017 for the Adriatic-Pannonian region - AP3H_v1 database, Earth Syst, Sci. Data 12 (2020), doi:10.5194/essd-12-2061-2020.
[2] W. Dansgaard, Stable isotopes in precipitation, Tellus 16 (1964) 436–468.
[3] H. Craig, Isotopic variation in meteoric waters, Science 133 (1961) 1702–1703.
[4] IAEA GNIP Precipitation sampling guide, http://www-naweb.iaea.org/napc/ih/documents/other/gnip_manual_v2.02_en_hq.pdf, 2020 (accessed 10 May 2020).
[5] W Roether, Water-CO$_2$ Exchange Set-up for the Routine ^{18}Oxygen Assay of Natural Water, Int. J. Appl. Radiat. Isot. 21 (1970) 379–387.
[6] S. Epstein, T. Mayeda, Variation of O^{18} content of waters from natural sources, Geochim. et Cosmochim. Acta 4 (1953) 213–224.
[7] J.M. Hayes, M.W. Johnson, Reagent and procedure for preparation of H$_2$ for hydrogen-isotopic analysis of water, Indiana University, Bloomington (Indiana, USA) (1988).
[8] M.L. Coleman, T.J. Shepherd, J.J. Durham, J.E. Rouse, G.R. Moore, Reduction of Water with Zinc for Hydrogen Isotope Analysis, Anal. Chem. 54 (1982) 993–995.
[9] A. Demény, H-isotope fractionation due to hydrogen-zinc reactions and its implications on D/H analysis of water samples, Chem. Geol. 121 (1995) 19–25.
[10] D. Paul, G. Skrzypek, I. Fórizs, Normalization of measured stable isotopic compositions to isotope reference scales – a review, Rapid Commun, Mass Spectrom. 21 (2007) 3006–3014.
[11] A. Demény, S. Kele, Z. Siklósy, Empirical equations for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70°C, Rapid Commun, Mass Spectrom. 24 (2010) 3521–3526.
[12] H. Qi, T.B. Coplen, L. Tarbox, J.M. Lorenz, M. Scholl, USGS48 Puerto Rico precipitation – a new isotopic reference material for δ^2H and δ^{18}O measurements of water, Isot. Environ. Health Stud. 50 (2014) 442–447.
[13] T.B. Coplen, J. Hopple, in: Audit of VSMOW distributed by the United States National Institute of Standards and Technology, IAEA-TECDOC-825 Reference and intercomparison materials for stable isotopes of light elements, IAEA, Vienna, 1995, pp. 35–38.
[14] S.J Prosser, C.M. Scrimgeour, High-precision determination of ^{2}H/^{1}H in H$_2$ and H$_2$O by continuous-flow isotope ratio mass spectrometry, Anal. Chem. 67 (1995) 1992–1997.
[15] G. Lis, L.I. Wassenaar, M.J. Hendry, High-Precision Laser Spectroscopy D/H and ^{18}O/^{16}O Measurements of Microliter Natural Water Samples, Anal. Chem. 80 (2008) 287–293.
[16] Gy. Czuppon, A. Demény, Sz. Leél-Őssy, M. Óvari, M. Molnár, J. Stieber, K. Kiss, K. Kármán, G. Surányi, L. Haszpra, Cave monitoring in the Béke and Baradla Caves (Northeastern Hungary): implications for the conditions for the formation cave carbonates, Int. J. Speleol. 47 (2018) 13–28.
[17] C.R. McKinney, J.M. McCrea, S. Epstein, H.A. Allen, H.C. Urey Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios, Rev. Sci. Instrum. 21 (1950) 724–730.
[18] T.B. Coplen, Reporting of stable hydrogen, carbon and oxygen isotopic abundances, Pure App. Chem 66 (1994) 273–276.
[19] L.I. Wassenaar, S. Terzer-Wassmuth, C. Douence, L. Araguas-Araguas, P.K. Aggarwal, T.B. Coplen, Seeking excellence: an evaluation of 235 international laboratories conducting water isotope analyses by isotope-ratio and laser-absorption spectrometry, Rapid Commun, Mass Spectrom. 32 (2018) 393–406, doi:10.1002/rcm.8052.