Acta Physica Universitatis Comenianae
Vol. L–LI, Number 1&2 (2009–2010) 143–153

# Spatial Distribution of Isotopes in Groundwater of Slovakia

P. P. Povinec[1], A. Šivo[1], M. Richtáriková[1], R. Breier[1], Ľ. Lúčan[2], P. K. Aggarwal[3], L. Araguás-Araguás[3]

[1]Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, SK-84248 Bratislava, Slovakia
[2]Department of Applied Informatics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia
[3]Isotope Hydrology Section, International Atomic Energy Agency, A-1400 Vienna, Austria,
*Povinec@fmph.uniba.sk*

**Abstract:** Spatial distribution of $^{14}$C, $^{13}$C and $^{18}$O in groundwater found on the territoty of Slovakia is presented for the first time. Preliminary investigations suggest large isotopic heterogeneity, although the data density is still not good enough to draw more precise conclusions. A vertical distribution of $^{14}$C in groundwater of the Žitný ostrov confirms that the majority of groundwater has $^{14}$C content below 20 pmc, except a small area on the north-west, where we see, at the surface and subsurface (around 500 m), younger waters with $^{14}$C values around 30 pmc. An interesting feature is the existence of old waters with $^{14}$C values below 10 pmc, which are surprisingly seen from the surface down to 200 m water depths.

## 1. Introduction

Isotopes as environmental tracers have been extensively used during the last decades to study the water cycle, to better understand the origin, dynamics and interconnections of the different elements of the hydrologic cycle. It has been possible to study the present day distribution of water isotopes in the atmosphere, in the rain water, river water, groundwater, and then trace the past isotopic compositions affecting many processes, such as atmospheric circulation, rain and snow formation, groundwater formation, ecology and paleoclimatology [1]. Radioactive and stable isotopes have been used to address the key aspects of the water cycle, e.g. the origin, dynamics and interconnections of the different elements of the water cycle [2–5].

Fortunately, with the development of the IAEA's Global Network of Isotopes in Precipitation (GNIP) database, it has been possible to use isotopes in hydrological, ecological and climate studies, as input functions have been available for many areas of the world [6]. A lot of isotope data have been collected and several isotope databases have been developed. The GNIP database (*www.GNIP.IAEA.org*) has provided the key data for the application of isotopes in hydrology, but also in climatic and ecological studies. Recently this monitoring activity has been enlarged to isotopes in the total water cycle, and the new isotope database (Isotope Hydrology Information System (ISOHIS; *www.ISOHIS.IAEA.org*), covering also

*) *Dedicated to Prof. Štefan Šáro and Assoc. Prof. Martin Chudý, Ing. Rudolf Janík to 75th and 70th anniversaries, respectively.*

groundwater data, enables together with the GNIP database, to study dynamics and spatial characteristics of groundwater [7].

However, a complex groundwater data compilation, evaluation and interpretation have been absenting, and the existing data have been mostly used only for specific hydrological applications. With the development of geostatistical methods of data treatment, which are based on the Geographical Information System (GIS), it is possible to map the spatial variability of the isotopic composition of water in selected regions of the world [8]. It is possible, in such a complex system, to trace the origin and pathways of different water masses on the basis of the developed isotopic maps, covering temporal and spatial distribution of hydrochemical and isotope data. Integrating isotope data into a relational database covering also hydrogeology and hydrochemistry, it will be possible, using GIS to visualize, and in this way to create the temporal-spatial isotope maps of groundwater [9]. Such an integrated attempt will gather new information on temporal and spatial variability of groundwater, on its dynamics, on anthropogenic and climatic impacts, and on its vulnerability.

Although radioactive and stable isotopes have been applied in a few groundwater studies, e.g. [10–13], there has not been done an integrated research yet, which would cover in full complexity the whole Slovakia, not to say that such a research should cover all Central Europe. The previous isotope hydrology work in Slovakia, e.g. on mineral and thermal waters [13], on formation and ages of travertines [14], etc., contributed to understanding of groundwater origin, however, temporal and spatial information has been missing, which could better characterize specific groundwater localities, groundwater ages, infiltration areas, recharging characteristics of groundwater reservoirs, danger of their contamination, climatic changes, etc., all important facts for protection and correct exploitation of groundwater from the long-term perspective.

Department of Nuclear Physics and Biophysics of the Faculty of Mathematics, Physics and Informatics of the Comenius University in Bratislava has 40 years of experience in radiocarbon measurements. The Radiocarbon laboratory started its operation in 1966 with analysis of radiocarbon in atmospheric carbon dioxide [15]. The developed methods included collection and pre-treatment of samples, sample preparation in the laboratory, lines for sample combustion, chemical dissolution and preparation of labelled gases (carbon dioxide, methane), low-background proportional counters with active gas filling, electronics for registration of pulses from proportional counters and low-background shields [16–20].

Samples of mineral and thermal waters, collected mostly in the south-western and north-western Slovakia [13] were analysed for stable isotopes and radiocarbon. The obtained results contributed to understanding of origin of these waters, however, temporal and spatial information, which could better characterize specific groundwater localities, groundwater ages, infiltration areas and recharging characteristics of groundwater reservoirs has been missing. The preliminary data show that groundwater was increasingly flowing mainly during the interglacial periods [21].

We started in 2007, in the framework of the IAEA Coordination Research Programme on "Geostatistical analysis of spatial isotope variability to map the sources of water for hydrology studies", a pilot study on the development of geostatistical tools for mapping the spatial isotope variability of groundwater in Slovakia and the Central Europe. The constructed isotope maps will be used to trace the origin of groundwater in the region, to identify areas, where additional isotope data are required, and to evaluate, assess and better manage resources of groundwater in the region. In the areas, where limited isotope data are available, new sampling campaigns and isotope analysis will be carried out over the Slovakia territory, and new data will be merged with the compiled Central Europe database. The radiocarbon ages plus $^{2}H$, $^{18}O$ and $^{13}C$ values will be determined in over 100 groundwater samples collected from about 70 localities. Geostatistical analysis of experimental data will be carried out with the aim to search for temporal and spatial variations in the distribution of water isotopes. A new hydrological isotope database for Slovakia and the Central Europe on the basis of all previous studies, as well as the data collected whitin the framework of this CRP will be developed. The developed hydrogeological-isotope maps of temporal and space variability of groundwater in Slovakia and the Central Europe will be important for the evaluation, assessment and management of water resources.

## 2. Sampling programme and methods

This work is based on samples collected in cooperation with the State Geological Institute of Dionýz Štúr in Bratislava. Mostly samples of Slovak thermal and mineral waters were collected (sampling sites are visible in the accompanying figures). Further sampling programme has been concentrated on the "Žitný ostrov" in the south-western Slovakia, north of the Danube River where over 100 samples of groundwater, river water (the Danube, the Small Danube, Váh) and precipitation have been collected and analysed for radioactive ($^{14}C$) and stable isotopes ($^{18}O$, $^{13}C$), as well as for anions, kations and trace elements. The obtained data will form the basis for the development of a 3D hydraulic model of the "Žitný ostrov", which will help to study the origin and flow of groundwater in the region as well as their connection with the Danube water. Isotopes will form an important part of the modelling exercise, especially from the point of view of calibration and validation of the model.

Experimental methods included large volume water sampling (~50 L) for radiocarbon dating, precipitation of carbonates in the form of $BaCO_3$ and its transport to the laboratory. Simultaneously small volume water samples (1 L) were collected for analysis of stable isotopes. Field analyses included the temperature, pH, Eh and electrical conductivity measurements.

Laboratory analyses included: analysis of stable isotopes ($^{18}O$, $^{13}C$) using mass spectrometers; preparation of gas fillings (carbon dioxide was released from $BaCO_3$ by addition of $H_3PO_4$); preparation of methane labelled with $^{14}C$ from a sample of carbon dioxide [16] and $^{14}C$ activity measurement by a gas proportional counter [17]. Quality management of all the analyses has been assured by analysis of reference materials, and by participation in intercomparison exercises.

## 3. Development of the relational database ISODAT

### 3.1. Structure of the ISODAT database

The sampling strategies are determined by the main objectives of the project which include development of a relational isotope database of groundwater of Slovakia, which will cover hydrogeological, hydrochemical and isotope data. Such databases, which enable to study temporal and spatial characteristics of groundwater are under preparation in several European countries.

The data evaluated in this paper were extracted from the Isotope Database (ISODAT) database, which has been developed whitin the framework of this project. The basic concept of the ISODAT database is described below to give an idea about the database structure and input-output functions, important for possible supply of data from other institutions, as well as for data extraction and use in research.

The ISODAT has been created to serve the following important functions:

- To provide the snap-shot of isotope data at any time, which may be used as the base-line for any assessment studies,
- To provide immediate and up-to-date information on the isotope levels in different environmental matrices,
- To permit investigation of temporal and spatial trends in environmental isotope levels and identify gaps in available information.

To satisfy these aims, the final system should be flexible and extendible and should be able to be interrogated by region, by time period, by isotope and by environmental matrix.

### 3.2. Data types and requirements

The data requirements for recording isotope measurements are relatively complex and extensive but can be functionally divided into two categories:

- definition of the environmental sample and its processing,
- analytical procedures undertaken and their results; a complete data profile provides sufficiently detailed information to ensure that the data verification and evaluation can be carried out.

Such detail requirements will help in the data interpretation and analysis and forms the basis of the data validation. The division into these two distinct data categories is reflected in the database structure which has two primary data files. The further reason for this structure is that a single sample will frequently give results on several isotopes.

Broad classes of sample type were defined, namely: water vapours, precipitation, river water, lake water, springs, wells, soil, sediment. These are the main environmental media considered for isotope studies. Associated with each are a number of further data fields which provide together the complete sample profile consisting of:

- sample description (including the volume, temperature, conductivity, oxygen content, pH, etc. as appropriate)
- sampling location
- sample pre-treatment
- method of analysis
- results.

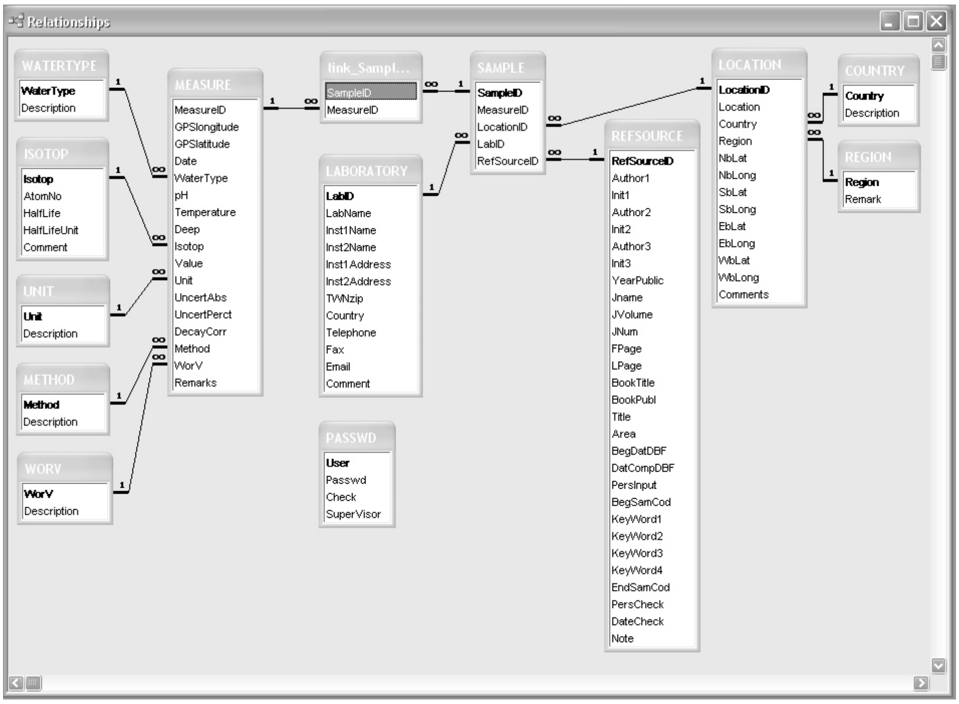


**Fig. 1.** Organisation of the ISODAT database.

The main considerations in the design of the data requirements were the different ways of reporting results, the difficulties in dealing with the limits of detection, the possibility of decay-corrected results and various uncertainties which should be quoted.

The information incorporated in the database is both current as well as retrospective. It reflects the current research and environmental priorities, as well as those of the past. In the initial development of the database, it was decided to undertake a retrospective search for data, making use of published literature and research reports. Currently, the database holds a great deal of historical data from a number of technical reports and papers from Slovakia. However, consideration has been given to prospective data entry, through electronic transfer of data from the source laboratory to the central database. Various data transfer protocols and programmes have been developed to facilitate the exchange of data. The data requirements have been broadly classified into several key areas, as presented below.

The general organisation of the database is shown in Fig. 1. The main relationship is given by the files, e.g. WATERTYPE, ISOTOPE, UNIT, METHOD, WORV (Weight or Volume), COUNTRY, REGION. Files MEASURE, LOCATION, LABORATORY and REFSOURCE covering the results, location and the bibliography. The arrangement is taking into account the intensity of the access into the database (the largest is for MEASURE, the smallest for REFSOURCE).

### 3.3. Database inputs

**Sample type.** Eight sample types were identified: water vapours, precipitation, river water, lake water, springs, wells, soil and sediment, corresponding to the environmental media most commonly used.

**Laboratory information.** As the primary data source, laboratory information provides the necessary background information. Only the very basic laboratory details are required. Participation in proficiency tests and intercomparison exercises provides a broad indicator of good laboratory practice and may be used in individual cases to assess the validity of the data.

**Sampling period.** The date of sample collection is required. Since temporal features will be an important analysis product from the database, these fields are essential and form the basis for temporal interrogation.

**Sample location.** All the data entered in the database are geographically registered. The degree of spatial registration recorded is precise (i.e. latitude and longitude). Provision has been made to include regional information as well.

**Sampling method.** Information on the specific sampling method used to collect the sample is requested. Although not considered as a central data requirement, availability of such information may be used in the data evaluation. A description of the water source is also included, e.g. well characteristics.

**Laboratory treatment.** A number of physical and chemical treatments may be applied to the sample prior to isotope analysis. General information on the processes to which the sample has been subjected is required as part of the profile. The primary function of these data is for data verification and in certain circumstances, e.g. in the identification of outliers, it may be used in the validation process. Again, when results from different laboratories are being combined, such information may be used to ensure the comparability of the results and to explain any observed discrepancies.

**Data source and reference.** Given a primary database function as a data archive and repository, it is important that the source of any data be fully referenced, thus part of the database system includes the full reference to the primary source (a published paper or internal laboratory report).

**Analytical information.** The information requested here has a number of features which must be accommodated within the primary data file. Key issues which had to be resolved included the different uncertainty structures, data recorded at the limit of detection, below detection or not detected and the information concerning the different analytical methods. The isotope is identified by the standard convention using scientific notation.

**Results and units.** Although an international convention on units does exist, it is noticeable and to be expected that results are presented in a variety of units. The primary database file holds the information on results in the original units. Later, the data management system converts the data to a standard form for further manipulation and analysis.

**Uncertainty and limit of detection.** Uncertainties in both absolute and percentage form are accommodated (at 1   level). Measurements made at the limit of detection or recorded as below detection or not detected are flagged in an additional character field.

**Method of measurement.** The particular analytical method of sample analysis is incorporated. The analytical data file also includes the sampling date (a secondary link to


**Fig. 2.** Format of inputs to the ISODAT database.

the environmental data file), the date of measurement, whether a decay correction has been made, and to which date.

**Bibliographic references.** The third basic information type gives details of the bibliographic information on the data source. It includes the authors/source of the data, if from a report, the full title and date of publication.

**Inputs and outputs.** The format of inputs (Access 2003) into the ISODAT database using fictive data is presented in Fig. 2. The file MEASURE allows for the same SAMPLE to include there all the measurements done on a given sample. Outputs from ISODAT cover temporal and spatial data for a given isotope, changes with time, 2D and 3D data visualisation, identification of gaps, modelling, etc.

The ISODAT is constructed using the PostgreSQL 8.3 software and its GIS version PostGIS, and based on the MS Access 2003 – first of all because of its easy availability and cross-connection with the Microsoft Office Excel, Word, PowerPoint and GIS visualisation software. The ISODAT will be available for users via the UNIBA web.

## 4. Results and discussion

Fig. 3 shows the preliminary distribution of $^{18}O$ in mineral and thermal waters of Slovakia. The $^{18}O$ values have varied between 11.6 ‰ and 5.8 ‰. Unfortunately, there are still great regional gaps, therefore more data are required to assure reasonable

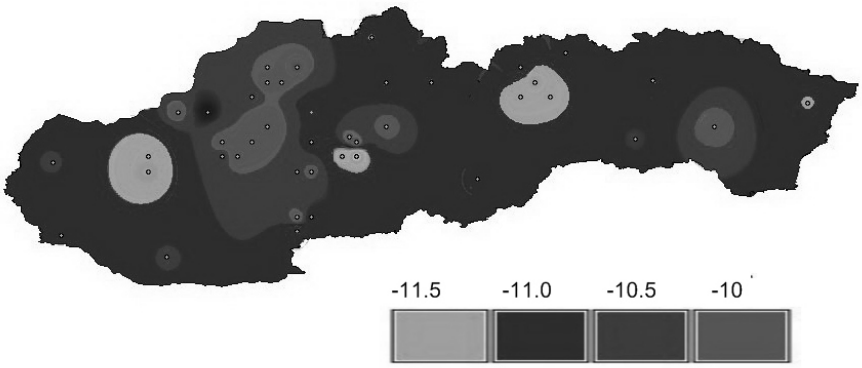


**Fig. 3.** Preliminary spatial distribution of $^{18}O$ (in ‰) in groundwaters of Slovakia.

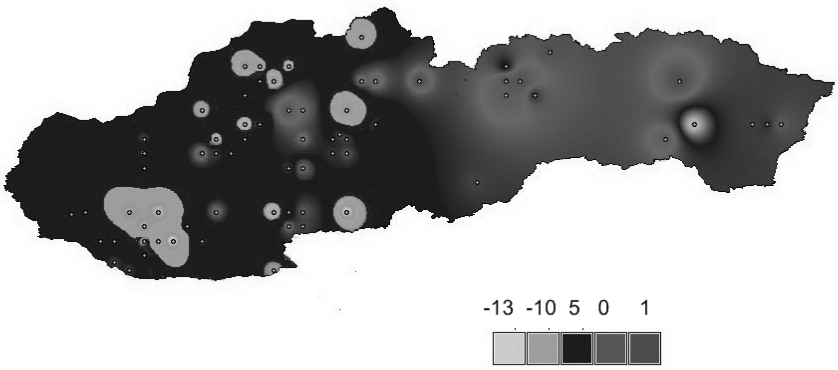


**Fig. 4.** Preliminary spatial distribution of $^{13}C$ (in ‰) in groundwaters of Slovakia.

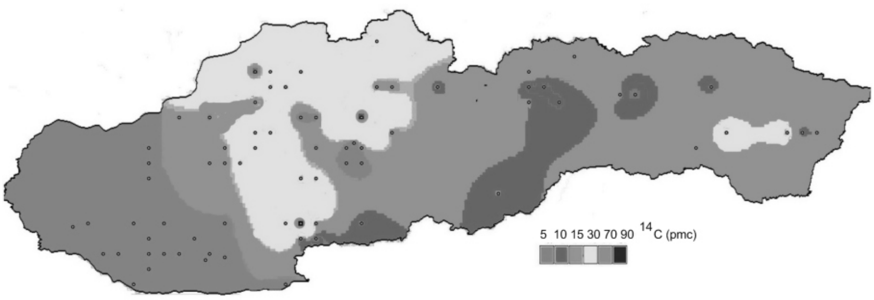


**Fig. 5.** Preliminary spatial distribution of $^{14}C$ (in pmc) in groundwaters of Slovakia.

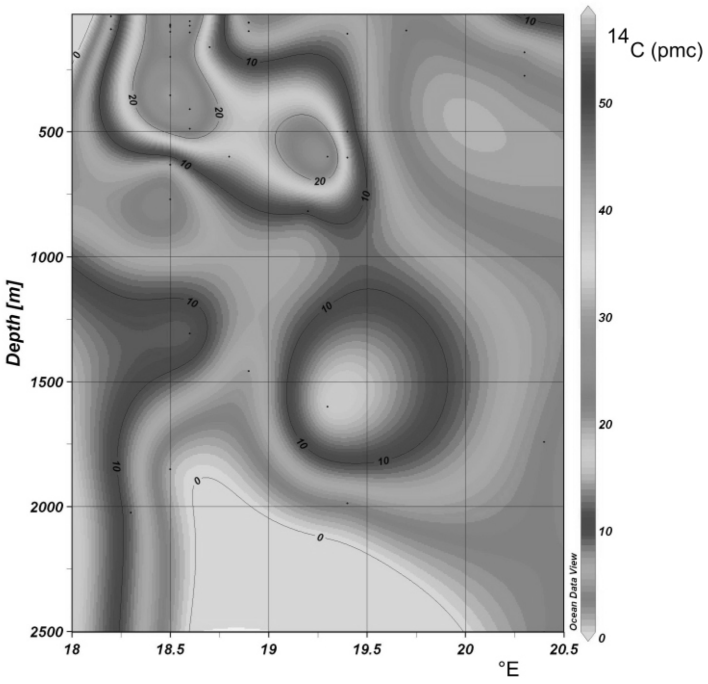


**Fig. 6.** Depth $^{14}$C profile in the groundwater of Žitný ostrov.

data density. Generally, it can be seen that in the north-western part of Slovakia the samples have been enriched in $^{18}$O, while there are a few island with depleted values. We hope to draw a better picture when more results will be available.

Spatial distribution of $^{13}$C in groundwater of Slovakia is presented in Fig. 4. The $^{13}$C values have varied between 13 ‰ and 1 ‰. Fortunately there the data density is better than in the case of $^{18}$O, however, still too far from being an optimal. There is an indication that in the north-western part of the Central Slovakia, where the samples have been enriched in $^{18}$O, they are depleted in $^{13}$C, and probably the same is valid for the northern part of the Central Slovakia.

The best available data density has been obtained for $^{14}$C. The data are plotted in Fig. 5 as percent modern carbon (pmc). We see that majority of the samples represent old groundwater with $^{14}$C content below 15 pmc. There have been only three localities in the Central Slovakia with much younger waters, around 90 pmc.

Fig. 6 shows the first attempt to construct the vertical distribution of $^{14}$C in groundwater of the Žitný ostrov. Generally, the depth distribution confirms that the majority of groundwater has $^{14}$C content below 20 pmc, except a small area on the north-west, where at the surface and subsurface (around 500 m) younger waters with $^{14}$C values around 30 pmc (similarly in the central part of the basin, at the water depths around 1500 m) can be seen. An interesting feature is the existence of old waters with $^{14}$C values below 10 pmc, which are surprisingly seen from the surface down to 200 m water depths.

## 5. Conclusions

Preliminary investigations of spatial variability of $^{14}$C, $^{13}$C and $^{18}$O suggest large isotopic heterogeneity in thermal and mineral waters of Slovakia, although the data density is still not good enough to draw more precise conclusions.

The vertical distribution of $^{14}$C in groundwater of the Žitný ostrov confirms that the majority of groundwater has $^{14}$C content below 20 pmc, except a small area on the north-west, where at the surface and subsurface (around 500 m) younger waters with $^{14}$C values around 30 pmc can be seen. An interesting feature is the existence of old waters with $^{14}$C values below 10 pmc, which are surprisingly seen from the surface down to 200 m water depths.

This new research approach will improve the capability and efficiency in using isotopic tools for deeper evaluation, more rigorous assessment and more efficient management of water resources in the region.

More detailed studies are underway and more information will be gathered when new isotopic data will be available, including new chemical and isotope analyses of samples collected during 2008 and 2009.

## Acknowledgements

The authors thank Dr. O. Franko, formerly with the State Geological Institute of Dionýz Štúr in Bratislava, for the long-term collaboration. A part of this research was supported by the International Atomic Energy Agency (RC No. 14301) and the Slovak Scientific Agency VEGA (grant No. 1/108/08).

## References

[1] C. Kendall, McDonnell: Isotope Tracers in Catchment Hydrology. Elsevier, Amsterdam 1999.
[2] V. I. Ferronsky, V. A. Polyakov: Environmental Isotopes in the Hydrosphere. Wiley 1982, 466p.
[3] D. Rank, W. Pepesch, V. Rainer: Environmental Isotope Study at Research Landfill (Breitenan, Austria). In: Proc. Intern. Symp. Isotopes in Water Resources Management. IAEA, Vienna 1995, 379 381.
[4] J. Deák: Isotope-Hydrogeology Studies in Hungary Focusing on the Requirements of the EU Water Framework Directive. In: Proc. Isotopenmethoden in der Hydrogeologie und Wasserwirtschaft, Vienna 2003, 1 9.
[5] P. K. Aggarwal, J. R. Gat, K. F. O. Froehlich (Eds.): Isotopes in the Water Cycle. Springer, Heidelberg 2006, 381p.
[6] P. K. Aggarwal, R. Froehlich, Gonfiantini, J. Gat: Isotope Hydrology: A Historical Perspective from the IAEA. In: P. K. Aggarwal, J. R. Gat, K. F. O. Froehlich (Eds.): Isotopes in the Water Cycle. Springer, Heidelberg 2006, 3 8.
[7] IAEA. Water and Environment News. Issue No. 22. IAEA, Vienna 2007.
[8] G. J. Bowen, L. I. Wassenaar, K. A. Hobson: Global Application of Stable Hydrogen and Oxygen Isotopes to Wildlife Forensics. Oecologia, 10.1007/s00442-004-1813-y, 2005.
[9] P. Aggarwal, L. Araguás-Araguás: CRP Proposal Geostatistical Analysis of Spatial Isotope Variability to Map the Sources of Water for Hydrology and Climate Studies. IAEA, Vienna 2006.
[10] P. Malík, J. Michalko, S. J. Mansell, M. Fendeková: Stable Isotopes in Karstic Groundwaters of Veľká Fatra Mountains, Slovakia. In: Proc. International Symposium on Isotopes in Water Resources Management, IAEA, Vienna 1995.
[11] J. Michalko: Stable Isotopes of Hydrogen, Oxygen and Sulphur in the Waters of Slovakia. Slovak Geol. Mag. **5** (1999) 63 67.

[12] O. Franko, J. Michalko, A. Šivo: Isotopes of Oxygen and $^{14}$C in the Geothermal Waters of Pliocene Sediments of Danube Basin. Proc. Conf. Nr. 45, PAN, Kraków 2000, 229  240.
[13] O. Franko, A. Šivo, M. Richtáriková, P. Povinec: Radiocarbon Ages of Mineral and Thermal Waters in Slovakia, In: 19th International Radiocarbon Conference, University of Oxford 2005, 261  262.
[14] P. P. Povinec et al.: Radiocarbon Dating of Travertines Collected in Slovakia (under preparation).
[15] P. Povinec, Š. Šáro, M. Chudý, M. Šeliga: The Rapid Method of Carbon-14 counting in atmospheric Carbon Dioxide. Int. J. Applied Radiation and Isotopes **19** (1968) 877  881.
[16] P. Povinec: Preparation of Methane Gas Filing for Proportional $^{3}$H and $^{14}$C Counters. Radiochem. Radioanal. Letters **9** (1972) 127  135.
[17] P. Povinec: Multiwire Proportional Counters for Low-Level $^{14}$C and $^{3}$H measurements. Nuclear Instruments and Methods **156** (1978) 441  445.
[18] S. Usačev, P. Povinec, M. Chudý, M. Šeliga: Bratislava Radiocarbon Measurements I. Radiocarbon **15** (1973) 443  450.
[19] P. Povinec et al.: Seasonal Variations of Anthropogenic Radiocarbon in the Atmosphere. Nuclear Instr. Methods B **17** (1986) 556  559.
[20] Š. Cimbák, A. Čechová, M. Grgula, P. Povinec, A. Šivo: Anthropogenic Radionuclides $^{3}$H, $^{14}$C, $^{85}$Kr, and $^{133}$Xe in the Atmosphere Around Nuclear Power Reactors, Nuclear Instruments and Methods B **17** (1986) 560  563.
[21] O. Franko, A. Šivo, M. Richtáriková, P. Povinec: Radiocarbon Ages of Mineral and Thermal Waters of Slovakia. Acta Phys. Univ. Comen. **49** (2008) 125  132.