ISOTOPIC TECHNIQUES IN HYDROLOGY: PRINCIPLES AND APPLICATIONS

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Received: 10.06.2026
Accepted: 07.07.2026
Published: 20.07.2026

Isotopic techniques represent an important and increasingly applied tool in hydrological research, providing valuable insights into the origin, movement, and distribution of water within the hydrological cycle. The application of stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$), together with radioactive isotopes, enables the investigation of groundwater recharge processes, surface water–groundwater interactions, evaporation, and water residence times in hydrological systems. The aim of this paper is to present the fundamental principles and potential applications of isotopic techniques in hydrology, with particular emphasis on their contribution to understanding hydrological processes and characterizing water resources. Special attention is given to the use of isotopic data as a complementary source of information for hydrological investigations, enabling a better understanding of water origin, movement, and connectivity between different components of the hydrological cycle. The integration of isotope-based approaches with conventional hydrological methods can also contribute to improving water resource monitoring, strengthening the assessment of hydrological processes, and supporting more effective, integrated, and sustainable water resources management.

Keywords: Isotopic techniques, stable isotopes, $\delta^{18}O$, $\delta^{2}H$, radioactive isotopes, hydrology, water resources management.

1. INTRODUCTION

Water is one of the most important natural resources, and its origin, movement, and distribution are governed by complex processes within the hydrological cycle. Understanding these processes is essential for assessing water availability, as well as for the effective protection and sustainable

Scientific Journal of Civil Engineering (SJCE)
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management of water resources. Although conventional hydrological and hydrogeological methods provide valuable information on water quantity, quality, and flow dynamics, they may not always be sufficient to determine water origin or establish the hydraulic and hydrological connections between different components of the hydrological system [1, 2].

In this context, isotopic techniques have become increasingly important in modern hydrological research. These techniques are based on analysing the natural isotopic composition of water, which reflects climatic and hydrological conditions and is influenced by processes such as evaporation, condensation, and mixing [3, 4]. Stable isotopes of oxygen and hydrogen ($\delta^{18}O$ and $\delta^{2}H$) are particularly valuable as natural tracers, enabling the identification of water sources, the investigation of seasonal and spatial variations in isotopic composition, the estimation of groundwater recharge areas and elevations, and the assessment of potential interactions between surface water and groundwater [5–7]. In addition, radioactive isotopes, such as tritium (^{3}H) and carbon-14 (^{14}C), provide valuable information for estimating groundwater age and residence time [1, 8]. Other natural radionuclides can also be used as hydrological tracers to investigate water movement, recharge processes, and exchange mechanisms within groundwater and surface water systems [9].

The integration of isotopic analyses with conventional hydrological, hydrogeological, and hydrochemical investigations provides a more comprehensive understanding and characterization of water resources [2, 5]. Isotopic information can therefore contribute to identifying hydrological connections between different water bodies, evaluating water origin and recharge processes, and improving the effectiveness of water resource monitoring. These applications are particularly relevant in the context of climate change and increasing pressure on freshwater resources, where reliable scientific information is essential for informed decision-making and sustainable water management [10, 11].

In the Republic of North Macedonia, the application of isotopic techniques in hydrological research represents an increasingly important opportunity, considering the country's diverse climatic, geological, and hydrogeological characteristics. The spatial and temporal variability of precipitation, complex groundwater recharge conditions, and interactions between surface water and groundwater highlight the need for complementary research approaches. In this regard, isotope analyses offer considerable potential for supplementing conventional hydrological data, improving the understanding of processes governing water availability and distribution, and establishing a scientific basis for systematic monitoring of the isotopic composition of water resources [7, 12, 13]. Further development of isotope hydrology in the country could also strengthen national research capacities and provide a more reliable scientific basis for long-term water resource planning and management.

Against this background, the objective of this paper is to present the fundamental principles of isotopic techniques and examine their potential applications in hydrological research, with particular emphasis on their contribution to understanding hydrological processes, characterizing water resources, strengthening monitoring activities, and supporting integrated water resources management.

2. FUNDAMENTAL PRINCIPLES OF ISOTOPE HYDROLOGY

Isotope hydrology is a scientific discipline that investigates the natural isotopic composition of water to improve the understanding of processes occurring within the hydrological cycle. Its fundamental principle is based on the presence of different isotopes of hydrogen and oxygen in water molecules, whose relative abundances vary under the influence of physical processes and environmental conditions. These variations provide a natural isotopic signature that can be used to trace water origin, movement, and interactions between different components of the hydrological system [1, 14].

Isotopes are atoms of the same chemical element that have an identical number of protons but differ in the number of neutrons, resulting in different atomic masses. According to their nuclear stability, isotopes are classified into two main groups: stable and radioactive isotopes. Stable isotopes do not undergo spontaneous radioactive decay, whereas radioactive isotopes are characterized by nuclear instability and gradually decay over time. These distinct properties determine their applicability in hydrological investigations, ranging from identifying water sources and tracing hydrological pathways to estimating groundwater age and residence time [1, 8].

One of the fundamental processes governing the isotopic composition of natural waters is isotopic fractionation, which refers to the unequal distribution of isotopes between substances or phases during physical, chemical, and biological processes. Within the hydrological cycle, isotopic fractionation is particularly significant during evaporation and condensation, as differences in isotopic mass result in different rates of phase transition for water molecules containing lighter and heavier isotopes. Consequently, the isotopic composition of precipitation, surface water, and groundwater reflects the climatic and geographical conditions under which water was formed, as well as the subsequent processes influencing its movement and transformation [4, 14].

The isotopic composition of water therefore provides an additional dimension of information that complements conventional hydrological observations and helps characterize processes that may otherwise be difficult to identify. Combining isotopic data with hydrological, hydrogeological, and hydrochemical investigations enables a more comprehensive assessment of water systems, their interactions, and their temporal and spatial dynamics [2, 15]. Furthermore, the reliability and comparability of isotopic measurements depend on the application of appropriate analytical techniques, internationally recognized reference materials, standardized measurement procedures, and rigorous quality assurance and quality control protocols [16, 17].

3. STABLE ISOTOPES IN HYDROLOGICAL RESEARCH

3.1 OXYGEN AND HYDROGEN ISOTOPES

Stable isotopes of hydrogen and oxygen are among the most widely used natural tracers in isotope hydrology. Hydrogen has two stable isotopes, protium (^1H) and deuterium (^2H), while oxygen has three stable isotopes (^{16}O, ^{17}O, and ^{18}O), Figure 1. In hydrological research, the $^2H/^1H$ and $^{18}O/^{16}O$ ratios are of particular importance, as variations in their relative abundance provide valuable information about water origin and the processes occurring within the hydrological cycle. The isotopic composition of natural waters is influenced by climatic and geographical conditions, as well as by processes such as evaporation, condensation, infiltration, and mixing [3, 14].

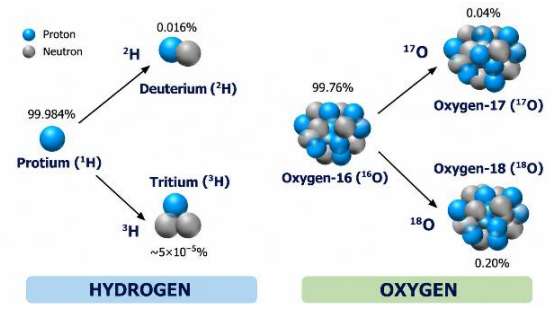


Figure 1. Isotopes of Hydrogen and Oxygen (Source: Authors)

The isotopic composition of water is expressed using delta notation (δ), which represents the relative difference between the isotopic ratio of the analysed sample and that of an internationally recognized reference standard. For stable isotopes of hydrogen and oxygen, measurements are conventionally reported relative to the Vienna Standard Mean Ocean Water (VSMOW) reference scale and expressed in per mille (‰). Delta values are calculated according to the following equation [18]:

$$\delta = [(R_p / R_s) - 1] \times 1000 \ (‰) \quad (1)$$

, where (R_p) represents the ratio of the heavier to the lighter isotope in the analysed sample, and (R_s) is the corresponding isotope ratio in the reference standard. Negative $\delta^{18}O$ and δ^2H values indicate depletion in heavier isotopes relative to the reference standard, whereas positive values indicate enrichment. Variations in isotopic composition are primarily associated with isotopic fractionation, through which water becomes relatively enriched or depleted in heavier isotopes depending on the physical processes and environmental conditions involved [4, 18].

One of the fundamental characteristics of stable isotopes in precipitation is the linear relationship between δ^2H and $\delta^{18}O$, described by the **Global Meteoric Water Line** (GMWL), originally established by Craig [19], (Figure 2):

$$\delta^2H = 8\delta^{18}O + 10 \quad (2)$$

The GMWL provides a global reference relationship for interpreting the isotopic composition of precipitation and other natural waters. However, climatic and geographical differences result in regional variations in this relationship. Consequently, Local Meteoric Water Lines (LMWLs) are established to better characterize the isotopic composition of precipitation under specific regional conditions. Deviations from the meteoric water line, particularly lower slopes, may indicate the

influence of evaporation, while variations in the intercept and slope can also reflect differences in atmospheric moisture sources, climatic conditions, and precipitation formation processes [3, 7].

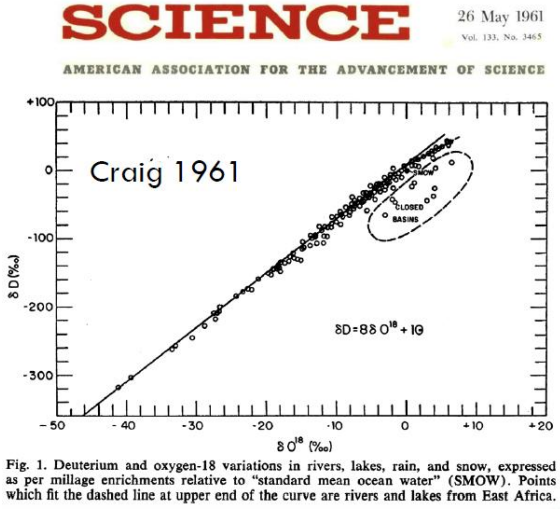


Figure 2. Global Meteoric Water Line GMWL (Source: Craig 1961 [19])

An additional parameter used in interpreting the isotopic composition of water is deuterium excess (d-excess), defined by Dansgaard [3] as:

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

Deuterium excess provides additional information about the conditions under which atmospheric moisture evaporates, particularly the relative humidity and sea-surface conditions in moisture source regions. It can also help identify changes in moisture sources and the influence of secondary evaporation during precipitation formation and falling. The combined analysis of $\delta^{18}O$, δ^2H, and d-excess therefore enables a more comprehensive investigation of seasonal and spatial variations in precipitation isotopic composition and their relationships with meteorological and climatic parameters [3, 7, 14].

In hydrological investigations, stable isotopes of hydrogen and oxygen are widely used to compare the isotopic characteristics of precipitation, surface water, and groundwater. Similarities and differences in their isotopic composition provide valuable information about potential recharge sources, the influence of elevation, seasonal variability, and the effects of evaporation and mixing processes. Furthermore, isotopic variations can help identify potential hydraulic connections between surface water and groundwater systems. Therefore, $\delta^{18}O$ and δ^2H represent important indicators for understanding hydrological processes, particularly when interpreted alongside meteorological, hydrological, and hydrochemical data [5, 14].

3.2 EVAPORATION AND ISOTOPIC FRACTIONATION

Isotopic fractionation is one of the fundamental processes governing the distribution of stable isotopes in the hydrological cycle. It occurs when physical, chemical, or biological processes cause the unequal distribution of isotopes between different substances or phases. In hydrology, isotopic fractionation is particularly important during evaporation and condensation, as differences in the mass of water molecules containing light and heavy isotopes influence their behavior during phase transitions. Consequently, these processes lead to variations in the isotopic composition of precipitation, surface water, and groundwater [3, 4, 14].

During evaporation, water molecules containing lighter isotopes (^1H and ^{16}O) have a higher probability of escaping from the liquid phase into the atmosphere than those containing heavier isotopes (^2H and ^{18}O). As a result, the remaining liquid water becomes progressively enriched in heavier isotopes, while the water vapor is relatively depleted. The extent of isotopic enrichment depends on environmental conditions, particularly air temperature, relative humidity, wind speed, and the isotopic composition of atmospheric moisture. These factors influence evaporation rates and the degree of isotopic fractionation occurring at the water–air interface [3, 4, 14].

Isotopic fractionation during evaporation is generally associated with two mechanisms: equilibrium fractionation and kinetic fractionation. Equilibrium fractionation occurs when isotopic exchange between liquid water and water vapor reaches thermodynamic equilibrium and is primarily temperature-dependent. Kinetic fractionation, on the other hand, occurs under non-equilibrium conditions and is associated with differences in the diffusion rates of water molecules containing different isotopes. It is particularly significant during evaporation into unsaturated air, where humidity and atmospheric conditions influence the degree of isotopic separation between the liquid and vapor phases [3, 4].

The effects of evaporation can be identified through changes in the relationship between δ^2H and $\delta^{18}O$. While precipitation generally follows the GMWL, evaporation from surface

water bodies and soils often produces an isotopic relationship with a lower slope, typically ranging between 3 and 6, depending on environmental conditions. This deviation reflects the preferential enrichment of heavier isotopes in the remaining water and is commonly associated with a reduction in d-excess values. Therefore, the slope and position of the evaporation line, together with changes in d-excess, provide useful indicators for identifying and evaluating evaporation effects in natural waters [3, 4].

Evaporation-induced isotopic fractionation is particularly relevant in hydrological investigations involving lakes, reservoirs, rivers, and shallow groundwater systems. By analyzing variations in $\delta^{18}O$ and $\delta^{2}H$, it is possible to distinguish between waters that have undergone significant evaporation and those that retain a predominantly meteoric isotopic signature. Furthermore, these variations can provide information about water residence, surface water–groundwater interactions, and the contribution of different water sources to hydrological systems. Consequently, understanding isotopic fractionation during evaporation is essential for correctly interpreting isotope data and assessing hydrological processes [5, 14].

4. RADIOACTIVE ISOTOPES AND GROUNDWATER DATING

Radioactive isotopes serve as significant natural tracers in hydrological research, particularly for estimating the age and residence time of groundwater. Unlike stable isotopes, they are characterized by unstable atomic nuclei that undergo gradual decay. The rate of decay is expressed by the half-life—the time required for half of the initial number of radioactive atoms to decay. This property enables their use in studying the movement and dynamics of groundwater [8, 20].

One of the most frequently used radioactive isotopes is tritium (^{3}H), a radioactive isotope of hydrogen with a half-life of approximately 12.32 years. It is produced naturally in the atmosphere under the influence of cosmic radiation and participates in the hydrological cycle as a component of water molecules. Its application allows for the identification of relatively young groundwater, the assessment of modern recharge, and the detection of mixing between waters of different ages [5, 21].

To determine the age of older groundwater, carbon-14 (^{14}C) is used, which has a half-life of approximately 5,730 years. Its analysis—most commonly within dissolved inorganic carbon—allows for the estimation of groundwater age, spanning a range from several thousand to tens of thousands of years. When interpreting the results, it is necessary to account for geochemical processes and the potential for the mixing of waters of different ages [1, 8].

In addition to tritium and carbon-14, other natural radionuclides—such as radon-222 (^{222}Rn) and radium isotopes—are used in hydrological research, enabling the study of exchange between surface water and groundwater. Combining radioactive isotopes with stable isotopes and conventional hydrological analyses contributes to a more comprehensive understanding of the origin, movement, and residence time of water [9, 20].

5. METHODS FOR DETERMINING THE ISOTOPIC COMPOSITION OF WATER

The determination of the isotopic composition of natural waters is performed using various analytical techniques, depending on the type of isotope, sample characteristics, and required measurement precision. For the analysis of stable isotopes of hydrogen and oxygen ($\delta^{2}H$ and $\delta^{18}O$), the most widely applied techniques include *Isotope Ratio Mass Spectrometry* (IRMS) and laser-based spectroscopy, particularly Cavity Ring-Down Spectroscopy (CRDS) and Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS), Figure 3. These techniques enable precise determination of isotope ratios and are extensively used in contemporary hydrological and environmental research [17, 22].

Isotope Ratio Mass Spectrometry (IRMS) is a well-established analytical technique based on the separation and detection of ions according to their mass-to-charge ratios. Prior to measurement, water samples undergo appropriate preparation to convert hydrogen and oxygen into suitable gaseous forms, typically hydrogen and carbon dioxide, respectively. The resulting gases are introduced into the mass spectrometer, where the relative abundance of isotopes is determined by comparing the measured isotope ratios with those of reference materials. IRMS provides high analytical precision and has traditionally been considered a reference technique for stable isotope measurements [17, 22].

Laser-based spectroscopy represents an alternative approach that has become increasingly important in isotope hydrology. Techniques such as CRDS and OA-ICOS determine isotopic composition by measuring the absorption of laser radiation at specific wavelengths corresponding to different isotopic forms of water vapor. The absorption characteristics allow the instrument to distinguish between molecules containing different isotopes and determine their relative abundances. These techniques offer several practical advantages, including relatively simple sample preparation, automated analysis, high sample throughput, and the possibility of performing measurements directly on water samples after vaporization [17, 22].

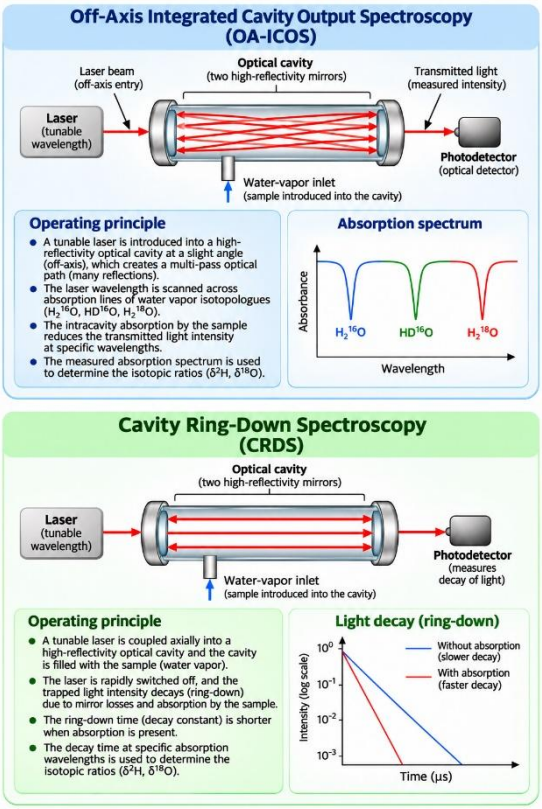


Figure 3. Schematic illustration of the operating principles of OA-ICOS (Los Gatos Research) and CRDS (Picarro) laser spectroscopy techniques for determining stable hydrogen and oxygen isotopes in water (based on Aemisegger et al [33] and Diamond [34])

For the determination of radioactive isotopes, analytical methods are selected according to the radioactive characteristics and concentration of the isotope being investigated. Tritium (^3H) is commonly determined using Liquid Scintillation Counting (LSC), a technique based on detecting light pulses generated by the interaction of beta particles emitted during radioactive decay with a scintillation medium [23]. Carbon-14 (^{14}C), particularly important for groundwater dating, can be measured using Accelerator Mass Spectrometry (AMS), which determines the abundance of ^{14}C relative to stable carbon isotopes and enables the analysis of very small quantities of the radioactive isotope [8].

Regardless of the analytical technique employed, the reliability and comparability of isotopic results depend on appropriate sample collection, handling, and storage, as well as instrument calibration and systematic quality control. The use of internationally recognized reference materials, laboratory standards, replicate measurements, and appropriate correction procedures is essential for ensuring measurement accuracy and analytical consistency. Results are conventionally reported relative to international reference scales, including VSMOW for stable hydrogen and oxygen isotopes [16, 17].

6. MAIN AREAS OF APPLICATION OF ISOTOPIC TECHNIQUES

Isotopic techniques are widely used in modern hydrological and hydrogeological research, as they enable the identification and investigation of processes that cannot always be directly assessed using conventional methods. One of their most important applications is determining water origin and identifying groundwater recharge areas. Spatial variations in the isotopic composition of precipitation, particularly those associated with altitude, temperature, and climatic conditions, provide valuable information for identifying potential recharge sources and estimating the conditions under which groundwater is recharged [5, 14, 24].

Another important application involves investigating hydraulic connectivity and water exchange between surface water and groundwater. By comparing the isotopic composition of rivers, lakes, and groundwater, potential interactions and exchange processes can be identified, as well as the contributions of different water sources to individual hydrological systems. Combining isotopic data with hydrological and hydrochemical measurements enables a more comprehensive assessment of water-flow dynamics, groundwater recharge mechanisms, and interactions within the hydrological system [2, 25].

Isotopic techniques are also valuable for identifying and evaluating processes such as

evaporation and the mixing of waters with different origins. Evaporation produces characteristic changes in the isotopic composition of water, particularly in the relationship between $\delta^{18}O$ and $\delta^{2}H$, while mixing processes can be investigated by examining the isotopic signatures of the contributing water sources. These approaches are particularly relevant for assessing water balance components and understanding hydrological processes in lakes, reservoirs, and other surface water bodies [4, 26].

Furthermore, monitoring seasonal and spatial variations in isotopic composition provides insights into the influence of climatic factors on the hydrological cycle. Variations in air temperature, precipitation amount, atmospheric humidity, and moisture source conditions can be reflected in the isotopic characteristics of precipitation and other water components. Long-term isotopic monitoring can therefore contribute to a better understanding of climate variability and its effects on water resources [10, 11].

The application of radioactive isotopes to estimate groundwater age and residence time represents another important area of isotope hydrology. Isotopes such as tritium (^{3}H) and carbon-14 (^{14}C) provide information about groundwater residence times and recharge history over different timescales. Their combined application with stable isotopes enables a more comprehensive investigation of water origin, recharge processes, movement, and mixing within aquifers. Such information is essential for evaluating groundwater renewability, understanding aquifer dynamics, and supporting the sustainable management of groundwater resources [8, 20, 21].

7. ISOTOPE MONITORING AND INTERNATIONAL MONITORING NETWORKS

Systematic monitoring of the isotopic composition of natural waters represents an important basis for investigating hydrological processes and assessing changes in water resources. The regular collection and analysis of samples from precipitation, surface water, and groundwater enable the development of long-term isotopic time series. These datasets provide valuable information on seasonal and spatial variations, the influence of climatic conditions, and changes in groundwater recharge and hydrological processes. Isotopic monitoring therefore complements conventional hydrological observations and contributes to a more comprehensive understanding of water system dynamics [5, 14].

At the international level, the Global Network of Isotopes in Precipitation (GNIP), established through cooperation between the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO), plays a particularly important role. GNIP supports the systematic collection and analysis of precipitation samples, providing data on the isotopic composition of precipitation, particularly $\delta^{18}O$, $\delta^{2}H$, and, at selected stations, tritium (^{3}H). Complementing this initiative, the Global Network of Isotopes in Rivers (GNIR) provides information on the isotopic composition of river water and supports investigations of hydrological processes and water-cycle dynamics at the river-basin scale [27, 28].

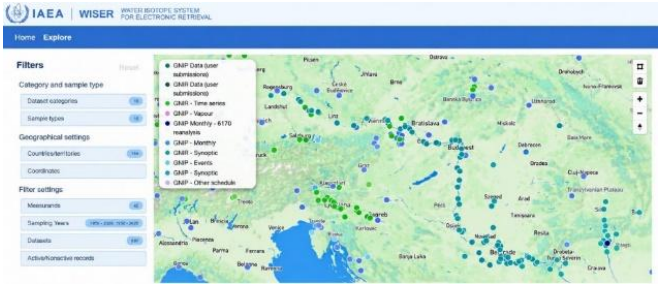


Figure 4. Portal for Accessing and Searching GNIP and GNIR Data (Source: IAEA WISER – Water Isotope System for Electronic Retrieval)

Data obtained through international monitoring networks enable comparisons of isotopic characteristics across different climatic and geographical settings and support regional and global hydrological investigations. These data are used to study water origin and movement, investigate hydrological connectivity, assess the effects of climate variability, and improve the development and validation of hydrological models. The establishment and continuous development of national isotope monitoring programmes, together with their integration into international databases, are essential for improving data comparability, strengthening scientific and technical capacities, and providing a sound scientific basis for the sustainable management of water resources [14, 28].

8. ISOTOPE RESEARCH IN THE REPUBLIC OF NORTH MACEDONIA

The application of isotope techniques in hydrological research in the Republic of North

Macedonia is very limited; existing studies are rare and primarily focus on individual water systems. Notable examples include research into the hydrological connection between Lake Prespa and Lake Ohrid, where the use of isotope and other methods confirmed the underground outflow of water from Lake Prespa toward Lake Ohrid [29]. Isotope techniques have also been applied to study the Rašče spring, with the aim of determining the origin of the water, recharge mechanisms, and the residence time of groundwater within the Žeden karst massif [30]. However, such studies remain isolated examples, while systematic, long-term monitoring of the isotopic composition of natural waters in the country remains underdeveloped.

Recently, initiatives have been undertaken to introduce a more comprehensive and systematic approach to isotope research. For the first time, a monitoring network has been established in the Vardar River basin for the continuous collection of precipitation samples at three locations: Tetovo, Skopje, and Gevgelija [31]. In parallel with the monitoring of precipitation, sampling from the Vardar River has also commenced, establishing a foundation for the integrated study of stable hydrogen and oxygen isotopes (δ^2H and $\delta^{18}O$) in precipitation, surface water, and groundwater [32]. This approach enables the investigation of spatial and seasonal variations in isotopic composition, the determination of meteoric water lines, and a better understanding of the hydrological connectivity between various water systems. Figure 5 shows the sampling points from the monitoring network in the Vardar River basin

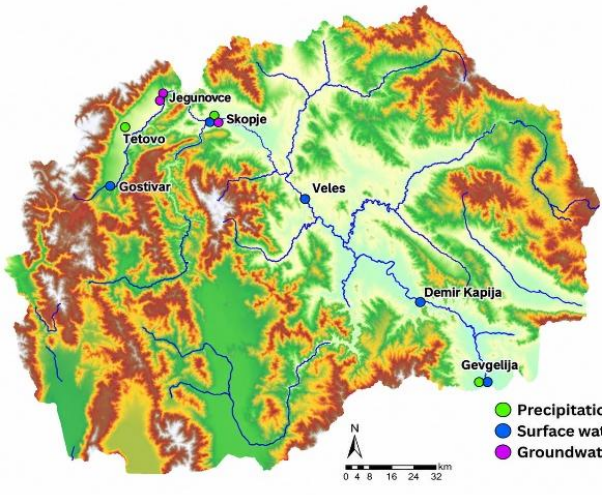


Figure 5. Monitoring network for stable isotopes in water in the Vardar River basin (Source: Authors)

The implementation of this approach represents a significant step toward the development of isotope hydrology in the Republic of North Macedonia. Continuous monitoring, the enhancement of laboratory capabilities, and the creation of an isotopic data repository will facilitate the expansion of research and its integration into international monitoring networks. Consequently, this establishes a basis for a better understanding of hydrological processes and provides additional scientific insights for the protection and sustainable management of water resources.

9. CONCLUSION

Isotope techniques represent a significant tool in modern hydrology, as they enable the acquisition of additional information regarding the origin, movement, and dynamics of water within the hydrological cycle. The application of stable isotopes of hydrogen and oxygen (δ^2H and $\delta^{18}O$) facilitates the identification of recharge areas, the study of seasonal and spatial variations, and the investigation of processes such as evaporation, mixing, and the connectivity between surface water and groundwater. On the other hand, radioactive isotopes—specifically tritium (^3H) and carbon-14 (^{14}C)—provide valuable insights into the age and residence time of groundwater.

Integrating isotope analyses with conventional hydrological, hydrogeological, and hydrochemical methods allows for a more comprehensive understanding of water systems and greater confidence in the interpretation of hydrological processes. The establishment of systematic, long-term isotope monitoring is of particular importance, as it enables the tracking of changes in water resources and the creation of relevant databases. Linking national monitoring programs with international networks, such as GNIP and GNIR, further contributes to the comparability of results and the advancement of hydrological research.

In the Republic of N. Macedonia, where the application of isotope techniques has thus far been limited to a small number of isolated studies, the establishment of integrated monitoring of the isotopic composition of precipitation, surface water, and groundwater represents a significant advancement. Further development of laboratory facilities, expansion of the monitoring network, and continuous collection of isotope data will create the conditions for more detailed research into

hydrological processes. In the long term, the application of these techniques can contribute significantly to a better assessment of available water resources, as well as their protection and sustainable management—particularly in the context of climate change and increasing pressure on water systems.

Acknowledgements

This paper was produced within the framework of the scientific research project "Analysis of Stable Isotopes in Precipitation, Surface Water, and Groundwater," funded by the Ministry of Education and Science of the Republic of North Macedonia.

REFERENCES

[1] Clark, I. D., Fritz, P. (1997), "Environmental Isotopes in Hydrogeology", CRC Press, Boca Raton.

[2] Kendall, C., McDonnell, J. J. (Eds.) (1998), "Isotope Tracers in Catchment Hydrology", Elsevier, Amsterdam.

[3] Dansgaard, W. (1964), "Stable isotopes in precipitation", Tellus, Vol. 16 No. 4, pp. 436–468.

[4] Gat, J. R. (1996), "Oxygen and hydrogen isotopes in the hydrologic cycle", Annual Review of Earth and Planetary Sciences, Vol. 24, pp. 225–262.

[5] Jasechko, S. (2019), "Global isotope hydrogeology—Review", Reviews of Geophysics, Vol. 57 No. 3, pp. 835–965.

[6] Hillaire-Marcel, C., Kim, S.-T., Landais, A., et al. (2021), "A stable isotope toolbox for water and inorganic carbon cycle studies", Nature Reviews Earth & Environment, Vol. 2, pp. 699–719.

[7] Rozanski, K., Araguás-Araguás, L., Gonfiantini, R. (1993), "Isotopic patterns in modern global precipitation", in Swart, P. K., Lohmann, K. C., McKenzie, J., Savin, S. (Eds.), Climate Change in Continental Isotopic Records, Geophysical Monograph Series, Vol. 78, American Geophysical Union, pp. 1–36.

[8] International Atomic Energy Agency (IAEA) (2013), "Isotope Methods for Dating Old Groundwater", IAEA, Vienna.

[9] Schubert, M., Lin, M., Clark, J. F., Kralik, M., Damatto, S., Copia, L., Terzer-Wassmuth, S., Harjung, A. (2024), "Short-lived natural radionuclides as tracers in hydrogeological studies – A review", Science of the Total Environment, Vol. 920, Article 170800.

[10] Rozanski, K., Araguás-Araguás, L., Gonfiantini, R. (1992), "Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate", Science, Vol. 258 No. 5084, pp. 981–985.

[11] Dee, S., Bailey, A., Conroy, J. L., Atwood, A., Stevenson, S., Nusbaumer, J., Noone, D. (2023), "Water isotopes, climate variability, and the hydrological cycle: recent advances and new frontiers", Environmental Research: Climate, Vol. 2 No. 2, Article 022002.

[12] Bowen, G. J., Wilkinson, B. (2002), "Spatial distribution of $\delta^{18}O$ in meteoric precipitation", Geology, Vol. 30 No. 4, pp. 315–318.

[13] Bowen, G. J. (2010), "Isoscapes: Spatial pattern in isotopic biogeochemistry", Annual Review of Earth and Planetary Sciences, Vol. 38, pp. 161–187.

[14] Bowen, G. J., Cai, Z., Fiorella, R. P., Putman, A. L. (2019), "Isotopes in the Water Cycle: Regional- to Global-Scale Patterns and Applications", Annual Review of Earth and Planetary Sciences, Vol. 47, pp. 453–479.

[15] International Atomic Energy Agency (IAEA) (2023), "Towards Best Practices in Isotope-Enabled Hydrological Modelling Applications: Final Report of a Coordinated Research Project", IAEA-TECDOC-2022, IAEA, Vienna.

[16] Skrzypek, G., Allison, C. E., Böhlke, J. K., et al. (2022), "Minimum requirements for publishing hydrogen, carbon, nitrogen, oxygen and sulfur stable-isotope delta results (IUPAC Technical Report)", Pure and Applied Chemistry, Vol. 94 No. 11–12, pp. 1249–1255.

[17] Brand, W. A., Coplen, T. B., Vogl, J., Rosner, M., Prohaska, T. (2014), "Assessment of international reference materials for isotope-ratio analysis", Pure and Applied Chemistry, Vol. 86 No. 3, pp. 425–467.

[18] Coplen, T. B. (2011), "Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results", Rapid Communications in Mass Spectrometry, Vol. 25 No. 17, pp. 2538–2560.

[19] Craig, H. (1961), "Isotopic variations in meteoric waters", Science, Vol. 133 No. 3465, pp. 1702–1703.
DOI: 10.1126/science.133.3465.1702

[20] Cook, P. G., Böhlke, J.-K. (2000), "Determining timescales for groundwater flow and solute transport", in Cook, P. G., Herczeg, A. L. (Eds.), Environmental Tracers in Subsurface Hydrology, Kluwer Academic Publishers, Boston, pp. 1–30.

[21] Cartwright, I., Morgenstern, U. (2016), "Using tritium and other geochemical tracers to address the 'old water paradox' in headwater catchments", Journal of Hydrology, Vol. 563, pp. 13–21.

[22] Gupta, P., Noone, D., Galewsky, J., Sweeney, C., Vaughn, B. H. (2009), "Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology", Rapid Communications in Mass Spectrometry, Vol. 23 No. 16, pp. 2534–2542.

[23] Copia, L., Wassenaar, L. I., Juvonen, R., Oikari, T. (2024), "Enhancing low-level tritium detection in environmental waters: assessing the Hidex ULLA liquid scintillation counter", Journal of Environmental Radioactivity, Vol. 280, Article 107545.

[24] Matiatos, I., Papadopoulos, A., Panagopoulos, Y., Dimitriou, E. (2023), "Insights into the influence of morphology on the hydrological processes of river catchments using stable isotopes", Hydrological Sciences Journal, Vol. 68 No. 11, pp. 1487–1498.

[25] Xia, C., Liu, Y., Meng, Y., Liu, G., Huang, X., Chen, Y., Chen, K. (2023), "Stable isotopes reveal the surface water-groundwater interaction and variation in young water fraction in an urbanized river zone", Urban Climate, Vol. 51, Article 101641.

[26] Yapiyev, V., Rossi, P. M., Ala-Aho, P., Marttila, H. (2023), "Stable Water Isotopes as an Indicator of Surface Water Intrusion in Shallow Aquifer Wells: A Cold Climate Perspective", Water Resources Research, Vol. 59 No. 2, Article e2022WR033056.

[27] International Atomic Energy Agency (IAEA) (n.d.), "Global Networks of Isotopes in Precipitation and Rivers (GNIP, GNIR)", IAEA, Vienna.

[28] Holko, L., Melikadze, G., Todadze, M., Chitanava, R., Chankvetadze, A., Chikadze, T., Gventsadze, A., Gaphrindashvili, M. (2023), "Stable isotopes of oxygen and hydrogen in precipitation and river water in Georgia", Journal of Hydrology and Hydromechanics, Vol. 71 No. 3, pp. 248–258.

[29] Anovski, T., Popov, V., Amataj, S., Anovska-Jovcheva, E., Jovchev, Z., Stojmenovska, I., Anovski, K., Milevski, J. (2012), "Study of Prespa Lake's Hydrology Using Isotopes and Other Relevant Techniques", WIT Transactions on Ecology and the Environment, Vol. 160, pp. 271–281.

[30] Anovski, T., Anovska-Jovcheva, E., Lisichkov, K., Dimitrovski, D., Kuvendziev, S., Leis, A., Benischke, R., Micevski, E., Arsov, L. (2019), "Application of environmental isotope techniques for determining the origin and mechanisms of recharge of the Rashche Spring", Environmental Earth Sciences, Vol. 78, Article 656.

[31] Faculty of Civil Engineering – Skopje (2025), "First phase of activities under project RER7017 completed – precipitation instruments installed," June 9, 2025. https://gf.ukim.edu.mk/завршена-прва-фаза-на-активностите-во/

[32] Faculty of Civil Engineering – Skopje (2025), "Project RER7017 – Ensuring Water Availability in a Changing Climate", July 11, 2025. https://gf.ukim.edu.mk/en/проект-rer7017-project-ensuring-water-availability-in-a-changing-climate/

[33] Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., Wernli, H. (2012), "Measuring variations of $\delta^{18}O$ and $\delta^{2}H$ in atmospheric water vapour using two commercial laser-based spectrometers: an instrument characterisation study", Atmospheric Measurement Techniques, Vol. 5 No. 7, pp. 1491-1511. https://doi.org/10.5194/amt-5-1491-2012

[34] Diamond, R. E. (2022), "Stable Isotope Hydrology", The Groundwater Project, Guelph, Ontario, Canada, 102 pp. https://doi.org/10.21083/978-1-77470-043-3