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Editorial

The Use of Environmental Isotopes in Hydrogeology

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1. Introduction

As a consequence of the population increase, there is a growing need for groundwater use worldwide, leading to the intensification of agricultural practices alongside the growth of industrial development. About 30% of the total available freshwater around the globe is found in aquifer systems (renewable water resources), with different replenishing rates depending on climatic conditions. National and international water authorities and experts on water problems worldwide are addressing water scarcity and overexploitation in available groundwater systems. Some of these aquifer systems are faced with anthropogenic contamination, namely surface and groundwater pollution of different origins such as those associated with agriculture practices, urban activities, and industry [1–5].

Isotope hydrology methodologies have been introduced in hydrogeological investigations for over fifty years, and the scope of their applications has increased throughout the world in different interdisciplinary fields. These methods are being applied as routine approaches in the characterization of water resources through the determination of the water molecule (δ^2H, ^3H, and $\delta^{18}O$) and the isotopic composition of the dissolved components (e.g., $\delta^{13}C$, ^{14}C, $\delta^{15}N$, and $\delta^{34}S$) present in the water. The knowledge of the isotopic composition of the dissolved ions is often crucial in the evaluation of groundwater contamination, enabling a "deeper" characterization of water resources.

The stable and radioactive isotopes naturally present in water can be used to identify its origin and the mean residence time and replenishment rates of groundwater systems. In aquifers, the assessment of replenishment rates and recharge sources is critical in supporting their function as reliable long-term water resources, for either human consumption or agriculture or industrial uses.

Understanding the chemical and dynamic evolution of groundwater along the flow paths is almost impossible without "looking" into the spatial and regional distribution and changeability of the environmental isotopes, using δ^2H, $\delta^{13}C$, $\delta^{18}O$, ^3H, and ^{14}C content. Among the available isotope hydrology methods, the determination of tritium, carbon-13, and nitrogen concentrations in water systems has often been demonstrated to be powerful in the identification/quantification of the main sources of contaminants [6–8].

According to Aggarwal and co-authors [9], research on isotope hydrology continues to be of prominence, as evidenced by the growing number of published research papers in scientific journals in which isotopes are often a key tool applied in hydrogeological studies. These authors compared the increasing number of studies from the early beginnings (1960–1965) with less than 100 scientific papers within 6 years to the exponential increase to approximately more than 7000 publications between 1995 and 2000 [9]. This increasing number of publications was the result of the new measurement methodology, i.e., the use of laser absorption spectroscopy (LAS), facilitating an inexpensive and faster measurement while requiring a smaller sample size [10–12].

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The use of isotope hydrology methodologies, together with the traditional hydrogeological approaches, raises significant awareness in understanding and characterizing the groundwater dynamics along flow paths. Isotope hydrology has proved particularly valuable in the following areas:

(i) The identification of mixture mechanisms between different water bodies (e.g., surface and groundwater systems);
(ii) The identification of the processes responsible for water mineralization;
(iii) Preferential recharge altitude assessments;
(iv) The assessment of mean groundwater flow velocities and the mean residence time.

This Special Issue, entitled "The Use of Environmental Isotopes in Hydrogeology", seeks to address the combination of isotopic and geochemical data interpretation in a hydrogeological context, a key topic for the proper sustainable management of water resources, in which a better understanding of isotope hydrology can eliminate inaccuracies, fill gaps, and rectify misconceptions often occurring along the flow path. In this Special Issue, seven original papers have been published, originating from different geographical locations, with different climatological and hydrogeological backgrounds.

2. Contributions

The seven papers published in this Special Issue showcase the different approaches related to the use of isotopes. The research articles address a variety of issues, from the characterization of the isotopic composition of precipitation networks to the characterization of complex aquifer systems and catchment areas.

2.1. Stable Isotope Signatures in Tehran's Precipitation: Insights from Artificial Neural Networks, Stepwise Regression, Wavelet Coherence, and Ensemble Machine Learning Approaches

The contribution by Mojtaba Heydarizad et al. leads this collection by presenting a combination of artificial neural networks with the measured stable isotope composition in Tehran, using the GNIP network database. The authors used different approaches, from stepwise regression to ensemble machine learning methods, to simulate the isotopic composition signatures observed/measured in precipitation in Iran. The accuracy of machine learning models is discussed, and the results are compared in the paper. The uncertainty in the simulations of the XGboost model indicates that this model most accurately predicted stable isotope values. The authors also indicated that the dominant factor influencing the stable isotope fingerprints of regional precipitation is temperature. This type of approach using environmental parameters provides valuable insights into the association between variations in the isotopic composition of precipitation and climatological parameters, which is of significance under the climatic change context.

2.2. Analysis of the Recharge Area of the Perrot Spring (Aosta Valley) Using a Hydrochemical and Isotopic Approach

The contribution by Santillán-Quiroga et al. is focused on the hydrogeological behavior of Perrot Spring, situated in the Monte Avic Natural Park (Valle d'Aosta, Italy), at 1300 m a.s.l., to identify and characterize the recharge areas and processes related to this spring. To achieve this, the authors used hydrochemical and isotopic methodologies. The results indicate two main sources contributing to the Perrot Spring input, i.e., a snowmelt input identified by a minor rise in flow and an autumn input derived from precipitation (rainwater) infiltration. Based on the low-temperature average values, together with the small variation in the annual temperature (between 4.8 °C and 6.5 °C), Santillán-Quiroga et al. suggest the existence of a sufficient groundwater deep flow. The spring's chemical analyses reflect water–rock interaction with regional lithological formations, explaining the calcium–magnesium bicarbonate hydrochemical facies of Perrot Spring waters. The stable isotopic results (δ^2H and δ^{18}O) of the regional precipitation and groundwater spring samples point to a preferential recharge altitude of around 2100 m a.s.l. The environmental isotope content used by the authors led to the identification of the main sources contributing to the spring discharge and allowed them to delineate its preferential recharge altitude areas. These achievements are important in the protection and sustainability of Perrot Spring, which supplies the municipality of Champdepraz.

2.3. The Integration of Stable Isotopes and Water-Level Monitoring for the Characterization of Groundwater Recharge in the Pra Basin, Ghana

The study by Manu et al. presents the regional stable isotope data in the Pra Basin (Ghana) concerning surface and groundwater problems. The obtained results were used to explore the hydrogeochemical processes occurring within the groundwater resources of the research area while considering the boundary conditions. The authors determined the isotopic content of the water samples together and measured the water levels to identify the potential recharge sources and recharge mechanisms. They observed depletion in the groundwater resources when the isotopic data involved surface water samples, ascribed to a short period of recharge water in the vadose zone. When associated with water levels, the field data regarding the stable isotope values indicate a potential hydraulic association between surface water and groundwater. This hypothesis is corroborated by the depleted isotopic composition of groundwater compared with the surface water values. Overall, this study provides an innovative understanding of groundwater recharge processes and their spatial quantification inside the Pra Basin. This type of characterization can be applied in groundwater flow and hydrogeochemical evolution conceptual models, which are fundamental for the effective sustainability, management, and protection of water resources in the region, i.e., in the framework of Pra Basin's Integrated Water Resources Management Plan.

2.4. Radiocarbon Dating and Stable Isotope Content in the Assessment of Groundwater Recharge at Santiago Island, Republic of Cape Verde

The research performed at Santiago Island by Carreira and co-authors aimed to distinguish the major mechanisms controlling groundwater salinization. This identification was achieved using different approaches, namely through the chemical characterization of aquifer systems and environmental isotopic and geophysical research. Concerning the geochemical data, a weak correlation was observed between the chemical composition of the water samples and geological formations. The authors enhanced the evolution trend by taking into account the mean seawater chemical composition; yet, attention was drawn to well location, making this hypothesis unfeasible and pointing to the importance of marine aerosol dissolution in the chemical evolution of water. Nonetheless, the stable isotopic composition allowed for the identification of (i) one group represented by groundwater samples from the eastern part of the island and (ii) another cluster mainly comprising the water points located all over the island, where the isotopic composition of groundwater is controlled by the recharge altitude. The "eastern group" of groundwater sources was considered as the result of ancient recharge from precipitation under different climatic regimes, where groundwater isotopic composition acted as a climatic archive of a paleoclimatic fingerprint. Tritium and carbon-14 concentrations indicated an active recharge of the aquifer systems, even though no tritium was detected in some locations. The radiocarbon-apparent ages obtained in the groundwater corroborated the assumption that the stable isotopic composition of the eastern group of samples is characterized by an ancient climatic pattern. Using the isotopic composition of C4 plants as a correction factor to estimate the ^{14}C-apparent groundwater ages, the authors dated these water samples between 3500 and 5000 years BP.

2.5. Isotope Discrimination of Source Waters, Flow Paths, and Travel Times at an Acid-Generating, Lead–Zinc–Silver Mine, Silver Valley, Idaho, USA

The paper presented by Langman and co-authors investigates a complex geological site at Bunker Hill, where alterations from past mining activities (a large pyritic zone) provided a heterogeneous environment. The environmentally stable and radioactive isotopes were used in the identification of the origin of infiltrated waters, associated with snowmelt and overland flow in the surrounding mountains. The relatively depleted stable isotopic content and the highest ^3H content were found in snowpack samples, setting one endpoint (baseline composition) for the identification of the origin of waters infiltrating at different depths in the mine. An isotopic evolution trend was observed along the mine levels, with depleted values in samples from the higher elevation creek, whereas a more enriched isotopic content was observed in the water samples from the lower elevation creek. The δ^2H and $\delta^{18}O$ concentrations present regional and temporal evolution trends. The water samples collected within the mine seem to represent a mix of different flow paths, i.e., from the contribution of snowmelt at a high altitude to infiltration/recharge at a lower elevation receiving downslope runoff and inflow waters from high mine levels. The different water contributions are reflected in different seasonal fluxes, with a primary contribution during the snow-melting period. Recharge contribution from high-elevation infiltration zones seems to intersect with regional pyritic layers, restricting water infiltration to natural flow paths (faults, fractures, and bedding planes). The infiltrated waters at higher elevations have a longer residence time and represent water with better quality and less variation over time.

2.6. An Interdisciplinary Approach and Geodynamic Implications of the Goutitir Geothermal System (Eastern Meseta, Morocco)

The geothermal site of Guercif Basin provides important fingerprints of geothermal volcanic activity at a surface or a relatively near-surface level. The study by El Mehdi Jeddi and co-authors presents the structural, lithological, and hydrogeochemical regional characterization of the groundwater system of the thermal spring of Goutitir. The isotopic results reveal a meteoric origin (regional precipitation) with preferential recharge altitude zones around 2000 m a.s.l., only observed at Middle Atlas Mountain, SW of the Goutitir thermal spring. The hydrothermal system's maximum depth is 3.5 km, calculated using chemical parameters. In this study, the authors characterized the water–rock interaction with the regional lithology basement of the Neogene Guercif Basin (mafic and mantle igneous rocks). However, they highlighted the maximum groundwater circulation depth since, the value obtained was significantly "higher" than the Mesozoic Reservoir, at 2 km depth, considered the main water reservoir within the Atlas region. The authors pointed to the structural analysis of the region, which confirmed a strong association between the thermal waters of Goutitir and the regional NE–SW fault network and E–W thrusts. The NE–SW faults are considered to favor flow paths for groundwater circulation, while E–W thrusts represent the ascent pathway structures from depth to the surface.

2.7. Review of Isotope Hydrology Investigations on Aquifers of Cameroon (Central Africa): What Information for the Sustainable Management of Groundwater Resources?

Bertil Nlend and co-authors present a review paper on the environmental isotopes in the characterization of groundwater resources in Cameroon in the past 30 years. Their work significantly improves our understanding of hydrological processes involved in recharge for the characterization of groundwater flow paths in Cameroon. The authors highlighted the isotopic database that was built using irregular short-period studies, where only a few series of data allow for long-term monitoring analyses. Even in restricted regions of the country, data exist regarding the long-term monitoring of the isotopic composition of rivers and rainfall. These data contribute to relevant information on the recharge of aquifer systems and allow for the identification of surface water–groundwater mixture. The isotopic studies started in Cameroon in the early 1990s, when isotope hydrology methods were applied for the first time in the far north region of the country. Currently, this type of research method is used more frequently; nevertheless, in the Sahelian domain (the far north region), the humid coastal region of Cameroon continues to be the most studied. Environmental radioactive isotopes remain rarely explored, leading to poor knowledge of deeper water resources. This published research is unique as, for the first time, an isotopic database gathering data from different regions of Cameroon with different geomorphological and climatic characteristics was generated and used to organize guidelines for future isotopic studies. The authors hope that this document may provide a better overall understanding of the evolution of water resources and assist in the long-term monitoring and planning of water resources.

3. Concluding Remarks

This collection of articles focused on enhancing the applicability of environmental isotopes in hydrology in different geographic, geomorphological, geological, and climatic conditions and showcasing a diverse range of research, indicative of the richness of this research field. Although a common topic was the foundation of this Special Issue, the novel research presented is also reflected in the different approaches and discussion of the results.

All contributions highlight the importance of groundwater, vital in the management of water resources worldwide. Groundwater quality can be affected by population growth and climate change, issues that were addressed with the environmental isotope approach. The scientific knowledge was enriched by the use of isotope techniques and methodologies, namely through the joint utilization of hydrogeochemical techniques and environmental isotopes of water (e.g., δ^2H, $\delta^{18}O$, and ^3H) for the contamination assessment of surface water–groundwater systems, which also contributes to the development of conceptual models of river–aquifer systems at the watershed level. The comprehension of groundwater flow dynamics, the identification of recharge sources, the meteoric origin of water sources, and information regarding karst aquifer systems can also result from the use of environmental isotopes. Moreover, isotope hydrology assists in the detection of possible contamination sources. Groundwater can be dated and residence times can be estimated with the use of tritium (^3H), a radioactive isotope.

This SI presents local and regional environmental isotope data of surface water, groundwater, and geothermal water sources, providing fundamental information to conceptualize joint hydrogeochemical and isotopic models that enhance groundwater evolution from recharge to discharge areas. In fact, a comprehensive understanding of the source and recharge mechanisms of groundwater plays a vital role in reaching its sustainable management.

The lack of comprehensive environmental isotopic studies involving the quantification of groundwater depletion and aquifer deterioration is a future challenge regarding the sustainable management of groundwater resources. Recognizing aquifer quality and vulnerability will help decision-makers supervise groundwater resources and relieve likely pollution sources. Water shortage is a major water problem in the world, which, due to population and economic growth, has increased during the 21st century. An assessment of the core spatial and temporal flow patterns is needed for the characterization of groundwater flow systems.

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