water

Editorial

Application of Stable Isotopes and Tritium in Hydrology

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The availability and quality of freshwater currently represent one of the great issues for mankind. Increasing demand for freshwater (both ground and surface water), environmental pollution, and climate change affects the water quality and changes its dynamics. Groundwater recharge and infiltration conditions, the mechanisms of mass transfer, and the mixing of water with different compositions and ages are among the basic problems of hydrology and hydrogeology that have been simultaneously tackled by both conventional hydrological methods and by isotope methods. Isotope studies applied to a wide spectrum of hydrological problems related to both surface and groundwater resources as well as environmental studies in hydro-ecological systems present today an established scientific discipline, often referred to as "Isotope Hydrology". Isotope hydrology techniques have proved to be effective tools for solving many critical hydrological problems and processes and in many cases, provide information that could not be obtained by conventional means only.

Isotopes of hydrogen (^{3}H, ^{2}H) and oxygen (^{18}O) are perfect candidates for groundwater tracers because they are constituent elements of the water molecule. Among them, ^{3}H (tritium) is the best candidate for the determination of groundwater age, if we assume that groundwater "age" is the travel time between recharge and discharge. Knowledge of the isotopic composition (δ^{18}O, δ^{2}H, including the derived quantity deuterium excess (*d*-excess), and ^{3}H activity concentration) in surface and groundwater and its relation to the isotopic composition of precipitation have found wide application in hydrology, such as the determination of the mean residence time of water in aquifers, the determination of recharge areas, the interconnections between aquifers, the origin of groundwater, and the dynamics of processes in surface waters.

A considerable number of studies on the use of isotope composition of various types of water have been published recently. In addition to the growing awareness of the usefulness of isotope studies in solving various hydrological problems, one of the main reasons for the increased number of isotope studies is the development of new measurement techniques [1] that enable fast measurement of a large number of small-sized samples at reasonably good precision and relatively low price.

This Special Issue (SI) of the MDPI journal *Water*, entitled "Application of stable isotopes and tritium in hydrology" addresses the current state-of-the-art applications of stable isotopes and tritium in studies of hydrological processes in various compartments of the water cycle. It can be considered as a sequel of the previous SI, "Use of Water Stable Isotopes in Hydrological Process" [2]. However, this SI is the only (closed) special issue of the journal *Water*—Hydrology and Hydrogeology Section that in the title explicitly mentions "tritium", the radioactive isotope of hydrogen of both natural (cosmogenic) and anthropogenic origin ([3] and references therein). The massive injection of anthropogenic tritium from atmospheric weapon tests in the 1950s and 1960s caused an almost 1000-fold increase in tritium activity concentration in precipitation, known as the "bomb peak". As precipitation is the ultimate source of groundwater, the bomb peak was quickly spread over the hydrosphere and the importance of tritium for studies of hydrological processes has been recognized by numerous researchers. In the last decades of the 20th century, tritium has been widely used to obtain time scales for physical processes in various hydrosphere compartments, mostly for dating modern water and distinguishing modern recharges from water older than about 50 years. After the cessation of atmospheric nuclear tests, a gradual decrease in tritium activity concentration in precipitation was observed worldwide until approximately the mid-1990s. After that, the mean annual tritium activity concentration in precipitation is almost constant approaching the pre-bomb tritium level and thus the present scientific value of tritium for hydrological applications has significantly declined [3].

This SI was announced and open for submission in November 2019, with a deadline of 24 May 2020. However, due to the pandemic and lockdown over most of the world in spring 2020, the deadline was extended to the end of July 2020. A total of nine papers were submitted for publication and they have undergone a scrutinized review process. Eventually, six papers passed the rigorous review by at least two recognized international reviewers and extensive editorial checks. The papers compiled in this SI show a wide variety of topics: isotope distribution in precipitation [4] and groundwater on regional scales [5], the relation between isotopes in precipitation and ground and drip water in a karst area [6,7], effects of evapotranspiration [8], and farming activities [9] on water isotope composition. Three out of six papers describe isotope studies in a karst area of Croatia [5–7], while the other papers consider the Iberian Peninsula [4], the United States of America [8], and China [9]. In what follows we shortly describe the most important aspects of the papers from this compilation and the main results presented.

Hatvani et al. [4] explored the spatial variation of oxygen and hydrogen stable isotope composition (δ_p) and *d*-excess of precipitation across the Iberian Peninsula. The data from 24 monitoring stations of the Global Network of Isotopes in Precipitation (GNIP) for October 2002–September 2003 were used, while for October 2004–June 2006, the 13 GNIP stations were merged with 21 monitoring stations from a regional network in NW Iberia. The research aimed to look for features of spatial variability of the isotope composition of precipitation in the Iberian Peninsula, to determine the spatial representativity of the regional precipitation monitoring network, and to provide an improved estimation for the spatial distribution of precipitation water stable isotopes across the Iberian Peninsula. Spatial autocorrelation structure of monthly and amount weighted seasonal/annual mean δ_p values were modeled, and two isoscapes were derived for stable oxygen and hydrogen isotopes in precipitation with regression kriging. Only using the GNIP sampling network, no spatial autocorrelation structure of δ_p could have been determined due to the scarcity of the network. However, in the case of the merged and much denser GNIP and NW dataset, for δ_p a spatial sampling range of ~450 km in the planar distance (corresponding to ~340 km in geodetic distance) was determined. The range of δ_p, which also broadly corresponded to the range of the *d*-excess, probably referred to the spatially variable moisture contribution of the western Atlantic-dominated and eastern Mediterranean-dominated domains of the Iberian Peninsula. The estimation error of the presented Iberian precipitation isoscapes, both for oxygen and hydrogen, was smaller than the ones that were reported for the regional subset of one of the most widely used global models, suggesting that the current regional model provided a higher predictive power. The authors concluded that a sparser network (e.g., GNIP) might be representative and suitable for the Iberian Peninsula, but its verification could only be done with a denser network. The results encourage the development of precipitation stable isotope models at a sub-continental scale in further regions.

Brkić et al. [5] presented an overview of isotope investigations in both karst and alluvial aquifers in Croatia at approximately 100 sites from the period 1997–2014. Stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) were used as indicators of the recharge condition, while tritium (^{3}H) was used to estimate an approximate mean groundwater age and for that the qualitative criteria were used to distinguish water recharged prior to the 1950s (<0.8 TU, sub-modern water), a mix of sub-modern and modern water (0.8 to about 4 TU), modern water (5 to 15 TU), waters containing "bomb" tritium (15–30 TU), and waters recharged in the 1960s to 1970s (>30 TU). The regional meteoric water lines (RMWL) were determined for the continental part

($\delta^2H_{p,cont}$ = (7.400 ± 0.005) $\delta^{18}O$ + (4.1 ± 0.5), R^2 = 0.99, n = 524) and the coastal part of Croatia ($\delta^2H_{p,coast}$ = (7.00 ± 0.08) $\delta^{18}O$ + (4.4 ± 0.5), R^2 = 0.96, n = 655). The composition of the stable isotopes of groundwater originated from recent precipitation and was described by regional groundwater lines (RGWL) that closely resembled the RMWLs: groundwater accumulated in the aquifers in the Pannonian (continental) part of Croatia can be described by $\delta^2H_{g,cont}$ = 7.4 $\delta^{18}O$ + 5.5, n = 255, R^2 = 0.93, and groundwater accumulated in the Dinaric karst of Croatia by $\delta^2H_{g,coast}$ = 7.0 $\delta^{18}O$ + 4.2, n = 340, R^2 = 0.96. The *d*-excess values of karst groundwater varied between 6‰ and 17‰ and increased with altitude; the catchment areas at relatively high altitudes and under the influence of the Mediterranean air masses showed the highest *d*-excess values, while the lowest *d*-excess values were determined in springs with catchment areas at relatively low altitudes and affected by the Atlantic air masses. The individual *d*-excess values of groundwater in the continental (Pannonian) region varied between 7.8‰ and 14.4‰. Higher values were again attributed to the influence of Mediterranean precipitating air masses. Most of the *d*-excess values in the groundwater samples in the Sava basin, Eastern Slavonia ranged from 10‰ to 12‰. Here the mean residence time of the groundwater was relatively long and, accordingly, the different individual precipitation contributions to groundwater were well mixed and their variations were dampened in the groundwater samples. Opposite to this, a wide range of *d*-excess values was found in the groundwater samples with relatively short mean residence time. The isotope content showed that the studied groundwater was mainly modern water making such water relatively vulnerable to the potential sources of environmental pollution. A mix of sub-modern and modern water was mostly accumulated in semi-confined porous aquifers in northern Croatia, deep carbonate aquifers, and (sub)thermal springs, which puts groundwater in these areas in a better position regarding vulnerability and pollution risks. This paper presents an important contribution to regional knowledge on groundwater hydrology obtained by applying tracers such as stable isotopes and tritium. The presented results may be useful for future studies on the isotopic composition of groundwater in Croatia and in nearby countries.

Although Brkić et al. [5] included about 100 sites from two regions in Croatia, they did not include the area of the Plitvice Lakes (PL) that presents a unique karst geomorphological system of 16 cascade flow-through lakes that are fed by three main springs and outflow to the Korana River. Krajcar Bronić et al. [6] presented various isotope studies of different types of water bodies (precipitation, groundwater, surface lake and river water, lake water from traps at certain depths) from the early period of isotope applications (since 1979) to the most recent ones (2018). The aim of the paper was to evaluate the most important hydrological inputs to the Plitvice Lakes and to detect possible effects of climate change on karst groundwater. The study included tritium, ^2H, and ^{18}O, and available climatological data (amount of precipitation, air temperature) in a search for evidence of climatological changes. An increase in the mean annual air temperature of 0.06 °C/year and the annual precipitation amount of 10 mm/year was observed for the PL area. The good correlation of the tritium activity concentration in the PL and Zagreb precipitation (discussed in detail in [3]) implied that the tritium data for Zagreb were applicable for the study of the PL area. The best local meteoric water line at PL was obtained by the reduced major axis regression (RMA) and precipitation-weighted ordinary least squares regression (PWLSR) approaches that gave also the best results for the closest precipitation stations Zagreb and Zadar: δ^2H_{PWLSR} = (7.97 ± 0.12) $\delta^{18}O$ + (13.8 ± 1.3), n = 36. The higher deuterium excess at PL (14.0 ± 2.2‰) than that at Zagreb (8.8 ± 0.8‰) in the same period reflected the higher altitude and influence of the Mediterranean precipitation at PL. The δ^2H in precipitation ranged from −132.4‰ to −22.3‰ and $\delta^{18}O$ from −18.3‰ to −4.1‰. The much narrower ranges in the groundwater (<1‰ in $\delta^{18}O$, <10‰ in δ^2H) indicated good mixing of waters in the aquifers. The higher average δ^2H in all three karst springs observed after 2003 was attributed to the increase in the mean air temperature. The mean δ^2H and $\delta^{18}O$ values in the surface and lake water increased downstream due to the evaporation of surface waters. It was shown that the stable isotope composition of surface and lake waters reacted to extreme weather conditions (intense precipitation events and snow melting).

Tritium activity concentration was used to determine the mean residence time (MRT) in three karst springs (range 2–4 years). Extreme hydrological conditions in 1983 (very low flow rate) and 1984 (high flow rate due to snow melting) enabled the determination of relative contributions of base-flow and precipitation in the three karst springs: the shorter the MRT, the higher proportions of precipitation. To conclude, the long-term and comprehensive isotope study of different water bodies in the area of the Plitvice Lakes can serve as an example of how the application of water isotopes (^{2}H, ^{18}O, ^{3}H) can help in the characterization of karst aquifers on regional and global scales.

Dinaric karst covers almost half of the Croatian territory [7], including islands and the Adriatic coast, high mountain regions, and part of central Croatia. The karst region is characterized by various forms of secondary carbonate sediments, like speleothem, tufa, or carbonaceous lake sediments. Speleothems deposited from cave drip waters retain in their calcite lattice isotopic records of past environmental changes and thus present the natural archives which confidentially record hydroclimate changes. Among other proxies, δ^{18}O is recognized as very useful for this purpose, but its accurate interpretation depends on understanding the relationship between precipitation and drip water δ^{18}O, a relationship controlled by climatic settings. Under equilibrium deposition conditions, speleothem δ^{18}O depends solely on cave air temperature and drip water δ^{18}O. In that case, the underground environmental changes respond to long-term climate changes and are recorded in the isotopic composition of slow-growing speleothems. Establishing cave hydroclimate monitoring is critical to assess variability in these two parameters. Surić et al. [7] analyzed isotope data of precipitation and drip water from 17 caves from different latitudes and altitudes in relatively small but diverse Croatian karst regions in order to distinguish the dominant influences. Stable isotope composition of precipitation collected at sites near the caves showed that local meteoric water lines (LMWL) lie between the Global MWL (δ^{2}H = 8 δ^{18}O + 10) and the Western Mediterranean MWL (δ^{2}H = 8 δ^{18}O + 13.7). Although slopes of the LMWLs were systematically lower (between 6.6 and 7.8) than the slope of the GMWL, a distinct difference was obtained between the northern continental stations (slope closer to 8) and maritime sites with lower slopes indicating enhanced secondary evaporation. Drip water δ^{18}O in colder caves generally resembled the amount-weighted mean of precipitation δ^{18}O. In these caves, in near-equilibrium calcite precipitation, speleothem δ^{18}O variations can reflect past meteoric precipitation and air temperature. At warmer sites, where evaporation played an important role, drip water δ^{18}O was usually more negative than the amount-weighted average δ^{18}O in precipitation. However, during glacial periods, today's "warm" sites were cold, changing the cave characteristics and precipitation δ^{18}O transmission patterns. Superimposed on these general settings, each cave has site-specific features, such as morphology (descending or ascending passages), altitude and infiltration elevation, (micro) location (rain shadow or seaward orientation), aquifer architecture (responsible for the drip water homogenization), and cave atmosphere (governing equilibrium or kinetic fractionation). This necessitates an individual approach to each cave and thorough monitoring for best comprehension. The authors stress that this approach should be the first and foremost guiding principle against which all actions need to be conducted worldwide in forthcoming studies of paleoclimate and paleo-environmental conditions based on cave speleothems.

Evapotranspiration (ET) is a process in the terrestrial hydrological cycle that accounts for evaporation (E) from the soil, open water, and canopy-intercepted water, and transpired (T) water from vegetation. ET constitutes a large percentage of the water cycle in most environments, and up to 95% in arid environments, being, therefore, an important water flux at a variety of spatial scales. Adkinson et al. [8] presented the potential of high-frequency partitioning ET into its constituent fluxes, T and E, which is important for understanding water use efficiency in forests and other ecosystems. Recent advancements in cavity ring-down spectrometers (CRDS) have made collecting high-resolution (temporal) water isotope data possible in remote locations, but this technology has rarely been utilized for partitioning ET in forests and other natural systems. To understand how the CRDS can be integrated with more traditional techniques, they combined stable isotope, eddy covariance, and sap flux techniques to partition ET in oak woodland in Texas, USA, using continuous water vapor CRDS measurements and monthly soil and twig samples processed using isotope ratio mass spectrometry (IRMS). They also wanted to compare the efficacy of δ^2H versus δ^{18}O within the stable isotope method for partitioning ET. The isotopic composition (δ^2H and δ^{18}O) of atmospheric and precipitation samples fell closely along the global meteoric water line (GMWL), while the soil samples fell to the right of the GMWL, indicating preferential evaporation of lighter isotopologues of water and soil enrichment with the heavier isotopologues. These results indicated the evaporative fractionation of soil water and an appropriate degree of separation between the signals of twig and soil water isotope ratios. It was shown that average daytime vapor pressure deficit and soil moisture could successfully predict the relative isotopic compositions of soil and xylem water, respectively. Contrary to past studies, δ^2H and δ^{18}O performed similarly, indicating CRDS can increase the utility of δ^{18}O in stable isotope studies. However, they found a 41–49% overestimation of the contribution of T to ET when utilizing the stable isotope technique compared to traditional techniques (reduced to 4–12% when corrected for bias), suggesting there may be a systematic bias to the Craig-Gordon Model in natural systems. This study demonstrated the utility of using a combination of stable isotopes, sap flux, and eddy covariance techniques to partition ET in oak woodland and introduced a novel methodology using CRDS water vapor isotopes. However, the authors pointed out the need for further refinement of the methodology, particularly in natural systems, to reconcile potential biases inherent in this approach, and to test the proposed models under various natural conditions.

Landform changes caused by human activities can directly affect the recharge of groundwater and are reflected in the temporal and spatial changes in groundwater stable isotope composition. These changes are particularly evident in high-intensity farming areas. Together with recent climate changes, they may influence local and regional water resources management and sustainability of local life. Liu et al. [9] tested and analyzed groundwater stable isotope samples at different elevations of rice terraces in a typical agricultural watershed of the Hani Terraces, a World Heritage Cultural Landscape in southwest China. They analyzed the features of the elevation effect on the oxygen and hydrogen isotopic composition of groundwater across month and year; analyzed and identified the influencing mechanisms of land-use change caused by farming activities on the elevation gradient of groundwater isotopes from a spatial perspective; estimated the recharge cycle and period of regional groundwater from a temporal perspective using the deuterium excess, and deepened the understanding of how farming activities can improve groundwater recharge efficiency and maintain agricultural sustainability. They determined the characteristic variations and factors that influence the temporal and spatial effects on groundwater stable isotopes in the Hani Terraces, which are under the influence of high-intensity farming activities. The relation between δ^2H and δ^{18}O in groundwater was described as $\delta^2\text{H} = 4.98\ \delta^{18}\text{O} - 15.01$, $R^2 = 0.92$, $n = 144$, with no significant difference between the rainy and dry seasons, and with the slope lower than the LMWL slope of 8.31. The elevation gradients of δ^{18}O and δ^2H in groundwater were significantly increased due to farming activities when compared to the altitude gradients of precipitation. The values were $-0.88‰\ (100\ \text{m})^{-1}$ and $-4.5‰\ (100\ \text{m})^{-1}$, respectively, and they changed with time. The authors proposed using the elevation gradient of groundwater as a key index for assessing groundwater recharge. The groundwater circulation cycle was determined to be approximately three months, based on variations in the deuterium excess value of groundwater. The authors used the special temporal and spatial variation characteristics of the groundwater isotopes to evaluate the source and periodic changes of groundwater recharge. In addition, high-intensity rice farming activities, such as plowing every year from October to January, can increase the supply of terraced water to groundwater, thus ensuring the sustainability of rice cultivation in the terraces during the dry season. This demonstrates the role of human wisdom in the sustainable and benign transformation of surface cover and the regulation of groundwater circulation.

Finally, we can proudly conclude that the six scientific papers belonging to this SI showed a wide variety of isotope applications in various studies performed locally or regionally, but the conclusions obtained may be valid worldwide. Precipitation, groundwater, and surface waters belong to classical water bodies, while evapotranspiration, effects of farming, and drip water in karst caves present relatively seldom applications of water isotopes.

As authors, guest editors, and reviewers of various manuscripts submitted to *Water* and other MDPI journals, we consider that the following reflections (or "lessons learned") could be useful for future publications. The use of appropriate and unified terminology is a major issue to be resolved by the joint effort of authors, reviewers, and editors. Correct and clear language is also indispensable for the flawless transfer of ideas and acquired knowledge. Suitable use of statistics (both the choice of statistical methods and statistical expression of results with uncertainties and significance levels) should be a prerequisite for scientific conclusions based on a large number of individual data, as is often the case in long-term studies. Clear graphical presentations and appropriate presentation of data in tables must not be forgotten, as well as the presentation of raw data, usually as supplementary files, and proper referencing.

The Guest Editors are looking forward to the continuation of this SI through the new Special Issue "Isotope Fingerprints of Precipitation in Groundwater, Lakes and Rivers" which is open for submission until 30 October 2021. As has been mentioned many times, precipitation is the ultimate source of groundwater and surface water. Recent climate change has also caused variations in the amount of precipitation and their isotopic composition. Lack of precipitation can cause deterioration of surface water discharges and a decrease in groundwater levels which can lead to water scarcity for both human consumption and ecosystem needs. On the other hand, an extreme amount of precipitation can cause problems such as flooding. Variations in the isotopic composition in precipitation are reflected in the isotopic composition of groundwater and surface waters (rivers and lakes), and, therefore, the isotope composition of all three water body types will help detect any change in these inter-dependent systems caused by climate change, anthropogenic activities, or natural disasters such as volcanic eruption, regional fires, etc. This new SI of *Water* will focus on this relationship, not just taking into account ^{18}O and ^{2}H but all isotopes and hydrogeological parameters that can provide information about water resources.

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