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Editorial

Applying Artificial and Environmental Tracing Techniques in Hydrogeology

Federico Cervi [1,*] and Alberto Tazioli [2]

1 Independent Researcher, 42122 Reggio Emilia, Italy
2 Department of Science and Matter Engineering, Environment and Urban Planning (SIMAU), Marche Polytechnic University, Via Brecce Bianche 12, 60131 Ancona, Italy
* Correspondence: fd.cervi@gmail.com

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This Editorial paper sums up the contents of the Special Issue named "Applying Artificial and Environmental Tracing Techniques in Hydrogeology". With reference to the topic of the Special Issue, here we recall that over the last decades, the use of artificial (i.e., intentionally introduced into the hydrogeological system, such as dyes) and environmental (i.e., entering as a part of the hydrological cycle, such as water isotopes) tracers in groundwater sciences has remarkably increased demonstrating their usefulness in solving hydrogeological problems at different spatial and time scales. Such tracers are used both in laboratory experiments (column tests) and field investigations (even at catchments and regional scales) and deal with water residence times lasting from few minutes to many millennia. They are recognized as powerful tools for obtaining information that cannot be gained by any other conventional means, such as depicting groundwater flow-paths and mixing processes among different end-members, identifying a connection between surficial water and groundwater, estimating the recharge areas of infiltrative water and quantifying pre-infiltrative evaporative processes and groundwater residence times. To date, many artificial and environmental tracers have been tested and the specific choice of a suitable one (or a subset of them; multi-tracing techniques) strictly depends on which hydrogeological investigation has to be conducted.

The Special Issue has collected eight papers, three of which [1–3] are based on artificial tracers while the other four on environmental ones [4–7]. The last paper has exploited a combined approach of environmental and artificial tracers [8]. The majority of the manuscripts are focused on hydrogeological relations between streams and groundwater at the catchments scale [1,5–7] while others deal with freshwater springs [3,4,8]. Another paper [2] refers to groundwater discharging from wells and drains in an underground tunnel. With reference to the manuscripts dealing with case studies based on environmental tracers, it is noteworthy to say that almost all of them exploit the stable isotopes of water $\delta^{18}O$ and $\delta^{2}H$ [4–8].

Below we briefly describe the main contents of each article included in this Special Issue. From a general point of view, the articles herein bulleted further demonstrate the suitability of artificial and environmental tracers for disentangling hydrogeological problems affected by high degrees of complexity (i.e., estimation of the recharge areas of groundwater feeding freshwater springs, identifying the time-windows in which recharge periods of groundwater takes place, elucidating hydrological connections occurring at the riparian scale between a river and its corresponding catchment, clarifying which part of the hydrological network conveys specific pollutants into a river, evidencing reaches of rivers in which streambed dispersions occur, assessing the advective velocity and effective porosity of the non-porous medium, verifying temperature-linked fractionation processes which could be further exploited to exclude or include components of recharge to groundwater or even quantifying each quotas in case of mixing, detecting earthquake-driven changes of groundwater flow-paths at the hillslope and catchment scale).

Several issues are still open and will need to be addressed as future perspectives. Firstly, the proper choice of the tracer (or better the tracers, as the use of multi-tracing techniques is preferable as it allows to reduce errors) is crucial and requires having a portfolio with the greatest number of environmental and artificial tracers available. In this case, it is evident that new research aimed at testing the possible use of new artificial (such as injection of water with known, $\delta^{18}O$-$\delta^{2}H$ content) and environmental (such as metal stable isotopes or pollutants-related compounds) tracers would be hopeful. In parallel to the aforementioned research activities, we believe it is necessary to spend efforts in providing common guidelines that attempt to harmonize the sets of tracers to be used according to the specific case study and the information that must be obtained, also including suggestions on time spans and number of sampling locations. By finding the correct balance between the necessary labor and cost, such guidelines can make the application of these methods more usable and bring a wider audience of interested parties (such as stakeholders in charge of river water and groundwater management).

Moreover, future works must be more pushed towards interdisciplinary by fostering collaborations among different geoscientific expertise (hydrogeology, geology, geochemistry, hydrology, etc.). In fact, tracing techniques are not to be used as a stand-alone tools as the final goal is to pave the way towards a better understanding of the hydrogeological systems under investigations.

As a final remark, we hope the innovative works presented here can stimulate further efforts in the field of tracing techniques and encourage the use of such tracers also by the stakeholders in charge of river water and groundwater management worldwide. The latter would benefit also from greater tracing tests data sharing (in form of "raw" data along with instrumental errors) to be pursued not only through supplementary materials along with scientific papers but also online self-service platforms.

In detail, Ref. [1] discussed the results of injections of artificial tracers (radioactive phosphorous ^{32}P and tritium ^{3}H) that were performed on a 2.6 km long stretch of a rural stream in Poland. The stream discharges from a flat area and was already found to be subjected to multiple sources of phosphorus contamination (namely: farmyard, urban and road runoff, sewage and wastewater disposal, fish ponds, and urban sprawl) that occurred intermittently (episodic inputs of inorganic phosphorous). The investigations were devoted to clarifying the transient storage of phosphorous transport with peculiar attention to the role of hydrological networks as well as the streambed sediments and beavers' dams.

Kim and Lee [2] presented a modified convergent tracing technique that has been tested by injecting a slug of sodium chloride into a single well and successively monitoring the breakthrough curves of the abovementioned tracer into an extraction well. The tests were carried out on several wells drilled in an underground tunnel and draining an aquifer hosted into a fractured rock mass from Korea; the results demonstrated the suitability of such an approach for assessing the advective velocity and effective porosity of the non-porous medium.

Thanks to a combined approach involving tracing tests and transient time-series analysis, Ref. [3] explained the significant hydrogeological variations (long-lasting decrease in discharge values from some springs meanwhile other springs and rivers showed a constant increase of discharges) that occurred in a carbonate aquifer following several seismic events in 2016–2017 in central Italian Apennines (Sibillini Massif). Here, the Authors performed injections of an artificial tracer (Sodium Fluorescein) to verify changes in groundwater flow-paths between pre-seismic and post-seismic periods and then exploited a sliding-window cross-correlation function for processing 6-year long datasets (covering the period between 1 November 2013 and 31 October 2019) of daily spring discharges/hydraulic heads (output of the aquifer) and snowmelt events/rainfalls (input to the aquifer) to check potential variations on the response time of the aquifer to the inputs. Co-seismic stresses have induced pore pressure propagation throughout the aquifer with void cleaning; the development of detachment surfaces as well as the internal collapse of the karst conducts have led groundwater divide to be shifted and the post-seismic groundwater flow to be finally modified.

Lucianetti et al. [4] used a stable water isotopes-based model to quantify the quotas of snowmelt and rainfall composing the discharges of nine relevant freshwater springs outflowing from an area of 240 km^2 within the Dolomites (Italian Alps). Water samples for further isotopic analyses came from rain gauges (rainfall), extended funnel gauges samplers (snowmelt), and the abovementioned nine springs. The two isotopic end members (i.e., pure rainfall and pure snowmelt) were identified starting from a temperature-based method in which the partitioning between them is carried out through a melt factor. The latter exploited the average monthly temperatures at the site. In the end, the Authors confirmed that the proportion between the two end-members is spatially variable throughout the mountain group according to the elevation of the spring recharge areas (predominance of the snowmelt fraction over the rain contribution in springs with the highest altitude of recharge areas and progressively greater quotas of rainfall for spring recharged at lowest altitudes). Furthermore, and with peculiar reference to the springs recharged at higher altitudes, a relatively rapid transmission of the recharge pulses to the spring waters was detected after intense snowmelt or rainfall events with consequent abrupt changes in percentages of the end-members (up to the nil of the non-contributing ones). Thus, the Authors argued that such variations may be linked to the strong seasonal and climate-dependent character of the storage processes although that does not exclude the presence of a well-mixed groundwater component with longer residence times.

To unravel hydrological connections occurring at the riparian scale between a river and its corresponding catchment (Henan province, China), Ref. [5] took advantage of multi-environmental tracers (physicochemical parameters, main hydrochemicals and isotopic data of ^{222}Rn, $\delta^{18}O$, and $\delta^{2}H$ collected during two short-time field investigations carried out during dry and wet seasons,) and further coupled a simplified two-components mixing model with a ^{222}Rn mass balance model. In detail, the two end members (i.e., surficial water from river and groundwater) were identified with several tracers separately (^{222}Rn, $\delta^{18}O$, $\delta^{2}H$, and Electrical Conductivity, respectively). In the end, the Authors identified river loss zones and gaining zones and found that the mixing extent with groundwater was greater in wet seasons than in dry seasons under the influence of an artificial sluice. The ^{222}Rn bass balance allowed the groundwater flux to the river to be quantified along the several investigated river reaches. Moreover, the study evidenced that untreated sewage discharge and fertilizer usage were the two main anthropogenic inputs of nitrate pollution in river water. The latter was driven by riparian groundwater with a remarkable increase of nitrates in the wet season as a result of higher fluxes toward the river.

Banda et al. [6] implemented a sampling network for the collection of surficial water along the course of the Shire River (Malawi). In addition, the Authors selected a representative number of wells from the aforementioned catchment to gather groundwater samples. All samples were collected in 2017–2018 (sampling campaigns in dry and wet periods) and further analyzed for obtaining physicochemical parameters along with main ions (150 samples) and stable isotopes of water (283 samples). Results suggest that groundwater is recharged by local precipitation predominantly during the peak months of the wet season. River flows during the wet seasons mostly arise from local precipitation, while dry-season flows are fed by increased groundwater contributions while still preserving the former isotopic composition (i.e., young water occurrence predominantly influenced by non-evaporated local rainfall recharge).

Martinelli et al. [7] used a dataset made up of hundreds of water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) from rain gauges, rivers, and groundwater hosted in five alluvial fans facing the northern Italian Apennines of Italy. The authors developed a statistical procedure based on monovariate and bivariate analyses involving also the deuterium excess (d^E). By assuming two main possible ways of recharge to groundwater (rainfall percolation from the topsoil and the streambed dispersions along the apical part of the alluvial fans), the approach allowed to verify whether a component of recharge for groundwater is prevalent or not.

To reach the scope, the Authors exploited the isotopic modification (mainly related to sublimation and evaporative/evapotranspiration processes) occurring in water from rivers when traveling along the mountainous sector of their catchments. The paper confirmed that groundwater from three alluvial fans out of five is likely to be mainly recharged by precipitations infiltrating in their apical areas. Groundwater hosted in the remaining two alluvial fans are found to be isotopically linked to river dispersions.

Fronzi et al. [8] developed a combined approach of environmental (physicochemical parameters, main cations, and anions, $\delta^{18}O$ and $\delta^{2}H$) and long-term artificial tracers tests (carried out with sodium fluorescein and Tinopal CBS-X) to propose a hydrogeological model of the upper Nera river catchment (central Italian Apennines). The area was affected by remarkable seismic-induced hydrogeological changes after the 2016–2017 earthquake sequence with the structural evidence of a new normal fault. Sampling activities were focused on a number of springs (punctual and linear; samplings carried out in 2017) as well as eight rain collectors installed at different altitudes (lasting over a maximum time window 2013–2019). The latter allowed the $\delta^{18}O$-elevation relation to be determined and consequently mean recharge altitude of freshwater springs recharge to be estimated. Artificial tracing tests were conducted in 2016 and 2017 in both pre-seismic and co-seismic time windows: the decoupled behaviors in quantity and time of tracer arrivals in some monitoring points among the tests confirmed that the newly mapped fault can act as a preferential flow path along its strike modifying permanently the conveys of groundwater flows and consequently the baseflow of adjacent creeks.

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