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Editorial

Environmental Tracers

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Abstract: Environmental tracers continue to provide an important tool for understanding the source, flow and mixing dynamics of water resource systems through their imprint on the system or their sensitivity to alteration within it. However, 60 years or so after the first isotopic tracer studies were applied to hydrology, the use of isotopes and other environmental tracers are still not routinely necessarily applied in hydrogeological and water resources investigations where appropriate. There is therefore a continuing need to promote their use for developing sustainable management policies for the protection of water resources and the aquatic environment. This Special Issue focuses on the robustness or fitness-for-purpose of the application and use of environmental tracers in addressing problems and opportunities scientifically, to promote their wider use and to address substantive issues of vulnerability, sustainability, and uncertainty in (ground)water resources systems and their management.

Keywords: environmental tracers; groundwater; stable isotopes; radioactive isotopes; water resource systems; water resources management

1. Introduction

Environmental tracers are ambient, natural or man-made compounds widely distributed in the Earth's near-surface. They may be injected naturally into the hydrological system from the atmosphere at recharge and/or are added/lost/exchanged inherently as waters flow over and through materials.

Because of possible issues of chemical equivalence in sampled groundwater signatures, to screen hypotheses and identify contributing processes typically detailed and/or quantitative groundwater investigations require consideration of multiple tracers of chemical reactions: ion ratios/correlations, minor/trace element determinands, mineralogy and reaction-path simulations, isotopic compositions, *etc.* These tracers separately or in conjunction may suggest a unique solution in detailing the hydrogeochemical processes operating. As for trace elements, environmental isotopic signatures of dissolved compounds, and the water molecule itself, can prove particularly sensitive tracers, as they occur generally at low levels of concentration and can be affected by chemical and physical fractionation effects shifting their signatures. Variations then in groundwater chemical abundances and isotopic compositions can be used as natural tracers to determine sources (provenance), pathways (of reaction or interaction), and also timescales (dating) of environmental processes. Dating may invoke their characteristic decay or accumulation functions (*i.e.*, radioactive *vs.* radiogenic compounds and isotopes) in a system, or the characteristic injection of sources. This then provides a handhold on timescales of processes and water residence times to be considered critically alongside hydraulic transit (flowthrough) and system turnover times. Moreover, environmental tracers in groundwater systems can give information both on current and past flow conditions independently of hydraulic analyses and groundwater modelling. Thus, generically environmental tracers are important tools for developing sustainable management policies for the protection of water resources (quantity and quality) and the aquatic environment. For example, where investigations are taking place in groundwater systems in which mixing is a potentially important process (*cf.* pumping flooded mines (see below) or even pumped public supply wells), the addition of even modest amounts of additional sampling and analysis for isotopic environmental tracers can greatly expand understanding of the flow and geochemical/water quality (mixing) dynamics of pumped groundwater systems [1].

Recent overviews (e.g., [2]) have highlighted how most environmental tracers systematics have now become well-established through proof-of-concept studies in geochemically and hydraulically simple aquifers. The challenge now lies in enhancing the way they are put to use by the hydrologic community and water resource managers in more complex systems, and how they may be used to address issues of vulnerability, sustainability, and uncertainty of water resources and their systems. Therefore the aim of this Special Issue is to disseminate and share findings especially on the robustness or fitness-for-purpose of the application and use of environmental tracers in water resource systems in addressing problems and opportunities scientifically. Original research papers were selected by rigorous peer-review process with the aim of rapid, accessible and wide dissemination of results.

2. Contributions

The selected papers presented in the Special Issue are highlighted in this section. They fall broadly into three categories: those focused particularly on the stable oxygen- and hydrogen-isotopes and also the radioactive hydrogen-isotope (tritium) of the water molecule to characterise its source(s), fractionation effects, and dating young groundwater systems (five papers); those focused on multi-isotope approaches (including the use of other radioisotopes, and significantly natural Uranium- and Thorium-series radionuclides) (three papers); and those using natural environmental tracers alongside or as applied tracers introduced into groundwater systems (three papers).

2.1. Stable Isotopes of Water (δ^2H, $\delta^{18}O$)

Three articles [3–5] look at the start of the hydrological cycle, at the origin of rainfall and its selection in groundwater recharge using characteristic, naturally-occurring δ^2H and δ^{18}O signatures in monthly samples. The concept of "deuterium excess", originally defined by Dansgaard [6] as d = δ^2H − 8.δ^{18}O, is used in case studies by Lambs *et al.* [3] in France and Yeh *et al.* [4] in Taiwan, to identify the predominance of different air masses contributing to rainfall patterns seasonally and the groundwater recharge at the regional/catchment scale. Buenning *et al.* [5] model specifically the δ^{18}O of annual rainfall across the western USA to identify mechanisms controlling interannual variations in isotopic signatures. Such signatures feed into groundwater systems and might be used as climate proxy for various surface archives and potentially [5] to monitor storm track changes. Overall, isotope mapping and monitoring on multiple spatial and temporal scales is helping recognise and characterise isoscapes, of use in a wide range of hydrological and other contexts [7].

A fourth contribution by Kabeya *et al.* [8] links a storm event over a 48-h. period to sediment production and transport in a forested headwater catchment in Japan. Their correlation is used to identify the source area for sediment, which might be linked potentially with mobilisation of radioactive caesium deposited following the recent Fukushima Daiichi nuclear power plant incident.

Doveri and Mussi [9] use both the stable isotopes (δ^2H, δ^{18}O) of water and its radioactive isotope (tritium, ^{3}H, with a half-life of 12.3 years) monitored in springs and wells (up to six times over a 2-year period) as natural environmental tracers to suggest a conceptual model of groundwater flow in the Scansano-Magliano region of southern Tuscany (Italy). The local sandstone aquifer here may provide a strategic alternative source for water supply given the overexploitation and contamination of known, local alluvial aquifers, and for supplying isolated villages on the Toscana ridge in this semiarid area.

2.2. Multi-Isotope Studies

In another regional aquifer study, and alongside the water isotopes (δ^2H, δ^{18}O, ^{3}H), Eastoe and Rodney [10] additionally utilise natural C-isotope systematics (stable δ^{13}C, and radioactive ^{14}C—this latter with a half-life of 5730 years) of dissolved inorganic carbon, and the S-isotope signature of dissolved sulfate (δ^{34}S). The environmental tracers are used to date groundwater residence times (^{3}H, ^{14}C) and to identify winter recharge at high-elevation in the Sacramento Mountains (USA) as the source of groundwaters in the regional carbonate aquifer and flanking basins. The authors highlight therefore that if winter rainfall decreases e.g., as a result of global climate change then aquifer recharge also will be affected. However, the authors also show that the use of stable isotopes of water equivocally here of themselves cannot help discriminate sources of groundwater for the more distant Roswell basin.

Swarzenski *et al.* [11] also combine stable and radioactive tracers alongside hydrochemistry in a coastal Los Angeles County (USA) study to investigate the complex groundwater scenario associated with a historical scheme to inject freshwater at three locations as a hydraulic barrier to saline intrusion. Here groundwater may be a "complex mixture of native groundwater, intruded seawater, non-native injected water, and oil-field brine water." The baseline geochemical study to discriminate sources and characterise groundwater dynamics and mixing included looking at natural Uranium- and Thorium-series radiogenic nuclides (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra, ^{222}Rn) particularly to study potential controls on the adsorption-desorption rates for dissolved cations. Schubert *et al.* [12] evaluate the use of the stable isotopes of water alongside natural radium isotopic ratios ($^{224}Ra/^{228}Ra$, $^{228}Ra/^{226}Ra$) and radon (^{222}Rn) contents to detect submarine groundwater discharge (SGD) in a submarine cave near Monaco. They found ^{222}Rn contents the most robust indicator in context and δ^2H, $\delta^{18}O$ suitable. They propose particularly therefore utilising ^{222}Rn contents alongside salinity for the investigation of offshore fresh groundwater reserves. Such SGD and offshore groundwater reserves have recently been highlighted as a global phenomenon potentially to be exploited [13]. Elsewhere, other authors [14] have used dissolved uranium and $^{234}U/^{238}U$ activity ratios and natural Uranium- and Thorium-series radiogenic nuclides, alongside dissolved noble gases (including ^4He, the stable by-product of U- and Th-series radioactive decay) to attest to the "fossil" water (palaeowater) status of groundwaters in the regional Continental Intercalaire aquifer of Algeria and Tunsia. Their abstraction is therefore akin to mining this groundwater resource. Where a freshwater/saline water interface is identifiable, even the use of scavenger well technology (e.g., [15,16]) must take into account the potential paleowater status of at least a component of the pumped water and the effect on the movement of the interface.

2.3. Investigations Using Natural Tracers in Combination with Applied Tracers

In complex hydrogeological settings the use of applied tracers to analyse system flow-through (transit) times and hydraulic connections can be problematic as the tracers can be diluted out, or if the mixing reservoir is overestimated there can be tracer breakthrough at concentrations exceeding environmental or analytical specifications.

Three further USA case studies [17–19] deploy applied tracers alongside ambient tracers. Cowie *et al.* [17] use a two-tier investigative approach in a flooded, abandoned, underground hard-rock mine system (USA). They monitored natural environmental tracers of water (δ^2H, $\delta^{18}O$, ^3H) to gain a conceptual understanding of the hydrogeology, and then injected applied tracers (here ionic and fluorescent tracers) at specific locations to focus their investigations. Remediation efforts for acid mine drainage (AMD) then can be targetted at separating and isolating or preventing sources of poor quality water. This approach then essentially follows the philosophy of Source-Pathway-Receptor (SPR) risk management (for Contaminated Land investigations) rather than a traditional end-of-pipe remedial solution for such waters. Elsewhere [1], monitoring of natural environmental tracers during pumping of AMD waters to control the water table in the system and prevent environmental impacts is used to characterise the sources, dynamics and evolution of mixing of waters and their water quality for flooded, abandoned coal mines.

Benson *et al.* [18] use injected, applied gas tracers (SF_6 and Xe) as nonpolar, partitioning tracers for the air-water interface in streams to monitor gas loss downstream and oxygen reaeration (K_{DO} or K_2, mass transfer coefficients). The link with environmental tracing is twofold, both because these two tracer gases are already present in the environment sourced from the atmosphere (albeit at very low ambient, dissolved concentrations which allows significant enhancement of dissolved concentrations for tracing), and because the loss rate for these gases could be used also for interpretation of ^{222}Rn measurements in the streams to study then groundwater-surface water interactions. Especially noble gases (like Xe) are perceived as "environmentally-friendly" tracers for stream reaeration and gas evasion/mass transfer (K) studies, as well as for characterising hydrodynamic properties [20].

Finally, Clark *et al.* [19] have applied (injected) the environmental gas tracers SF_6 and Xe in groundwater to characterise hydraulic connections between recharge facilities and production wells of a Managed Aquifer Recharge (MAR) site. MAR involves a strategy of injecting "surface waters into aquifers for storage and later extraction". Each tracer was injected separately and following an intervening period of a decade between the two tests to assess whether operation of the MAR facility (including any changes in recharge conditions) therefore had impacted the system response.

3. Conclusions

Eleven original research articles have been selected for this Special Issue. The research findings are novel and timely in informing the hydrological and water resources management communities on up-to-date research and practice. Sixty years or so after the first isotopic tracer studies applied to hydrology the use of isotopes and other environmental tracers are still not necessarily routinely applied in hydrogeological and water resources investigations where appropriate. We trust that the collation of these papers contributes to piquing further interest in how environmental tracers can contribute and be used to address substantive issues of vulnerability, sustainability, and uncertainty in (ground)water resources systems and their management.

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Conflicts of Interest

The author declares no conflict of interest.

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