An insight into the present and future of noble gas sampling methods, natural variabilities, and numerical modeling

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Noble gas radioisotopes (i.e. ³⁹Ar, ³⁷Ar, ⁸¹Kr, ⁸⁵Kr, ²²²Rn) are increasingly used as tracers of groundwater flow paths and residence times on scales from days to millions of years. Their inertness in the subsurface, combined with the continuous decrease in the required amount of water for sample analysis, and the improvement of measurement precision have placed them at the forefront of the tracer scene. Yet, with every vividly investigated topic, new questions and potential challenges arise. In this respect, we offer a *tour d'horizon* of the current knowledge and prospects for sampling methods, natural biases, and numerical modeling of radio-noble gases.

For example, actively pumping groundwater creates biases towards more permeable pore volumes. Passive sampling overcomes this issue but results in other complications such as small-scale variability. The sampling method should therefore reflect the purpose of the investigation. ⁸⁵Kr, ³H/³He, and ³⁷Ar can now also be sampled by means of membrane modules directly inserted in boreholes [1,2] or placed in riverbeds. The disturbances of the natural flow system are thus reduced and a better representation of the age stratigraphy with depth is possible. Other advantages are the simplification of the sampling regime and the possibility of automated continuous sampling.

Dating methods based on ³⁹Ar, ⁸¹Kr, and ⁸⁵Kr commonly assume negligible sources underground. Recently, this prerequisite was challenged by field data that induced a reevaluation of underground production in rocks and in the water phase [3–5]. Conversely, ³⁷Ar and ²²²Rn are indicators of residence times solely based on their accumulation rate in the subsurface and offer, in combination with numerical modeling [8], exciting new applications in the field of river–groundwater interactions [6–9] and hence drastically increase the potential to understand complex hydrogeological systems in the future.

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