



A new approach to constrain basal helium flux into aquifers for better estimation of groundwater ages by Helium 4

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Estimation of groundwater age through the combined use of isotope methods and groundwater flow modelling is the common approach used for developing the required level of knowledge in the case of groundwater pumped from deep aquifers. For more than 50 years radiocarbon and tritium have been the common tools used in isotope hydrology studies to provide first estimates of groundwater age and dynamics. The half-life of carbon-14 (5730 years) and the complex geochemistry of carbon species in most environments have limited the proper characterization of groundwater flow patterns in large sedimentary basins and deep aquifers to ages more recent than about 40 000 years. Over the last years, a number of long-live radionuclides and other isotopes have been tested as more reliable age indicators by specialised laboratories. Among these methods, chlorine-36 (half-life of 300 000 yr) has been used with mixed results, mainly due to problems derived from in-situ production of this radionuclide. Uranium isotopes have also been used in a few instances, but never became a routine tool. Accumulation of helium-4 in deep groundwaters has also been proposed and used in a few instance, but one major obstacle in the 4He dating method is a difficulty in assessing a rate constant of 4He input into aquifers (namely, the entering basal 4He flux).

In this context, recent breakthrough developments in analytical methods allow the precise determination of dissolved noble gases in groundwater as well as trace-level noble gas radionuclides present in very old groundwaters. Atom trap trace analysis, or ATTA, has dramatically improved over the last years the processing of very small amount of noble gases, providing now real possibilities for routine measurements of extremely low concentration of exotic radionuclides dissolved in groundwater, such as krypton-81 (half-life 229 000 years). Atom trap trace analysis involves the selective capture of individual atoms of a given isotope using six laser beams, minimizing the size of the sample to be processed for analysis. Being a noble gas, krypton does not form compounds in the aquifer and is only derived from atmospheric sources. The long half-life and the lack of geochemical interactions make this radionuclide an excellent tracer to estimate groundwater ages in deep aquifer systems.

Krypton-81 results offer also the possibility of calibrating groundwater ages derived from helium-4 accumulation method. Until recently, helium-4 ages were calibrated to account for the basal helium flux on carbon-14 ages, but the relatively short half-life of carbon-14 often led to inaccurate age estimates for groundwater ages older than about 100 000 years. We will present a new approach to utilize 81Kr to optimize the parameters of conceptual groundwater flow model and the size of 4He basal flux, which yielded a reasonable agreement between 81Kr and 4He ages in two large and old aquifers in Brazil (Aggarwal et al., *Nature Geoscience*, 8, 35-39, 2015) and in the North China Plain.