



## First dating of groundwater with Atom Trap Trace Analysis of $^{39}\text{Ar}$ - application

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Groundwater from the intermediate aquifer layers of the Rhine Graben sediments in the Rhein-Neckar metropolitan region is strongly exploited for the purpose of drinking water supply. Isotope hydrological investigations of the regional groundwater dynamics have been initiated with the ultimate goal of improving the protection of this important water resource. However, these studies are hampered by the fact that the groundwater falls in the age dating gap of classical isotope methods between about 50 and 1000 years of water age, which can only be bridged by the extremely rare isotope  $^{39}\text{Ar}$ . Here we report and discuss the first  $^{39}\text{Ar}$  groundwater ages obtained by the new analytical method Atom Trap Trace Analysis (ATTA).

Groundwater samples from the Upper Rhine Graben aquifers were collected and analysed by established methods for a large range of tracers, including tritium, stable isotopes, noble gases, and  $^{14}\text{C}$ . For  $^{39}\text{Ar}$  analysis, several tons of water were degassed in the field using a membrane contactor. In the laboratory, a gas-chromatographic system at cryogenic temperatures was used to separate pure argon from the extracted gas. ATTA was then used to isolate and count  $^{39}\text{Ar}$  atoms from these samples. In parallel, samples for  $^{39}\text{Ar}$  analysis by low-level counting at the University of Bern were taken to enable comparison of the two analytical techniques.

The resulting  $^{39}\text{Ar}$  groundwater ages in the range of several hundred years are in accordance with the indications obtained from the classical dating tracers. They provide quantitative information on the groundwater travel time for an important, strongly exploited part of the investigated aquifer system, which could not be obtained from the other tracers. These results significantly improve the knowledge of the time scale of groundwater renewal in the aquifer layers of intermediate depth. Furthermore, the combination of the  $^{39}\text{Ar}$  age scale with noble gas recharge temperatures and stable isotope data has the potential to provide a reconstruction of the regional paleoclimate on the time-scale of the past millenium.