



## **Groundwater dating and geochemical conditions in an artesian, siliciclastic transboundary aquifer, under pristine conditions and after one decade of exploitation using radiocarbon, tritium, SF<sub>6</sub>, CFCs.**

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Continental siliciclastic Pliocene deposits of the Rhine Graben form a small (77 km<sup>2</sup>) transboundary aquifer system, shared between France and Germany, laterally delimited by roughly N-S-striking faults. This three-layer aquifer system, with artesian outflow from the deep aquifer, overlies several 100 m of Oligocene marlstones. The system has been studied in some detail in 1999 through a multi-isotope study including radiocarbon and tritium dating. In 2010, a new geochemical and isotopic snapshot has been taken, allowing assessing the impact of one decade of groundwater exploitation on the age structure and hydrochemistry of the aquifer system. The recharge area of all 3 aquifers proved to be very limited (<10 km<sup>2</sup>) and the mean thickness of the deep artesian aquifer (12 m) is negligible compared to its lateral extension. Tracer transport is thus well described by pure piston flow.

The surface and intermediate aquifers contain <sup>3</sup>H (surface aquifer) and NO<sub>3</sub> (surface and intermediate aquifer), whereas the artesian waters of the deep aquifer are nitrate- and tritium-free except one point nearest to the recharge zone, tritium free (<1TU) but containing NO<sub>3</sub>. CFC and SF<sub>6</sub> concentrations, measured in 2010, indicate a modern component in the middle aquifer and close to the recharge zone in the deep aquifer.

There is a continuous downgradient decrease of <sup>14</sup>C activity (from 83 to 42 pmc in 1999, and 88.6 to 43.5 pmc in 2010) at constant  $\delta^{13}\text{C}$  (-14.5 ± 1.1 ‰ vs.PDB in 1999, -15.0 ± 0.75 ‰ in 2010). From 1999 to 2010, all individual A<sup>14</sup>C values were shifted to higher values, by 8.7 pmc close to the recharge zone and by 1.1 pmc for the most downgradient points. The siliciclastic deep aquifer is virtually carbonate-free but contains some ligneous organic debris. The constant  $\delta^{13}\text{C}$  suggests that there is no significant C-input from carbonates or organic matter at depth so that uncorrected radiocarbon ages can be used as a first approximation of groundwater residence times.  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values are similar to modern regional surface waters and show no influence of Pleistocene recharge.

There is a clear downgradient evolution of most inorganic compounds, well correlated with <sup>14</sup>C activities, with an increase of Na, K, silica, B, Br and Sr whereas Ca, Mg and Cl concentrations are constant or increase only slightly in the deepest part of the deep aquifer. The strong rise of Sr contents from 0.2 to 1.2 ppm is accompanied by <sup>87</sup>Sr/<sup>86</sup>Sr ratios increasing from 0.7086 to 0.7098 in 1999, systematically shifted to more radiogenic values in 2010. This evolution of groundwater chemistry is interpreted in terms of exchange of the deep aquifer with the underlying aquiclude, as the boron and strontium isotope values are incompatible with water-rock interaction with the aquifer material itself. Diffusive flow from the interstitial porosity of the thick argillaceous series, combined with water-rock interactions (ion exchange, desorption) may explain the input of monovalent cations, Sr, B and Br (to a lesser extent Cl). Diffusive flow of <sup>14</sup>C from the aquifer towards the aquiclude might lower A<sup>14</sup>C at constant  $\delta^{13}\text{C}$  thus suggesting too high groundwater ages. The evolution of the A<sup>14</sup>C from 1999 to 2010 indicates some acceleration of the groundwater flow through continuous pumping. Evidence of recent groundwater inflow in the deep aquifer was found only close to the recharge zone. Hydrodynamic modelling is currently undertaken and results will be compared with geochemical and isotopic age estimations.