## Isotopic Tracers (Sr, C, B, S, O, H) Reflecting Flow Conditions in an Artesian Siliciclastic Aquifer

Wolfram Kloppmann (w.kloppmann@brgm.fr), Susanne Schomburgk & Philippe Elsass

BRGM, Orléans, BP 6009, F 45060, France

Continental siliciclastic Pliocene deposits of the Rhine Graben (France, Germany) form a small (77 km<sup>2</sup>) aquifer system laterally delimited by faults of the graben shoulder. In the aim of protecting this transboundary water resource from over-exploitation, a Franco-German research project has studied recharge and flow conditions by means of hydrodynamic modelling and geochemical and isotopic tracers. The recharge area proved to be very limited (<10 km<sup>2</sup>) and the mean thickness of the lowermost aquifer (12 m), which is mainly artesian confined by clay layers, is negligible compared to its lateral extension. Tracer transport is thus well described by pure piston flow (Zuber, 1986). We observe a clear downgradient evolution of major ion chemistry from Ca-HCO<sub>3</sub> to Na-Ca-HCO<sub>3</sub> waters, with Na, K and Sr increasing by a factor of 6 at constant Ca, Mg and Cl concentrations and constant Br/Cl values. The shallow groundwater contains <sup>3</sup>H (max 20 TU) and NO<sub>3</sub> (max 57 ppm), whereas the artesian waters are nitrate- and tritium-free. There is a continuous downgradient decrease of <sup>14</sup>C activity (from 83 to 42 pmc) at constant  $\delta^{13}$ C (-14.5 ±1.1‰ vs. PDB). Initially, water infiltrates through loess layers dissolving calcite and then enters the virtually carbonate-free siliciclastic aquifer. The constant <sup>13</sup>C suggests that there is no significant C-input at depth and that the <sup>14</sup>C decrease mainly reflects radioactive decay. The <sup>14</sup>C ages reach several thousand years in the deep aquifer.  $\delta^{18}$ O and  $\delta^{2}$ H values are similar to modern regional surface waters and show no influence of Pleistocene recharge.  $\delta^{34}S$  and  $\delta^{18}O$  of sulphates in the shallow groundwater reflect atmospheric input, whereas the deep groundwater values fall in the field of Triassic or Tertiary evaporites. Some direct or indirect sulphate input from Triassic sandstones or the underlying Tertiary marls may cause the isotopic enrichment downgradient, accompanied by a slight increase in sulphate concentrations.  $\delta^{11}B$  from +4 to +12‰ vs. NBS 951 lie in the range of crystalline rocks (Palmer and Swihart, 1996). The strong downgradient increase of B is attributed to silicate weathering. 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. The good linear correlation of 1/Sr and <sup>87</sup>Sr/<sup>86</sup>Sr (Fig. 1) is interpreted as an "evolution line" rather than a mixing line and may reflect low-kinetics interaction (Bullen et al., 1996) of recharge water with a silicate end-member such as K-feldspars with a homogeneous radiogenic isotope signature. The evolution of <sup>87</sup>Sr/<sup>86</sup>Sr ratios is closely related to the residence time of the groundwaters (Fig. 1) and intimately reflects the flow pattern in the aquifer. Sr isotopes can thus been used together with <sup>14</sup>C to establish a relative residence time scale and to constrain hydrodynamic boundary conditions. It becomes clear that in the central part of the aquifer, a zone of preferential flow exists and that some zones near the boundary faults are poorly connected to the main aquifer leading to prolonged water-rock contact.

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Figure 1: Sr isotope ratios of groundwaters from the Pliocene aquifer system plotted vs. 1/Sr (l/mg) and vs. <sup>14</sup>C activity of DIC