

## A multi tracer study of groundwater origin and transit-time in the fore deep basin of the Southern Alps

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A multi tracer study <sup>3</sup>H-<sup>3</sup>He, <sup>4</sup>He, <sup>14</sup>C, <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>36</sup>Cl (Rebeix *et al.* this issue), <sup>224</sup>Ra, <sup>226</sup>Ra, <sup>228</sup>Ra, <sup>222</sup>Rn, <sup>18</sup>O, <sup>2</sup>H, cations, anions, has been carried out in the Venice Plain aquifers (Italy) to determine origin, transit times and mixing proportions of different groundwaters (GW) between the Brenta (B) and Piave (P) rivers. Phreatic GW from the upper plain yielded <sup>3</sup>He-<sup>3</sup>H recharge years 1970-2008 and an infiltration rate of about 1 km/y. Tritiogenic <sup>3</sup>He matches well the IAEA Vienna <sup>3</sup>H record in precipitations, indicating no dilution with older GW. Artesian GW in the lower plain has instead lower tritiogenic <sup>3</sup>He, i. e. contains modern GW having <sup>3</sup>H-<sup>3</sup>He recharge ages 1970-1963, significantly diluted with old GW having model - corrected <sup>14</sup>C ages in the range of 1 to 12 ka. The latter are consistent with <sup>226</sup>Ra – <sup>222</sup>Rn data and yield apparent GW velocity of ca. 1-10 m/y. Older GW contains also higher radiogenic <sup>4</sup>He, and shows slight changes in the hydrochemistry. Noble gas atmospheric excesses are very high in all samples. <sup>87</sup>Sr/<sup>86</sup>Sr allows a clear distinction between GW originated from B- and P- rivers, due to the presence of <sup>87</sup>Sr- radiogenic granitoids in B catchment. Older GW are less <sup>87</sup>Sr- radiogenic probably because of water-limestones exchanges in the aquifer.

## Noble gas composition and reactive gas fluxes: Indicators for natural attenuation processes in contaminated aquifers

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At petroleum hydrocarbon contaminated sites, it often remains difficult to identify the most active regions of biodegradation and to quantify rates of contaminant destruction. We evaluate the suitability of noble gases (He, Ne, Ar, Kr, and Xe) to delineate the fate of contaminants in the saturated and vadose zones of a contaminated aquifer. In addition, we assess the use of CO<sub>2</sub> efflux measurements at the ground surface to estimate depth-integrated rates of contaminant degradation. To this end, noble gas data and CO<sub>2</sub> fluxes were measured in a petroleum-hydrocarbon contaminated shallow aquifer near Bemidji, MN. At this site, O<sub>2</sub> is locally depleted in the saturated and vadose zones and biodegradation of hydrocarbons takes place mostly under anaerobic conditions, generating CO<sub>2</sub> and CH<sub>4</sub>.

In the vadose zone, the observed noble gas composition confirms the occurrence of reaction-induced advective gas transport. The results reveal that the heavier noble gases provide the strongest signal for identifying gas advection as a result of their lower diffusion coefficients. Biogenic gas generation in the saturated zone promotes gas exsolution and leads to the depletion of dissolved noble gas concentrations in relation to atmospheric values. The lightest noble gases provide the strongest signal for gas exsolution due to their low solubility and noble gas ratios provide insight into the occurrence of ebullition of gas bubbles to the vadose zone. Results from the CO<sub>2</sub>-efflux measurements indicate that this method is able to adequately delineate the extent of the source zone, to distinguish between the rates of natural soil respiration and contaminant degradation, and to provide an estimate of overall contaminant degradation rates.

Overall, our results demonstrate that the measurement of the composition and fluxes of reactive and non-reactive gases at contaminated sites can be effectively used to further constrain and quantify conceptual models of processes affecting contaminant fate.