

A new analytical field method for the *in situ* determination of the oxygen dynamics in groundwater

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The knowledge of oxygen dynamics in groundwater is fundamental to understand biogeochemical processes. However oxygen dynamics can only be studied if the underlying physical gas exchange processes are understood in a mechanistic and quantitative way. In recent years gas exchange processes in porous media were thoroughly studied. The resulting conceptual and quantitative models describe gas/water partitioning in groundwater and yield mechanistic insight in the formation of excess air, a commonly observed super saturation of dissolved atmospheric gases (e.g. oxygen or noble gases) in ground waters. The initial oxygen concentrations typically exceed the atmospheric equilibrium concentration considerably (>20%). Quantification of excess air is therefore crucial to study the biogeochemical turnover of oxygen in natural groundwater.

The solubility and diffusion coefficients of O₂ in water are similar to those of Ar. However, the Ar concentration in the groundwater is unaffected by the geochemical processes of oxygen turnover. Hence, the concentration of dissolved Ar is a direct proxy that allows quantification of the initial oxygen concentration at recharge. The difference of the initial oxygen concentration with the concentration observed in a groundwater sample corresponds to the oxygen consumed since recharge of this water.

We developed a massspectrometric system for *in situ* analysis of O₂ and Ar concentrations in groundwater during field work. The gas probe consists of a membrane inlet that is submerged in the groundwater and separates the water from the gas phase to be analysed. The probe is connected to a quadrupole mass spectrometer (QMS200, SRS) via a tube of several meters length to allow *in situ* analyses in groundwater wells. A continuous vapor flow transports the gases to be analysed (Ar, O₂, N₂, and possibly also CH₄ and CO₂) from the probe to the mass spectrometer. The short response time of the system (seconds to minutes) allows continuous analysis of the dissolved gas concentrations in groundwaters. This enables us to study the O₂ dynamics, e.g. during bank infiltration of groundwater in response to the hydraulic conditions of the infiltrating river.

Iron removal enhancement of a two step calcite passive treatment system at the Iberian Pyrite Belt

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The previous calcite passive treatment systems developed at Monte Romero (SW, Iberian Pyrite Belt) have shown a significant effectiveness in iron and aluminum removal from the highly polluted acid mine drainage (AMD) emerging from the mine shaft. However, in previous experiments using two reactive tanks in series filled with calcite Dispersed Alkaline Substrate (Calcite-DAS), Al and Fe were not completely removed. The system was modified to improve treatment efficiency.

Anoxic acid discharge of Monte Romero mine flows across several iron terraces where the acidophilic microbes and atmospheric oxygen diffusion cause some iron oxidation and subsequent removal. To enhance this natural attenuation, a 100m³ dam was built after several meters of the iron terraces, and before the input of the passive treatment system (two 3m³ reactive tanks, Calcite-DAS, connected in series with two decantation ponds).

AMD treated at Monte Romero has a pH of 3-3.5, a net acidity over 1800 mg/L as CaCO₃ equivalents and contains 440 mg/L Zn, 330 mg/L Fe (98% Fe²⁺), 100 mg/L Al, 3750 mg/L SO₄ and 0.1-3 mg/L Cu, As, Pb, Co, Ni and Cd.

The natural attenuation (fomented by the dam) and the passive treatment system showed excellents results. In the dam almost 50% of ferrous iron were oxidized and 25% of ferric iron precipitated. As well, 75% of As and 7% of net acidity (140 mg/L as CaCO₃) were removed from the emerging AMD. Without the presence of the dam the oxidation and removal of Fe in the iron terraces would be only 6% and 3% respectively. The passive treatment system (Calcite-DAS) eliminated a net acidity of more than 1300 mg/L as CaCO₃ equivalents (72%) and removed 100% of Fe, Al, Cu, As, Cr and Pb from the AMD.

This pretreatment by the dam requires only minimal maintenance and no additional input of alkaline reagents.