4.5.P13

Chemical speciation and saturation state in Alpine cave dripwaters

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The seasonal dripwater chemistry variability analysed in 17 caves located in Trentino (Alps of Northern Italy) allow to recognize altitudinal and latitudinal effects on trace element composition and seasonality. The monitored caves open at different elevations: from the valley bottom (Bus del Diaol: 225 m a.s.l.) to above the timberline (Grotta del Torrione di Vallesinella: 2320 m a.s.l.). The passages of the caves are commonly cut in dolomite (slightly calcian to ideal) and pure limestones.

A linear decrease of calcite saturation index (SIcc) and alkalinity were measured in the drips of shallow caves (i.e. with rock overburden < 50 m) that open at progressively higher elevations. In particular, the SIcc shows a diminution of –0.57 units per 1,000 meters, so that in the caves located above 1500 m a.s.l. the drips are commonly undersaturated. This trend is related to the altitudinal decrease of mean annual soil CO_2 concentration, which was detected by measurements of soil air PCO_2. With respect to seasonal variability, the SIcc of the dripwaters show maximum values during winter and the lowest values in summer. At the same sampling sites, we did not observe any clear correlation between SIcc and total Ca content: we, therefore, suggest that a straightforward correlation between Ca concentration and SIcc, as proposed in theoretical models for hypogean waters, might not be always valid.

The Cl^-, Na^+, and SO_4^{2-} concentrations in cave drips are positively correlated, and decrease with the increase of the catchment elevation: the highest concentration (up to 11 mg/l SO_4^{2-}) was measured in caves located at the lowest elevation (Bus del Diaol). We infer that this phenomenon is related to a combination of altitude effect and distance from the source of water vapour. The co-variance of Cl^-, Na^+, and SO_4^{2-} - three ions that are mainly derived from the regional rainwaters through the aerosols of marine and anthropogenic-related provenance – is indicative of moisture source influence on cave dripwater chemistry. In fact, we observed a marked N-S increase of the Cl/HCO_3 Na/HCO_3, and SO_4/HCO_3 ratios in the drip-waters, from northernmost Torrione di Vallesinella to the southern Bus del Diaol. This trend reflects the distance from the Po Plain (the sulphate source), as well as from the Mediterranean (source of Na and Cl). Cave dripwater chemistry, therefore, can be a useful tool to reconstruct regional storm-track trajectories.

4.5.P14

Dedolomitization induced by dissolution of $CaSO_4$ fertilizers in loess sediments of the Szigetvár area, SW Hungary

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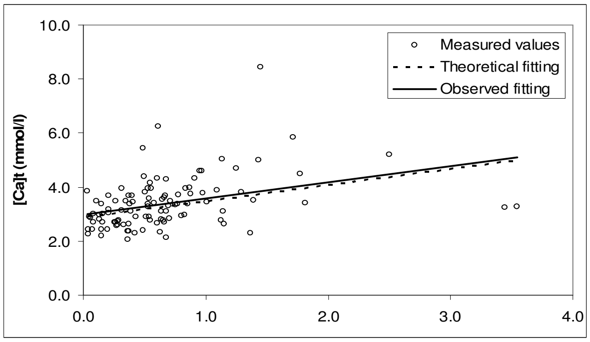
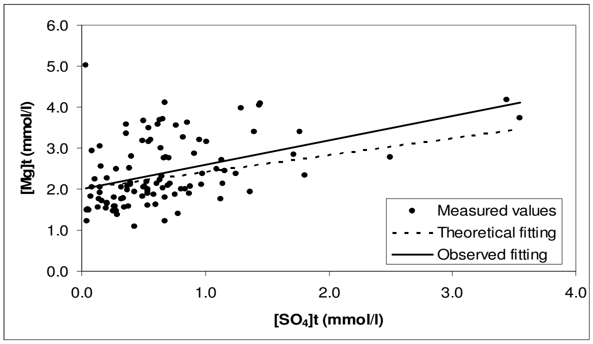
Usually, dedolomitization occurs when aquifers contain CaMg-carbonates mixed with gypsum layers, but we suggest that it can occur when gypsum-free aquifers containing calcite and dolomite are fed with farmland calcium-sulfate fertilizers.





The studied loess aquifer has calcite (cc) and dolomite (dol). Supersaturation with respect to cc and dol is given by SI_{cc}=0.85 and SI_{dol}=1.68. The groundwater is periodically fed with significant amounts of dissolved calcium-sulfate fertilizers. An eventual process of dedolomitization in such case is described by:

$$1.7CaSO_4+0.7CaMg(CO_3)_2 \rightarrow 1.4CaCO_3+Ca^{2+}+0.7Mg^{2+}+1.7SO_4^{2-}$$

The theoretical fittings between Ca/Mg and SO_4, in agreement with this stoichiometry, are represented in the figure by the dashed lines. In both cases they are followed closely by the actual fittings (solid lines). In view of these results it is reasonable to suggest that dedolomitization induced by continuous maintenance of agriculture in the study area is actively dissolving dolomite beyond its state of equilibrium.