



Anomalous CO₂ content in the Gallicano thermomineral spring (Serchio Valley, Italy) before the 21 June, 2013 Alpi Apuane earthquake (M = 5.2)

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Since late 2002, in the framework of a project funded by the Regional Seismic Service, a continuous automatic monitoring network (CAMN) has been installed in Tuscany (Italy), to investigate the geochemical response of selected aquifers to local seismic activity, and eventually identify possible hydrogeochemical precursors of earthquakes. At the present, the CAMN consists of 6 stations operating in selected areas of high seismic risk in Tuscany, i.e. Serchio Valley, Magra Valley, Mugello, Tiber Valley and Mt. Amiata. In this contribution, we present a CO₂ anomalous variation registered in the Gallicano thermomineral spring (Serchio Valley, Italy) 20 days before the M=5.2 Alpi Apuane earthquake of 21 June 2013.

The Gallicano automatic station is equipped to measure (sampling frequency 5 minutes) water temperature (T), pH, electrical conductivity (EC), redox potential (Eh), CO₂ and CH₄ dissolved concentrations. In addition to continuous monitoring, the Gallicano spring has also been investigated by discrete sampling and measurement of T, pH, EC, alkalinity, dissolved concentrations of major and selected minor (F, B, SiO₂) chemical components, and isotope composition of water ($\delta^{2}H$, $\delta^{18}O$, UT).

The monitored feature is a thermal spring issuing from carbonate outcrops on the Apuan (i.e. western) side of the Serchio Graben. Two different components contribute to the outflow of the spring: i) hydrothermal waters of Na-Cl-Ca-SO₄ type, likely uprising through the major NW-SE local fault system, and ii) dilute groundwaters of Ca-HCO₃ composition connected to shallow circulation circuits. The lack of an impermeable cover upstream of the emergence point, allows for minor dilution of the ascending branch of the local, low-enthalpy hydrothermal circuit, with surficial cold waters. Due to the mixing of these two components, Gallicano spring waters have a Na-Ca-Cl geochemical signature, positive Eh values (average +389 mV), and temperatures between 23.4°C and 25.2°C. Total dissolved salinity (TDS) ranges from 2.4 to 4.2 g/l, and CO₂ concentrations in dissolved gases are around 2.6% by vol.. Under these conditions, anomalies of the geochemical signal can be detected by inspection of multi-parameter correlations.

In the case of M=5.2 earthquake of 21 June 2013, a significant positive anomaly of CO₂ dissolved concentration, not correlated to T, EC and variations in rainfall amounts, was observed about 20 days before the seismic event, on 30 May 2013. This feature has been interpreted as a clear evidence of sudden gas release at depth within the system. The existence of a CO₂ anomaly has also been validated by signal processing techniques, based on the analysis of CO₂ residuals (CO₂ autocorrelogram, time lag up to 48 h).