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## Santa Cesarea Terme, a sulphuric acid speleogenetic system intensely influenced by marine waters

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Santa Cesarea Terme (SCT) karst system opens along the Adriatic coastline of Apulia (southern Italy) and is composed of four sub-horizontally caves Fetida, Sulfurea, Gattulla and Solfatarata. Being influenced by rising sulphidic waters, it is used as thermal spa for human health treatments. The caves show interesting signs of hypogene sulphuric acid speleogenetic (SAS) activity such as peculiar morphologies and mineralogical by-products. From the geomorphological standpoint it is possible to observe ceiling cupolas, megacusps (former megascallops), rising channels, submerged feeders, weathered walls, replacement pockets, whereas for mineralogy sulphur, gypsum and jarosite deposits have been recorded. Despite the presence of extensive SAS features, SCT is also intensely influenced by marine water.

All these observations induced us to conduct a long-lasting (2015-2018) geochemical monitoring to understand intensity and tendency of the two main domains (rising acidic vs. marine).

Water sampling was done every 3-4 months at 4 sites in Fetida (2 in areas influenced by sea water movements, and 2 in the innermost zone, less but still influenced by sea), and 1 site in Gattulla. Moreover, 1 sampling site located along the coastline (sea water) was constantly monitoring for comparative reasons.

Collected groundwaters exhibit mean temperatures of 23 °C (7 °C higher than average annual air temperature) and circumneutral pH. All samples belong to the Na-Cl-SO<sub>4</sub> type of waters. Sea waters display the highest pH (ranging between 8.15 and 8.20), [Na<sup>+</sup>], [K<sup>+</sup>], [Mg<sup>2+</sup>], [Cl<sup>-</sup>], [SO<sub>4</sub><sup>2-</sup>], and total dissolved solids (TDS), and on the other hands one of the innermost sampling site in Fetida Cave showed the highest values of temperature (29 °C), [HS<sup>-</sup>], [Ca<sup>2+</sup>] and the lowest pH (6.76). In addition, the Ba<sup>2+</sup>/Sr<sup>2+</sup> ratio compared with Ca<sup>2+</sup>/HCO<sub>3</sub><sup>-</sup> or Ca<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> clearly exhibit the presence of two main domains: rising acid and marine. In particular, the samples collected in the Adriatic Sea are always in the domain of marine influence, whilst all the others from Gattulla and Fetida, depending on sampling conditions (tides, waves, etc..), can fall in both domains.

Our investigations demonstrated rising sulphidic fluids to reach the surface through deep tectonic fractures and karst flowpaths, but seasonal effects due to modest water head variations (tides) and meteomarine conditions affect the geochemical variability, even in the innermost portion of the caves, inducing these slightly thermal acidic fluids to partially mix with marine waters.