

The fate of CH₄ in shallow aquifers: the case study of “*warm water wells*” in Emilia-Romagna Region (central-northern Italy)

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After the destructive seismic sequence that struck the Emilia-Romagna Region (central-northern Italy) in May-June 2012, scientists and population has focused their attention on the so-called “Geological Anomalous Events (GAEs)”, i.e. persistent gas bubbling in wells, gas-water-mud burst, ground fracturing and collapsing events, fish death episodes in small lakes or channels and so forth. Among the GAEs, the most reported and recurrent are those related to abrupt temperature increases (up to 55°C) of shallow (depth \leq 10 m) groundwaters recorded in domestic water wells. Currently, more than 30 heating episodes were reported by citizens and recorded by the Geological, Seismic and Soil Survey of the Emilia-Romagna Region. In order to understand the mechanism responsible for this anomalous process and its relationship with the structural setting and the seismotectonic activity, a geochemical survey was carried out on several selected water wells by deploying sensors for the continuous monitoring of water temperature, electrical conductivity and hydrometric level and direct periodic sampling to determine the chemical and isotopic composition of water and dissolved gases. During quiescent periods, meteoric water is the sole contribution that feeds the studied wells and the composition of the dissolved gas phase is dominated by atmospheric species (N₂, Ar, and O₂) similar to that of ASW (air-saturated water). The results of our geochemical survey highlighted that the water heating episodes affect the dissolved gas phase since significant concentrations of CH₄ and subordinate contents of CO₂ occur, which are also accompanied by an abrupt drop of the oxygen partial pressure. On the other hand, the water chemistry does not show any substantial modification. Moreover, CH₄ shows a relatively positive isotopic composition ($\delta^{13}\text{C}$ and δD up to -20.7 ‰ and -58.5 ‰ respectively), strongly different from that recorded within the reservoirs of natural gas, which are widely distributed in the subsurface of the Emilia-Romagna Region. Contribution of warm water from the underlying marine formations as the cause of the temperature increase seems unlikely due to both the very low local geothermal gradient (\leq 25°C/km) and the absence of any change in the water chemistry. Presently, the most reliable explanation is the exothermic oxidation of diffusively uprising methane by methanotrophic bacteria under aerobic conditions at very shallow depths. The same process was recently invoked for explaining the anomalous high temperature (up to 48.5 °C) in the soils from “Terre Calde di Medolla” (literally, “Warm Grounds of Medolla”), a site located in a farming area close to some of the monitored water wells. Where the methane comes from and if and how this phenomenon might be related to the structural and seismotectonic context are still matter of debate. Despite this, looking in a 4D perspective, this biological mechanism could represent an important sink for CH₄, preventing its release into the atmosphere in all the investigated area but also in other subaerial sedimentary basins around the world.