DIPARTIMENTO
DI SCIENZE DELLA TERRA
SAPIENZA
UNIVERSITÀ DI ROMA

DOTTORATO DI RICERCA
IN SCIENZE DELLA TERRA

Research activity

Groundwater and seismicity relationship: hydrogeological monitoring to identify hydrosensitive sites in central-southern Italy

General objective: Hydrogeological and hydrogeochemical characterization of the main springs in central-southern Apennines in order to identify specific sites for a potential future national monitoring network.

Specific objective: Expanding our understanding of the cause-effect relationship between groundwater and seismicity to define "hydrosensitive" sites in central-southern Italy.

State of the art: Earthquake-induced groundwater and gas changes have been widely documented in seismogenic areas worldwide. Several studies have highlighted the sensitivity of fluid behaviour related to the seismic cycle both in terms of hydrogeological and hydrogeochemical anomalies[1-3]. In detail, variations, including changes in spring discharge[4], groundwater level[5], geochemical content[6], isotope composition[7], dissolved and free gases[8] have been observed in sensitive monitoring sites at different distances from epicentres. In literature, various mechanisms have been proposed to explain groundwater level and discharge changes such as: pore-pressure response to crustal elastic strain[9], permeability changes caused by seismic waves[10], and fluid migration along dilatant cracks or deep crustal fractures[11]. Besides, variations in geochemistry and isotopic signature of groundwater have been also defined as the results of the following processes: deep and hydrothermal fluid upwelling[12], mixing of waters from different aquifers, and rock weathering enhancement in new rupturing[13]. Studies carried out by international research teams argue that focusing on hydrogeological and hydrogeochemical earthquake-related effects is a promising target for seismic investigation. Indeed, in many countries all over the world (e.g., Italy, Iceland, Japan, China, and Korea)[14-18], the set-up of hydrogeochemical networks has been already established or is currently in progress in order to identify responses induced by earthquakes. Scientific efforts are now moving towards this direction to obtain more observations and to build up appropriate hydrogeochemical models associated with different geo-tectonic contexts. In detail, hydrogeochemical anomalies during the 2016-2017 Amatrice-Norcia seismic sequence in central Apennines were ascribed to the deep CO_2 upwelling into the regional shallow aquifer along tectonic discontinuities[14,19,20]. Thus, considering previous results, and hydrogeological and seismological constraints, the central-southern Apennines represent a natural promising laboratory for monitoring geofluids as markers of active seismogenic processes, owing to the great abundance of groundwater resources and the nature of the regional aquifers hosted by fractured Meso-Cenozoic carbonates that enhances the response to deep fluids uplift, allowing fast and concentrate changes in groundwater close to tectonic lines. Additionally, the intense seismic activity, affecting the above-mentioned area, confirms the relevance of the research to better understand the interactions between seismicity and hydrogeology. Therefore, this PhD project has the dual purpose of identifying potential earthquake-induced groundwater and gas changes, and of analysing deep and shallow fluid contributions to a regional groundwater circulation model in an active seismic area.

Activity and workplan: The bibliographic study concerning the topics related to the project was carried out and will be continuously updated in order to better develop the research. Based on the results of the first year of research, respect with the entire central-southern Apennines, two focus areas characterized by optimal conditions of water-gas system were selected. Thus, by considering both logistic conditions and hydrogeological characteristics, I focused the study mainly on the Matese, and the Contursi sites, since deep fluids contributions are more evident. In detail, I performed monthly surveys at four springs in the Matese area (i.e., Rio Freddo, Grassano, Telese Terme, and Capovolturno) in order to investigate potential changes in groundwater hydrogeochemistry induced by seismicity. Additionally, I performed continuous hydrogeological,

hydrogeochemical, and gas-geochemical monitoring by using multiparametric probes whose installation was established within a previous research project. Specifically, the Hydrolab HL4 probe was used for the continuous measurements of temperature, electrical conductivity, pH, and dissolved oxygen; the Mini CO_2 probe for the continuous measurement of dissolved CO_2 concentration; the Alphaguard probe for the detection of dissolved radon concentration. Recorded data can be monitored and downloaded in real-time through an online system of data acquisition. It is noteworthy that analyzing both discrete and continuous data, collected and recorded at Grassano spring, hydrogeochemical changes were observed before the onset and during the 2019-2020 Benevento seismic sequence, including dissolved CO_2 increase, pH lowering, and anomalies in major ions (i.e., Ca^{2+}, Na^{+}, HCO_3^{-}). The study shed light on the possibility of having pre-seismic hydrogeochemical signals in groundwater of Apennines also for small-intermediate earthquake magnitude (mainshock: M_w 3.9 San Leucio del Sannio), at least in the areas where deep fluids contribution to groundwater is evident. Besides, the obtained results confirm a geochemical process in the fractured carbonate aquifers, similar to the one proposed in literature for the stronger 2016-2017 Amatrice-Norcia seismic sequence[14,19,20]. Moreover, I performed a sampling survey in 22 springs with different geochemical features (e.g., from low to high mineralization, abundance or absence of free gases) in the Contursi area. Attempts to build a detailed deep circulation conceptual model, defining mixing between deep and shallow fluids, are now in progress. Hence, I worked on field, in laboratory, as well as in data processing. In each sampling campaign chemical-physical parameters (temperature, pH and electrical conductivity) were measured on-site through the multiparametric probe WTW Multi 3420. Samples for the determination of major ions and trace element concentrations were analyzed using the anionic and cationic chromatograph, and the ICP-MS spectrometer, respectively, at the Geochemistry Laboratory of Earth Sciences Department of Sapienza University of Rome. Samples for analysis of the water isotopes ($\delta^{18}O$, δD, and ^{3}H), dissolved and free gases (He, CO_2, H_2, N_2, O_2, CH_4) and isotopic ratio ($^{3}He/^{4}He$, $\delta^{13}C$, $\delta^{34}S$) were collected and sent to the laboratories of Isotope Tracer Technologies Europe Srl, and to ones of the National Institute of Geophysics and Volcanology (section of Palermo). Analyses of samples and data processing allowed the determination of the hydrogeochemical facies, the degree of mineralization, and the origin of the gaseous contribution. In addition to the two areas treated as "core" of the project, the research activity extended to other areas in Italy (i.e., Val d'Agri, Pantelleria, Pontina Plain) by starting collaborations with research teams of Sapienza University. Such areas are suitable for expanding knowledge about the origin and mixing of deep fluids and the water-rock-gas interactions in aquifer systems. During the last year, I will continue to perform monthly sampling surveys coupled with continuous multiparametric monitoring in the Matese area. Processing and data interpretation will be carried out in order to identify periodicity, trends and relations with local, seasonal conditions, and potential characteristic trends associated with seismicity. For seismic investigation, I will select earthquakes of different magnitudes (recorded by the National Seismic Network) that occurred in the same period of the hydrogeochemical monitoring. Furthermore, a detailed hydro-gas-geochemical characterization of the Contursi area will be realized through further sampling and analyses. An in-depth study of the deep and shallow fluid contributions to a regional groundwater circulation flow in an active seismic area will be useful for improving groundwater monitoring aimed at identifying geochemical signals related to crustal deformation processes and potentially to seismic activity. I will contribute further to the above-mentioned "extra" activities that I started during the second year of PhD. Among the activities of the third year, a period abroad at the Department of Ecology and Geology of the University of Malaga (Andalusia, Spain) is planned to improve the interaction with researchers involved in scientific research. Finally, I will also write papers and the PhD thesis.

References: 1. Montgomery & Manga (2003). *Science* 300, 2047-2049; **2.** Doglioni et al. (2014). *Geosci. Front.* 5, 767-780; **3.** Wang & Manga (2021). Water and Earthquakes (p. 387) *Springer Nature;* **4.** Petitta et al. (2018). *Hydrogeol. J.* 26, 1009-1026; **5.** Lan et al. (2021). *Hydrogeol. J*. 29, 1329-1341.; **6.** Kim et al. (2020). *Geochem, Geophys. Geosyst.* 21; **7.** Hosono, et al. (2020). *Nat. Commun*. 11, 2776; **8.** Kawabata et al. (2020). *J. Hydrol.* 584, 124712; **9.** Wakita (1975). *Science* 189*,* 553-555; **10.** Elkhoury et al. (2006). *Nature* 441, 1135-1138; **11.** Tsunogai & Wakita (1995). *Science* 269*,* 61-63; **12**. Hosono et al. (2018). *Sci. Rep.* 8, 14809; **13.** Claesson et al. (2004). *Geology* 32, 641-644; **14.** Barberio et al. (2017)*. Sci. Rep.* 7, 1-12; **15.** Skelton et al. (2019) *J. Geophys. Res. Solid Earth* 124*,* 2702-2720; **16.** Hosono & Masaki (2020). *J. Hydrol.* 580, 124340; **17.** Chen & Wang (2021). *Environ. Pollut*. 284, 117125; **18.** Lee et al. (2021). *Water*, 13, 2448; **19.** Boschetti et al. (2019) *Geochem. Geophys. Geosyst*. 20, 2303-2317; **20.** Barbieri et al. (2020) *J. Hydrol.* 582, 124495.

Gantt chart

PhD activity	First year		Second year		Third year	
	First semester	Second semester	First semester	Second semester	First semester	Second semester
University courses	x	x	x	x		
Bibliographic study	x	x	x	x	x	x
Sampling of springs	x	x	x	x	x	x
Installation of stations			/	/	x	
Further activities (contribution to other research projects)*				x	x	
Training period abroad				/	x	
Analysis and comparison of processed data		x	x	x	x	x
Data interpretation		x	x	x	x	x
Publications		x		x		x
Seminars and conference	x	x	x	x	x	x
Thesis						x

The original time schedule was modified: the activities that were not realized during this year are displayed in grey, while the new ones are reported with (*)

Research products

a) Publications (ISI journals)

- **Gori, F.**, & Barberio, M. D. (2022). Hydrogeochemical changes before and during the 2019 Benevento seismic swarm in central-southern Italy. *Journal of Hydrology*, *604*, 127250.
- Barbieri, M., Barberio, M. D., Banzato, F., Billi, A., Boschetti, T., Franchini, S., **Gori, F.**, & Petitta, M. (2021). Climate change and its effect on groundwater quality. *Environmental Geochemistry and Health*, 1-12.
- Barbieri, M., Franchini, S., Barberio, M. D., Billi, A., Boschetti, T., Giansante, L., **Gori, F.**, Sigurjón, J., Petitta, M., Skelton, A., & Stockmann, G. (2021). Changes in groundwater trace element concentrations before seismic and volcanic activities in Iceland during 2010–2018. *Science of the Total Environment*, *793*, 148635.
- Barberio, M. D., **Gori, F.**, Barbieri, M., Boschetti, T., Caracausi, A., Cardello, G. L., & Petitta, M. (2021). Understanding the Origin and Mixing of Deep Fluids in Shallow Aquifers and Possible Implications for Crustal Deformation Studies: San Vittorino Plain, Central Apennines. *Applied Sciences*, *11*(4), 1353.
- Barberio, M. D., **Gori, F.,** Barbieri, M., Billi, A., Caracausi, A., De Luca, G., Franchini, S., Petitta, M., & Doglioni, C. (2020). New observations in Central Italy of groundwater responses to the worldwide seismicity. *Scientific Reports* 10, 17850.
- Barberio, M. D., **Gori, F.**, Barbieri, M., Billi, A., Casalati, F., Franchini, S., Lorenzetti, L., & Petitta, M. (2020). Optimization of dissolved Radon monitoring in groundwater to contribute to the evaluation of the seismic activity: an experience in central-southern Italy. *SN Applied Sciences*, 2(8), 1-12.
- Barberio, M.D., **Gori, F.**, Barbieri, M., Billi, A., Devoti, R., Doglioni, C., Petitta, M., Riguzzi, F., & Rusi, S. (2018). Diurnal and Semidiurnal Cyclicity of Radon (^{222}Rn) in Groundwater, Giardino Spring, Central Apennines, Italy. *Water*, 10, 1276.

b) Publications (NON ISI journals)
c) Manuscripts (submitted, in press)
d) Abstracts

- **Gori**, **F.**, Buttitta, D., Barberio, M.D., Barbieri, M., Caracausi, A., Paternoster, M., Petitta, M. – Hydrogeochemical and isotopic studies of groundwater in the Contursi area (southern Apennines). *1st Italian Geochemical Society Congress "From theoretical to applied geochemistry, Genoa 2022*
- **Gori, F.**, Barberio, M.D., Barbieri, M., Billi, A., Doglioni, C., Franchini, S., Petitta, M. – New insights on the groundwater-seismicity relationship: experiences from the hydrogeological network in central-southern. *5th edition of Flowpath, the National Meeting on Hydrogeology, Naples 2021.*
- **Gori, F.**, Barberio, M.D., Barbieri, M., Billi, A., Franchini, S., Petitta, M. – Hydrogeochemical changes before and during the 2019 Benevento seismic swarm in central-southern Italy. *1st National Congress of Italy for Young Geoscientists (BeGeo), Naples 2021.*

- Petitta, M., **Gori, F.**, Barberio, M.D., Barbieri, M., Billi, A., Franchini, S. – Investigating groundwater-seismicity relationship: the preliminary hydrogeological monitoring network of central-southern Italy**.** *47th IAH Congress, São Paulo Brazil 2021*
- Barberio, M.D., **Gori, F.**, Barbieri, M., Boschetti, T., Caracausi, A., Cardello, G.L., Petitta, M. – Hydrogeochemistry and geothermometry of fractured carbonate aquifers controlled by deep-seated faults: two study cases from Central Italy*. 5th edition of Flowpath, the National Meeting on Hydrogeology, Naples 2021.*
- Barberio, M. D., Barbieri, M., Billi, A., Boschetti, T., Caracausi, A., Doglioni, C., Franchini, S., **Gori, F.**, Petitta, M. – Deep fluid source contribution to groundwater in Central Apennine: from regional to local scale*. MinWat 2020, 3rd International Multidisciplinary Conference on Mineral and Thermal Waters*
- Barberio, M. D., **Gori, F.**, Barbieri, M., Billi, A., Franchini, S., Petitta, M., Doglioni, C. – First observation of multi-groundwater level responses to the strongest worldwide seismicity in Central Apennines (Central Italy). In *EGU General Assembly Conference Abstracts (p. 5659). Vienna, 2020.*
- **Gori, F.**, Petitta, M., Barberio, M. D., Doglioni, C., & Caracausi, A. – Groundwater and seismicity relationship: hydrogeological monitoring to identify "hydrosensitive sites" in central-southern Italy. In *Roma chiama Roma. Earth Science Department of Roma Tre University. Rome, 29-30 January 2020*
- Barberio, M.D., Barbieri, M., Billi, A., Doglioni, C., Gallo, T., **Gori, F.**, Franchini, S., Lacchini, A., Mariani, J., Petitta, M., Rusi, S. – Monitoring groundwater and earthquake relationships: "hydrosensitive zone" concept and experiences from Central Italy. *45th IAH congress. Korea, 9-14 September 2018*