Geochemical characterization of groundwater quality in Hellenic karst systems

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Karst aquifers are considered to be one of the most important aquifer types, as they constitute the main drinking water resource for the majority of the global population (Ford et al., 2007). They are generated from the dissolution of carbonate rocks (e.g. limestone, dolomite, marble etc.), a phenomenon commonly known as "karstification". This process is mainly caused by the acidity of water enriched in dissolved CO_2, with the concentration of the latter being dependent on both the temperature and the CO_2 partial pressure of the atmosphere in contact with the water (Bakalowicz, 2005).

Carbonate rocks cover about 35% of the land surface of Greece and are mainly located in the western, central and southern parts of the country (Daskalaki et al., 2008). The Hellenic karst aquifer resources are more abundant in the western part of Greece, which receives the highest amount of precipitation (1800 mm/a) (Mimikou, 2005). The karst system constitutes a strategic resource of water in the region and preserving its quantity and quality is of the utmost importance for the sustainability of the area.

Seventy samples of natural water were collected from karst springs in the northern (Macedonia-Thrace) and in the central parts of Greece, during 3 campaigns from 2016 to 2018. Sampling sites were selected on the basis of the springs flow rates (> 50 L/s). Water temperature, pH, Eh and electric conductivity were measured in situ with portable instruments; major ions were determined by Ionic Chromatography (IC) on filtered (anions) or filtered and acidified (cations) samples, whereas trace elements were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on filtered and acidified samples. All analyses were performed at the laboratories of INGV of Palermo.

Chemical compositions were compared with the limits fixed by the Directive 98/83/EC, which is the most recent EU legislation that sets quality standards for drinking water. Regulations concerning the quality of drinking water as established by the Directive allow Member States to adapt the monitoring of water quality to local conditions (Karavoltsos et al., 2008).
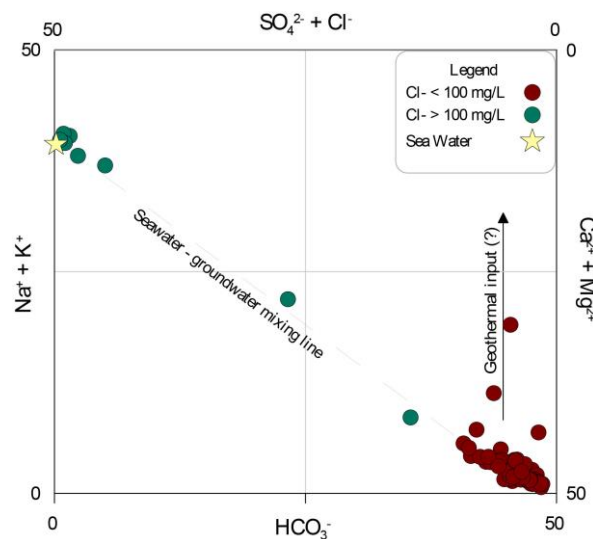

Figure 1. Langelier Ludwig diagram showing the chemical composition of the sampled karstic groundwater of northern and central Greece.

Temperatures of the sampled waters ranged from 8 to 25 °C, pH from 6.5 to 8.4, whilst Total Dissolved Solids (TDS) from 206 to 15,418 mg/L. The highest concentrations of sodium, potassium, chloride and sulfate were found in the karst springs of Central Greece (26.6-5610 mg/L; 1.56-204 mg/L; 81.06-9467 mg/L; 15-2420 mg/L, respectively), where values had sometimes exceeded the limits set by the Directive 98/83/EC, indicating a contamination due to sea water intrusion. Based on the chloride concentrations, samples were subdivided into low (Cl^- < 100 mg/L) and high (Cl^- > 100 mg/L) chloride karst waters. All water samples were plotted in a Langelier Ludwig diagram (Fig. 1) with the low chloride waters presenting a typical alkaline-earth bicarbonate composition. Exception is the samples of Kaliakuda, Sidirokastro and Koromilia that display enrichment in alkalis possibly due to hydrothermal activity. On the other hand, the most chloride-rich waters plot close to the sea water composition point while two samples (Rema, Mylos Kokkosi) are aligned

along the seawater-groundwater mixing line (Fig. 1).

Concentration ranges of major and trace elements for all waters are presented in Fig. 2, with low and high chloride samples being plotted with different symbols. High chloride group displays much higher values for Mg, SO_4, Cl, Na, K, Sr, B, Li, Rb and Cs with respect to low chloride, with differences in the median values between two and three orders of magnitude. Species deriving from carbonate dissolution (Ca and HCO_3) show the lowest range of concentrations both for low and high chloride waters (Fig. 2). Low chloride waters show a wide range of concentrations (three to four orders of magnitude) for trace elements such as Li, Fe, Rb, As, Mn, Cu and Cs.

Trace elements were above the legislation limits (Directive 98/83/EC) mostly in the case of high chloride karst springs, showing elevated concentrations of Boron (up to 1861 μg/L), Strontium (up to 5026 μg/L) and Arsenic (up to 12.1 μg/L). In terms of Boron and Strontium, the exceeding values seem to be generally related to the intrusion of sea water. On the other hand, Arsenic, whose maximum admissible level is 10 μg/L, was above limit also in the low chloride water (17 μg/L) of Tempi, Thessalia. Few low chloride waters show a metal enrichment, such as Tempi (Sr = 242 μg/L, Mo = 2.27 μg/L, and Cs = 1.57 μg/L) and Kaliakuda (V = 3.89 μg/L, Mn = 3.65 μg/L, Fe = 71.26 μg/L, Cu = 11.55 μg/L, Zn = 22.61 μg/L, Rb = 54.7 μg/L), whilst nitrate concentrations that could indicate contamination from fertilizers or from septic tanks, are always below the maximum admissible value (50 mg/L).

Most of the analyzed waters can be considered suitable for human consumption. Water quality deterioration of Hellenic karst springs is mainly due to sea water intrusion, whilst only few low chloride waters show significant enrichments in trace metals that rarely exceeds the drinking water standards. These higher contents are probably of natural origin due to local geological setting.
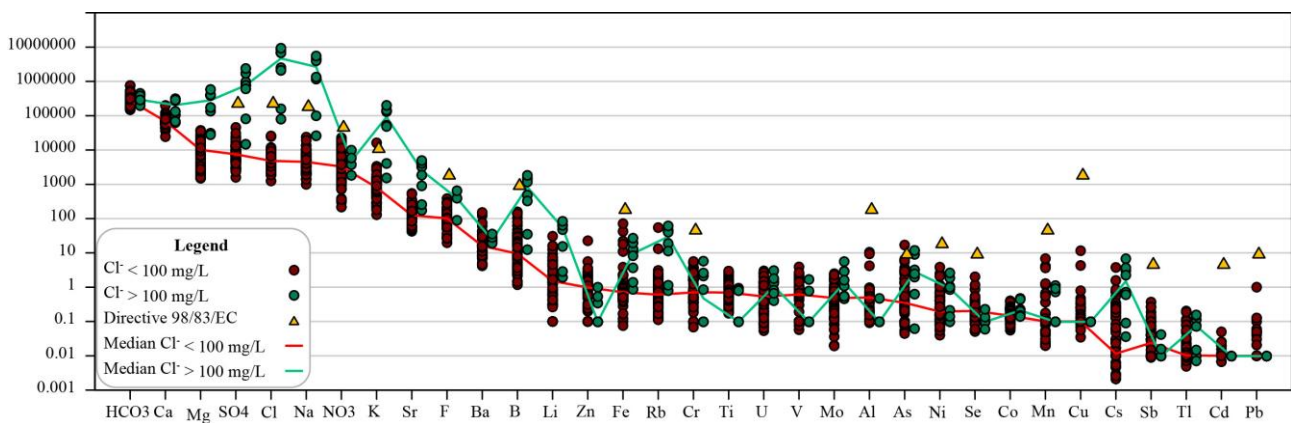

Figure 2. Distribution of major and trace elements in μg/L. Limits set by the Directive 98/83/EC are plotted with yellow triangles.

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