HYDROGEOCHESTRY OF KARST SPRINGS IN THE TRANSBOUNDARY AREA ITALY – SLOVENIA (KANIN MOUNTAIN)

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INTRODUCTION

Karst aquifers are considered by scientific community one of the most important globally water resources; in fact, approximately 25% of the world's drinking water comes from karst groundwater systems (Drew & Hoetzl, 1999). They are also the landscape most vulnerable to environmental impacts (Veni *et al.*, 2001). Global environmental change studies have therefore become increasingly important for environmental scientists, as well as the relationships between ground water and climate for ground water hydrologists and hydrogeochemistry.

The direct effect of the global warming is the redistribution of water resources on the Earth (Waggoner, 1990). As an important component of the global hydrologic cycle, ground water not only contains information about environmental changes, but it is directly affected by those changes (Zhang *et al.*, 1997). Isotopic and hydrochemical studies were made to find out the most sensitive indicators of environmental changes (Edmunds, 1996; Grasso & Jeannin, 1998; Plummer *et al.*, 1999).

This research was focused on geochemical study of springs located in the transboundary area Italy-Slovenia (Kanin Montain) of the Isonzo river basin. Kanin Mountain, due to their geological and hydrogeological features, houses a very important karst aquifer system that feeds springs with extraordinary flow rate and quality. This work integrates, with geochemical studies, the activities of characterization of transboundary aquifers of Isonzo/Soca River within ASTIS Project (Italy-Slovenia 2007-2013, Cross-Border Cooperation Programme).

The main topic of this study was the geochemical characterization of spring waters of the Kanin Mountain karst aquifer, through water-rock interaction studies as well as geochemical mobility analyses of some chemical elements, in order to identify by meteo-climatic analysis, the possible geochemical markers that could depend on climatic variability, especially seasonal changes.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The study area is located in the Kanin massif at the western part of the Julian Alps (Italian-Slovenian border). It is a typical karst area very famous for the high numbers of deep caves.

The present landforms of this area are the results of tectonics, karstic, fluvial and glacial processes (Telbisz *et al.*, 2011). The most common lithotype around Kanin Massif is represented by the Upper Triassic poorly karstifyng Main Dolomite ("Dolomia Principale") with a thickness grater than 1000 meters. It is overlain by the well karstifyng Dachstein Limestone, which is also Upper Triassic and has similar thickness. The great thickness of the Dachstein limestone strata has influenced the development of the karst as well as the nature and the position of the karst springs. Jurassic limestones are found in a limited extent only at the western and southeastern part of Kanin massif. Quaternary glacial, fluvioglacial and detrital sediments are present mainly in the valleys and at the foot of steep slopes (Buser, 1986; Carulli, 2006; Jurkovšek, 1987). The location and characteristics of the springs below the Kanin massif depend on the geological features. They are usually located where the geological structure allows water to outflow from the karst massif, mostly at fissure zones and along stratigraphic structures. The springs at the lowest altitudes were mostly formed from erosion at base level or at the contact between permeable carbonate rocks and less permeable flysch. The water is also directed to the springs at the bottom of the Bovec Basin by the stratigraphic and tectonic structure (syncline) and by impermeable crushed zones formed at thrusts and faults. Hydrodinamic of Kanin massif is characterized by short and fast water circulation toward the springs that border the recharge zones.

METEORIC REGIME

The study area is located close to the head of the Isonzo/Soca Valley and presents very peculiar climatic characters due to its morphology. To define the climate of the study area it has been selected the meteorological station of Kredarica, that has continuous long-term daily data from 1961 to today. The Kredarica station is located at an altitude of 2,515 m and it well describes the climate of the more elevated areas of Kanin massif.

The climate of the region is alpine, with an annual average temperature of -10 °C, minimum average temperature of -8.1 °C in February (coldest month) and maximum average temperature of 6.90 °C in July (warmest month). The area is characterized by annual precipitation ranging from 1500 to 2900 mm and annual average snowfall of 1029 cm.

Meteo-climatic analysis (2011-2014)

Statistical analyses were carried out on meteorological daily data in order to correlate the climatic variations (Fig. 1) and the geochemical composition of spring waters, in the period 2011-2014.

In the analyzed period significant variations in the annual average temperatures were not observed. Values below the average seasonal temperatures were observed in the second part of winter 2012 (-23 °C T_{min}; Fig. 1).

As concern the precipitations (rain and snow), the 2011-2012 winter season was characterized by long phases of dry periods, due to North-Western fronts producing low precipitations (especially snowfall).

Conversely, the 2013-2014 winter period was characterized by southern streams with abundant precipitations. In this time, the snow precipitations were the highest with snowfall of 1400 cm (2013) and 1700 cm (2014) compared to the average annual snowfall of 1029 cm.

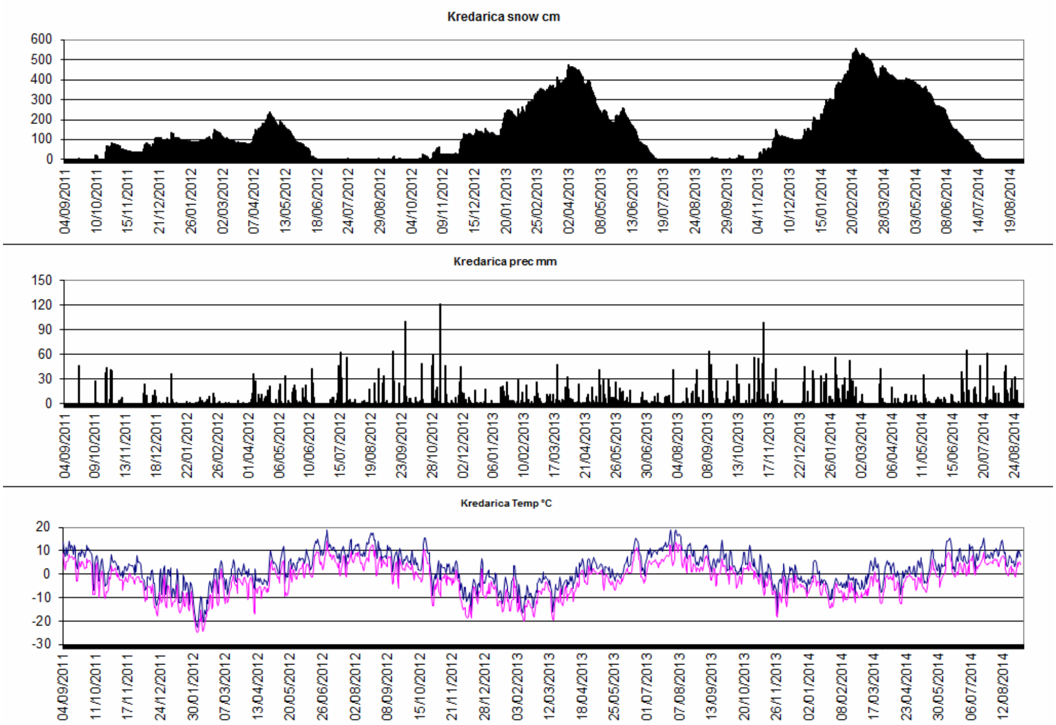

Fig. 1 -Temperature, rain precipitation and snowfall (daily data for the period 2011-2014) at the meteorological station of Kredarica.

MATERIALS AND METHODS

The investigated 10 springs are located in the Kanin Mountain area. The main topic of the research was the monitoring of water samples during 3 different years from 2012 to 2014; we performed seasonal sampling (spring, summer, and autumn), *i.e.*, during the recharge and discharge of the aquifer. Altitudes, minimum and maximum flow rates were measured during the sampling based on recent studies (Casagrande *et al*., 2011a).

The samples were collected in 50 ml HDEP bottles. For cations and trace elements analysis the samples were acidified with 0.5 mL of concentrated Suprapur HNO_3, whereas for anions and alkalinity analsysis the samples were not acidified. Each water sample was filtered by a 0.45 μm Minisart® NML syringe cellulose acetate filter. For $\delta^{18}O$ and δD analyses samples were collected without filtering in 50 ml HDEP bottles.

Alkalinity was determined with standard neutralization titration with 0.1 M HCl (Clesceri *et al.*, 1998). Cations ($Ca^{2+,}$ $Mg^{2+,}$ Na^+, K^+) and trace elements were measured by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument on samples previously diluted (1:10) by deionized Milli-Q water (resistivity of *ca*. 18.2 MΩ×cm), also introducing known amount of Re and Rh as internal standard; in each analytical session, the analysis of samples were verified by comparison with the reference materials (EU-L-1 and ES-L1) provided by SCP-Science. Anions (Cl^-, SO_4^{2-}, NO_3^-) were determined by ion chromatography using a Shodex IC SI-90 4E separation column (250 mm × 4 mm). A mixture of sodium carbonate and sodium bicarbonate in water (1.8 mM: 1.7 mM) with a flow rate of 1 mL min^{-1} was used as the mobile phase. The injection volume was 50 μL. For quantification purposes a calibration curve in the range from 0.5 mg L^{-1} to 50 mg L^{-1} was prepared. The coherence of chemical data were verified by checking the ionic balance, as the sum of cation (expressed in meq/L) approaches that of anions; the relative error [(Σcations−Σanions)/(Σcations+Σanions)]×100, was generally less than 5%. Geochemical model for pCO_2 and saturation index of calcite and dolomite, were obtained using GWB (The Geochemist's Workbench) with subprogram SPEC8.

RESULTS AND DISCUSSION

The results of chemical analyses highlighted that the springs waters are mainly characterized by Ca-Mg – HCO_3, whereas other major elements (Na^+, K^+, NO_3^-, SO_4^{2-}, Cl^-) are presents in low concentrations (Fig. 2).

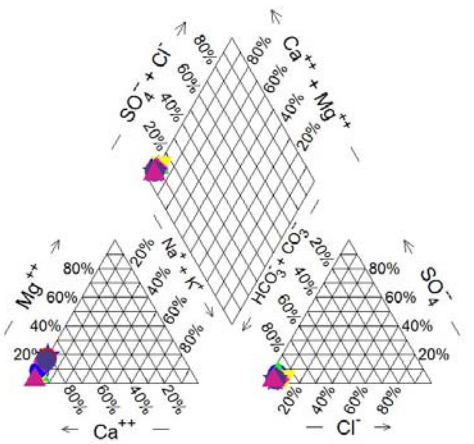

Fig. 2 - Piper Diagram for the analyzed spring waters.

During the studied period major elements evidenced a good homogeneity with few variations of chemistry; conversely trace elements evidenced a higher seasonal variability. In particular, the springs water evidenced high concentration of As (> 10 μg/L) higher than the limits set by the Drinking Water Directive 2000/60/EC.

High concentrations of As were presents in summer, whereas in spring and autumn the concentrations were below the regulatory limits. As concern to other trace elements, Fe was present in amounts higher than the regulatory limits (> 200 µg/l) set by the Drinking Water Directive 2000/60/EC during the spring seasons.

In order to provide an overview for all the geochemical components and to estimate if the climate variability affects the geochemical characteristics of waters, it was necessary to analyze and to study the behavior of the stable isotopes of water $\delta^{18}O$ and δD, which are, as is widely known, excellent tracers for water and excellent indicators for climate variability.

The δD and $\delta^{18}O$ isotopic ratios have been measured for Kanin spring waters sampled in distinct hydrological periods from 2012 to 2014; *i*) in summer seasons, the δD ranged from -86.14 to -75.45‰, whereas $\delta^{18}O$ from -12.35 to 10.34 ‰.; *ii*) in spring seasons δD ranged from -75.21 to 65.56‰, whereas $\delta^{18}O$ from -0.71 to -9.78 ‰; *iii*) in autumn seasons δD ranged from -68.54 to -51.45 ‰, whereas $\delta^{18}O$ from 10.01 to 8.96 ‰. The isotopic compositions of hydrogen and oxygen in Kanin water springs mainly reflected the isotopic composition of the meteorological precipitations, particularly snow in summer periods and rain in autumn season.

Water - rock interaction

As showed by chemical results, the water-rock interaction was checked by parameters as pH, pCO_2, calcite and dolomite saturation index, and, finally, $Mg^{2+/}Ca^{2+}$ ratio. Weathering of rocks provides a significant part of HCO_3^- in most water systems and therefore plays an important role in carbon cycle (Barth *et al.*, 2003).

The Kanin area is characterized mainly by carbonate lithotypes in which carbonate dissolutions take place. Mg^{2+} *vs.* Ca^{2+} values were used to determine the relative contribution of the weathering of dolomite and calcite to spring waters. It can be observed that calcite dominates the water chemistry of Kanin springs since Mg^{2+}/Ca^{2+} ratio aprossimately range from 0.1 to 0.33. All of the springs was oversaturated with CO_2 relative to the atmosphere.

Saturation of springs is pH dependent; lower pH results in higher pCO_2, except for some springs in summer period which showed low PCO_2 values. In spring and autumn, most of the water springs are close to saturation or are slightly supersaturated with respect to calcite, whereas in summer some spring waters are supersatured with respect to dolomite.

Undersaturation of dolomite was expected from water chemistry of springs, since it is controlled by calcite dissolution. Comparing the Canin springs water with other karst systems water (Szramek *et al.*, 2007) it was observed that Canin springs deviate from the equilibrium reaction $2HCO_3^- = Ca^{2+} + Mg^{2+}$, falling in the field of $Ca^{2+} + Mg^{2+}$ due to carbonate weathering.

As - Fe and climate effect

The climate data analysis evidenced that the investigated area is influenced mainly by meteoric regime. This research has focused on geochemical parameters changes with respect to climate variability. The most sensitive geochemical indicators of seasonal variability resulted As and Fe.

Comparing the isotopic composition of the water springs *vs*. As concentrations in summer, it resulted that the higher values of As were reached in summer. At the same time the isotopes values are comparable to the isotopic composition of snow. For these reasons, it may therefore be estimated that higher As values in water could be derived by atmospheric deposition, mainly concentrated in the snow.

In addition, it is known that atmospheric arsenic is mainly related to fine aerosol particles (less than 2.5 µm) which can be transported for relatively long distance (Cullen & Reimer, 1989); due to their relatively high specific surface, these particles often are more concentrated than in rain or in snow (Rattigan *et al.*, 2002). Finally, the arsenic species are more concentrated in snow than rain (Dousova *et al.*, 2007).

CONCLUSION

Hydrogeochemistry of the investigated spring is influenced by meteo-climatic variability; in particular. it was observed a seasonal variability correlated to water-rock interaction (carbonates solubility) and to the presence of As and Fe (aquifer vulnerability).

The multifactorial relationship between Mg/Ca ratio, pH, pCO_2, and the saturation index of calcite and dolomite showed that the karst processes are influenced by the continuous CO_2 availability and by the quick runoff, which, in some case can modify the water-rock interaction. Comparing stable isotopes values and arsenic concentrations, it was possible to hypotize that the arsenic could be derived by atmospheric deposition and that it is concentrated more in the snow than in the rain. Considering the geological and the hydrogeological setting as well as the high hydraulic conductivity, Kanin Mountain could have a high degree of vulnerability with possible negative effects on water quality.

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