

THE IMPORTANCE OF GEOCHEMICAL AND ISOTOPICAL ANALYSES IN THE GROUNDWATER FLOW DYNAMICS:

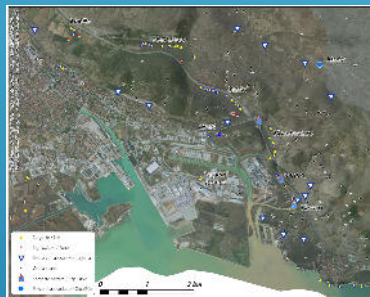
THE REKA-TIMAVO AQUIFER SYSTEM (ITA-SLO)

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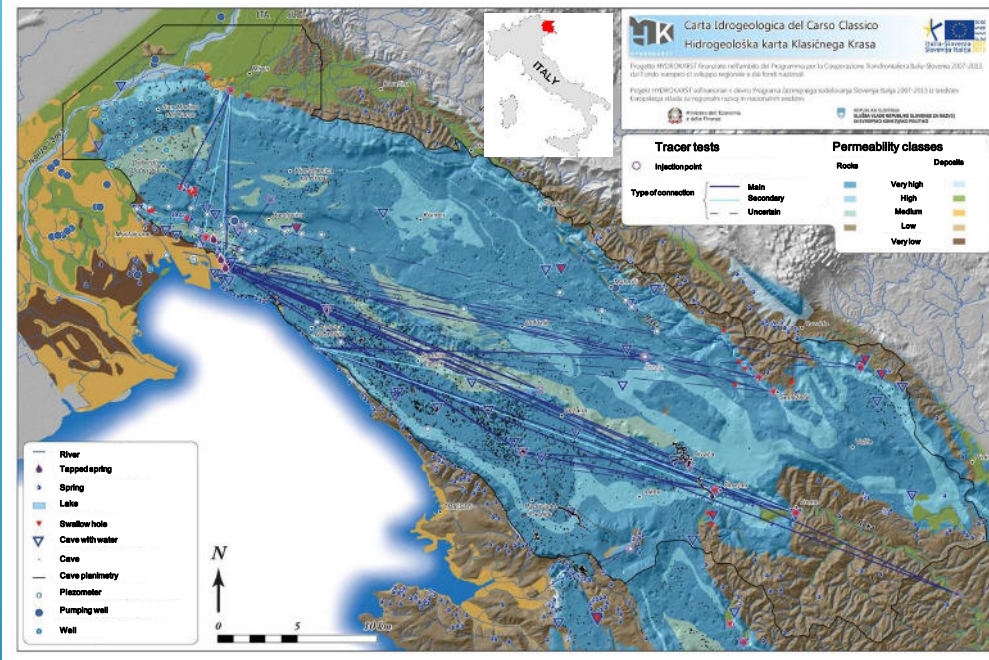
ABSTRACT

In a territory shared between two neighboring countries as Italy and Slovenia, in a highly karstified carbonate plateau is present an important hydrostructure. The plateau, slightly inclined towards NW is worldwide known with the name of Classical Karst, an area of about 750 km² bounded by the Isonzo/Soča and Vipacco/Vipava rivers, Pivka River basin, Cicarija/Cičarija structure and the Gulf of Trieste (northern Adriatic Sea). This area has always been of strategic importance due to the water exploitations for the city of Trieste and the surroundings. However, even though the first studies date back to the end of 1800s the groundwater dynamics presents still shadow sides. For sure, three water sources contribute to the Reka/Timavo aquifer system recharge: the effective infiltration (20.6 m³/s), the sinking of the Reka river in the Skočjan cave (8.3 m³/s) and the input coming from the Isonzo/Soča alluvial aquifer (10.0 m³/s). However, how the groundwaters are flowing inside into the conduits and/or the fractures still requires more insights. From 2012 to 2014, in the framework of the Hydrokarst Project, funded by the European Union, a monitoring campaign was realized during which, for 50 selected water points, several physico-chemical and isotopical analysis were performed. Major ions, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ isotopic ratio were analyzed. The isotopic $^{87}Sr/^{86}Sr$ ratios as the $\delta^{18}O$ values have proved to be a good tool for understanding the residence time and the groundwaters mixing due to the three different inputs. The W sector of the aquifer is recharged by the leakage of the Isonzo/Soča and Vipacco/Vipava rivers. The E sector, during floods, is mainly influenced by the Reka-Timavo River. During low water conditions instead, the effective infiltration in the catchment seems to play the main role.



Timavo spring area.

The image was shot during a flood. It is in fact possible to see the groundwater plume outflowing from the three branches of Timavo spring. The image is a Bing map image (Microsoft Corporation).

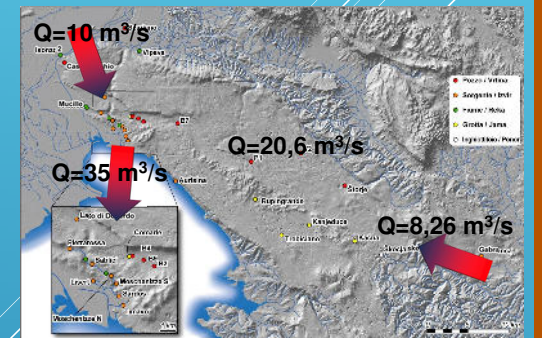


HYDROGEOLOGICAL CHARACTERIZATION

In 1995, the researchers of the Trieste University – D.M.G. jointly with Slovenian researchers, began with the study of the Timavo/Reka hydrodynamics in order to enrich the knowledge of the Classical Karst aquifer. In this framework, a monitoring network made of devices for continuous recording of physical parameters (electrical conductivity, temperature and water level) and sampling surveys was updated. The main caves reacting groundwaters were analyzed as well as the available piezometers and the recognized lakes and springs. The aquifer recharge is represented by:

- 1) a concentrated allogenic recharge due to Reka River inputs,
- 2) a diffuse autogenic recharge due to effective precipitations,
- 3) a diffuse allogenic recharge due to the Isonzo/Soča contribution (Zini et al., 2013).

As defined by the data recorded at Timavo/Timava and Sardos/Sardoč springs, contributions from the different sectors of the hydrostructure, differs due to the water flow regime: in high water flow, Reka and effective precipitations represent the main inputs, while during low water flow regime, Isonzo/Soča groundwater input prevails.



GEOLOGICAL FRAMEWORK

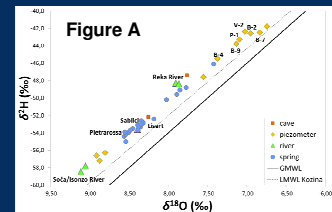
The "Classical Karst" is a wide morpho-karstic unit that extends from the Isonzo River (ITA) as far as Postojna (SLO). It contains epigeal and hypogeal karst forms, whose concentration, dimension and type have made this area the worldwide symbol of karst phenomena. The Trieste Karst belongs to the "karst-Friuli carbonate platform", the northern portion of the "Adria plate", formed by a thick sequence of carbonate rocks ranging from the Triassic to the Eocene (Cocchi and Zini 2007). In the area of interest the following outcrops occur: the "Calcarei di Monte Coste", the "Formazione di Monrupino", the "Calcarei di Aurisina", the "Formazione Ilbunica" and the "Calcarei ad Alveoline e Nummuliti". The Calcarei di Monte Coste (Aptian – Albian) represent the most ancient part of the platform and are characterized by well-layered blackish-grey bedding mudstone typical of a shallow-water carbonate platform (shelf lagoon and tidal flats). At its base, the Formazione di Monrupino (Cenomanian), has monogenic breccias with dolomitic clasts. The prevailing lithologies are grey dolomite and blackish-grey calcareous dolomite. They are characteristic of shallow-water carbonate platforms (shelf lagoon and reefs). The Calcarei di Aurisina (Late Cenomanian) are largely grey bioclastic limestones with very frequent radiolites and hippuritids. They are typical of two slightly different shallow-water carbonate platform depositional environments: reef and open and inner platform and reef. The Formazione Ilbunica (Late Campanian – Thanetian) is largely characterized by two typical lithologies: a) light grey very fossiliferous (Rudist) limestones (a superfacial platform) and b) blackish-grey bedding mudstone (tidal flats). The Calcarei ad Alveoline e Nummuliti limestones (Late Thanetian – Ypresian) are characterized by very light grey and very fossiliferous (Foraminifera and Gasteropoda) limestones initially deposited on a subtidal marine environment, and later on an open slope. At the top of the carbonatic sequence, the carbonates are overlain by Flysch (Lutetian) made up of marl and sandstone interbeddings. (Cocchi and Piano 2013).

Schematic cross-section



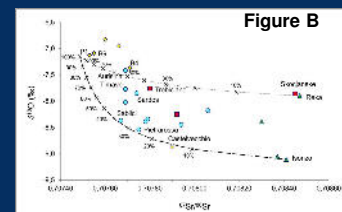
Red dots represent the location of the monitored water points into the caves or in the spring area.

GEOCHEMICAL CHARACTERIZATION



The oxygen $\delta^{18}O$ and hydrogen δ^2H isotopes are an excellent tool to be used in a karst context because the isotopic ratio is function of the temperature at which the precipitations occur and the catchment altitude: ratios are more negative during the colder months and decrease with increasing altitude.

Analyzing the graph of Figure A ($x = \delta^{18}O$, $y = \delta^2H$), it is clear that the samples deviate from the Global Meteoric Water Line (GMWL) to a position in proximity to a Local Meteoric Water Line (LMWL) already identified in Kozina. Even if we analyze a single survey, it emerges the presence of different recharging areas conditioning the springs. During the springtime, in correspondence of the snow melting, the $\delta^{18}O$ isotopic values of the Isonzo/Soča waters are very negative and can be used as natural tracer. The proportions and values of the Isonzo/Soča contribution are also depending on the water regime: during low water regime, the Isonzo/Soča contribution is more evident affecting the most part of the springs except Aurisina one. During high flow water regime instead, the influence of Isonzo/Soča waters is limited to the western springs: Mucelle, Pietrarossa, Sablici and Moschenizza Nord. In all the other springs, with different percentages, the influence of Reka/Timavo waters are dominant. From the analysis of Figure A, it emerges that the piezometers B-2, B-7, B-9, P-1 e V-2 represent a separate group, with $\delta^{18}O$ and δ^2H isotopic values higher on average and this indicates a mixing and a recharge probably derived from the local precipitations (Klarici, $\delta^{18}O = -6.85\%$). Klarici pumping station (B-4) as Reka is not end-member of the mixing process (Cocchi et al., 2015).

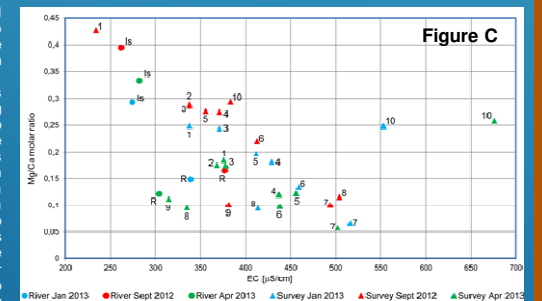


Unlike the oxygen and hydrogen ratios, Sr is a non-conservative element and therefore the concentration and isotopic composition vary according to the water-rock interaction: if the resident times are long, the water can reach the isotopic equilibrium with the rock. Even if the technique is known and used in hydrology already long, no one adopted it in the Classical Karst area. So, data on $^{87}Sr/^{86}Sr$ isotopical ratio are here described for the first time. The analysis show that both the Isonzo/Soča River and the Reka/Timavo River have a similar isotopic composition of Sr more radiogenic than the other samples. The waters of these rivers gradually interacting with carbonate rocks, having a lower isotopic composition, tend to lower their isotopic ratio without ever reaching the equilibrium with carbonates as observed in the different springs. The spring, well and karst cave waters show intermediate values between the isotopic composition of the Isonzo/Soča and Reka/Timavo rivers and those in equilibrium with Cretaceous carbonates (mean isotopic composition = 0.70750). If we look at all the samples, it is possible to conclude that all the analyzed waters indicate a mixing process. To quantify the contribution of Reka/Timavo and Isonzo/Soča rivers to the different springs, caves and wells we used a graph where in the x-axis are the isotopic ratio of $^{87}Sr/^{86}Sr$ and in the ordinate the values of $\delta^{18}O$. The curves represented in Figure B, show the trend of binary mixing between a water in equilibrium with carbonates as regards the isotopic composition of Sr ($^{87}Sr/^{86}Sr = 0.70750$) and with oxygen isotopic composition equal to the mean local precipitations ($\delta^{18}O = -7.2\%$) and the values of the Isonzo/Soča and Reka rivers defined while sampling.

CONCLUSIONS

Seen that the Classical Karst is evolving since at least 10 million years, its underground network is highly developed and complex. It is possible to distinguish two main sectors: the south-eastern one between Skočjan sinkhole and Timavo Springs, and the north-western one where waters through the Isonzo alluvial plain flow towards karst hydrostructure. The first sector is characterized by a high gradient influenced, in its evolution, by the sinking waters of Skočjan sinkhole. It is the so called underground Timavo system characterized by large conduits quickly transferring Reka waters directly into the spring area. The north-western sector (Soča/Isonzo system) is instead characterized by lower gradients in a karst fractured system spread along the edge of the plain. To the two allogenic inputs is necessary to add also the contribution due to the effective precipitation on both sectors. The two sectors are anyway draining waters from the hydrostructure and this is glaring along all the coastal springs. From Aurisina to Timavo, springs are strongly connected to the Timavo system, while the western as Moschenizza, Lisert and Sablici there is an involvement with a north-western hydrodynamic system. Linking point between the two systems are the Sardos and Timavo springs. During low water regime, both springs are draining waters mainly coming from the Isonzo system. In high water regime water drained are instead coming from Timavo system; Timavo Springs are draining only Timavo waters, while Sardos spring is draining mixed waters (from Timavo and Isonzo systems). During normal flow, Timavo Springs are draining mainly Timavo waters and Sardos spring is draining Isonzo waters.

The major ion analysis indicates that surface- and ground-waters have similar chemical composition, belonging to the Ca-HCO₃ and Ca-Mg-HCO₃ hydrofacies. No meaningful differences are observed during low- and high-water flow regime. On the basis of electrical conductivity (EC) and Mg/Ca molar ratio instead, it is possible to recognize a defined draft trend in the waters (Figure C). To better understand this correlation, three sampling surveys realized in three different regimes were analyzed: September 2012 (red – very low water), April 2013 (green – after the peak flood event) and January 2013 (blue – during a flood event). During very low water regime, Isonzo/Soča inputs are prevailing over the others enhancing low EC values and high Mg/Ca molar ratio. Reka influence is recognizable only at Aurisina spring (7) and Trebiciano Abyss (8). The situation changes during flood event: at Aurisina (7) and Timavo (6) the contribution of Reka river, characterized by low Mg/Ca ratios and high EC values prevails. Moschenizza Sud (4) and Sardos (5) are influenced by Isonzo/Soča waters and Reka River in different proportions according to different regimes. The other spring points are characterized by the Isonzo/Soča inputs. A separate discussion is required for Klarici pumping station (10) tapping the water at about -30/-50m a.s.l. During low water regime it is heavily influenced by Isonzo/Soča inputs. During floods, an increased EC is observed, mainly due to the increased Cl value that ranges from 13.5 mg/l up to 60 mg/l.



EC vs. Mg/Ca molar ratio during different water regimes. Is-Isonzo River, R-Reka River. 1=Doberdo, 2=Pietrarossa, 3=Moschenizza Nord, 4=Moschenizza Sud, 5=Sardos, 6=Timavo, 7=Aurisina, 8=Trebiciano Abyss, 9=Skocjan cave, 10= Klarici pumping station (B4).