

Geochemical characterization of the submarine spring of Izola (Gulf of Trieste, N Adriatic Sea)

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Abstract: First results of the geochemical research performed in a submarine spring near Izola are presented. It was found that the spring discharge of nutrients to the southern part of the Gulf is of less importance relative to the other freshwater discharges, representing <4 % of the total freshwater nutrient input.

Key words: groundwater, coastal zone, discharge, measurements

INTRODUCTION

Submarine groundwater springs are a widespread coastal phenomena which occur wherever hydrogeological gradients enable lateral and upward groundwater transport (JOHANNES, 1980). Karstic coastlines (BACK ET AL., 1979; PAULL ET AL., 1990), modern and paleo-river channels (CHAPELLE, 1997), geopressed aquifers (MANHEIM, 1967; KOHOUT ET AL., 1976), geothermal aquifers (KOHOUT, 1967), mountainous shorelines with large tidal amplitudes and lagoons with heightened evaporation (SIMMS, 1984) are most important locales for submarine groundwater discharges. A submarine spring derived from meteoric and seawater mixing within an aquifer can be considered a subterranean estuary because it displays many of the key chemical features of surface estu-

ary (MOORE, 1999). In subterranean estuaries, geochemical reactions between the mixed waters and host aquifer materials can enhance sediment/water geochemical exchange and significantly affect the coastal water mass balance of nutrients and other reactive constituents (SWARZENSKI ET AL. 2001 and references therein).

The aim of the present study is to determine the complete geochemical composition of a submarine spring located 0.8 km offshore of Izola (Gulf of Trieste, northern Adriatic Sea) to identify the source(s) of spring water and to determine via comparison with conservative tracers (e.g. Cl, Mg) the significance of geochemical reactions occurring at the mixing zone.

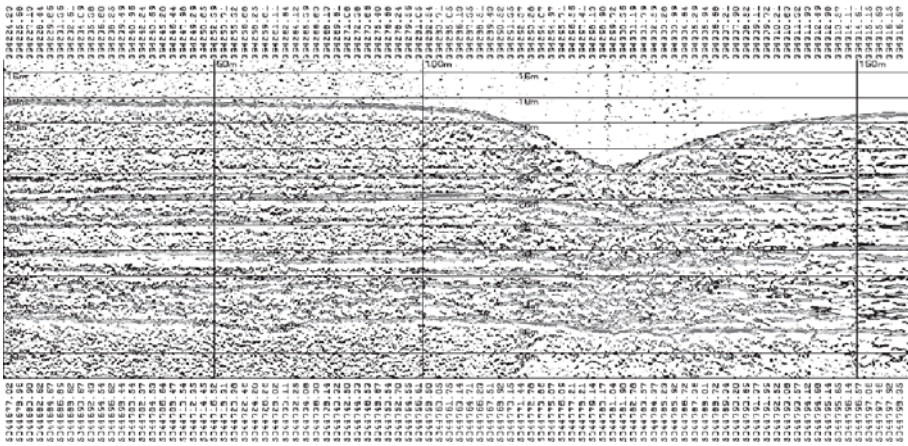


Figure 1. Parametric acoustic profile of Izola submarine spring (Courtesy of Harphasea Koper, Slovenia)

MATERIALS AND METHODS

Samples - Water samples were collected in November 2003 at the Izola submarine spring (45° 32.911 N, 13° 38.752 W). To obtain the most pristine sample of the spring water, SCUBA divers inserted a polyethylene tube (6 mm i.d.) into the well and samples were collected by syringe. Water samples were filtered through 0.45 mm Millipore HA membrane filters in a N₂-filled glove bag under N₂ pressure of 0.4 MPa. In spring water pH, total alkalinity (TA), dissolved inorganic carbon (DIC), ¹³C composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$), sulphide, and N and P nutrients were analyzed immediately. Water samples for cation determinations were acidified using “ultrapure” HNO₃.

Analyses - The pH of spring waters was measured using a UniFET microelectrode. TA was determined by Gran titration. Ammonia, phosphate and sulphide were analyzed colorimetrically and Cl⁻ titrimetrically

(GRASSHOFF ET AL., 1986). Analyses of the following elements (Ca, Mg, Na, K, Sr, Ba, B, Mn, Fe, Zn, Si, Li and Al) were performed by ICP-OES. The concentrations of DIC were determined on a UIC Coulometrics CO₂ Coulometer. The precisions, based on replicate analyses, were ± 0.01 for pH, $\pm 1\%$ for TA, and $\pm 2\%$ for DIC and metals, and $\pm 5\%$ for nutrients, chloride and sulphide, respectively. The stable isotopic composition of DIC was determined with the modified method of extraction (CAPASSO ET AL., 2003). The isotope ratios of extracted CO₂ was then determined directly from the headspace by Isotope Ratio Mass Spectrometer - IRMS (Europa Scientific 20-20) with preparation module for trace gas samples ANCA-TG equipped with a Gilson autosampler. The results are reported using conventional delta (d) notation relative to PDB in per mil (‰). Overall analytical error was $\pm 0.2\%$. All measuring data are collected in Table 1.

Table 1. Chemical composition of the Izola spring water, "average" seawater and karst groundwater from SW Slovenia (KUKAR, 1998)

Solutes	Izola spring	Seawater	Groundwater
Na (mM)	73.7	468.03	0.21
Mg (mM)	3.14	53.08	0.19
K (mM)	1.96	10.21	0.02
Ca (mM)	8.12	10.25	2.23
Sr (mM)	0.11	0.09	0.003
B (mM)	0.12	0.27	-
Si (mM)	0.67	0.007	0.15
Al (μ M)	0.33	0.02	0.11
Ba (μ M)	0.487	0.073	0.385
Mn (μ M)	0.404	0.004	0.013
Fe (μ M)	0.351	0.036	0.08
Zn (μ M)	0.05	0.002	0.04
Li (μ M)	26.3	26.1	72.5
DIC (mM)	4.03	2.33	4.33
$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	-3.5	-0.9	-12.0
NH_4^+ (mM)	0.06	0.001	-
TDN (mM)	0.08	0.02	-
PO_4^{3-} (μ M)	1.4	0.1	-
TDP (μ M)	1.5	0.15	-
pH	7.09	8.15	7.70
Salinity (‰)	5	35	

RESULTS AND DISCUSSION

The solute composition of Izola spring water was compared to typical groundwater from SW Slovenia and to the composition of the average seawater (Table 1). The salinity of submarine spring water was 5 consistent with dilution in ambient seawater by advection and mixing. The reducing submarine spring water is evidenced by the presence of sulphide (0.22 mM). The spring water is rich in Ca-DIC. The concentrations of Na, K, Mg and Sr are much higher in spring water compared to the groundwater and, except for Ca, about 10-fold lower than in seawater. The calcite saturation index indicates that calcite dissolution is thermodynamically favored in the spring water. The enrichment

of DIC in the Izola spring relative to the seawater can be explained by oxidation of organic matter within the spring which could be also seen in the lower $\delta^{13}\text{C}_{\text{DIC}}$ value. Additionally, the realised of CO_2 can also promote calcite dissolution in the spring.

Therefore, mixing of seawater supersaturated with respect to calcite with fresh groundwater saturated with respect to calcite results in the solution where calcite dissolution occurs. This mechanism can be explained by non-linear dependence of activity coefficient on ionic strength and by the non-linear dependence of calcite solubility on pCO_2 (PLUMMER, 1975; MOORE, 1999).

Selected elements (Fe, Mn and Ba) suggest some interesting deviations from seawater values as well. Mn and Fe concentrations were up to 10 to 100-times higher than in the average seawater and groundwater. The behavior of these two redox couples conforms to a predictable oxidation state transformation in the reducing groundwaters from more particles reactive to more soluble +2 states. Ba was also enriched in spring water relative to seawater probably due to biologically mediated precipitation of barite (BaSO_4) in seawater. Concentration of Al and Zn in spring water were close to onshore groundwater and higher than the average seawater. Nutrient data from the submarine spring water show that N is mostly (75 %) and P almost totally present as NH_4^+ and PO_4^{3-} , respectively, which could also be the consequence of organic matter degradation present in the spring. Concentration level of Si was, on the other hand, very similar to pore waters concentrations (ČERMELJ ET AL., 1997), and B very similar to seawater concentrations. On the other hand, the seawater concentrations of nutrients were an order of magnitude lower than the spring water concentrations.

These results suggest that meteoric waters discharged off Izola are geochemically similar to karst groundwater, characteristic of those in SW Slovenia, mixed with about 15 % of the seawater based on the comparison with conservative tracers (e.g. Cl, Mg). Hence, the onshore flow regime appears to extend onto the Gulf of Trieste. The concentrations of major solutes in the spring water are similar to those found in the study of SWARZENSKI ET AL. (2001) of the submarine spring off Crescent Beach in Florida. As is the case in Izola, the source aquifer for the spring water is not a single geological formation, but a more diffuse and complicated karst-influenced mixing regime. Considering the spring discharges in the Gulf of Trieste of $1 \text{ m}^3/\text{min}$ it seems that the flux of metals and nutrients to the southern part of the Gulf of Trieste is of lesser importance compared to other fresh water discharges (TURK & POTOČNIK, 2001) representing <0.2 % and <4 %, respectively, of the freshwater input.

Acknowledgement

This research was financially supported by IAEA under Contract No. 12156/R0.

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