



Hydrogeochemical conditions of submarine and terrestrial karst sulfur springs in the Northern Adriatic

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Abstract

Submarine springs near Izola, in the Northern Adriatic Sea, appear in funnel-shaped depressions and smell strongly of sulfur. Along the Mediterranean coast there are many submarine karst springs containing brackish or fresh water, but submarine sulfur springs are not particularly common. Three submarine sulfur springs and one terrestrial sulfur spring were investigated to better understand the water properties, water–rock interaction within the aquifer, and to explore the origin of the spring water. Groundwater and seawater samples were also collected for comparison. Based on the geological setting, physicochemical parameters, hydrogeochemical data, and stable isotope data ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$), we can affirm that (1) the large concentration of seawater in the submarine springs samples is due to sampling challenges; (2) springs recharge from precipitation where confined karst aquifers outcrop; (3) deep water circulation is indicated; (4) redox conditions can provide a suitable environment for bacterial reduction of the marine or organic sulfate to the odorous H_2S ; (5) geological data suggests that the coals beneath the alveolinic-nummulitic limestones are the source of sulfur. A multi-parameter and interdisciplinary approach has proven important in assessing submarine sulfur springs affected by seawater input.

Keywords Terrestrial and submarine sulfur springs · Karst groundwater · Hydrogeochemistry · Stable isotopes · Slovenia

Introduction

Submarine spring, a term often used to describe point-source conduit flow of submarine groundwater discharge (SGD) in a karst environment (Swarzenski et al. 2001; Fleury et al. 2007; Dimova et al. 2011; Parra et al. 2015; Moosdorf and Oehler 2017; Bakalowicz 2018), is a peculiar coastal feature that provides insight into the functioning of the aquifer system, its relation with seawater, and the geological setup that influences hydraulic flow in the aquifer. Seawater-groundwater mixing, rock-groundwater interaction, and the source of the spring's water can be investigated by analyzing the water's geochemical and isotopic data. Knowledge of SGDs is especially important in assessing geochemical

matter-related cycles and nutrient input in coastal environments (Slomp and Van Cappellen 2004; Lee et al. 2009; Moore 2010; Pavlidou et al. 2014; Tamborski et al. 2020), SGD discharge and its impact on the global water budget (Taniguchi et al. 2002; Burnett et al. 2006; Kwon et al. 2014), and studying water resources, as SGDs are often useful for public needs (Moosdorf and Oehler 2017).

Karst submarine springs are the most reported form of SGD (Taniguchi et al. 2002) and are particularly common along the Mediterranean coast (Fleury et al. 2007; Bakalowicz 2018). They are usually affected by the intrusion of seawater (Bonacci and Roje-Bonacci 1997; Fleury et al. 2007; Parra et al. 2015; Gemici et al. 2016; De Filippis et al. 2016; Xu et al. 2019; Liso and Parise 2020). As a result, understanding the connection between groundwater and seawater is important for the protection of water resources. The Slovenian coastal aquifer is also influenced by seawater, as Brenčič (2009) reported the mixing of seawater (31%) and groundwater (69%) in the carbonate aquifer under reducing conditions in the Slovenian coastal town of Lucija (Lu-1, Fig. 1b), located some 5 km by air from Izola. Seawater and carbonate groundwater

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mixing was also reported by Petrini et al. (2013) from nearby thermal waters in Tržič/Monfalcone in Italy (Gulf of Trieste/Trieste). Seawater interactions are often a topic in SGD research, where the determination of temperature (T), electrical conductivity (EC), geochemical, and sometimes isotopic composition are common tools used to assess seawater intrusion and to identify main water types (Stüben et al. 1996; Swarzenski et al. 2001; Slomp and Van Cappellen 2004; Charideh and Rahman 2007; Parra et al. 2015; Pétré et al. 2020).

Apart from mixing with seawater, specific geochemical and thermal features are not particularly common in karst submarine springs and are usually associated with volcanic or tectonic activity (Caramanna et al. 2021; Corliss et al. 1979; Michard et al. 1993; Prol-Ledesma et al. 2004; Varnavas and Papavasiliou 2020; etc.). Italy is known for its many thermal sulfuric acid caves formed as a result of the deep circulation of H₂S-rich fluids in a karst and evaporite environment (D'Angeli et al. 2019). Based on geochemical and sulfate isotopic data, the Santa Cesarea Terme system in Apulia was found to be recharging from the seawater via localized fault damage zones, circulating at a depth of about 2–3 km at 85 °C, and then interacting with evaporites and limestones, while sulfide is produced by bacterial reduction (Santaloia et al. 2016; D'Angeli et al. 2021). The Crescent Beach springs in Florida are one of the best-known submarine sulfur karst springs. Their recharge is also associated with the fracture zone. Geochemical tracers show that the spring water is the result of a complex mixing of seawater and artesian groundwater (Swarzenski et al. 2001).

Izola, a coastal town in Slovenia (Northern Adriatic Sea), has been known for centuries to have springs of warm, sulfur-rich water (Kramar 2003). Only two decades ago, submarine springs with the same properties were discovered nearby (Žumer 2004, 2008). In addition to the submarine and terrestrial sulfur springs of Izola, only four other sulfur springs are known in Slovenia (all terrestrial): the Žveplenica dolomite spring (Zega et al. 2015; Mulec et al. 2015) with sulfur that may have derived from pyrite (Zega et al. 2015), the Smrdljivec spring with sulfur of possible coal-related origin (Mulec et al. 2021), the Žvepovnik karst spring with sulfur of evaporite or barite origin (Žvab Rožič et al. 2022), and Riharjev studenec (not yet investigated).

The first geochemical research of the submarine sulfur springs of Izola was conducted by Faganelli et al. (2005), who identified the hydrogeochemical characteristics of the spring water. However, said research did not provide sufficient results to fully understand the origin of the water and the hydrogeochemical processes in the Izola karst aquifer.

Isotopic composition can provide further information about the water source and interactions. In addition to physicochemical and geochemical analysis, the isotopic

composition of H and O has been used to trace the origin of the water and to compare the isotopic signal with precipitation, as was done in the study of groundwater flow in Zagreb, Croatia (Marković et al. 2013), and Syrian submarine springs (Charideh and Rahman 2007). Stable carbon isotopes are useful indicators of dissolved inorganic carbon (DIC) sources in groundwater systems. DIC is the main species in carbonate environments. Changes in DIC concentrations result from the addition or removal of carbon from the DIC pool, while changes in $\delta^{13}\text{C}_{\text{DIC}}$ values result from fractionation accompanying the transformation of carbon or the mixing of carbon from different sources. Major sources of carbon to aquifer DIC loads consist in the dissolution of carbonate minerals, soil CO₂ derived from root respiration, and microbial decomposition of organic matter (Aucour et al. 1999; Li et al. 2005; Kanduč et al. 2007, 2012). Dissolved sulfate in aquatic environments has multiple sources: atmospheric deposition, evaporite dissolution, oxidation of sulfide minerals, soil sulfate, and sewage (Otero and Soler 2002; Rock and Mayer 2009; Gammons et al. 2013). Given that the investigated springs have a strong sulfurous odor and that layers of sulfur-bearing coal are present in the study area (Pleničar et al. 1973; Benedik and Rožič 2002; Brenčič 2009), the sulfur isotope of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) was used to identify the source of SO_4^{2-} , as has been done for some other sulfur springs (Zega et al. 2015; Santaloia et al. 2016; D'Angeli et al. 2021; Žvab Rožič et al. 2022). A combination of $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ is widely used and provides more conclusive information for the qualitative tracing of sources of dissolved SO_4^{2-} in aquatic systems (Zhang et al. 2015, 2021; Cao et al. 2018). The reduction of sulfate to sulfide is usually associated with redox conditions and an acidic environment, which poses a risk to groundwater quality. The origin of sulfur and the contamination of karst groundwater from anthropogenic activities has been successfully determined using hydrogeochemical and isotopic characterization in various studies of karst environments (Dogramaci et al. 2017; Sun et al. 2017, 2021; Tang et al. 2021).

The aim of this study was to expand on our knowledge of the sulfur springs of Izola, which is important in better understanding the conditions of the coastal environment, geochemical cycles, and for planning the use and management of water resources. The main objectives were to determine a geological and hydrogeochemical characterization of the submarine and terrestrial karst sulfur springs of Izola, to identify the potential sources of H, O, C, and S, to determine the origin of the spring water, and to create a conceptual model of water flow in the area. The findings in this study emphasize the importance of using diverse methods in assessments of submarine sulfur springs in order to obtain more conclusive results when mixing with seawater.

Research area

Previous research on the thermal and sulfidic groundwater of Izola

The first mentions of thermal and sulfidic waters in Izola date back to the seventeenth century by Bishop Tommasini. The first analysis of terrestrial spring water was carried out in the nineteenth century by Eduard Papp, who noted the presence of ammonium, sulfur, magnesium, nitrate, copper, and chlorate, as well as a distinctive smell of sulfur. Soon after, thermal baths were built, but they were not in operation for long (Kramar 2003). In 2002, a 501 m deep borehole LIV-1 (Fig. 1c) was drilled in Izola for geological and hydrological analyses of the aquifer and the thermal water. The report noted the presence of coal and organic-smelling water, with a temperature of 23.2 °C at a depth of 500 m (Benedik and Rožič 2002).

Submarine springs with similar physical and chemical properties were discovered in 2002 by Žumer (2004, 2008). He reported that the submarine springs have a temperature of 29.9 °C and a strong sulfurous odor. Water analysis was performed by Faganeli et al. (2005), who reported higher Na, K, Mg, and Sr concentrations than those of groundwater and 10-times lower than seawater. The spring water was enriched in DIC, which, together with lower $\delta^{13}\text{C}_{\text{DIC}}$ values, suggests oxidation of organic compounds in the spring. The presence of sulfide points to the reducing conditions in the submarine spring water (Faganeli et al. 2005).

Location and shape of the submarine sulfur springs of Izola

Submarine sulfur springs of Izola are located in the SE part of the Gulf of Trst/Trieste, about 400–1000 m from the coast of the town of Izola (SW Slovenia) and are clustered into three groups: Izola (springs notations M01, M02, M03), Bele skale (M04, M05), and Ronek (M06, M07, M08, M09, M10, M11, M12) (Fig. 1c, Table 1); the smell of sulfur is also present in the terrestrial sulfur spring (K04).

Submarine sulfur springs flow out of Quaternary sediments in funnel-shaped depressions in the seafloor at depths of 19–32.2 m below sea level, with the deepest depression (M03; 11.1 m) having a diameter of 41 m at the top (Slavec 2012; Table 1) and about 2 m at the bottom (Žumer 2004). The mixing of spring water, seawater, and sediment occurs in the funnel.

Coordinates of K04, VK01, SW01, SW02 and SW03 are available in the Pangaea data repository (Žvab Rožič et al. 2023).

Geological setting

SW Slovenia and Istria are characterized by two major rock associations (Fig. 1b). The basal unit consists of Cretaceous to Lower Eocene limestones of the Dinaric/Adriatic carbonate platform with intercalations of coal layers in the Liburnia Formation of Late Cretaceous–Early Paleogene (Pleničar et al. 1969, 1973; Jurkovšek et al. 2013). The limestones gradually pass through transitional marls into Eocene Flysch, which consist of alternating marl and turbiditic sandstone beds. Sporadic calciturbidites also occur within the flysch, mainly as thin- to medium-bedded, graded calcarenites, but several calciturbiditic/calcodebritic megabeds are also intercalated (Pavšič and Peckmann 1996; Placer et al. 2004; Vrabc and Rožič 2014) and can be used for detailed geological mapping (e.g. Rožič and Žvab Rožič 2023).

Structurally, the investigated area belongs to the External Dinaric Imbricated Belt, which is characterized by structural shortening in the SW direction (Fig. 1b). The most prominent structural element is a Palmanova/Črni kal thrust fault that runs along the SW slopes of the Kras (Karst) Plateau, which is otherwise dominated by limestone formations. Rather a large number of thrust-sheets are associated with the main thrust fault and, in this zone, limestone and flysch successions are quickly alternating. Further to the SW, the area of the Slovenian coast and Istria shows only minor internal tectonic deformation and, with the exception of the Izola anticline limestone core, consists entirely of Eocene flysch. This area is known as the Istria-Friuli Underthrust Zone. The recognized structures are, from the NE towards the SW, the Buzet thrust fault, the already mentioned Izola anticline, and the Sv. Križ thrust fault (Fig. 1b). This structural unit is confined further to the SW by the Buje fault in Croatia, while the transition from flysch back to limestones occurs slightly earlier in the Sečovlje area. This contact is partly stratigraphic and partly in the form of a vertical fault (Pleničar et al. 1969, 1973; Placer 2005, 2007; Placer et al. 2010).

Cretaceous to Paleogene rock formations are overlain by Pliocene to Quaternary deposits. Below the sea, these deposits are divided into two units. The lower unit consists of the Pliocene–Pleistocene fluvial deposits (mainly sand, gravel, and silty clay) and is occasionally interrupted by marine and brackish sediments. The upper unit is represented by Holocene marine fine-grained clastic sediments (sandy silt, clayey silt, silt, and silty sand) with frequent foraminifera, bivalve, and gastropod shells (Ogorelec et al. 1981, 1987, 1991, 1997; Covelli et al. 2006). The upper unit of the Holocene marine deposits varies in thickness, ranging from 0 m in coastal areas to several tens of meters in the central part of the gulf (Romeo 2009; Slavec 2012; Vrabc et al. 2014;

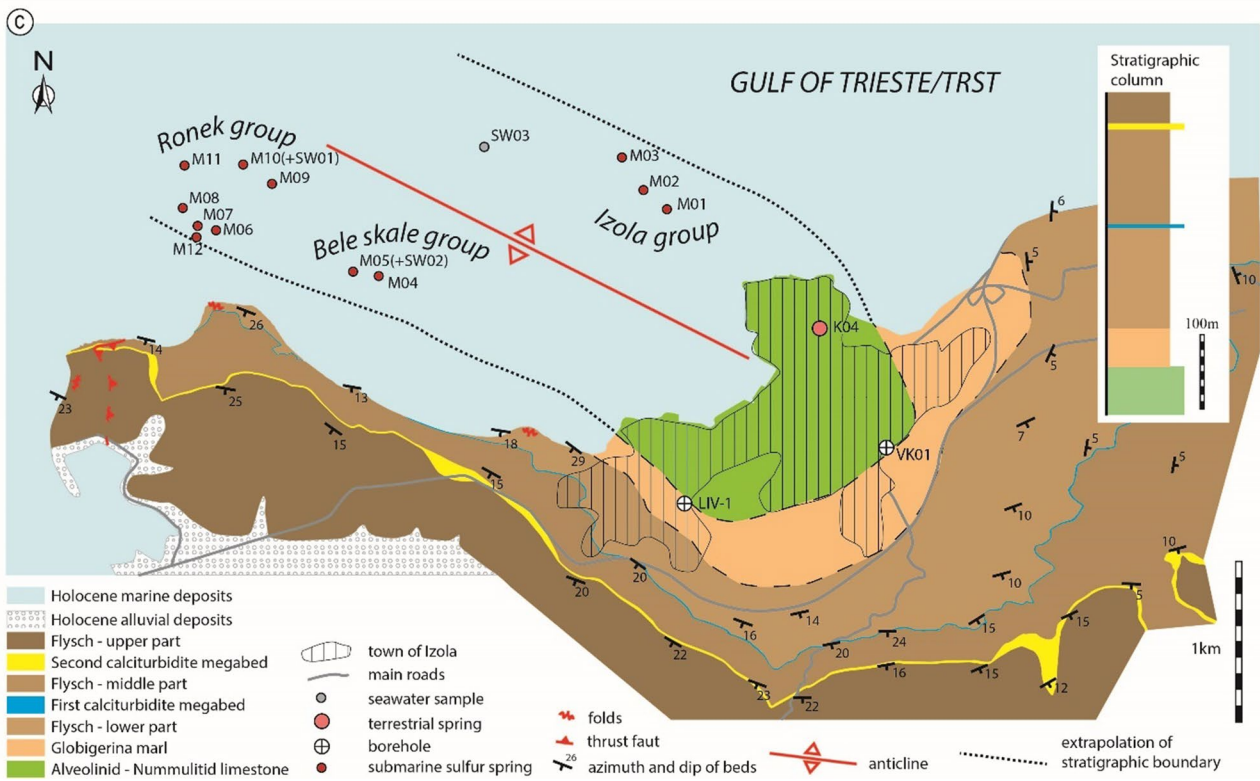
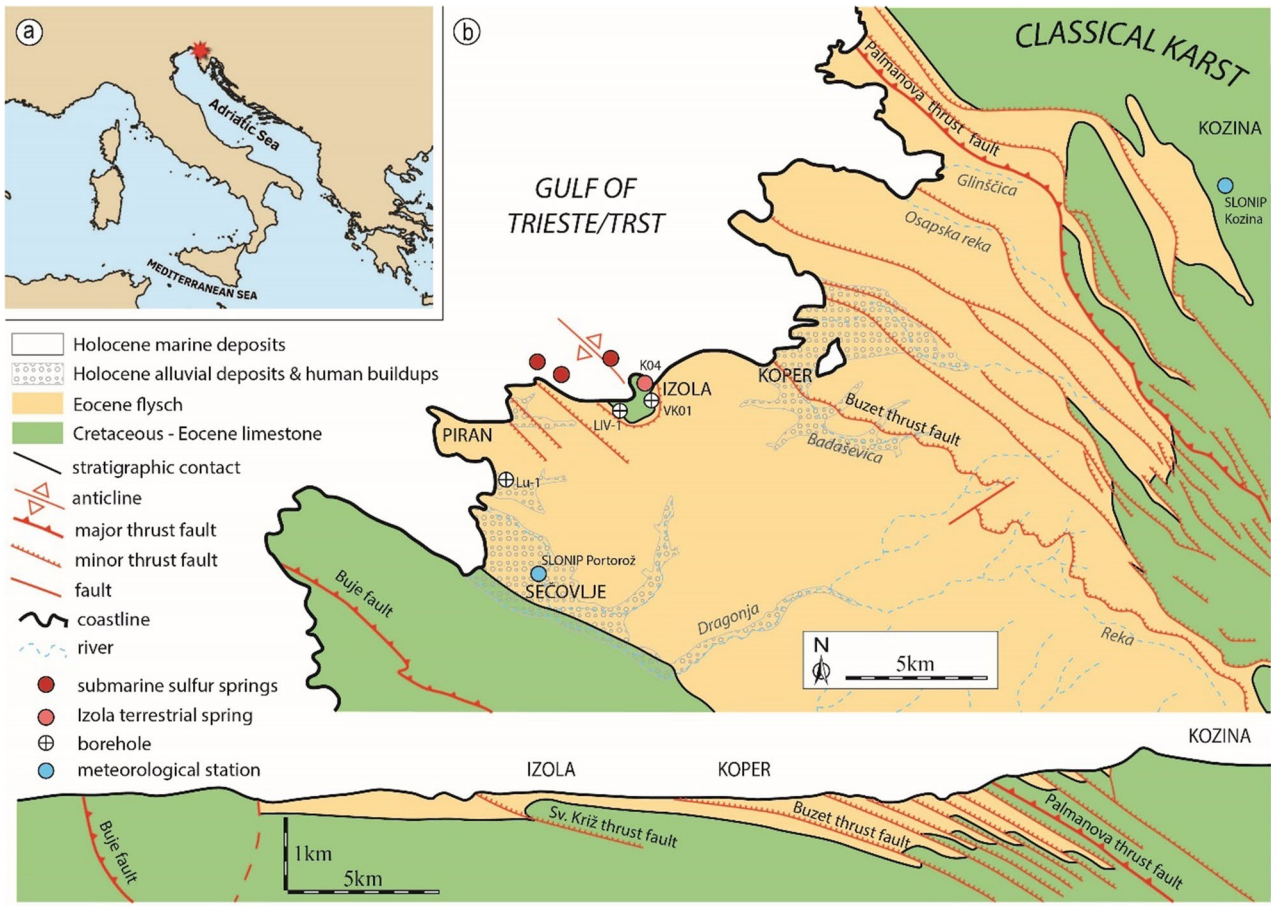


Fig. 1 **a** Map of the location of springs on the N Adriatic Sea. **b** General geological map and cross-section of investigated area (simplified after Pleničar et al. 1973 and Placer et al. 2010). Note that the lithology colors also mark their hydrogeological characteristics, with limestone (green) representing a karst aquifer and flysch (ocher) generally acting as a groundwater barrier. **c** Detailed geological map of the Izola area with the schematic stratigraphic column: sulfur springs are located at the stratigraphic contact between limestone and flysch on both limbs of the Izola limestone core in areas with thin Quaternary sediment cover (adopted from Rožič and Žvab Rožič 2023)

Trobec et al. 2018). At the same time, on the mainland, the Holocene is characterized by fluvial deposits covering valley floors with brackish or (anthropogenic) saline environments at river mouths (Pleničar et al. 1973; Ogorelec et al. 1981; Kovač et al. 2018).

Recent detailed geological mapping of the Izola area has revealed that the Izola submarine sulfur springs occur on both limbs of the Izola anticline limestone core with an axial orientation of WNW-ESE (Fig. 1c). All of them occur at the stratigraphic boundary between limestone and flysch. The springs are found in those areas where the Quaternary deposits are thin enough to be washed out, resulting in a funnel-shaped depression morphology of the springs. The Izola group is situated on the NE limb, while the Bele Skale and Ronek groups are located along the SW limb.

Hydrogeological setting

The research area is positioned at the coastal karst aquifer. Outcropping limestones of the Izola anticline are covered by the town's infrastructure, therefore the recharge by precipitation is negligible here. The surrounding flysch covers the underlying limestones and represents a barrier with very low permeability. The groundwater in Izola is most likely connected to and recharged from a karst aquifer of Classical

Karst in the NE area in Fig. 1b (Petrič et al. 2002). The flysch layers covering the limestones are several hundred meters thick, therefore deep groundwater of the Izola area presents deep regional flow with artesian pressure. There is very little hydrological data on groundwater in the Izola area, and no water table map or groundwater flow pattern are yet available. The piezometric level in the Izola area rises towards the sea and is found at a depth of 36 m in the Izola town center (Benedik and Rožič 2002).

Sampling and analyses

Field sampling and measurements of physicochemical parameters

Field samples of sulfur springs were collected from three submarine sulfur springs (one from each group; M03, M05, M11) and one terrestrial sulfur spring (K04; Fig. 1c). Groundwater samples from a well (VK01) and seawater (SW01, SW02, SW03) were also collected for comparison and interpretation of the source of the submarine sulfur springs. Physicochemical measurements were accompanied by sampling and were conducted in three sampling campaigns: in June and July 2020 on water samples from M05, M11, K04, and SW01, in October 2020 on samples from M03, M05, K04, VK01, and SW02, and in April 2021 on samples from M03, M05, M11, K04, VK01, and SW03 (Žvab Rožič et al. 2023).

Submarine spring water samples were collected by professional divers who sampled the water with 100-ml syringes inserted into the spring opening in the seabed sediment. The seabed sediment covering the limestones from which the springs emerge is silty and loose. The seawater and the spring water mix in the loose sediment. The divers could not

Table 1 Submarine sulfur spring locations, depths, and sizes; data from Slavec (2012)

Label	LAT (°)	LONG (°)	Group	Total depth (m)	Depression depth (m)	Seabed depth (m)	Depression diameter (m)	Slope angle (°)
M01	45.54567	13.64964	Izola	19.0	1.0	18.0	70	18
M02	45.54673	13.64775	Izola	21.8	3.2	18.6	24	39
M03	45.54853	13.64594	Izola	30.8	11.1	19.7	41	57
M04	45.54160	13.62654	Bele skale	23.6	6.0	17.6	27	27
M05	45.54181	13.62447	Bele skale	24.6	7.4	17.2	10	62
M06	45.54403	13.61335	Ronek	22.1	1.2	20.9	18	20
M07	45.54423	13.61190	Ronek	23.7	2.3	21.4	33	17
M08	45.54527	13.61068	Ronek	24.1	1.6	22.5	27	36
M09	45.54670	13.61784	Ronek	24.1	1.6	22.5	13	23
M10	45.54781	13.61543	Ronek	24.9	1.8	23.1	43	15
M11	45.54767	13.61077	Ronek	32.2	9.1	23.1	46	50
M12	45.54363	13.61180	Ronek	21.8	0.8	21.0	9	12

reach the spring opening at the limestone because working deeper in the loose sediment is dangerous for divers.

Measurements of the physicochemical parameters of the water samples, such as temperature (T), pH, electroconductivity (EC), and dissolved oxygen (DO), were performed in the field as soon as the divers brought the samples on board using a calibrated Multi 3430 (WTW GmbH, Weilheim, Germany).

Samples for oxygen and hydrogen isotope analysis ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were collected in high-density polyethylene (HDPE) bottles. Samples for hydrogeochemical (cations and anions), dissolved inorganic carbon isotope ($\delta^{13}\text{C}_{\text{DIC}}$), total alkalinity (TA) and sulfur isotope ($\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$) analysis were filtered through 0.45 μm pore-sized membrane filters and stored in 30-mL HDPE bottles and 12-mL Labco glass vials with septum, without headspace for the $\delta^{13}\text{C}_{\text{DIC}}$ analyses. Samples for hydrogeochemical analysis were acidified with HNO_3 . Samples for sulfur isotope analysis were acidified on site with a few drops of 2N HCl and then treated with BaCl_2 in the laboratory to collect filtered BaSO_4 . All samples were refrigerated until further analysis.

Analysis of major, minor and trace elements

Hydrogeochemical analysis was performed at the Actlabs laboratory (ActLabs 2021) using inductively coupled plasma mass spectroscopy (ICP-MS) for major, minor, and trace elements (ActLabs Code 6-HR-ICPMS), and ion chromatography for anions (ActLabs Code 6B-Ion Chromatography). Reference materials, independent quality control, and detection limits for each element or compound for the methods ICP-MS and IC are described and reported on the ActLabs website (ActLabs 2021).

Concentrations of HCO_3^- were not determined directly by laboratory analysis but were obtained from total alkalinity values. It should be noted that while the two parameters are related, total alkalinity is not strictly equivalent to HCO_3^- concentration but is a good estimate, and the difference between the two values in the measured pH range in the field is less than 1%.

Analysis of isotopic composition of hydrogen and oxygen

The isotopic composition of oxygen and hydrogen was determined at the Jožef Stefan Institute using $\text{H}_2\text{-H}_2\text{O}$ (Coplen et al. 1991) and $\text{CO}_2\text{-H}_2\text{O}$ (Epstein and Mayeda 1953; Avak and Brand 1995) equilibration on a Finnigan MAT DELTA plus dual inlet isotope ratio mass spectrometer with an HDOeq 48 automatic $\text{CO}_2\text{-H}_2\text{O}$ and $\text{H}_2\text{-H}_2\text{O}$ equilibrators. Cu was added to the sulfur springs samples prior to measurements. The CO_2 and H_2 gasses were used as working standards for water equilibration. Results are

expressed as δ -values in per mil (‰). Two laboratory reference materials (LRM) calibrated to the international scale VSMOW-SLAP were used to normalize the data. Reference materials LRM W-45, W-53, USGS 45, USGS 46 and USGS 47 were used for independent quality control of the measurements (Kanduč et al. 2020, 2021; Žvab Rožič et al. 2021). The average repeatability of the samples was 0.02‰ for $\delta^{18}\text{O}$ and 0.3‰ for $\delta^2\text{H}$.

The isotopic composition of monthly composite precipitation samples is regularly monitored at the Portorož station (Fig. 1b) by the Jožef Stefan Institute as part of the Slovenian Network of Isotopes in Precipitation (SLONIP) since 2000 (Vreča et al. 2022); in the past, it was also monitored at Kozina. Both stations are located in the recharge area (Fig. 1b) and represent the source of investigated groundwater, therefore we used the available data for the interpretation of our results.

Analysis of total alkalinity

The water sample was passed through a 0.45 μm nylon filter into an HDPE bottle and kept refrigerated until analysis. First, pH was measured in the laboratory using a pH meter (Mettler Toledo AG 8603, Schwerzenbach, Switzerland). Within 24 h of sample collection, the Gran titration method (Gieskes 1974) was used to determine TA with an accuracy of $\pm 1\%$. Approximately 8–10 g of the water sample was weighed into a plastic container and placed on a magnetic stirrer. A calibrated pH electrode (7.00 and 4.00 ± 0.02) was placed in the sample and the initial pH was recorded. Reagencon HCl 0.05 N (0.05 M) was used for the titration. Titration was performed using a CAT titrator (Ingenierbüro CAT, M. Zipperer GmbH Ballrechten-Dottingen, Germany). The method is described in detail by Zuliani et al. (2020). Two replicates were measured.

Analysis of the isotopic composition of dissolved inorganic carbon

The isotopic composition of carbon from dissolved inorganic carbon was determined using the Spötl procedure (Spötl 2005; Kanduč 2006). Ampoules of saturated phosphoric acid (100–20 μL) were flushed with helium, 5 mL of the water sample was added according to the alkalinity, and then CO_2 was generated. $\delta^{13}\text{C}_{\text{DIC}}$ was measured using the Europa Scientific 20–20 isotope mass spectrometer (Sercon Limited, Crewe, UK) with the ANCA-TG preparation module. Standard solution Na_2CO_3 (Carlo Erba CE, Val de Ruil, France aqua preparation (8 mg $\text{Na}_2\text{CO}_3/12$ mL distilled water) with a known $\delta^{13}\text{C}_{\text{DIC}}$

value of $-10.8‰ \pm 0.2‰$ and tap water (Reactor Center Podgorica) with a value of $-13.0‰ \pm 0.1‰$ were used as control materials. The CE standard was used for normalization of the results. Two replicates of each sample were measured.

Analysis of isotopic composition of carbonates ($\delta^{13}\text{C}_{\text{CaCO}_3}$)

The isotopic composition of carbon from carbonate ($\delta^{13}\text{C}_{\text{CaCO}_3}$) was determined using an Europa Scientific 20–20 isotope-ratio mass spectrometer (Sercon Limited, Crewe, UK) with ANCA-TG preparation module. Samples were first ground and homogenized. 10 mg of limestone, 20–30 mg of marl and 50 mg of sandstone were weighed into 12 mL glass ampoules and flushed with helium. Then, 0.5 mL of H_3PO_4 was added (McCrea 1950). Reference materials: NBS 18 ($\delta^{13}\text{C} = -5.014‰ \pm 0.035$, $\delta^{18}\text{O} = -23.2‰$) and IAEA CO-1 ($\delta^{13}\text{C} = +2.492 \pm 0.030$, $\delta^{18}\text{O} = -2.4‰ \pm 0.1$) were used for the normalization of $\delta^{13}\text{C}$ measurements. Five replicates for each sample were performed.

Analysis of isotopic composition of sulfur and oxygen in sulfate

The water was filtered through a 0.45- μm filter membrane to remove any dirt in the water samples and the clean, clear water was then transferred to a beaker. We added a few drops of 2N HCl solution to the water to prevent the precipitation of BaCO_3 . While heating, we added a few drops of a 0.5 M BaCl_2 solution to precipitate BaSO_4 . The BaSO_4 powder was then carefully collected from a dry filter for $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ measurements.

The sulfur isotope composition of sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) was analyzed at The University of Arizona with SO_2 gas using a ThermoQuest Finnigan Delta PlusXL continuous-flow gas-ratio mass spectrometer with coupled elemental analyzer (Costech). Samples were combusted at 1030 °C with O_2 and V_2O_5 . Standardization is based on international standards OGS-1 and NBS123, and several other sulfide and sulfate materials that have been compared between laboratories. Calibration is linear in the range -10 to $+30‰$. Precision is estimated to be $\pm 0.15‰$ or better based on repeated internal standards (The University of Arizona 2021). The oxygen isotope composition of sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$) was measured on CO gas using a continuous-flow gas-ratio mass spectrometer (Thermo Electron Delta V) with coupled elemental analyzer (ThermoQuest Finnigan). Samples were combusted with excess C at 1350 °C. Standardization is based on international standard OGS-1. Precision is estimated to be $\pm 0.3‰$ or better based on repeated internal standards (The University of Arizona 2021).

Geochemical modelling

Saturation indices of calcite (SI_{cal}), dolomite (SI_{dol}), anhydrite (SI_{anh}), gypsum (SI_{gyp}) and CO_2 (SI_{CO_2}) were calculated using major cations and anions determined by ActLabs and the PHREEQC program (WATEQ4F database). Other elements and phases were not included in the calculations, since they were not detected in all samples. Saturation indices were calculated for each sample and then averaged for each group (submarine, terrestrial sulfur springs, groundwater, seawater).

Mixing with seawater was estimated using a simple mixing model based on Cl^- concentration and EC values to estimate the seawater content in the springs (Eq. 1):

$$w(\%) = \frac{x_{\text{(sample)}}}{x_{\text{(seawater)}}} \times 100\%, \quad (1)$$

where w percent of seawater in the sample, x Cl^- or EC.

The conservative mixing equation assumes that the parameters (i.e., Cl^-) on which the calculation is based are conserved during the mixing processes, therefore, the chloride ion was used in the calculation of the effect of mixing with seawater. Seawater sample S03 was used for this calculation, as its location is independent and does not coincide with the location of the submarine sulfur spring sampling (as is the case for SW01 and SW02, Fig. 1c).

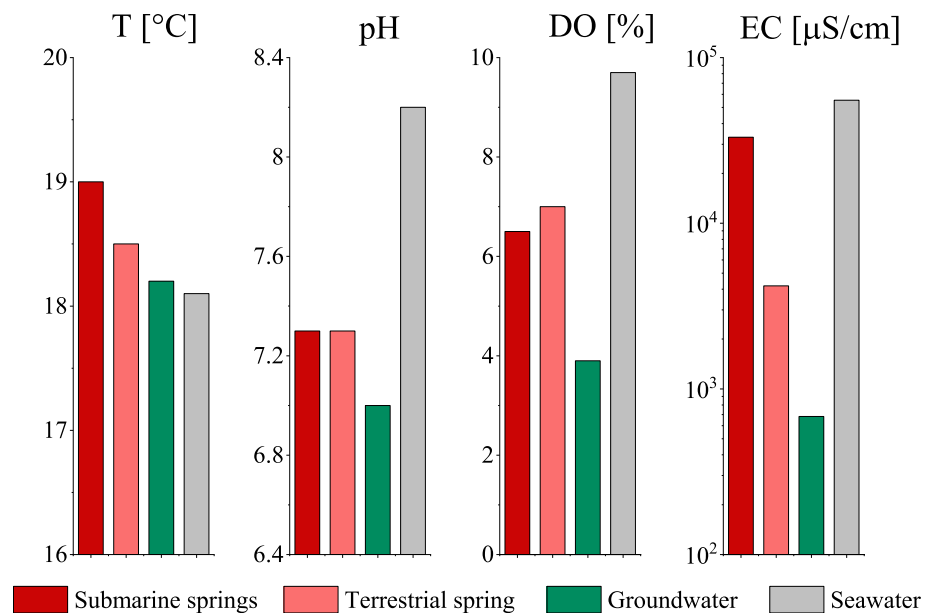
Results and discussion

All results of the physicochemical parameters, geochemical and isotopic analyses are freely available in the Pangaea data repository (Žvab Rožič et al. 2023). The results presented in this paper focus on submarine sulfur springs (M03, M05, M11) and a terrestrial sulfur spring (K04) compared to non-sulfurous groundwater (VK01) and seawater samples (SW01, SW0, SW03).

Physicochemical parameters of submarine and terrestrial sulfur springs, groundwater and seawater

The temperature of the submarine sulfur springs was not constant throughout the seasons, with mean values as follows: 22.2 °C, 20.5 °C and 14.2 °C in the summer and autumn of 2020 and the spring of 2021, respectively. The temperature of the terrestrial sulfur spring was more constant, with a mean value of 18.5 °C for all three sampling events. The mean pH value of 7.5 for the submarine and terrestrial sulfur springs is lower than the mean pH of seawater (8.2) and higher than the groundwater from well VK01 (7.0).

Fig. 2 Mean values of physicochemical characteristics of investigated submarine sulfur springs (M03, M05, M11), terrestrial sulfur spring (K04), groundwater (VK01) and seawater (SW01, SW02, SW03)



The EC values of the submarine sulfur springs are high and vary significantly, from 16,900 to 58,000 $\mu\text{S}/\text{cm}$. The EC values of the terrestrial sulfur spring are less variable and lower, ranging from 3370 to 5410 $\mu\text{S}/\text{cm}$. The mean DO content of 7.46 mg/L of all sulfur springs was lower than that of seawater (9.69 mg/L) and higher than that of groundwater (3.88 mg/L) (Fig. 2, Table 2).

Although we observed large temperature fluctuations in submarine sulfur springs throughout the year and temperatures in submarine sulfur springs were not as high as previously reported (29.6 °C; Žumer 2004, 2008), we measured temperatures of up to 4.2 °C higher for submarine sulfur springs in April 2021 than seawater and we also see elevated mean temperatures of the spring water as well. Assuming that submarine sulfur springs and a terrestrial sulfur spring represent the outflow of the same aquifer, the higher temperatures of the terrestrial sulfur spring also indicate the thermal nature of the springs. High EC values indicate mixing with seawater, which is more present in the submarine sulfur springs than in the terrestrial sulfur spring.

Hydrogeochemical characteristics of submarine and terrestrial sulfur springs, groundwater and seawater

Submarine sulfur spring water is dominated by Na^+ (3.77–11.10 mg/L) and Cl^- (7.14–23.20 mg/L) ions. High concentrations of Mg^{2+} (300–1.05 mg/L) and SO_4^{2-} (1.10–3.00 mg/L) are also present in the submarine sulfur springs. These results point to mixing with seawater, since seawater contains the highest concentrations of Na^+ , Mg^{2+} and Cl^- ions. The Ca/Mg ratio is below 1 for

all submarine sulfur springs, while the terrestrial sulfur spring has a Ca/Mg ratio of 0.98–1.74. In addition to the predominant Na^+ and Cl^- ions, the terrestrial sulfur spring also shows high levels of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} . In contrast to the submarine sulfur springs, which are characterized by the Na–Cl water type, the terrestrial sulfur spring has a higher proportion of the Ca– HCO_3^- type, characteristic of groundwater (VK01) that is dominated by Ca^{2+} and HCO_3^- ions and which is typical of limestone dissolution.

High Na^+ and Cl^- concentrations in both the submarine and terrestrial sulfur springs indicate mixing with seawater. The results of the mixing model based on the Cl^- concentration and the EC values show that the lowest calculated seawater content was observed in samples M03 from October (44% based on EC values, pure seawater based on Cl^-), M03 from April 2021 (48% seawater based on Cl^- and 71% of seawater based on EC values), M05 from July 2020 with 31–33% seawater, M05 from October 2020 with 40–47% seawater, and M11 from April 2021 with 29–35% seawater (Table 3). Since other samples (M05 from April 2021, M11 from July 2020) show seawater contents of greater than 80% we suspect that the syringe sampling is not optimal, and we sampled spring water mixed with seawater in the sediment covering the spring opening. In the future, it may be worth developing a more sophisticated sampling method in order to generate more accurate and conclusive results.

The results of other ions are freely available in the Pangaea data repository (Žvab Rožič et al. 2023) and largely reflect seawater mixing or are below the detection limit. Higher levels of Fe and Mn ions were detected in the sulfur springs and groundwater, with the submarine sulfur springs containing up to 34.4 $\mu\text{g}/\text{L}$ of Mn, the terrestrial sulfur spring with Mn up to 361 $\mu\text{g}/\text{L}$, and groundwater containing

Table 2 Temperature, pH, electrical conductivity, and dissolved oxygen values for submarine sulfur springs (M03, M05, M11), terrestrial sulfur spring (K04), groundwater (VK01) and seawater (SW01, SW02, SW03)

Sample	Date	T (°C)	pH	EC (µS/cm)	DO (mg/L)
M03	8 Oct 2020	20.1	7.1	25200	4.8
M03	16 Apr 2021	13.4	7.3	40800	9.4
M05	9 July 2020	23.6	7.1	18830	3.5
M05	8 Oct 2020	21.0	7.2	27200	4.5
M05	23 Apr 2021	16.6	8.1	56400	10.1
M11	9 July 2020	22.6	7.4	46200	7.0
M11	23 Apr 2021	15.4	7.1	16900	6.2
	Mean	19.0	7.3	33076	6.5
	Minimum	13.4	7.1	16900	6.5
	Maximum	23.6	8.1	56400	10.1
	St. Dev.	3.6	0.3	13821	2.3
K04	17 June 2020	19.9	7.6	3800	7.5
K04	8 Oct 2020	18.5	7.3	3370	5.7
K04	14 Apr 2021	17.0	7.2	5410	7.9
	Mean	18.5	7.3	4193	7.0
	Minimum	17.0	7.2	3370	5.7
	Maximum	19.9	7.6	5410	7.9
	St. Dev.	1.2	0.2	878	0.9
Seawater (SW01, SW02, SW03)	Mean	18.1	8.2	55333	9.7
	Minimum	12.4	8.2	53000	8.7
	Maximum	21.2	8.3	57400	11.0
	St. Dev.	4.1	0.0	1806	1.0
Groundwater (VK01)	Mean	18.2	7.0	681.50	3.9
	Minimum	18.1	7.0	668.00	2.9
	Maximum	18.3	7.1	695.00	4.8
	St. Dev.	0.1	0.1	13.50	1.0

the highest Mn concentration of 540 µg/L. 50 µg/L of Fe ions were detected in the terrestrial sulfur spring and up to 990 µg/L of Fe in the groundwater sample. Fe in the submarine sulfur springs was below the detection limit, which was raised following sample dilution due to high TDS. Elevated Fe and Mn concentrations may point to redox conditions in the aquifer, comparable to that of submarine sulfur springs in Florida, since the reduced Fe and Mn are more soluble (Swarzenski et al. 2001).

Geochemical modelling of submarine and terrestrial sulfur springs

Calcite saturation indices of the submarine sulfur springs and the terrestrial sulfur spring are close to the equilibrium state, while SI_{dol} values show a slight oversaturation of dolomite in submarine sulfur springs; dolomite oversaturation in the seawater is even higher. Such oversaturation of

dolomite in karst groundwaters is typical due to the problematic precipitation of dolomite (Verbovšek and Kanduč 2016). All samples are undersaturated with gypsum and anhydrite (Table 4). The partial pressure of CO_2 (pCO_2) in the submarine sulfur springs ($10^{-2.24}$ atm) is almost 20 times the normal atmospheric value ($10^{-3.39}$ atm; Žvab Rožič et al. 2022), while the pCO_2 of the terrestrial sulfur spring is 33-times the atmospheric pCO_2 . Other phases and minerals were not included in the geochemical modelling, as their element concentration were low and the presence of these minerals not expected.

Isotopic characteristics of submarine and terrestrial sulfur springs, groundwater and seawater

The isotopic value of the submarine sulfur springs had a range of 44.6‰ for δ^2H , with the lowest negative value of -38.8‰ to the highest positive value of +5.8‰. The $\delta^{18}O$

Table 3 Calculated seawater content in the samples based on Cl^- concentrations and EC values

Sample	Date	w_{Cl^-} (%)	w_{EC} (%)
M03	8 Oct 2020	102	44
M03	16 Apr 2021	48	71
M05	9 July 2020	31	33
M05	8 Oct 2020	40	47
M05	23 Apr 2021	97	98
M11	9 July 2020	83	80
M11	23 Apr 2021	35	29
K04	17 June 2020	4	7
K04	8 Oct 2020	4	6
K04	14 Apr 2021	7	9
VK01	8 Oct 2020	0	1
VK01	16 Apr 2021	0	1
SW01	17 June 2020	88	92
SW02	8 Oct 2020	33	97
SW03*	16 Apr 2021	100	100

SW03* is the reference sample

of submarine waters showed a range of 6.60‰, from -5.88 to $+0.72$ ‰ (Fig. 3). The hydrogen and oxygen isotopic composition of the terrestrial sulfur spring, groundwater, and seawater is less variable. The mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the terrestrial sulfur spring K04 were -41.5 ‰ and -6.59 ‰, respectively (Fig. 3). Local groundwater samples from the well VK01 are also presented for comparison, with mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of -41.0 ‰ and -6.12 ‰, respectively, and seawater samples with mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of $+7.5$ ‰ and $+0.94$ ‰, respectively (Fig. 3). The isotopic composition of precipitation at Portorož with weighted mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of -40.5 ‰ and -6.38 ‰ for the period 2011–2020 is characteristic for the coastal areas of the northeastern Adriatic and similar to the mean values observed for the 2001–2003 period at Portorož (Vreča and Malenšek 2016). All $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data related to the investigated samples are plotted near the global meteoric water line (GMWL; $\delta^2\text{H} = \delta^{18}\text{O} \times 8 + 10$; Craig 1961) and the reduced major axis precipitation amount weighted local meteoric water line (LMWL Portorož, 2011–2020; $\delta^2\text{H} = 7.87 \times \delta^{18}\text{O} + 9.77$; Šušmelj et al. 2022). Therefore, the main source of water in all samples is local precipitation. However, the submarine sulfur springs and groundwater data

plot slightly below the GMWL and LMWL along the mixing line (ML) between the seawater and the weighted mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for Kozina (Vreča and Malenšek 2016) (Fig. 3). Values for the terrestrial sulfur spring are positioned between the precipitation values characteristic for Portorož and Kozina, reflecting the infiltration of modern precipitation in the recharge area of the springs. The submarine sulfur spring samples M03 from October 2020, M05 from July 2020, M05 from October 2020, and M11 from April 2021 plot closer to the terrestrial waters and LMWL, indicating less mixing with seawater and a higher proportion of groundwater originating from precipitation. The isotopic composition of the groundwater is also very similar to the isotopic composition of the Smrdljivec sulfur karst spring, which is located in the Classical Karst (Mulec et al. 2021), which is in one of the presumed recharge areas of the Izola sulfur springs.

All investigated water samples are enriched with heavier isotopes (i.e. ^2H and ^{18}O) due to the proximity to the Mediterranean and the Adriatic Sea. In comparison, other karst and fractured aquifers in central Slovenia (Verbovšek and Kanduč 2016; Žvab Rožič et al. 2022) (Fig. 3) are affected by the continental isotopic effect, as an increasing depletion of ^2H and ^{18}O is observed in the precipitation in Slovenia with distance from the sea (Vreča et al. 2006; Kern et al. 2020).

The mean $\delta^{13}\text{C}_{\text{DIC}}$ values of submarine sulfur springs (M03, M05, M11), terrestrial sulfur spring (K04), and groundwater (VK01) were -1.4 ‰, -12.2 ‰, and -12.3 ‰, respectively. The seawater in Izola (SW01, SW02, SW03) had an average $\delta^{13}\text{C}_{\text{DIC}}$ value of $+0.7$ ‰. The measured $\delta^{13}\text{C}_{\text{DIC}}$ of the submarine sulfur spring M03 from the study of Faganelli et al. (2005) was -3.5 ‰ at a salinity of 5‰ (lower salinity than this research, approximately 14‰ of seawater in the sample), while $\delta^{13}\text{C}_{\text{DIC}}$ of the seawater was -0.9 ‰ and salinity 35‰.

The results of $\delta^{13}\text{C}$ from different rock types from Izola Bay (sandstone in the flysch formation, marl in flysch formation and nummulite limestone) vary from -0.6 ‰ (carbonate from the flysch formation) to $+2.2$ ‰ (limestone) with an average value of $+0.4$ ‰.

Geochemical processes were calculated as follows: Line 1 (with a value of 1.2‰) dissolution of limestone according to the average $\delta^{13}\text{C}_{\text{CaCO}_3}$ (2.2‰) value—predicted value (Kanduč et al. 2012) causing 1‰ enrichment in ^{12}C in DIC

Table 4 Mean values of saturation indices SI_{cal} , SI_{dol} , SI_{anh} , SI_{gyp} of investigated waters in the Izola area

	SI_{cal}	SI_{dol}	SI_{gyp}	SI_{anh}	SI_{CO_2}
Submarine sulfur springs (M03, M05, M11)	0.07	0.63	-0.64	-0.87	-2.24
Terrestrial sulfur spring (K04)	0.21	0.36	-1.31	-1.55	-1.91
Groundwater (VK01)	0.19	-0.45	-2.31	-2.56	-1.47
Seawater (SW01, SW02, SW03)	0.78	2.29	-0.70	-0.93	-3.31

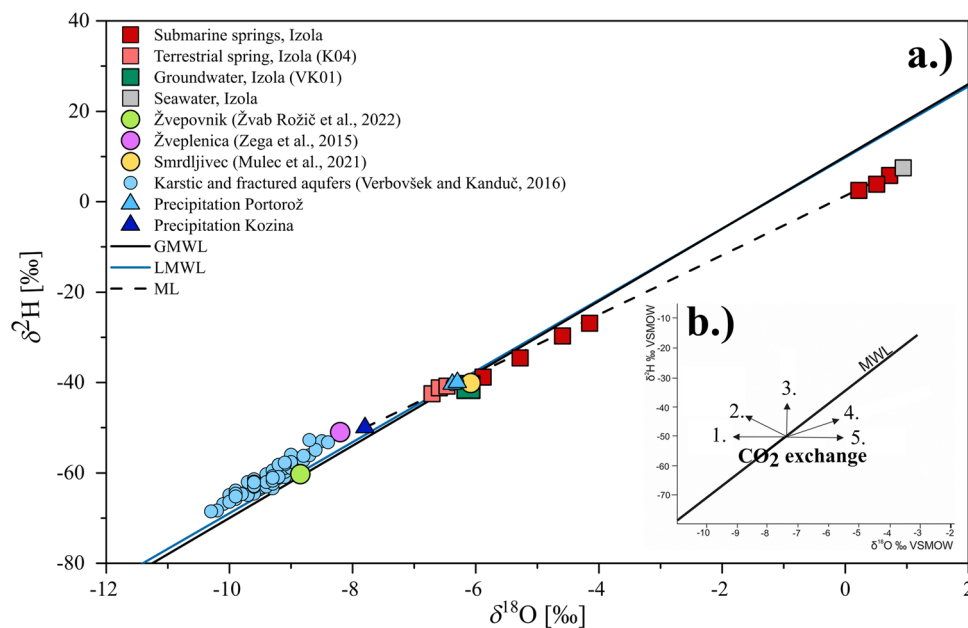


Fig. 3 a $\delta^2\text{H}$ versus $\delta^{18}\text{O}$, values of submarine sulfur springs of Izola, terrestrial sulfur spring, groundwater, seawater (this study in squares) and other studies: Smrdljivec sulfur spring (Mulec et al. 2021), Žvepovnik sulfur spring (Žvab Rožič et al. 2022), Žveplenica sulfur spring (Zega et al. 2015) and groundwater from central Slove-

nia (Verbovšek and Kanduč 2016). b $\delta^2\text{H}$ and $\delta^{18}\text{O}$ fractionation processes: 1. low-T mineral reactions, 2. hydration of silicates, 3. H_2S exchange, 4. evaporation from surface, 5. high-T exchange with minerals (modified after Karolytė et al. 2017)

(Romanek et al. 1992), line 2 with a value of -12.5‰ non-equilibrium carbonate dissolution by carbonic acid produced from soil zone CO_2 (Kanduč et al. 2012), and line 3 (with a value of -18.2‰) open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}\text{C}_{\text{soil}} = -27.2\text{‰}$ (Kanduč et al. 2012) (Fig. 4).

Seawater falls around equilibration line 1, while samples from the submarine sulfur springs (from limestone) fall between equilibration lines 1 and 2. Terrestrial sulfur spring K04 (from nummulite limestone and flysch rocks in the hinterland (Fig. 1a)) fall close to equilibration line 2 and show carbonate and soil CO_2 contribution. Groundwater in Izola (VK01) is also near equilibration line 2 but has higher total alkalinity (longer retention time) in comparison to the terrestrial sulfur spring (K04), but a similar $\delta^{13}\text{C}_{\text{DIC}}$ value (Fig. 4). Groundwater (VK01) and the terrestrial sulfur spring (K04) fall along the same fractionation line 2 as the previously studied Žvepovnik (Žvab Rožič et al. 2022) and Žveplenica sulfur karst spring (Zega et al. 2015) (Fig. 4). These two previously studied sulfur springs, VK01 and K04, have similar $\delta^{13}\text{C}_{\text{DIC}}$ to karst groundwater from SW Slovenia (Kukar 1998) and most karst and fractured aquifers in central Slovenia (Verbovšek and Kanduč 2016) (Fig. 4). Springs from North Slovenia have a more variable $\delta^{13}\text{C}_{\text{DIC}}$ due to their different geological backgrounds (Kanduč et al. 2012).

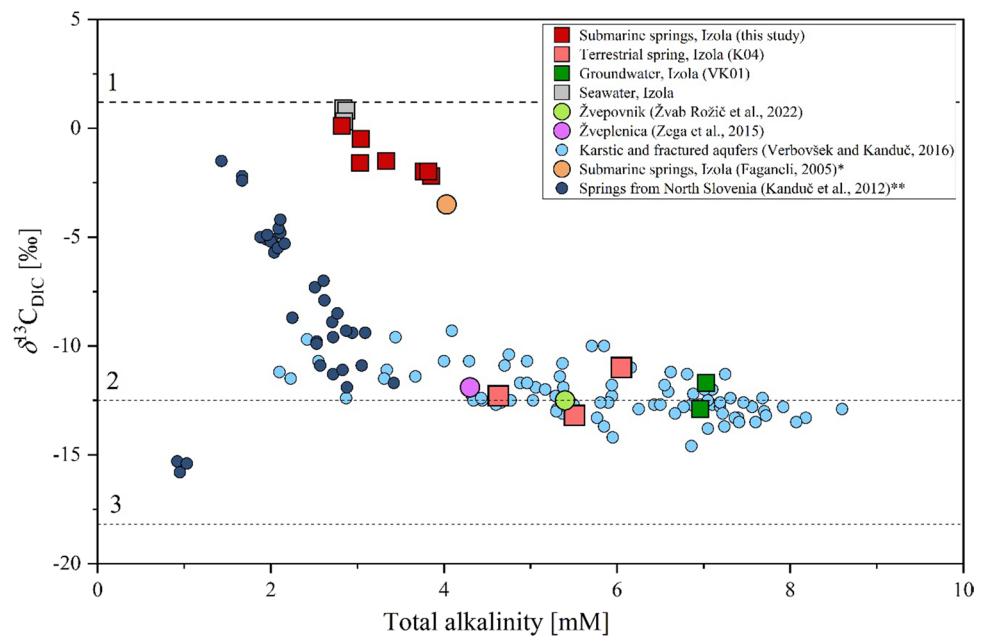
Alkalinity and $\delta^{13}\text{C}_{\text{DIC}}$ values (Fig. 4) indicate that the seawater near Izola has the highest $\delta^{13}\text{C}_{\text{DIC}}$, while

the submarine sulfur springs near Izola have total alkalinity and $\delta^{13}\text{C}_{\text{DIC}}$ values between those of seawater and the terrestrial sulfur spring and the groundwater in Izola (Fig. 4). The higher $\delta^{13}\text{C}_{\text{DIC}}$ value of the submarine sulfur spring is also due to the mixing with seawater with $\delta^{13}\text{C}_{\text{DIC}}$ of $+0.7\text{‰} \pm 0.3\text{‰}$, in addition to the dissolution of carbonates (fractionation line 1). It is impossible to say how much of a contribution comes from the dissolution of carbonates (with value of $\delta^{13}\text{C}_{\text{DIC}}$ of $+1.2\text{‰}$) and how much from the mixing with seawater (with an average value of $+0.7\text{‰}$), which in our case is considerable.

Sulfate isotope analysis was performed once, in the spring of 2021. The $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values of the submarine sulfur spring sample M03 are $+9.1\text{‰}$ and $+22.2\text{‰}$, respectively. Sample M11 shows slightly higher values, $\delta^{18}\text{O}_{\text{SO}_4} = +11.2\text{‰}$ and $\delta^{34}\text{S}_{\text{SO}_4} = +23.6\text{‰}$. The $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values of the terrestrial sulfur spring K04 are $+11.0\text{‰}$ and $+20.3\text{‰}$, respectively. Sulfate concentrations in the submarine sulfur springs ranged from 1100 to 2770 mg/L, reaching concentrations similar to those in seawater (2640–3000 mg/L), whereas they were much lower in the terrestrial sulfur spring, ranging from 182 to 283 mg/L.

Although the $\delta^{34}\text{S}_{\text{SO}_4}$ values for the submarine sulfur springs of Izola are typical of seawater and evaporites (Krouse and Mayer 2000), the negative SI_{anh} and SI_{gyp} and the local geologic setting do not indicate an evaporative origin. Since high proportions of seawater were detected in the springs, we can conclude that the marine sulfate in the sulfur springs water

Fig. 4 $\delta^{13}\text{C}_{\text{DIC}}$ versus TA, values of submarine sulfur springs, terrestrial sulfur spring, groundwater, seawater, and other studies: submarine sulfur springs of Izola (Faganeli et al. 2005; *TA values as HCO_3^- concentration), Žvepovnik sulfur spring (Žvab Rožič et al. 2022), Žveplenica sulfur spring (Zega et al. 2015), springs from North Slovenia (Kanduč et al. 2012; **data from all seasons) and groundwater from central Slovenia (Verbovšek and Kanduč 2016). Please refer to the text for an explanation of dotted lines 1, 2, and 3, indicating biogeochemical processes



samples reflects the mixing of seawater with spring water in the samples. The origin of the sulfate from which the sulfide is formed remains undefined. According to the geological data, a highly probable source of sulfur is the coal of the Liburnian Formation, which underlies the alveolinic-nummulitic limestones in Izola. We did not detect sulfate from FeS_2 oxidation as found in the karst groundwater in China, with a negative $\delta^{34}\text{S}_{\text{SO}_4}$ value (Tang et al. 2021), therefore any particular potential risk to the marine environment is excluded.

Characterization and origin of the groundwater in the sulfur springs of Izola

The submarine and terrestrial sulfur springs of Izola exhibit elevated mean temperatures and a distinctive smell of sulfur, which is consistent with the reports on the use of Izola thermal waters for spa purposes in the nineteenth century (Kramar 2003) and the first reports on submarine sulfur springs by Žumer (2004, 2008). Elevated temperatures indicate deep water circulation, presumably more than 100 m deep, in accordance with the expected temperature at a depth of 100 m of around 17 °C in this area (Rajver 2016). The spring water has a higher mean temperature than the groundwater (VK01) at a depth of 180 m and thus rises from a greater depth. The spring water flows deep beneath the flysch that surrounds and covers the limestones of Izola, separating them from the limestones of Karst and the Croatian border area (Fig. 5). At depths of several hundred meters, the water warms up and then rises and springs at the stratigraphic

boundary of the limestones of the Izola anticline and the surrounding flysch (Rožič and Žvab Rožič 2023). Heat, lower salinity, and artesian pressure may also play a role in water rise and spring formation.

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ show that the source of the freshwater component in the sulfur springs is local precipitation, with a limited influence of evaporation and/or geochemical processes that could modify the stable isotopic composition of the water, since the terrestrial sulfur spring and local groundwater plot on or close to the LMWL (Fig. 3). Limestones in Izola are largely covered by the urban area, where water drains into sewers, therefore greater infiltration is not possible. The water from the Izola sulfur springs could originate from the same recharge area as that of the isotopically similar Srdljivec sulfur spring (Mulec et al. 2021), in the Classical Karst region, about 25 km E to 30 km NE from Izola. Outcrops of alveolinic-nummulitic limestones at the Croatian border, near the Dragonja river and the Sečovlje coal mine, represent other possible recharge areas. The isotopic composition from this area, recorded at station Portorož and Kozina (Fig. 1b), confirms these assumptions.

The sulfur spring water is highly mineralized as it mixes with seawater in the sediment at the spring depression. Groundwater–seawater mixing within the aquifer, as present in Lucija (Lu-1), 5 km from Izola (Fig. 1b; Brenčič 2009), is unlikely, since groundwater in Izola (VK01) with a Ca-HCO_3 facies shows no signs of mixing with seawater at a depth of 180 m.

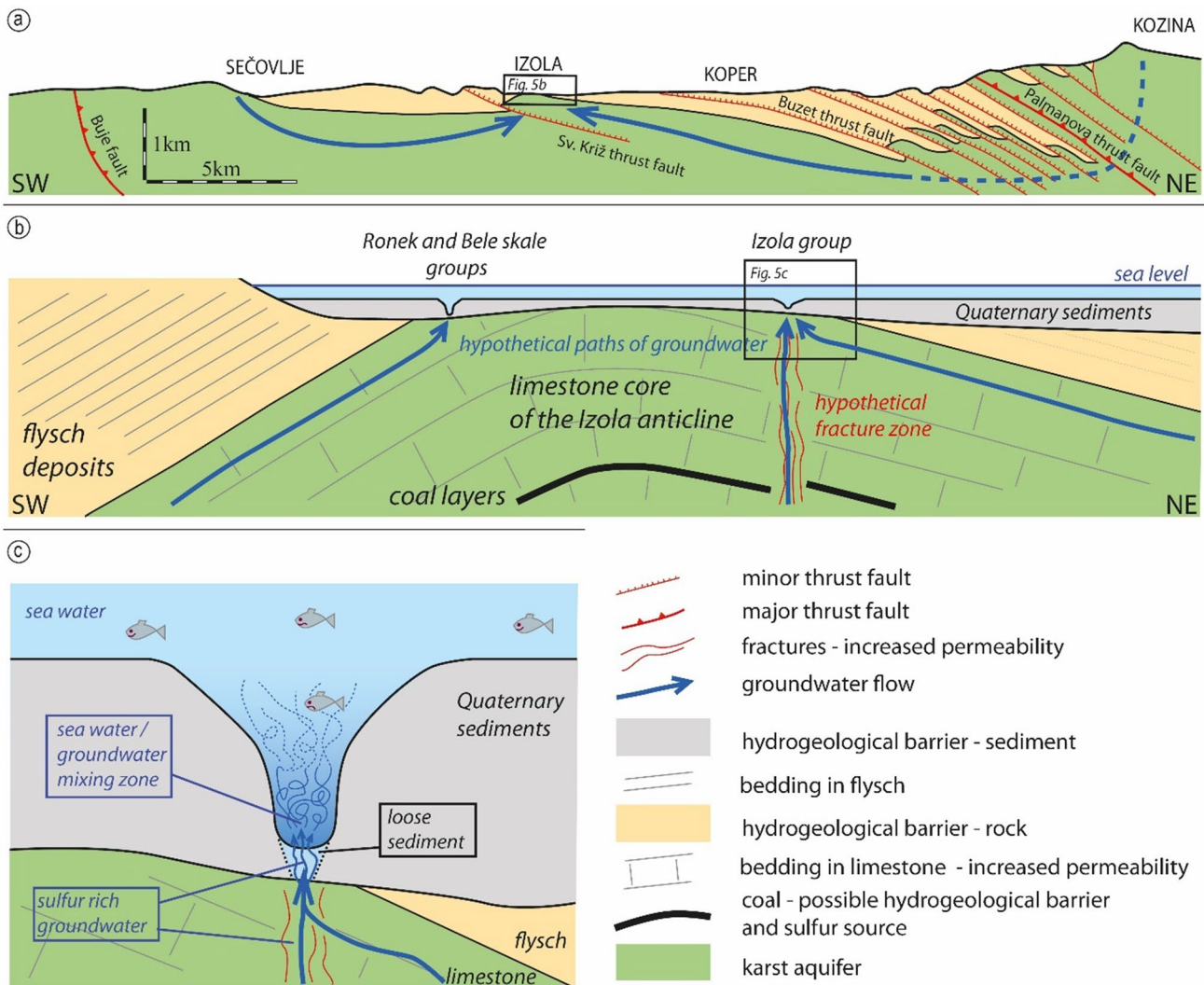


Fig. 5 **a** General geological/hydrogeological cross-section between the Istra Peninsula and the Kras (Karst) Plateau with possible regional groundwater flow pathways (modified from Placer et al. 2010; major modification is in Izola area with the representation of the outcropping Izola anticline limestone core and in Sečovlje area, where the data from the coal mine (Turk 1955) does not show major fault displacement); **b** hydrogeological model of the submarine sulfur springs near Izola with the indicated possible groundwater flow

paths; the springs occur near the boundary between the karst aquifer (limestone core of the Izola anticline) and the hydrogeological barrier (flysch limbs of the Izola anticline). The micro-locations of the springs could be governed by fracture zones and the thickness of the overlying Quaternary deposits; **c** detailed hydrogeological cross-section of a spring: groundwater springs from a limestone, penetrates a thin cover of loose sediments, and mixes rapidly with seawater within the funnel-shaped depression.

$\delta^{13}\text{C}_{\text{DIC}}$ and alkalinity confirm that the spring water is coming from a limestone aquifer, yet the terrestrial sulfur spring water is also in contact with organic matter, as some carbonate dissolution occurs due to carbonic acid. The presence of coal in the layers below the alveolinic-nummulitic limestones of Izola (Pleničar et al. 1973; Benedik and Rožič 2002; Brenčič 2009) is a possible source of the organic matter in contact. High Fe and Mn concentrations also indicate

mild redox conditions, which are likely the cause of the hydrogen sulfide production by bacterial reduction of evaporite or marine sulfate, as is the case in the thermal springs of the Santa Cesarea Terme system in Italy (Santalioia et al. 2016; D’Angeli et al. 2021), or by the reduction of organic (coal-derived) sulfates. $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ suggest that the sulfate is of marine origin; however, said results are affected by the mixing with seawater (Fig. 5).

Conclusions

Physical, geochemical, and isotopic data were used to characterize submarine and terrestrial sulfur springs on the Slovenian coast. The results provide us with a better understanding of the source areas of water and interactions within the aquifer, all of which play an important role in water management (use of water on the coast or management of discharges into the sea). Namely, the presence of seawater, sulfide, and other special properties of the investigated springs may represent a harmful or beneficial contribution to the environment and community.

The applied methodologies provide us with valuable results from which we can draw the following conclusions:

1. Seawater mixing with submarine sulfur springs in the sediments was confirmed by high EC values, high concentrations of Cl^- , Na^- , and other elements characteristic of seawater, such as enrichment with $^{13}\text{C}_{\text{DIC}}$. Not all springs mixed with seawater equally, as samples of submarine sulfur springs consisted of 29–98% of seawater. The terrestrial sulfur spring also mixed with seawater and consisted of 4–9% seawater. Although natural mixing with seawater is to some degree present in the sulfur springs, the very high proportions of seawater in some submarine spring samples point to problematic sampling.
2. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ have shown that the origin of the water in the terrestrial sulfur spring can be traced to the infiltration of local modern meteoric water. The source of the freshwater component in the submarine sulfur springs is the same as that in the terrestrial sulfur spring, as they plot on the mixing line between the terrestrial sulfur spring and the seawater.
3. $\delta^{13}\text{C}_{\text{DIC}}$ and alkalinity in the terrestrial and submarine sulfur springs of Izola show that most of the dissolved inorganic carbon in the groundwater and the terrestrial sulfur springs with $\delta^{13}\text{C}_{\text{DIC}}$ around -12‰ originates from the dissolution of nummulite limestone and the flysch formation with soil CO_2 contribution, while in the submarine sulfur springs the dissolution of nummulite limestone prevails with seawater mixing, which is not negligible. Even though mixing with seawater was present in the submarine sulfur springs, we can conclude from this and previous investigations that carbonate dissolution constitutes the main process at work in the recharge area of submarine sulfur springs.
4. $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ indicate that the sulfate is of marine origin, which reflects spring water mixing with seawater, thus the exact origin of the sulfur is still unclear. Another possible source of sulfur is the coal layers of the Liburnian formation underneath the alveolinic-

nummulitic limestones, which are rich in organic matter and sulfur. The higher concentrations of soluble Fe and Mn in the sulfur springs are consistent with the reducing conditions and the bacterial reduction of marine or organic sulfates, which could explain the sulfurous odor. However, further analyses is required to better understand the sulfur cycle in the spring's aquifer. Moreover, new sampling methods have to be developed to sample submarine karst springs under the unconsolidated silty sediment.

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Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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