

# Study of dilution processes of sulfidic aquifer hosted by the Fiume-Vento karstic complex, Frasassi (Central Italy)

## *Studio dei processi di diluizione della falda solfurea interna al complesso carsico Fiume-Vento, Frasassi (Italia centrale)*

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### Riassunto

Le grotte ipogeniche, caratterizzate da speleogenesi da acido solforico, sono diffuse in tutto il mondo. In Italia centrale, il complesso carsico del Fiume-Vento rappresenta il più importante sistema ipogenico attivo che ospita diversi laghi interconnessi in cui le acque sotterranee drenano verso sorgenti solfuree che emergono lungo il torrente Sentino. Fenomeni di stratificazione e diluizione acqua dolce-acqua solfurea si verificano in molti laghi sotterranei, anche se non è ancora chiaro se questi processi sono legati alle interazioni torrente-acquifero o all'apporto delle acque di stillicidio. La conoscenza speleologica del sistema, unita alle indagini geochimiche, aiuta a comprendere la circolazione delle acque sotterranee sia nelle porzioni interne che esterne del sistema carsico. Le analisi geochimiche su campioni d'acqua prelevati lungo il torrente Sentino, all'interno delle grotte (acque di stillicidio e dei laghi) e nelle sorgenti solfuree hanno permesso di stabilire che le acque di stillicidio sono responsabili dei processi di diluizione. Tuttavia, non è da escludere un apporto di acqua superficiale dal torrente verso l'acquifero nelle porzioni del complesso carsico prossime al T. Sentino, in particolare durante gli eventi di piena (interazioni torrente-acquifero). La portata delle sorgenti solfuree, stimata con il metodo del bilancio di massa con traccianti naturali (ioni cloro e sodio), è risultata tra 11 e 65 L/s. I risultati presentati in questo studio possono aiutare a comprendere i fenomeni di circolazione e diluizione delle acque sotterranee in altri sistemi carsici caratterizzati da speleogenesi da acido solforico.

### Abstract

*Sulfuric acid caves are widespread worldwide. In Central Italy, the Fiume-Vento karstic complex represents the most important active hypogenic cave system hosting several interconnected lakes where groundwater moves towards sulfidic springs emerging along the Sentino Stream. Stratification and dilution phenomena between freshwater and sulfidic water occur in many underground lakes, even if they remain still open if these processes are driven by stream-aquifer interaction or dripping water. The speleological knowledge coupled with geochemical surveys can help study groundwater circulation in the karst system's inner and outer portions. The geochemical analyses on water samples taken along the Sentino Stream, inside the caves (dripping and lakes water) and in sulfidic springs allow establishing the origin of the dilution water in the dripping water. However, stream-aquifer interactions cannot be excluded during flood events. Using the tracer mass balance method (chloride and sodium ions), the discharge of the sulfidic springs ranges between 65 and 11 L/s. The results presented in this study may help understand groundwater circulation and dilution phenomena in other karst systems characterised by sulfuric acid speleogenesis type.*

## Introduction

Sulfuric Acid Speleogenetic (SAS) caves are widespread worldwide (Piccini et al. 2007; Klimchouk 2009; Palmer 2011; Laurent et al. 2021), with most examples in Central-Southern Italy (e.g., Galdenzi and Menichetti 1995; De Waele et al. 2014; Vattano et al. 2017; D'Angeli et al. 2019; D'Angeli et al. 2021). As reported by Galdenzi and Maruoka (2003), and Jones et al. (2015), the SAS caves are mostly formed above the water table by abiotic and/or biotic oxidation of hydrogen sulfide ( $H_2S$ ) deriving from a deep source (hypogenic caves). According to De Waele et al. (2016), the dissolution of carbonate rock in these conditions is extremely fast compared to normal epigenic caves and can cause the formation of sizeable cavities. In Central Italy, the Fiume-Vento karstic complex represents the most important SAS system characterized by hypogenic caves affected by an active flow of sulfidic water (Galdenzi et al. 2008). The water chemistry, rich in  $H_2S$ , is related to a deep-water circulation from the evaporitic Triassic formation of Anidriti di Burano (Centamore et al. 1975; Cambi et al. 2010; Di Matteo et al. 2016). Sulfuric acid ( $H_2SO_4$ ), resulting from the oxidation of  $H_2S$  in the upper part of the aquifer, is considered the main cause of the corrosive phenomena that have generated the caves over time. The oxidation of  $H_2S$  can occur through the interaction of the sulfidic aquifer with freshwater rich in gaseous oxygen ( $O_2$ ) (Galdenzi 1990 a,b). The latter, less dense than the sulfidic one, tends to stratify above the aquifer contributing in some cases also to the dilution of sulfidic water; this is clearly recognisable within the underground lakes (Cocchioni et al. 2003; Galdenzi 2004). The origin of freshwater responsible for dilution, stratification and oxidation processes is debated in the literature, including hypotheses of the interaction of groundwater with dripping water or with surface waters of the Sentino Stream (e.g., Gambelli et al. 1978; Tazioli et al. 1990; Ciancetti and Pennacchioni 1993; Dragoni and Verdacchi 1993; Caprari et al. 2001; Cocchioni et al. 2003; Galdenzi et al. 2008).

The morphology of the Fiume-Vento karstic system is characterized by different superimposed sub-horizontal levels connected by wells, karst ducts and tunnels (Bocchini and Coltorti 1990; Galdenzi 2004), which allow reaching the sulfidic aquifer in several points. A new hydrogeochemical campaign has investigated the origin of freshwater in 2020-2021 it has been carried out on underground lakes, sulfidic springs, dripping water, and some stream sections, clarifying the interaction processes between the different water types.

## Hydrogeological and geochemical setting

The Frasassi karst area hosts the Fiume-Vento karst complex, located in the central-western part of the Marche Region, forty kilometers from the Adriatic Sea (Fig. 1). This area develops on the eastern side of the Umbria-Marche Apennines, along an asymmetrical anticline with NNW-SSE axial direction and Adriatic vergence. The main caves and karst networks developed between the core and the eastern side of the Valmontagnana Mt.-Frasassi Mt. anticline

(Fig. 1), at altitudes between 200 and 500 m a.s.l. The erosion by the Sentino Stream produced a deep incision (Frasassi Gorge), allowing the outcropping of the Calcarea Massiccio formation hosting the main karst features. This formation deposited on a structural high, hosts an important hydrogeological complex (the Basal Limestones Complex, BLC, Fig. 1) overlaid by the low permeability Bugarone formation belonging to the Calcareous Siliceous Marly Complex (CSMC). In the eastern sector of the Frasassi anticline, the BLC is in tectonic contact with the Maiolica hydrogeological Complex (MAC) by a normal fault system (Fig. 1). The MAC is in stratigraphic contact with the low permeability Marne a Fucoidi Complex (MFC), representing the no-flow boundary, responsible for the emergence of sulfidic groundwater along the right bank of the Sentino Stream. The recharge area of these springs is about 6 km<sup>2</sup> (Baldoni et al. 2010). Lithological and structural factors strongly influence the groundwater circulation within the Frasassi anticline. The main aquifers are hosted in the BLC and MAC, feeding the Sentino Stream (Cocchioni et al. 2003). Two main groundwater types characterize the inner circulation: the bicarbonate one, rich in  $O_2$ , and the sulfidic one, rich in  $H_2S$  (Fig. 2). Water circulation occurs in submerged karst conduits, except in some areas of the north-eastern portion of the karst complex (Fig. 3). The water table can be reached in the inner part of the karst system, at the same level as the Sentino Stream. The groundwater flow is, in general, very slow, and flowing water is only found in the north-eastern part of the karst system (Galdenzi and Maruoka 2003). In the western part of the system, water stratification phenomena in many underground lakes have been documented (Galdenzi 2001; Cocchioni et al. 2003). Some experimental tests with marble disk probes placed at different depths in some lakes have been carried out by Galdenzi et al. (1997) and Mariani et al. (2007), observing the different dissolution with increasing water depth. Galdenzi (2001) pointed out that the bicarbonate water (less dense) is superimposed on the denser sulfidic one (Fig. 2). In a few cases, mixing phenomena occur, responsible for the partial dilution of groundwater (Cocchioni et al. 2003). NS-oriented faults control the groundwater flow coupled with a dense network of joints distributed in the NE-SW and NW-SE directions (Menichetti 2013).

The Fiume-Vento karst system (Fig. 2) comprises several superimposed levels, primarily horizontal and with dense ramifications, linked to the discontinuous deepening of the surface water network due to the alternating glacial-interglacial periods during the Pleistocene (Bocchini and Coltorti 1990). Each level represents periods of stability of the phreatic surface characterised by slow groundwater flow, which lasted long enough to fully develop the morphologies linked to the oxidation processes of  $H_2S$  (Galdenzi 1990 a,b). It is possible to distinguish environments that have developed entirely in groundwater and environments that recognize the effects of corrosive actions in the gaseous phase above the original phreatic level (Galdenzi 1990 a,b). Nowadays, the most ancient karst levels are not affected by the oxidation processes of  $H_2S$ , while the epigenic karst is still active.

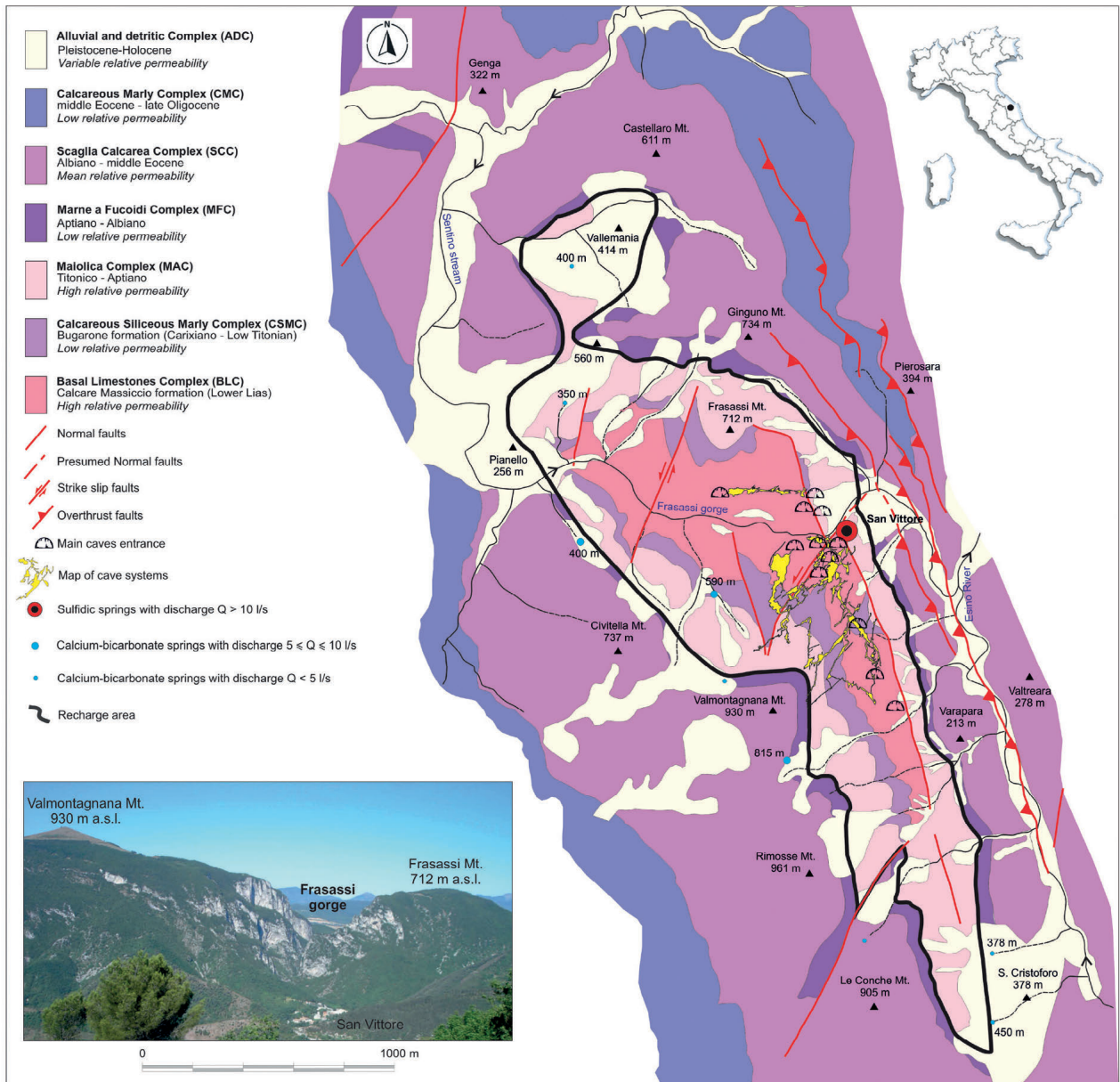


Fig. 1 - Hydrogeological map of the study area.

Fig. 1 - Carta idrogeologica dell'area di studio.

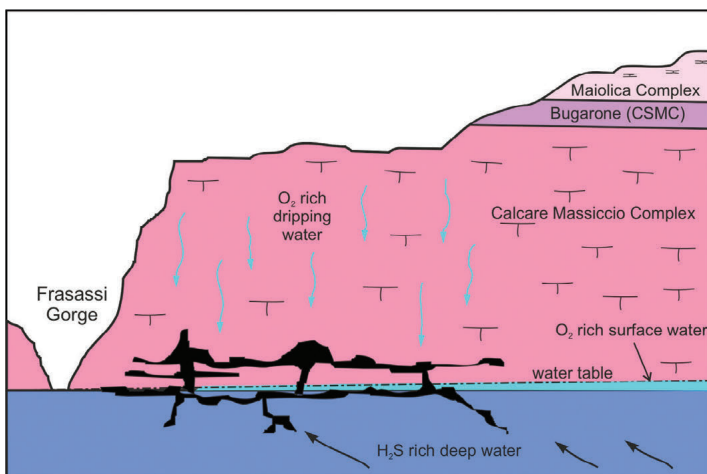


Fig. 2 - Scheme of the karst aquifer hosted in Frasassi Caves (modified from Galdenzi 2001).

Fig. 2 - Schema dell'acquifero carsico interno alle Grotte di Frasassi (modificato da Galdenzi 2001).

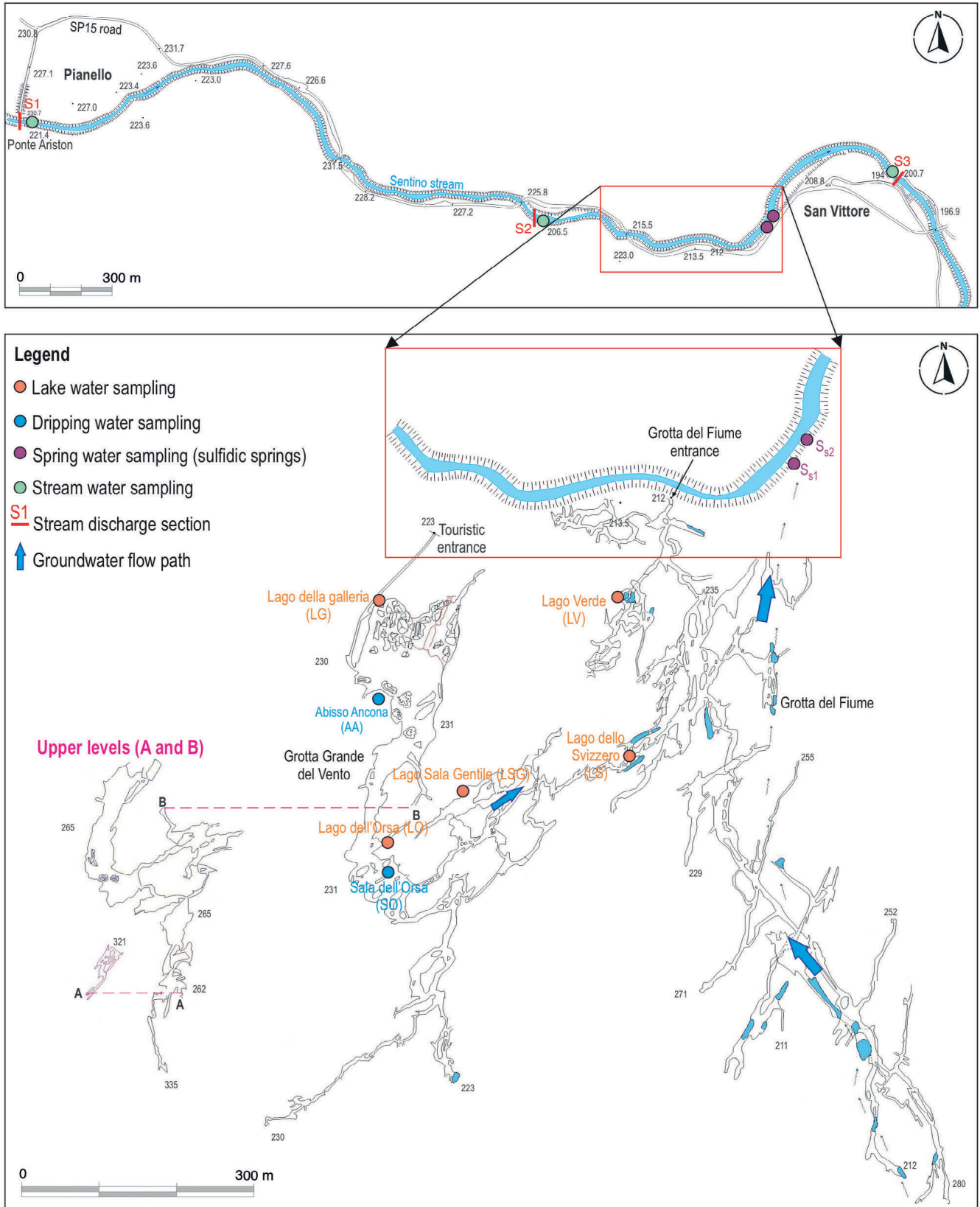


Fig. 3 - Schematic map of the "Fiume-Vento" karstic complex and Sentino Stream, with water samples location.

Fig. 3 - Planimetria del complesso carsico "Fiume-Vento" e schema del torrente Sentino, con ubicazione dei punti di campionamento.

## Materials and methods

### Sampling sites

To determine the origin of the bicarbonate water responsible for dilution and stratification of the sulfidic aquifer inside the “Fiume-Vento” karst system, a detailed hydro-geochemical study of the different types of water that characterize the groundwater circulation system of the area was performed. The geochemical analyses were carried out on Sentino Stream water, sulfidic springs water, dripping water, and groundwater in two different seasons, November 2020, May and June 2021 (Fig. 3). Sampling points coupled with discharge measurements are located at Pianello, upstream of the Frasassi Gorge (S1); close to the tourist entrance of the Frasassi Caves (S2); and in San Vittore village (S3). The water of sulfidic springs was sampled at Sorgente Libera and Sorgente Briglia ( $S_{s1}$  and  $S_{s2}$  in Fig. 3), located downstream of the entrance of Grotta del Fiume. Groundwater samples were collected on the surface of five lakes emerging in the lower portions of the karstic complex, such as Lago Verde (LV), Lago dello Svizzero (LS), Lago di Sala Gentile (LSG), Lago dell’Orsa (LO) and Lago della Galleria (LG) (Fig. 3). Dripping water was sampled in the abundant percolation areas inside the Grotta Grande del Vento in Sala Abisso Ancona (AA) and Sala dell’Orsa (SO) sites.

### Surveying techniques

The determination of the chemical-physical properties of sampled waters was carried out both on-site and at the Geochemistry Laboratory of the Department of Physics and Geology of Perugia University. Temperature (T), electrical conductivity (EC), pH, and redox potential (Eh) measurements were carried out using a portable multiparameter probe WTW pH/Cond 3320 SET 2. Moreover, the concentration of bicarbonates was determined on-site by acid titration with 0,01 N HCl, using methyl orange as an indicator.

Two 100 ml samples were taken from each sampling site (Fig. 3) for the laboratory analyses. One of the sample aliquots was filtered upon sampling through a 0.45  $\mu\text{m}$  membrane filters and then acidified with 1% of 1:1 diluted HCl, to avoid the precipitation of Ca and Mg in carbonate minerals. Cations concentration were determined by Atomic Absorption Spectroscopy (AAS), on the acidified sample, while anions concentration were determined by Ion Chromatography (IC).

To investigate discharge increases or decreases along the Frasassi Gorge and the interaction of streamflow with the karstic system, two discharge measurements (November 2020 and May-June 2021) were carried out using a digital Flow Tracker of the SonTek/YSI company (velocity accuracy  $\pm 1\%$  of measured velocity in the range 0.001- 4.0 m/s). Figure 4 shows the water sampling operations inside the karst system and the discharge measurement in section S2 (Fig. 3).

### Tracer mass balance method

In karst hydrogeology, natural tracers can give information about the spring discharge. As shown in Figure 3, the main springs ( $S_{s1}$ - $S_{s2}$ ) are located along the Sentino River between two sections (S2 and S3), whose flow rate was measured during the 2020-2021 campaign. In this situation, by considering the river discharge and water chemistry, it is possible to estimate the spring discharge by the mass balance method (see Böhme 2011). This method requires measuring of a selected conservative ion concentration on S2 (upstream the springs), springs, and S3 (downstream the springs). According to Atkinson et al. (2015), tracers may be conservative or have well-defined non-conservative behavior. Chloride and sodium are the most used among the natural conservative tracers for hydrogeological investigations (e.g., Tazioli and Palpacelli 2013). Some other study suggests using magnesium in areas with abundant dolomite (Sappa et al. 2017; De Filippi et al. 2021).

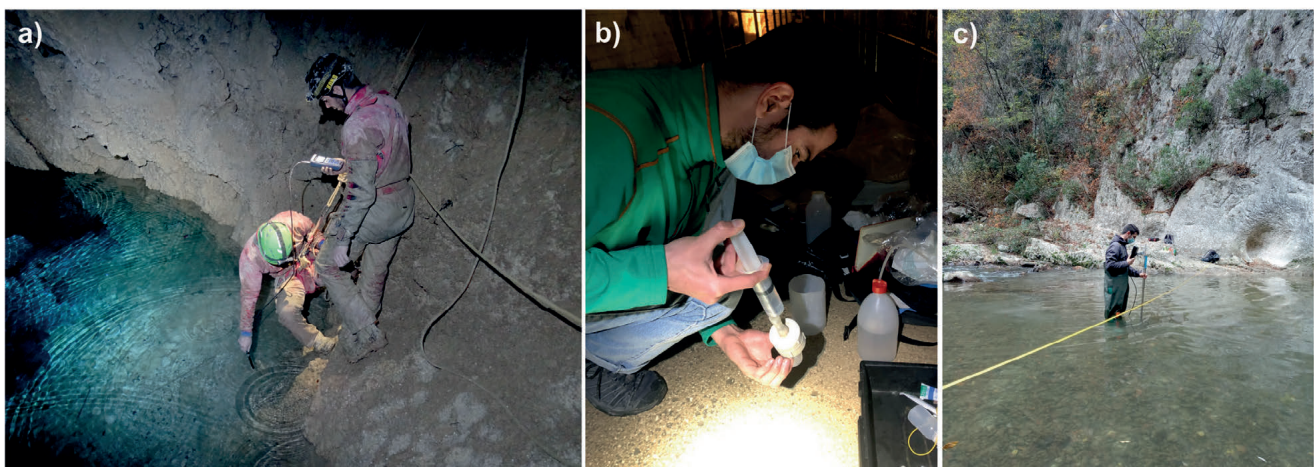


Fig. 4 - a) Measurement of EC in Lago dell’Orsa (LO); b) Filtering of dripping water in Abisso Ancona chamber AA); c) Discharge measurement on Sentino Stream in Ingresso Grotte section (S2).

Fig. 4 - a) Misura della conducibilità elettrica nel Lago dell’Orsa (LO); b) Filtraggio dell’acqua di stillicidio prelevata nella Sala Abisso Ancona (AA); c) Misura della portata del torrente Sentino nella sezione Ingresso Grotte (S2).

Equation 1 shows the tracer mass balance approach for determining groundwater inflow rates, particularly where the inflow is concentrated in discrete reaches of the river.

$$Q_{in} = \frac{Q_{dw} \cdot C_{dw} - Q_{up} \cdot C_{up}}{C_{in}} \quad (1)$$

Where:

- $Q_{in}$  = groundwater inflow rate ( $m^3/s$ );  
 $Q_{dw}$  = stream flow downstream ( $m^3/s$ );  
 $Q_{up}$  = stream flow upstream ( $m^3/s$ );  
 $C_{in}$  = groundwater concentration of tracer (mg/L);  
 $C_{dw}$  = concentration of tracer in the downstream water (mg/L);  
 $C_{up}$  = concentration of tracer in the upstream water (mg/L).

## Results and discussion

The results of geochemical analyses carried out in two different periods (November 2020, May and June 2021) are shown in Table 1.

Data in Table 1 were analysed to identify differences in water chemistry of samples collected within the karst complex. According to Galdenzi (2012), the main flow direction moves from NW-SE to N following the main tectonic lineament

(Figs. 2, 3), feeding the sulfidic springs ( $S_{s1}$ - $S_{s2}$ ) located in the north-eastern portion of the karst system. In addition, secondary flow direction follows the E-NE oriented fractures (Fig. 2). As shown in Table 1, the water electrical conductivity at the S3 section of the Sentino Stream is higher than that recorded at S1-S2 sites due to the contribution of sulfidic waters of  $S_{s1}$ - $S_{s2}$  springs. Between S2 and S3 sections, an increase of about 4-6 mg/L of  $SO_4$  content is registered due to the contribution of sulfidic springs.

Figure 5 shows the Langelier - Ludwig classification diagram, which identifies two distinct water types: Ca-Mg- $HCO_3$  water and Na-Cl- $SO_4$  water. Referring to Figure 3 for the location of the sampling sites, the Sentino Stream water (S1-S2-S3), dripping water (AA-SO) and the shallow part of lakes' water (LS-LSG-LO) belong to Ca-Mg- $HCO_3$  water. In contrast, waters of the sulfidic springs ( $S_{s1}$ - $S_{s2}$ ) and LV belong to Na-Cl- $SO_4$  water.

In the two periods considered, the geochemical characteristics of the sampled water were almost the same, except for Lake LG, that moved from the group of Ca-Cl- $SO_4$  water (November 2020) to the group of Na-Cl- $SO_4$  water (May-June 2021). Within the group of Na-Cl- $SO_4$  water, the sulfidic springs ( $S_{s1}$  and  $S_{s2}$ ) were distinguished from

Tab. 1 - Chemical-physical parameters of the sampled waters: T(°C); EC ( $\mu S/cm$ ); Eh (mV); Ion concentrations (mg/L).

Tab. 1 - Parametri chimico-fisici delle acque campionate: T(°C); EC ( $\mu S/cm$ ); Eh (mV); Concentrazioni ioniche (mg/L).

Sampling water	Site	ID	DATA	T	pH	EC	Eh	Ca	Mg	Na	K	$SO_4$	Cl	$HCO_3$	$NO_3$	F
Sentino Stream	Ponte Ariston	S1	14/11/2020	11.3	8.34	467	269.4	76.80	3.40	10.87	1.15	10.54	5.84	280.60	1.03	0.05
			10/05/2021	13.8	8.25	434	81.8	71.00	3.25	9.72	1.05	14.71	13.90	305.00	0.50	0.13
	Ingresso Grotte	S2	14/11/2020	12.1	8.45	456	137.1	75.60	3.28	10.77	1.18	18.34	13.17	257.40	0.98	0.13
			10/05/2021	17.5	8.38	430	104.9	72.00	3.24	10.28	1.00	14.58	14.54	309.88	0.01	0.13
	San Vittore	S3	14/11/2020	12.0	8.39	546	-195.1	77.80	4.12	24.96	1.71	23.80	35.17	279.40	1.98	0.14
			10/05/2021	15.2	8.34	488	-230.0	72.10	3.69	16.80	1.31	18.27	26.42	323.30	0.07	0.14
Sulfidic springs	Sorgente Libera	$S_{s1}$	19/11/2020	13.8	7.28	2170	-321.7	109.35	18.70	272.80	13.64	119.04	449.18	275.70	0.24	0.66
			10/05/2021	13.7	6.87	2190	-321.5	113.20	18.70	301.20	13.88	124.16	435.23	362.34	0.00	0.69
	Sorgente Briglia	$S_{s2}$	19/11/2020	13.7	7.27	2130	-363.3	108.20	18.40	278.40	13.24	118.30	438.57	278.20	0.23	0.59
			10/05/2021	13.5	7.25	2130	-330.2	111.20	18.08	328.80	13.12	120.60	408.36	368.44	0.05	0.72
Dripping	Abisso Ancona	AA	19/11/2020	14.1	8.23	457	178.2	75.10	2.05	12.96	0.20	3.94	25.55	256.20	0.28	0.40
			15/05/2021	13.9	8.02	462	45.0	74.20	2.03	14.28	3.53	4.08	29.15	305.00	0.11	0.40
	Sala dell'Orsa	SO	19/11/2020	13.8	7.61	420	211.5	71.80	1.53	8.19	0.04	2.52	17.56	244.00	0.25	0.88
			15/05/2021	13.6	7.56	431	57.8	73.90	1.55	8.36	0.29	2.77	18.13	317.20	0.00	0.96
Lakes	Lago Verde	LV	20/11/2020	14.1	7.18	2920	-332.9	127.20	26.00	386.40	21.12	186.90	653.50	280.60	0.00	0.75
			11/05/2021	14.1	7.22	3190	-359.0	134.20	31.64	447.00	28.04	210.38	698.53	411.14	0.16	0.84
	Lago dello Svizzero	LS	20/11/2020	14.1	7.18	2920	-332.9	127.20	26.00	386.40	21.12	186.90	653.50	280.60	0.00	0.75
			11/05/2021	13.2	7.11	475	-25.6	47.30	2.43	12.04	1.42	5.64	25.05	190.32	0.17	0.50
	Lago Sala Gentile	LSG	20/11/2020	14.2	7.97	372	196.3	58.30	2.98	17.48	1.20	7.30	32.50	174.50	8.64	0.27
			07/06/2021	14.3	8.10	379	60.5	49.60	3.21	17.74	2.05	7.50	31.81	195.20	8.38	0.28
	Lago dell'Orsa	LO	20/11/2020	14.2	8.04	420	155.0	50.40	3.64	23.16	1.27	10.77	40.37	178.10	1.04	0.57
			07/06/2021	13.9	7.88	502	87.5	55.60	3.77	33.16	1.96	15.10	53.36	219.60	0.76	0.62
	Lago Galleria	LG	20/11/2020	14.2	8.11	546	166.8	49.70	4.36	44.98	3.55	31.84	75.67	131.80	15.16	0.42
			07/06/2021	13.0	7.95	1223	146.8	72.00	9.16	137.20	8.89	77.09	212.10	183.00	11.39	0.54

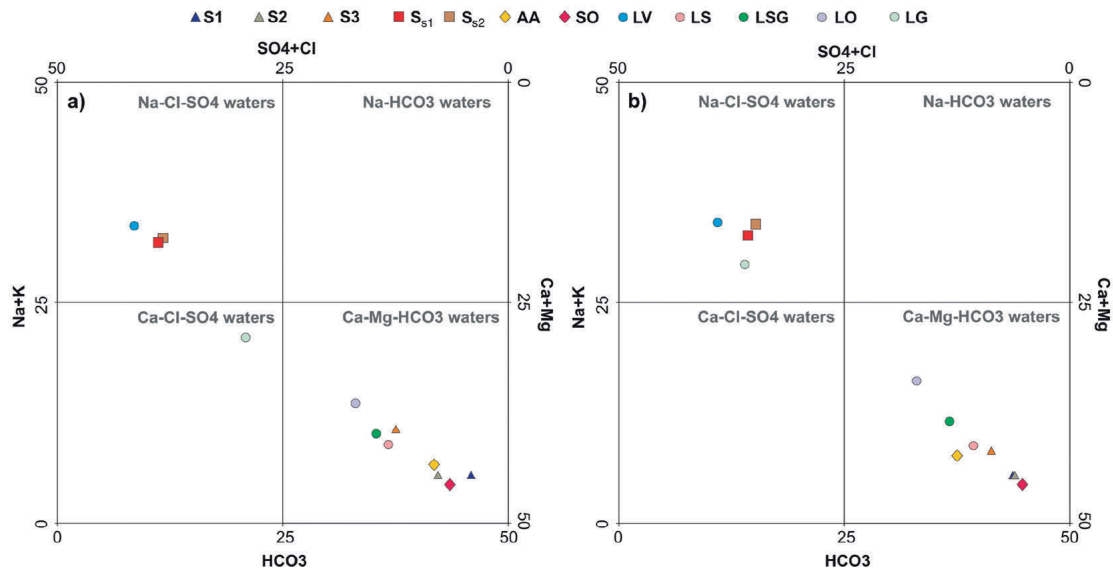


Fig. 5 - Langelier – Ludwig (L-L) compositional diagram: a) November 2020; b) May/June 2021.

Fig. 5 - Diagrammi classificativi di Langelier – Ludwig (L-L): a) Novembre 2020; b) Maggio/Giugno 2021.

LV, which is saltier. Figure 6 shows the mean electrical conductivity values (EC) recorded in the 2007 and 2020-2021 sampling periods. Marked similarity can be observed between the water of Sentino Stream (S1-S2-S3), the dripping water (AA and SO), and the surface water of LO, LSG, and LS lakes. On the contrary, the EC of the sulfidic springs (S<sub>s1</sub>-S<sub>s2</sub>) and LV lake is much higher. As reported by Cocchioni et al. (2003) and Galdenzi et al. (2008), the water of LV rises by means a deep feeder (sub-vertical karst conduit) from the deepest parts of the aquifer to the most shallow portion of the lake. This phenomenon occurs locally only in some part of the karst system due to the role of the fault systems (Galdenzi and Maruoka 2003). For example, the portion of the karst system hosting the LV lake developed along a joint system related to NW-SE and SW-NE oriented faults (Fig. 1).

For the LG lake, the EC values are between the two groups and show more significant variability.

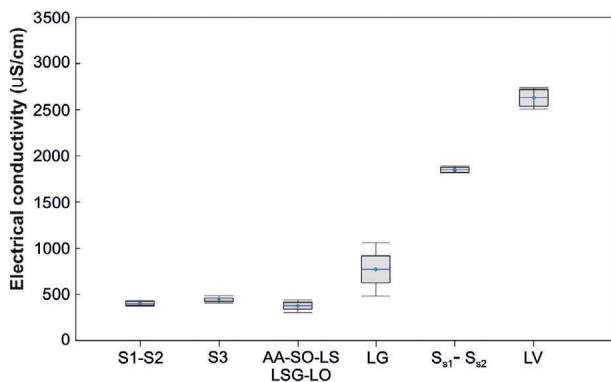


Fig. 6 - Boxplot graphs of the sampling sites based on data in Table 1 integrated with those presented by Baldoni et al. (2010) for May-December 2007.

Fig. 6 - Grafico boxplot dei siti di campionamento geochimico basato sui dati di Tabella 1 integrati con quelli di Maggio e Dicembre 2007 di Baldoni et al. (2010).

The results help to discuss the karst system processes, considering the results and interpretations coming from previous studies (Dragoni and Verdacchi 1993; Galdenzi 2001; Cocchioni et al. 2003; Baldoni et al. 2010).

The different chemical compositions of the analysed lakes surface water are related to the freshwater input responsible for the stratification and dilution phenomena on the free surface of the lakes. Freshwater was found at the top of lakes LO, LS and LSG. Due to their lower density, this water stratifies above the denser sulfidic water. Although the sampling was not carried out at different depths in the present work the water stratification in lakes has been well documented by Galdenzi (2001), Cocchioni et al. (2003), Mariani et al. (2007), and Galdenzi et al. (2008). In detail, Galdenzi (2001) reported thicknesses of freshwater in the inner areas of the karst system that can reach up to 5 m above the sulfidic water. Geochemical analyses on sulfidic water sampled in LO at a depth higher than 4.5 m has been carried out by Cocchioni et al. (2003) in September 2001. The results indicate an EC = 1413 µS/cm, which is lower than that of sulfidic springs (EC = 1859 µS/cm); thus, the latter is the result of mixing phenomena with saltier water.

Since the dripping waters (AA-SO) are characterised by electrical conductivity and chemical composition very similar to those of the stream water (S1-S2), it had not been possible until now to prove the origin of the freshwater responsible for the dilution and stratification of the water table. Due to the proximity of the stream to the karst system, several studies have hypothesized dilution phenomena of the sulfidic water due to the Sentino Stream water ingress into the karst aquifer (Gambelli et al. 1978; Tazioli et al. 1990; Ciancetti and Pennacchioni 1993; Dragoni and Verdacchi 1993; Caprari et al. 2001). This process has been hypothesized in the central-western portion of the Frasassi Gorge, where the stream level is higher than the piezometric surface of the

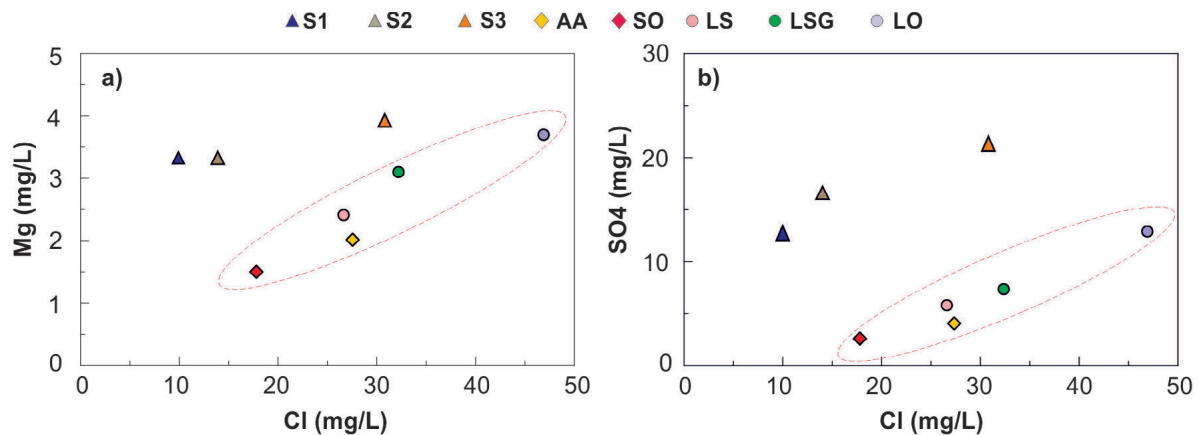


Fig. 7 - Cl-Mg (a) and Cl-SO<sub>4</sub> (b) relationships for Sentino Stream, dripping and surface water of the innermost underground lakes. S1, S2, S3 = stream sections; AA and SO = dripping water; LS, LSG and LO = shallow part of inner lakes' water.

Fig. 7 - Diagrammi Cl-Mg (a) e Cl-SO<sub>4</sub> (b) delle acque del T. Sentino, di stillicidio e della superficie dei laghi interni. S1, S2, S3 = sezioni fluviali; AA e SO = acque di stillicidio; LS, LSG e LO = acque dei laghi interni nella parte più superficiale.

aquifer. In the latest studies (Galdenzi et al. 2008; Galdenzi and Campagnoli 2015), thanks to the installation of data loggers to measure potentiometric surface in some lakes (e.g., LV and LG), new hypotheses of dilution produced by dripping have been proposed. By studying a flood event of Sentino Stream in July 2008, Galdenzi and Campagnoli (2015) highlighted that stream level and discharge variations directly affect groundwater levels only in the outermost parts of the karst complex close to the stream. The geochemical data obtained in our study allow to better understand the role of dripping water in the dilution processes of sulfidic water in the different lakes (see Table 1). Based on the Cl-Mg and Cl-SO<sub>4</sub> relationships (Fig. 7), a close correlation is observed between the dripping water (AA-SO) and those of the LS-LSG-LO, whose points tend to align on a straight line. On the contrary, points belonging to the Sentino Stream do not fall on this line (Fig. 7). Findings of Figure 7 indicate the presence of a dilution process of sulfidic water by dripping water, confirming the hypothesis of Cocchioni et al. (2003), Baldoni et al. (2010) and Galdenzi et al. (2008). In other

words, geochemical analyses strengthen the hypothesis that stream-aquifer interactions do not propagate to the inner parts of the system.

Locally, due to possible differences in the hydraulic head, there is an increase in mineralization of the surface waters of some lakes, regardless of seasonality. The accumulation of infiltration waters in some lakes is responsible for siphoning phenomena that produce the rise of saltier waters towards neighbouring lakes; the EC water documents this for LG Lake, which moves towards the Na-Cl-SO<sub>4</sub> waters (e.g., May-June 2021 campaign, Fig. 5).

Figure 8 shows the Cl-Mg and Cl-SO<sub>4</sub> relationships for all the lakes and springs investigated. As the figure shows all the data points align along a straight line. It is interesting to point out as the sulfidic springs show both Cl-Mg and Cl-SO<sub>4</sub> values which fall between those of LV and LS-LO-LSG-LG, suggesting water mixing phenomena, especially occurring in the north-east portion of the karst aquifer just upstream of the springs (e.g., due to the contribution of very salty water of LV lake area).

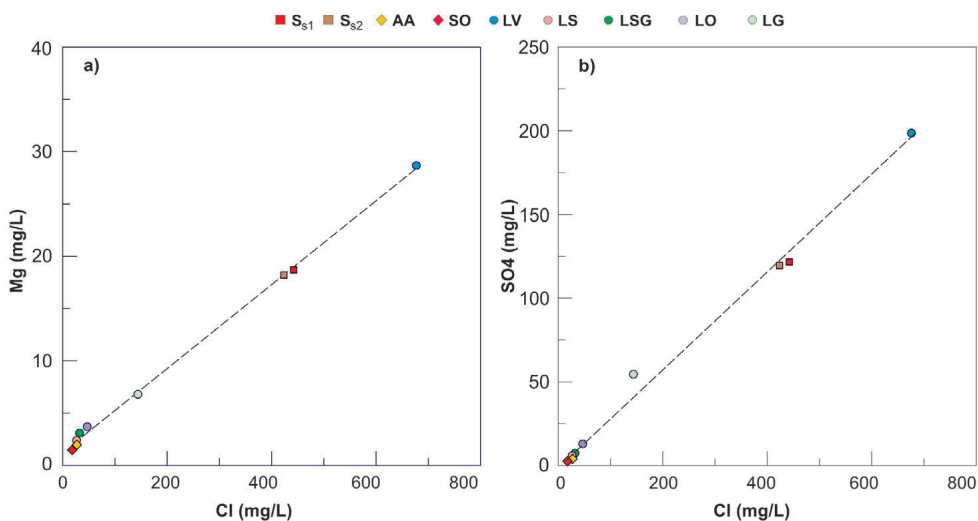


Fig. 8 - Cl-Mg (a) and Cl-SO<sub>4</sub> (b) relationships for all the lakes and springs investigated. S<sub>s1</sub> and S<sub>s2</sub> = sulfidic springs; AA and SO = dripping water; LV, LS, LSG, LO, and LG = shallow part of lakes' water.

Fig. 8 - Diagrammi Cl-Mg (a) e Cl-SO<sub>4</sub> (b) delle acque di tutti i laghi del sistema carsico e delle sorgenti sulfuree. S<sub>s1</sub> e S<sub>s2</sub> = sorgenti sulfuree; AA e SO = acque di stillicidio; LV, LS, LSG, LO e LG = acque dei laghi interni nella parte più superficiale.



Tab. 2 - Sulfidic springs discharge  $Q$  ( $S_{s1}$ - $S_{s2}$ ) estimated with chloride and sodium ion concentrations and Sentino Stream discharge measured in sections S2 and S3.

Tab. 2 - Portate delle sorgenti solfuree ( $S_{s1}$ - $S_{s2}$ ) stimate con le concentrazioni dello ione cloro e sodio e con le portate del torrente Sentino misurate nelle sezioni S2 e S3.

Period	Q S2 (L/s)	Q S3 (L/s)	Cl <sup>-</sup> S2 (mg/L)	Cl <sup>-</sup> S3 (mg/L)	Cl <sup>-</sup> $S_{s1}$ and $S_{s2}$ (mg/L)	Q $S_{s1}$ and $S_{s2}$ (L/s)
Nov 2020	959.4±11.5	1139.0±11	13.17	35.17	443.5	61.8±0.6
Jun 2021	449.7±6.0	478.6±5.0	14.54	26.42	421.5	14.5±0.1
Period	Q S2 (L/s)	Q S3 (L/s)	Na <sup>+</sup> S2 (mg/L)	Na <sup>+</sup> S3 (mg/L)	Na <sup>+</sup> $S_{s1}$ and $S_{s2}$ (mg/L)	Q $S_{s1}$ and $S_{s2}$ (L/s)
Nov 2020	959.4±11.5	1139.0±11	10.77	24.96	275.6	65.2±0.6
Jun 2021	449.7±6.0	478.6±5.0	10.28	16.80	315.0	10.8±0.1

Thanks to the tracer mass balance (eq. 1), using the Cl<sup>-</sup> and Na<sup>+</sup> concentrations and discharge data (downstream and upstream of the springs) it has been possible to evaluate the discharge of the sulfidic springs ( $S_{s1}$ - $S_{s2}$ ). Table 2 summarises the results of the mass balance analyses considering the uncertainty related to each discharge value: it should be noted that in the two observation periods, the discharge at section S3 is higher than S2, with very close values in June 2021. For both investigation periods, the spring discharge estimations give similar results using both Cl<sup>-</sup> and Na<sup>+</sup> tracers. Due to the slight difference in Mg<sup>2+</sup> concentration between the two river sections (0.84 mg/L) and the karst aquifer's lithological characteristics, this tracer has not been used to compute spring discharge. Although the discharge data of sulfidic springs estimated by the mass balance method are obtained only on two periods, the values presented increase the knowledge on the groundwater inflow to the Sentino Stream by the karst aquifer. Previous studies carried out using the tracer mass balance method reported 50 L/s in winter 1990 (Dragoni and Verdacchi 1993) and about 40 L/s in December 2007 (Baldoni et al 2010).

## Conclusions

The present study updated the knowledge of the groundwater circulation in the Fiume-Vento karst system, focusing on the phenomena of dilution and stratification of the high salinity sulfidic aquifer. The results presented allow us to make robust hypotheses on the possible origin of the water responsible for the dilution. The geochemical analyses on samples collected both outside and inside the caves, in two different periods, have permitted to establish the origin of the dilution water in the dripping waters. The oxygen carried by dripping water is indispensable for the oxidation of H<sub>2</sub>S (coming from the deepest parts of the aquifer), allowing the development of the sulfuric acid speleogenesis (Galdenzi and Maruoka 2003). The lens of bicarbonate water stratified above the sulfidic ones prevents H<sub>2</sub>S exhalations and, therefore, corrosive actions in an aerated environment in large sectors of the karst system, including the touristic part. These new interpretations seem to exclude, in the present hydrodynamic conditions, water contributions from the Sentino Stream to the aquifer, except locally and near the outermost portions of the karst system, only during very intense floods.

By integrating the geochemical analyses with discharge measurements upstream and downstream of the springs, the groundwater inflow to the Sentino Stream (sulfidic springs), evaluated on two periods (November 2020 and May-June 2021), ranges between about 65 and 11 L/s. These results, although preliminary, indicate that it is possible to have a reliable evaluation of the discharge of the Fiume-Vento karst system, especially considering that there is no quantitative monitoring system for both the stream and the karstic springs. The results presented in this study may help understand groundwater circulation and dilution phenomena in other karst systems characterised by SAS-type speleogenesis.

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## Competing interest

The authors declare no competing interest.

## Author contributions

Collection of data, Nicolini R, Baldoni F, Valigi D; data processing, Nicolini R, Di Matteo L, Valigi D; interpretation of results, Nicolini R, Di Matteo L, Valigi D, Galdenzi S, Frondini F; writing-original draft preparation, Nicolini R, Di Matteo L, Valigi D; writing-review and editing, Nicolini R, Di Matteo L, Galdenzi S, Baldoni F, Frondini F, Valigi D; visualization, Nicolini R, Di Matteo L, Galdenzi S; supervision, Valigi D. All authors have read and agreed to the published version of the manuscript.

## Additional information

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## REFERENCES

- Atkinson AP, Cartwright I, Gilfedder BS, Hofmann H, Unland NP, Cendon DI, Chisari R (2015) A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry. *Hydrological Processes* 29(1):1-12. <https://doi.org/10.1002/hyp.10122>.
- Baldoni F, Cardellini C, Cambi C, Di Matteo L, Frondini F, Valigi D (2010) Contributo alla conoscenza della circolazione idrica del sistema carsico di Valmontagnana-Frasassi (Italia centrale). Atti "VIII Convegno Nazionale dei Giovani Ricercatori di Geologia Applicata". "Contribution to the knowledge of the water circulation of Valmontagnana-Frasassi karstic system (Central Italy)". *Proceedings "VIII National Congress of Young Researchers in Applied Geology"*, 18-19 February 2010, Perugia, Italy, 4-6.
- Bocchini A, Coltorti M (1990) Il complesso carsico Grotta del Fiume Grotta Grande del Vento e l'evoluzione geomorfologica della Gola di Frasassi. "The karstic complex Grotta del Fiume Grotta Grande del Vento and the geomorphological evolution of the Frasassi Gorge". *Mem. Ist. It. Speleol.* 2(4):155-180. Available from: [https://www.researchgate.net/publication/253644244\\_Il\\_complesso\\_carsico\\_Grotta\\_del\\_Fiume\\_-\\_Grotta\\_Grande\\_del\\_Vento\\_e\\_l%27evoluzione\\_geomorfologica\\_della\\_gola\\_di\\_Frasassi\\_Appennino\\_umbromarchigiano#fullTextFileContent](https://www.researchgate.net/publication/253644244_Il_complesso_carsico_Grotta_del_Fiume_-_Grotta_Grande_del_Vento_e_l%27evoluzione_geomorfologica_della_gola_di_Frasassi_Appennino_umbromarchigiano#fullTextFileContent) - last accessed 10/06/2022.
- Bohme D (2011) Evaluation of brine discharge to rivers and streams: Methodology of rapid impact assessment. *Limnologica* 41(2):80-89. <https://doi.org/10.1016/j.limno.2010.08.003>.
- Cambi C, Valigi D, Di Matteo L (2010) Hydrogeological study of data-scarce limestone massifs: the case of Gualdo Tadino and Monte Cucco structures (central Apennines, Italy). *Bollettino di Geofisica Teorica ed Applicata* 51(4):345-360. Available from: [https://www.researchgate.net/publication/255963847\\_Hydrogeological\\_study\\_of\\_data-scarce\\_limestone\\_massifs\\_The\\_case\\_of\\_Gualdo\\_Tadino\\_and\\_Monte\\_Cucco\\_structures\\_central\\_Apennines\\_Italy#fullTextFileContent](https://www.researchgate.net/publication/255963847_Hydrogeological_study_of_data-scarce_limestone_massifs_The_case_of_Gualdo_Tadino_and_Monte_Cucco_structures_central_Apennines_Italy#fullTextFileContent) - last accessed 10/06/2022.
- Caprari M, Galdenzi S, Nanni T, Ramazzotti S, Vivalda P (2001) La sorgente di Gorgovivo. Analisi idrogeologica finalizzata all'individuazione della zona di tutela, rispetto e protezione: dati preliminari. "The Gorgovivo spring. Hydrogeological analysis aimed at identifying the area of protection, respect and protection: preliminary data". *Mem. Soc. Geol. It.* 56:157-169. Available from: [https://www.researchgate.net/publication/32887372\\_CAPRARI\\_M\\_GALDENZI\\_S\\_NANNI\\_T\\_RAMAZZOTTI\\_S\\_VIVALDA\\_P\\_2001\\_-\\_La\\_sorgente\\_di\\_Gorgovivo\\_analisi\\_idrogeologica\\_finalizzata\\_all%27individuazione\\_delle\\_zone\\_di\\_tutela\\_rispetto\\_e\\_protezione\\_Dati\\_preliminari\\_Mem#fullTextFileContent](https://www.researchgate.net/publication/32887372_CAPRARI_M_GALDENZI_S_NANNI_T_RAMAZZOTTI_S_VIVALDA_P_2001_-_La_sorgente_di_Gorgovivo_analisi_idrogeologica_finalizzata_all%27individuazione_delle_zone_di_tutela_rispetto_e_protezione_Dati_preliminari_Mem#fullTextFileContent) - last accessed 10/06/2022.
- Centamore E, Catenacci V, Chiocchini M, Chiocchini U, Jacobacci A, Martelli G, Micarelli A, Valletta M (1975) Note Illustrative della Carta Geologica d'Italia alla scala 1:50.000, Foglio 291, Pergola. "Explanatory Notes of the Geological Map of Italy at the scale of 1:50,000 (291), *Serv. Geol. d'It. Roma*".
- Ciancetti GF, Pennacchioni E (1993) Idrologia superficiale ed alimentazione della falda dell'area carsica di Frasassi. "Surface hydrology and groundwater supply of the Frasassi karst area". *Geologia Applicata ed Idrogeologia* 28:285-293.
- Cocchioni M, Galdenzi S, Amici V, Morichetti L, Nacciarriti L (2003) Studio idrochimico delle acque nelle Grotte di Frasassi. "Hydrochemical study of the waters in the Frasassi Caves". *Le Grotte d'Italia* 4:49-61.
- D'Angeli IM, Parise M, Vattano M, Madonia G, Galdenzi S, De Waele J (2019) Sulfuric acid caves of Italy: A review. *Geomorphology*, 333:105-122. <https://doi.org/10.1016/j.geomorph.2019.02.025>.
- D'Angeli IM, Nagostinis M, Carbone C, Bernasconi SM, Polyak VJ, Peters L, De Waele J (2019) Sulfuric acid speleogenesis in the Majella Massif (Abruzzo, Central Apennines, Italy). *Geomorphology* 333:167-179. <https://doi.org/10.1016/j.geomorph.2019.02.036>.
- D'Angeli IM, De Waele J, Fiorucci A, Vigna B, Bernasconi SM, Florea LJ, Parise M (2021) Idrogeologia e geochimica delle sorgenti sulfuree carsiche di Santa Cesarea Terme (Puglia, Italia meridionale). "Hydrogeology and geochemistry of the sulfur karst springs at Santa Cesarea Terme (Apulia, southern Italy)". *Hydrogeology Journal* 29(1):481-498. <https://doi.org/10.1007/s10040-020-02275-y>.
- De Filippi FM, Iacurto S, Grelle G, Sappa G (2021) Magnesium as Environmental Tracer for Karst Spring Baseflow/Overflow Assessment-A Case Study of the Pertuso Karst Spring (Latium Region, Italy). *Water* 13(1):93. <https://doi.org/10.3390/w13010093>.
- De Waele J, Galdenzi S, Madonia G, Menichetti M, Parise M, Piccini L, Sanna L, Sauro F, Tognini P, Vattano M, Vigna B (2014) A review on hypogene caves in Italy. In: Klimchouk A, Sasowsky I, Mylroie J, Engel SA, Engel AS (Eds.) *Hypo-gene Cave Morphologies*. Karst Waters Institute Special Publication 18. Leesburg, Virginia.
- De Waele J, Audra P, Madonia G, Vattano M, Plan L, d'Angeli IM, Nobécourt JC (2016) Sulfuric acid speleogenesis (SAS) close to the water table: examples from southern France, Austria, and Sicily. *Geomorphology* 253:452-467. <http://dx.doi.org/10.1016/j.geomorph.2015.10.019>.
- Di Matteo L, Menegon S, Rossi A, Liti S (2016) Understanding karst environments by thermo-hygrometric monitoring: preliminary results from the Cesi Mountain karst system (Central Italy). *Italian Journal of Groundwater* 5(1):25-32. <https://doi.org/10.7343/as-2016-197>.
- Dragoni W, Verdacchi A (1993) First results from the monitoring system of the Karstic complex "Grotte di Frasassi-Grotta Grande del Vento" (Central Apennines, Italy). *IAHS Publ* 207:107-117.
- Galdenzi S (1990a) Litostratigrafia giurassica e speleogenesi nella struttura di Frasassi. "Jurassic lithostratigraphy and speleogenesis in the structure of Frasassi". *Mem. Ist. It. Spel.* 2:53-64.
- Galdenzi S (1990b) Un modello genetico per la Grotta Grande del Vento. "A genetic model for the Grotta Grande del Vento". *Mem. Ist. It. Spel.* 2:123-142. Available from: [https://www.researchgate.net/publication/281994204\\_Un\\_modello\\_genetico\\_per\\_la\\_Grotta\\_Grande\\_del\\_Vento](https://www.researchgate.net/publication/281994204_Un_modello_genetico_per_la_Grotta_Grande_del_Vento) - last accessed 9/06/2022.
- Galdenzi S, Menichetti M (1995) Occurrence of hypogene caves in a karst region: examples from central Italy. *Environmental Geology* 26:39-47. <https://doi.org/10.1007/BF00776030>.
- Galdenzi S, Menichetti M, Forti P (1997) La corrosione di placchette calcaree ad opera di acque sulfuree: dati sperimentali in ambiente ipogeo. "Corrosion of limestone tablets by sulfidic waters: experimental data in a hypogeous environment. Proceedings 12th International Congress of Speleology, 10-17 August 1997", Le Chaux-de-Fonds, Switzerland, 1:187-190. Available from: [https://www.researchgate.net/publication/284582678\\_La\\_corrosione\\_di\\_placchette\\_calcaree\\_ad\\_opera\\_di\\_acque\\_sulfuree\\_Dati\\_sperimentali\\_in\\_ambiente\\_ipogeo](https://www.researchgate.net/publication/284582678_La_corrosione_di_placchette_calcaree_ad_opera_di_acque_sulfuree_Dati_sperimentali_in_ambiente_ipogeo) - last accessed 10/06/2022.
- Galdenzi S (2001) L'azione morfogenetica delle acque sulfuree nelle Grotte di Frasassi, Acquasanta Terme (Appennino marchigiano - Italia) e di Movile (Dobrogea - Romania). "The morphogenetic action of sulfidic waters in the Frasassi, Acquasanta Terme (Marche Apennines - Italy) and Movile (Dobrogea - Romania) caves". *Le Grotte d'Italia* 2:49-61. Available from: [https://www.researchgate.net/publication/284026363\\_L%27azione\\_morfogenetica\\_delle\\_acque\\_sulfuree\\_nelle\\_Grotte\\_di\\_Frasassi\\_Acquasanta\\_Terme\\_Appennino\\_marchigiano-Italia\\_e\\_di\\_Movile\\_Dobrogea-Romania](https://www.researchgate.net/publication/284026363_L%27azione_morfogenetica_delle_acque_sulfuree_nelle_Grotte_di_Frasassi_Acquasanta_Terme_Appennino_marchigiano-Italia_e_di_Movile_Dobrogea-Romania) - last accessed 10/06/2022.
- Galdenzi S, Maruoka T (2003) Gypsum deposits in Frasassi Caves, central Italy. *Journal of Cave and Karst Studies* 65(2):111-125. Available from: <https://caves.org/pub/journal/PDF/V65/v65n2-Galdenzi.pdf> - last accessed 10/06/2022.
- Galdenzi S (2004) Il carsismo nella regione Marchigiana. "The karst in the Marche region". In: Galdenzi S (Ed.) *Frasassi 1989-2004: gli sviluppi nella ricerca. Frasassi 1989-2004: Developments in Research* 6-20. Available from: [https://www.researchgate.net/publication/319314276\\_Il\\_carsismo\\_nella\\_regione\\_marchigiana](https://www.researchgate.net/publication/319314276_Il_carsismo_nella_regione_marchigiana) - last accessed 10/06/2022.

- Galdenzi S, Cocchioni M, Morichetti L, Amici V, Scuri S (2008) Sulfidic ground-water chemistry in the Frasassi Caves, Italy. *Journal of Cave and Karst Studies* 70(2):94-107. Available from: <https://digital.lib.usf.edu/content/SF/S0/05/24/97/00001/K26-02048-cave-70-02-94.pdf> - last accessed 10/06/2022.
- Galdenzi S (2012) Corrosion of limestone tablets in sulfidic ground-water: measurements and speleogenetic implications. *International Journal of Speleology* 41(2):3. <http://dx.doi.org/10.5038/1827-806X.41.2.3>.
- Galdenzi S, Campagnoli A (2015) Piano quotato dell'acquifero carsico di Frasassi. "Datum of the Frasassi karst aquifer". Proceedings of the XXII National Congress of Speleology, 30 May-2 June 2015, Pertosa-Auletta (SA), Italia.
- Gambelli G, Recchioni R, Santolini C (1978) Complesso carsico del Monte Valmontagnana. "Monte Valmontagnana karstic complex". Preprints XIII National Congress of Speleology, 30 September-4 October 1978, Perugia, Italy.
- Jones DS, Polerecky L, Galdenzi S, Dempsey BA, Macalady JL (2015) Fate of sulfide in the Frasassi cave system and implications for sulfuric acid speleogenesis. *Chemical Geology* 410:21-27. <https://doi.org/10.1016/j.chemgeo.2015.06.002>.
- Klimchouk A (2009) Morphogenesis of hypogenic caves. *Geomorphology* 106(1-2):100-117. <https://doi.org/10.1016/j.geomorph.2008.09.013>.
- Laurent D, Durllet C, Barré G, Sorriaux P, Audra P, Cartigny P, Gaucher EC (2021) Epigenic vs. hypogenic speleogenesis governed by H<sub>2</sub>S/CO<sub>2</sub> hydrothermal input and Quaternary icefield dynamics (NE French Pyrenees). *Geomorphology* 387:107769. <https://doi.org/10.1016/j.geomorph.2021.107769>.
- Mariani S, Mainiero M, Barchi M, Van Der Borg K, Vohnhof H, Montanari A (2007) Use of speleologic data to evaluate Holocene uplifting and tilting: an example from the Frasassi anticline (northeastern Apennines, Italy). *Earth and Planetary Science Letters* 257(1-2):313-328. <https://doi.org/10.1016/j.epsl.2007.02.045>.
- Menichetti M (2013) Karst processes and carbon flux in the Frasassi Caves, Italy. Proceedings of the 16<sup>th</sup> International Congress of Speleology, July 21-28, Brno, Czech Republic, 3:376-378. Available from: [https://www.speleogenesis.info/directory/karstbase/pdf/seka\\_pdf13456.pdf](https://www.speleogenesis.info/directory/karstbase/pdf/seka_pdf13456.pdf) - last accessed 8/06/2022.
- Palmer AN (2011) Distinction between epigenic and hypogenic maze caves. *Geomorphology* 134(1-2):9-22. <https://doi.org/10.1016/j.geomorph.2011.03.014>.
- Piccini L, Forti P, Giulivo I, Mecchia M (2007) The polygenetic caves of Cuatro Ciénegas (Coahuila, Mexico): morphology and speleogenesis. *International Journal of Speleology* 36(2):83-92. <http://dx.doi.org/10.5038/1827-806X.36.2.4>.
- Sappa G, Ferranti F, De Filippi FM, Cardillo G (2017) Mg<sup>2+</sup>-based method for the Pertuso spring discharge evaluation. *Water* 9(1):67. <https://doi.org/doi:10.3390/w9010067>.
- Tazioli GS, Coltorti M, Dramis F, Cocchioni M, Mariani M (1990) Circolazione idrica e chimismo delle acque sotterranee dell'area carsica di Frasassi nelle Marche. "Water circulation and chemistry of the groundwater of the Frasassi karst area in the Marche region". *Mem. Ist. It. Spel.* 4(2):93-108.
- Tazioli A, Palpacelli S (2013) Scelta del tracciante ideale per indagini idrogeologiche: risultati preliminari da test in laboratorio. "Choosing of the appropriate tracer for hydrogeological investigations: preliminary results from laboratory testing". *Italian Journal of Groundwater* 59-64. <http://dx.doi.org/10.7343/AS-021-13-0000>.
- Vattano M, Madonia G, Audra P, D'Angeli IM, Galli E, Bigot JY, De Waele J (2017) An Overview of the Hypogene Caves of Sicily. In: Klimchouk A, N. Palmer A, De Waele J, S Auler A, Audra P (eds) *Hypogene Karst Regions and Caves of the World. Cave and Karst Systems of the World*. Springer, Cham. [https://doi.org/10.1007/978-3-319-53348-3\\_12](https://doi.org/10.1007/978-3-319-53348-3_12).