DOI: https://doi.org/10.3986/ac.v52i2-3.13149


# GROUNDWATER DILUTION AND FLOW CONDITIONS IN SULFURIC ACID CAVES: THE CASE STUDY OF FRASASSI (ITALY).

# MEŠANJE PODZEMNE IN POVRŠINSKE VODE TER POGOJI PRETAKANJA V JAMAH Z ŽVEPLOVO KISLINO: PRIMER JAMSKEGA SISTEMA FRASASSI (ITALIJA)

Sandro GALDENZİ[1]

**Abstract** UDC 551.442:546.221.1(450.571)

***Sandro Galdenzi: Groundwater dilution and flow conditions in sulfuric acid caves: the case study of Frasassi (Italy)***

This study analyzes the dilution process of the sulfidic groundwater in the Frasassi caves due to the recharge of $O_2$-rich freshwater and its influence on the sulfuric acid speleogenesis and morphogenesis. The drainage pattern and the seasonal changes of the chemo-physical characteristics of the groundwater through a year-long monitoring and the measurements of the groundwater levels are presented. The inflow of water infiltrating from the karst surface influenced the sulfidic groundwater parameters, reflecting the seasonal meteoric cycle. On the contrary, the Sentino River, which represents the local base level, directly influenced the groundwater only in the most external part of the cave. The water level measurements evidenced a low hydraulic gradient (~3‰), due to the high karstification, and also some differences in the permeability depending on the drainage direction. Most cave pools are isolated on the surface and connected to each other through a network of submerged passages. In the present conditions, a surface layer of bicarbonate water forms above the sulfidic water in a large part of the cave, where it impedes subaerial corrosion by released acidic gases. Conversely, the distribution of residual gypsum deposits and corrosional wall features in the upper old cave levels demonstrate that large interfaces between sulfidic water and cave atmosphere existed during some periods of the cave history. Here, the release of acidic gases ($CO_2$ and $H_2S$) and the production of $H_2SO_4$ from $H_2S$ oxidation caused the widespread subaerial corrosion which significantly contributed to the morphogenesis. The comparison between these residual morphologies and the active processes shows that morphogenesis in the cave has evolved through time, influenced by hydrodynamic conditions, in turn depending on the general morphological and hydrogeological setting of the whole karst area.

**Key words:** sulfuric acid speleogenesis, hypogenic caves, sulfidic groundwater, Frasassi caves, central Apennines.

**Izvleček** UDK 551.442:546.221.1(450.571)

***Sandro Galdenzi: Mešanje podzemne in površinske vode ter pogoji pretakanja v jamah z žveplovo kislino: primer jamskega sistema Frasassi (Italija)***

Študija analizira proces mešanja sulfidne podzemne vode in sveže infiltrirane vode bogate s kisikom v jamskem sistemu Frasassi in vpliv mešanja na hipogeno speleogenezo in morfogenezo zaradi delovanja žveplove kisline. Predstavljene so sezonske značilnosti pretakanja ter kemijsko-fizikalne lastnosti podzemne vode na osnovi celoletnega vzorčenja ter zveznih meritev nivojev, temperature in električne prevodnosti podzemne vode. Dotok vode, ki pronica s kraškega površja, vpliva na sestavo sulfidne parametre podzemne vode, pri čemer se izraža sezonski cikel meteornih voda. Nasprotno pa reka Sentino, ki predstavlja lokalno erozijsko bazo, neposredno vpliva na podzemno vodo le v najbolj zunanjem delu jame. Meritve vodostaja so pokazale nizek hidravlični gradient (~3 ‰) zaradi močne zakraselosti in nekatere razlike v prepustnosti glede na smer toka vode. Večina jamskih bazenov je na površju izoliranih, med seboj pa so povezani z mrežo potopljenih rovov. V sedanjih razmerah se nad sulfidno vodo tvori plast bikarbonatne vode, ki preprečuje stik sulfidne vode z zrakom in korozijo sten zaradi sproščenih kislih plinov. Nasprotno pa ostanki sadre in korozijske oblike sten v zgornjih starih jamskih nivojih kažejo, da so v preteklosti obstajale velike mejne površine med sulfidno vodo in jamsko atmosfero. Tu sta sproščanje kislih plinov ($CO_2$ in $H_2S$) in nastajanje $H_2SO_4$ pri oksidaciji $H_2S$ povzročila razširjeno površinsko raztapljanje, ki je pomembno prispevalo k morfogenezi jamskih sten. Primerjava med rezidualnimi jamskimi oblikami in aktivnimi procesi kaže, da se je morfogeneza v jami skozi čas razvijala pod vplivom hidrodinamičnih razmer, te pa so bile odvisne od morfoloških in hidrogeoloških pogojev v širšem kraškem območju.

**Ključne besede**: speleogeneza žveplove kisline, hipogene jame, podzemna voda s sulfidi, jame Frasassi, Centralni Apenini.

[1] Geology Division, School of Science and Technology, University of Camerino, Italy, e-mail: sandro.galdenzi@unicam.it

Prejeto/Received: 12. 7. 2023

# 1. INTRODUCTION

In the last decades, many cave systems were related to the upward flow of deep-seated fluids coming from depth. These caves were defined as hypogenic (Palmer, 2000; Klimchouk, 2007) and an increasing number of examples are reported globally (Klimchouk et al., 2017, with references therein). Hydrogen sulfide ($H_2S$) bearing fluids represent one of the most common causes of aggressiveness in the carbonate rocks, in particular where rising fluids interact with the oxygen present in the atmosphere or dissolved in the groundwater, producing sulfuric acid. This process, sulfuric acid speleogenesis (SAS), is involved in the development of some of the world's largest caves, as in the Guadalupe Mountains of New Mexico, USA (Hill, 2000; Jagnow et al., 2000; Palmer, 2007).

The sulfuric acid production and limestone dissolution can proceed in the phreatic zone, but the release of acidic gases produces significant corrosion also in the cave atmosphere. Rims of replacement gypsum typically form as a consequence of the oxidation of $H_2S$ to sulfuric acid on moist cave walls and ceilings. The role of the SAS in the cave development is recognized in a continuously increasing number of cave systems (Galdenzi & Menichetti, 1985; Klimchouk et al., 2017; D'Angeli et al., 2019). Sulfuric acid caves have many subaerial and subaqueous morphologies common to those of the other hypogene caves (Audra et al., 2009; Palmer, 2013; De Waele et al., 2016;) and often host gypsum deposits (Galdenzi & Maruoka, 2003; 2019).

Experimental studies have also tried to quantify the importance of sulfuric acid corrosion above and below the water table through the results of chemical analyses (Engel et al., 2004, Jones et al., 2015) or by quantifying the weight loss of limestone tablets fixed in the Frasassi caves (Galdenzi et al., 1997; Galdenzi, 2012). The dissolution values show rates up to 68-119 mm $ka^{-1}$ for non-turbulent water and similar maximum values for subaerial corrosion. These researches highlighted the importance of sulfide concentration and flow conditions (Galdenzi, 2012; Jones et al., 2015).

The Frasassi caves offer an extraordinary opportunity to access the groundwater surface in many different points from the lower branches, where active processes are presently occurring in different conditions. Furthermore, active SAS processes can be compared to the relict features and deposits in the upper levels within the same large cave system. The present research aims to analyze the present flow conditions in the cave in order to discuss their possible influence on the morphogenetic processes, in the present condition and during the cave history.

# 2. BACKGROUND

## 2.1 GEOLOGICAL SETTING

The object of this study is a cave system located in the Frasassi Gorge (12°57'E, 43°24'N), a 500 m deep canyon incised by the Sentino River in the Northern Apennines, Italy (Figure 1). The area has a mountainous landscape (maximum elevation ~1000 m) and the climate is subcontinental, with an annual average temperature of ~13 °C, rainfall of ~1000 mm $y^{-1}$ and quite dry summer seasons.

The gorge cuts a cross section inside a small northeastern verging anticline (Figure 2) which involves the Umbria Marche Meso-Cenozoic carbonate succession (Centamore et al., 1975; Deiana, 2009). At the core of the fold the steep walls expose over 500 m of pure Lower Jurassic limestone (Calcare Massiccio), deposited in an epicontinental carbonate platform.

In the area, the Calcare Massiccio is overlain by the Bugarone Fm, a 60 m thick Jurassic unit comprising limestones, marls and cherts, which represents an aquitard, and by a 200 m thick Lower Cretaceous permeable cherty limestone (Maiolica). These two limestone units are in hydraulic continuity due to a tectonic contact in the eastern limb of the anticline and form a single hydrostructure with sulfidic groundwater (Figure 2). A 30 m thick Lower Cretaceous marl Group. (Marne a Fucoidi) represents the local aquiclude which influences the recharge area and the spring location at the outlet of the gorge (Nicolini et al., 2022). Above this unit, the carbonate succession is completed by cherty limestone and marls of Upper Cretaceous and Tertiary age, non involved in the described karst processes. Downward, the Mesozoic succession includes a thick Upper Triassic evaporitic Formation, not cropping out in the region, consisting mainly of anhydrite and dolomite (Anelli et al., 1994).

The tectonic uplift of the region, interfering with the Pleistocene climate changes, produced an alternation of downcutting and gravel overfilling in the valley (Coltorti & Dramis, 1995; Nesci et al., 2012) that influenced the

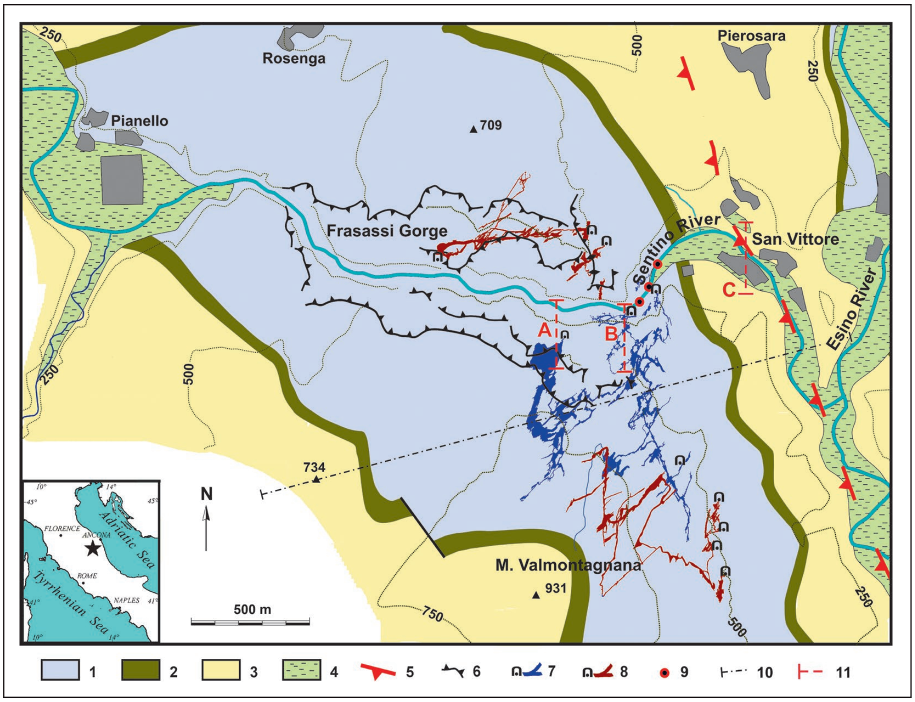


**Figure 1:** *Simplified geo-lithological map of the Frasassi karst area. Legend: 1) Jurassic and Lower Cretaceous limestone; 2) Upper Cretaceous marl; 3) Upper Cretaceous and Cenozoic limestone and marl; 4) Pleistocene alluvial deposits; 5) thrust, presumed or buried; 6) escarpment edge; 7) lower caves (with entrances); 8) upper caves (with entrances); 9) sulfidic springs (in 2023); 10) geological cross section of Figure 2; 11) schematic sections of Figure 6.*

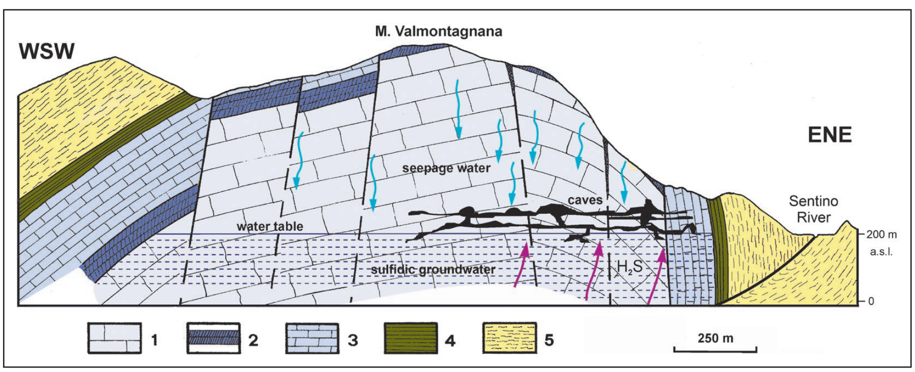


*Figure 2: Geological cross section, modified after Cocchioni et al., 2003. Legend: 1) Calcare Massiccio; 2) Bugarone Group (aquitard); 3) Maiolica; 4) Marne a Fucoidi (aquiclude); 5) Upper Cretaceous and Cenozoic limestone and marl.*

height of the water table and the development of the cave on sub-horizontal levels (Cattuto, 1976; Bocchini & Coltorti, 1990).

### 2.2 THE CAVE SYSTEM

The caves develop mainly in the core and the eastern limb of the fold in the Calcare Massiccio and subordinately in the Maiolica (Figure 2). They consist of a network of ramified, mainly sub-horizontal passages, distributed on superimposed and interconnected levels. A single large cave complex comprising Grotta del Fiume, Grotta Grande del Vento, Grotta Sulfurea and Grotta Bella extends south of the gorge on two main levels at 225 and 250 m a.s.l., near the present local base level represented by the Sentino River, at 200 m a.s.l. (Figure 1). These levels developed in a hydrogeological setting similar to the present one, following the progressive incision of the river valley during the Middle and Late Pleistocene, as confirmed by correlation with the surface terraced deposits (Bocchini & Coltorti, 1990) and by uranium series dating (Taddeucci et al., 1992). In some periods, probably during the pauses in the deepening of the valley, the river water carried sediments mainly silt-clayey, but also some sands, inside the cave. More ancient cave levels are present at higher elevations, up to 500 m a.s.l. (Figure 1).

Solutional processes responsible for the cave development reached the highest rate close to the water table, where the supply of oxygen from the infiltrating meteoric water and cave atmosphere enhances the redox processes (Galdenzi, 1990). The largest passages and some isolated domes developed along old water table levels, with coexisting subaerial and subaqueous corrosional features (Galdenzi, 1990; Galdenzi & Maruoka, 2003). Here, the release of $H_2S$ to the cave atmosphere and its oxidation on the limestone walls formed rims of replacement

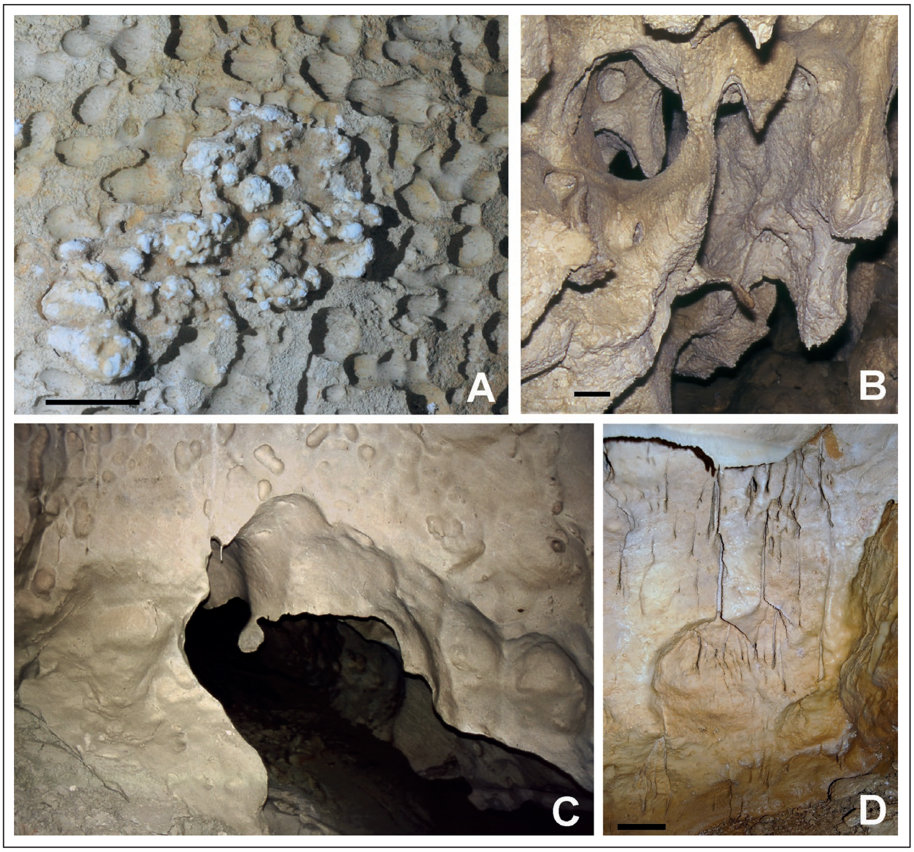


**Figure 3:** *Wall morphologies produced by sulfuric acid speleogenesis (scale bars ~10 cm). Subaerial: A) replacement gypsum growing from pockets on the limestone surface; subacqueous: B) spongework corrosion of the rock; C) smoothed walls with cupolas and pendants (pendant size ~30 cm); D) rills produced by ascending fluids from a half cupola (Photos: S. Galdenzi).*

gypsum and, together with the high $CO_2$ levels, acted to enlarge walls and ceilings (Figure 3A).

In the shallow phreatic zone the ascending flow of sulfidic water created wide shafts and articulated systems of small passages, often with an irregular looping profile and smoothed surfaces, rounded pendant, blades, and spongework (Figures 3B and 3C). Grooves and channels produced by rising aggressive fluids (Figure 3D) can be dominant in some locations (Galdenzi, 2019). These systems of small phreatic passages generally interconnect the large water table passages or represent their feeder conduits.

### 2.3 GROUNDWATER

The sulfidic water emerges mainly from cave passages located on the shores of the river, but also from alluvial gravel in the riverbed or, locally, directly from the bedrock. The location of springs in detail underwent small shifts due to the changes in the river bed over time. Perrone (1911) reported an average spring discharge of 27 L $s^{-1}$, measurements which can no longer be repeated as most water is presently rising along the riversides or directly in the riverbed. A more recent evaluation with a chemical method provided values between about 11 and 65 L $s^{-1}$, respectively in May-June 2021 and November 2020 (Nicolini et al., 2022).

Tazioli et al. (1990) suggested a meteoric origin for the sulfidic groundwater, with a recharge area at the elevation of 600-1000 m in the neighboring reliefs and a brief residence time to the aquifer, based on $\delta^{18}O$, $\delta^{2}H$, and tritium content. They also suspected the contribution of river water sunk at the entrance of the gorge to the sulfidic groundwater circulation, reporting a 10% loss of discharge from the river itself. However, subsequent measurements did not confirm a loss of discharge in the river (Ciancetti & Pennacchioni, 1993; Caprari et al., 2001; Baldoni, 2007; Nicolini et al., 2022). Baldoni (2007) also noted that the correlation lines for $\delta^{2}H$ and $\delta^{18}O$ proposed at Frasassi by Tazioli et al. (1990) differ significantly from those obtained in the Apennines (Celico, 1984; Longinelli & Selmo, 2003) and calculated that the average altitude of the recharge area varies between 458 and 612 m a.s.l. in the different outcropping Formations.

The groundwater chemistry of the Frasassi cave system is well known (Tazioli et al., 1990; Sighinolfi, 1990; Cocchioni et al., 2003; Galdenzi et al., 2008). The sulfidic water is not thermal (~13°C) with salinity values (up to 2 g $L^{-1}$) higher than the bicarbonate water infiltrating from the karst surface (Figure 4). It is enriched in sodium and chloride, and contains sulfate and hydrogen sulfide, probably derived from the interaction with the underlying Triassic anhydrite formation (Anelli et al., 1994).

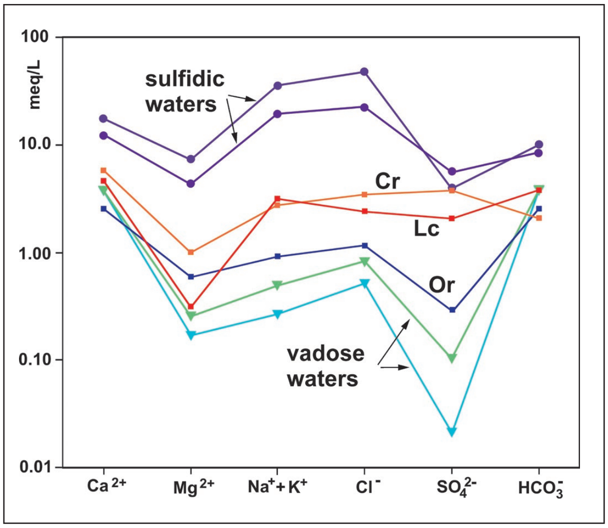


*Figure 4: Schoeller diagram for the cave water (Data from Cocchioni et al., 2003). For sulfidic and vadose water, lines representative of the composition range are reported. Intermediate-water samples were taken in Pozzo dei Cristalli (Cr), Laghi di Lucia (Lc), Lago dell'Orsa (Or).*

The composition of sulfidic groundwater varies seasonally as a result of the direct infiltration of surface meteoric water into the karst system (Galdenzi et al., 2008). In the Lago Verde and nearby pools, the ionic concentration is higher and the seasonal dilution is only weak as they are probably fed more directly from a deeper zone of the aquifer (Galdenzi et al., 2008). Compared to the water chemistry of these pools, the spring water would be influenced by a further contribution of freshwater that varies seasonally between 30% and 60% (Galdenzi et al., 2008).

A surface layer of water with bicarbonate or intermediate composition forms in many cave pools near the water table due to its lower salinity (Galdenzi et al., 2008). The surface layer thickness ranges from a few dm up to 5 m in different places. The ion ratios show that these surface layers are recharged by seepage water from the karst surface rather than from the river (Nicolini et al., 2022). Where $H_2S$-rich water directly emerges at the water table, it may form anoxic and microoxic streams and lakes with dissolved sulfide concentrations up to 650 μM.

## 3. METHODS

The research integrates a large-scale analysis of the distribution of subaerial and subaqueous morphotypes in the cave, based on direct field observation, with the measurements of the characteristics and absolute levels of the groundwater.

The local flow conditions were verified in over 30 groundwater pools. Typical characteristics, such as sulfide smell, microbial mats, oxidized or reduced deposits, made it possible to recognize bicarbonate or sulfidic groundwater at the surface. In the presence of stratified groundwater, direct depth measurements and *in situ* conductivity tests, where necessary, helped to define the thickness of the upper layer of bicarbonate water.

In order to know the absolute groundwater level in the cave, with the essential support of the speleological team, we selected ten stations distributed inside the cave area and three outside the cave, in the riverbed. The stations were equipped with small metal plates from which it was possible to directly measure the water level with a plumb line or phreatimeter. We measured the elevation of these stations using a theodolite and a hydraulic level, and standardized the values with respect to a height zero, located at the main spring (Figure 5). We made simultaneous water level measurements at all stations in December 2006 and June 2009. In the spring area, we performed a detailed survey of other cave pools with the hydraulic level during June 2007, in a period of absolutely

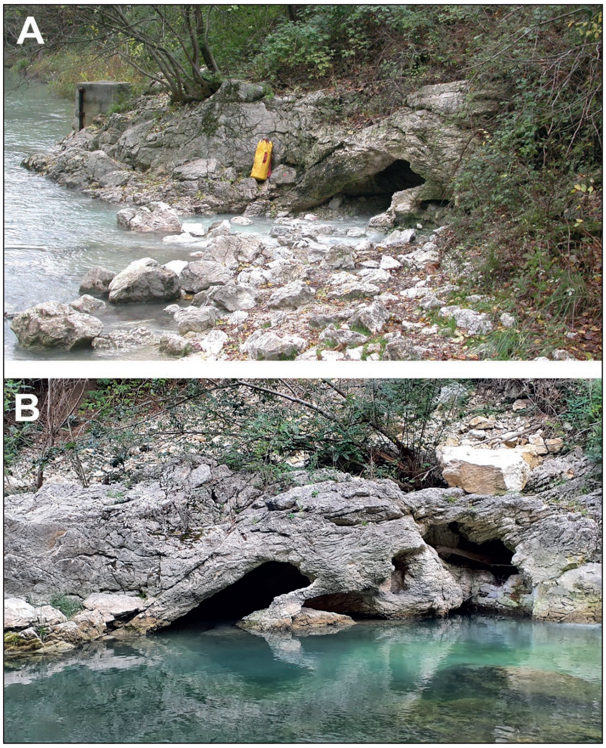


*Figure 5: A) The main spring during the research (2006-2010). The height zero corresponded to the river level in low flow conditions. B) The same place in 2023, after two major floods modified the river profile.*

stable water level which ensured the comparability of the measurements.

We used the hydraulic digital level (Ziplevel) to join the cave stations and the water pools to the preexisting closed survey line, already measured with a theodolite (Topcon, mod. GTS-229 – Angle measurement accuracy: 9"; distance accuracy: ± 3 mm + 3‰ measure) by a speleologist team led by Alfredo Campagnoli (personal communication). The accuracy of the digital level was 0.2 mm for measurements <1 m, 2‰ for measurements <3 m, 3.5‰ for measurements between 3 and 6 m in height. Owing to the number of readings for each traverse, the uncertainty of height values of most stations was lower than ± 25 cm and increased up to ± 44 cm in the longest traverse, which required 44 reading. Repetition of the survey in some traverses provided differences in height slightly higher than those calculated analytically. Along the river, we used the same theodolite already employed for the cave survey.

After the preliminary field analysis, six crucial cave pools representative of different conditions and the river station were equipped with the remote loggers for water level, temperature and electric conductivity (Eijkelkamp, Netherlands. Accuracy: ± 0.5 cm; ± 0.1 °C; ± 1% of conductivity reading). The acquisition interval was set at one hour, and the monitoring continued from November 2007 to December 2008. Monitoring of a cave pool was repeated from December 2009 to July 2010 to assess vertical changes of the water characteristics. The recorded levels were corrected for barometric pressure changes, measured by an independent logger placed near the cave entrance. The water parameters were then related to meteoric precipitation in the nearby station of Colleponi.

## 4. CAVE HYDROLOGY

### 4.1 CAVE MORPHOLOGY AND DRAINING STRUCTURE

The cave can be roughly divided into two sectors according to partly different morphology and structure, the south-western and north-eastern sector. The southwestern sector develops in the core of the mountain, over 500 m below the subaerial karst surface. Here, the morphologies produced by SAS are generally well preserved, with

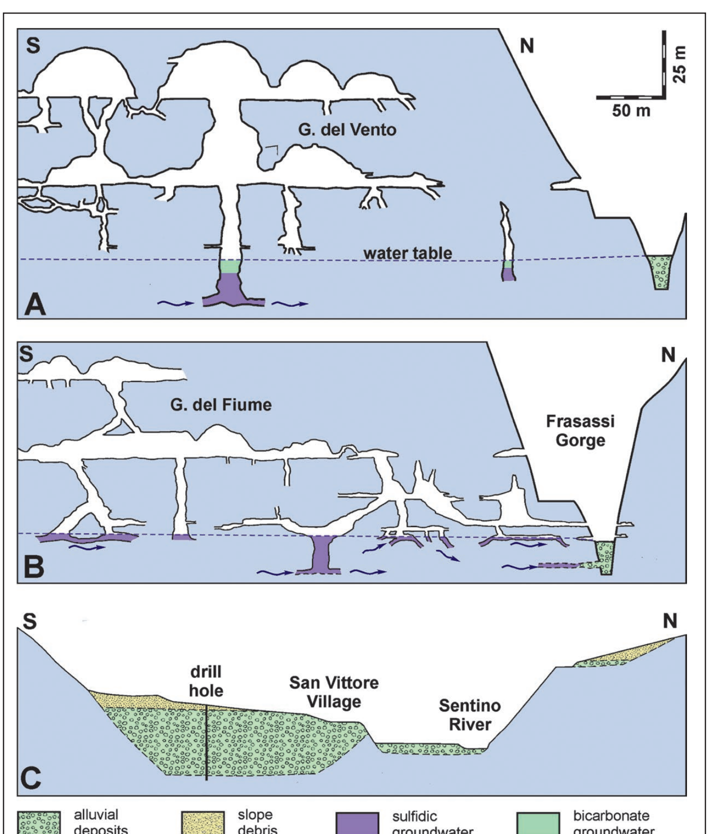


*Figure 6: Sketches of the cave structure. The projected schematic cave profiles are exaggerated in vertical. Location as shown in Figure 1. A) Schematic section of the Vento cave area; B) Schematic section of the Fiume cave and spring area; C) Section of the continental deposits in the San Vittore village, ~500 m downstream of the sulfidic springs and karstified limestone.*

minor subsequent changes due to corrosive or depositional action of descending vadose water (Figure 6A). The northeastern sector is more directly exposed to the inflow of meteoric water from the surface, which also carried allochthonous gravel during periglacial periods (Bocchini & Coltorti, 1990). In this area, some minor cave levels extend between the water table and the overstaying main cave level at 225 m (Figure 6B).

The groundwater can be reached at the end of descending passages or directly at the bottom of shafts. Only in the north-eastern cave region an evident flow occurs in small pools and short streams (Figure 7). These are the only places where intense active subaerial SAS is presently occurring. In the remaining part of the cave the water surface is stagnant and stratification phenomena can often be observed in the same pool (Figure 8). The non-sulfidic layer of water at the groundwater surface is present in most cave sectors. It has an important morphogenetic effect, as it prevents degassing towards the cave atmosphere and consequently the possibility of subaerial SAS. In the few pools with stagnant sulfidic water subaerial SAS processes are weak or completely absent.

Most of the pools with stagnant water are isolated from each other, but a well-developed draining system ensures connections below the groundwater surface (Figures 6A and 6B). Underwater exploration discovered wide sub-horizontal passages at the bottom of a subaqueous shaft in the Sala dell'Orsa pools group (Figure 8A). In this water body, a clearly perceptible movement of the sulfidic water was felt at a depth of more than 10 m below the water surface, beneath a 4.5 m thick stagnant layer of bicarbonate water. A wide system of submerged passages developing for many hundreds of meters was also explored in the inner cave sectors (Mariani, personal communication).

Submerged stalagmites, located at up to 4.3 m below the present water surface in the Sala dell'Orsa pools group, prove that karstification had proceeded in subaerial condition before the water level raised. These low

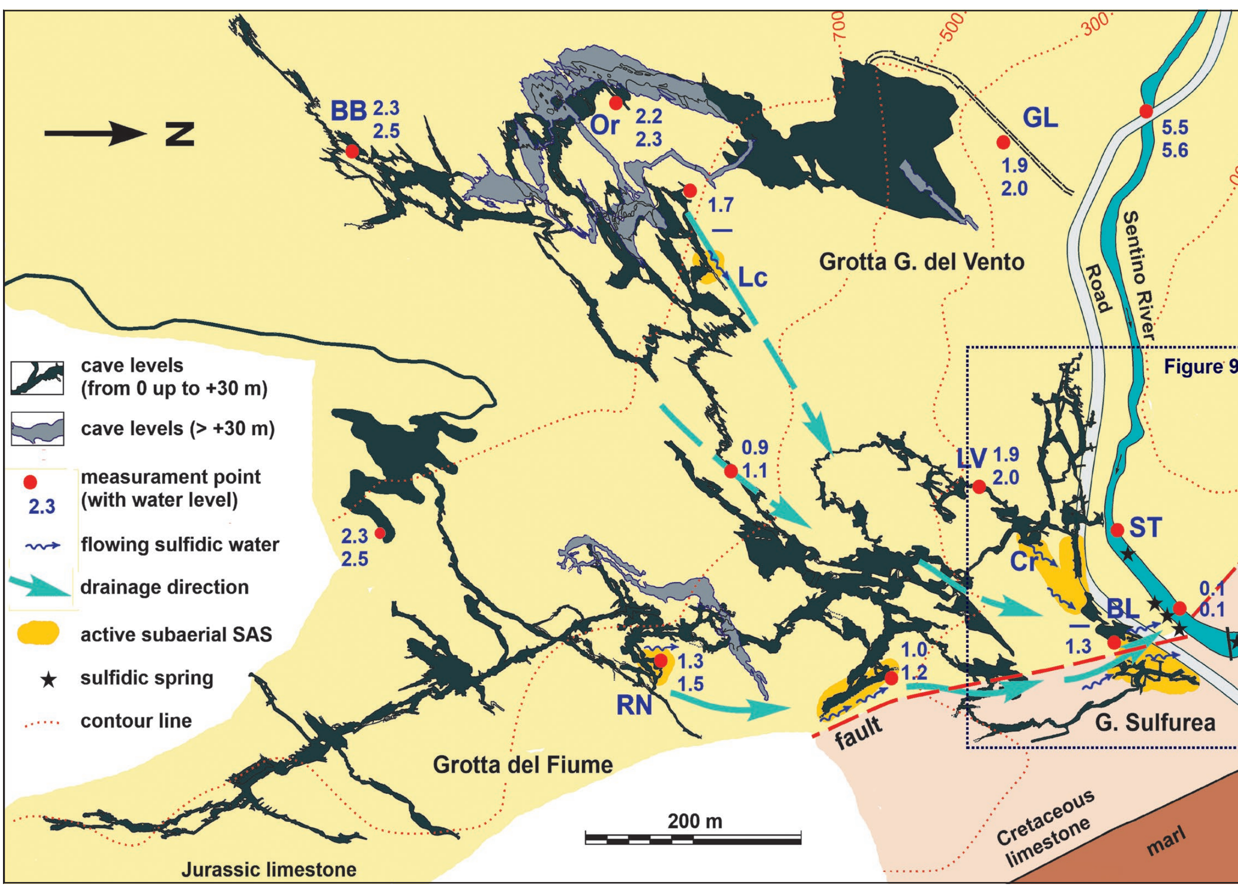


*Figure 7 : Hydrological map of the Fiume-Vento cave system at Frasassi. All the heights are expressed in meters and referred to to the river level in low flow conditions at the main spring. The reported water levels were measured in December 2006 (above) and June 2009 (below). Monitoring stations: BB) Budellone Basso; BL) Grotta Bella; GL) Lago Galleria; LV) Lago Verde; RN) Lago del Rinoceronte. Other cited sites: Cr) Pozzo dei Cristalli; Lc) Laghi di Lucia; Or) Orsa lakes. Cave map drawn from surveys of the Speleological groups of FSM (Speleological Federation of the Marche region).*

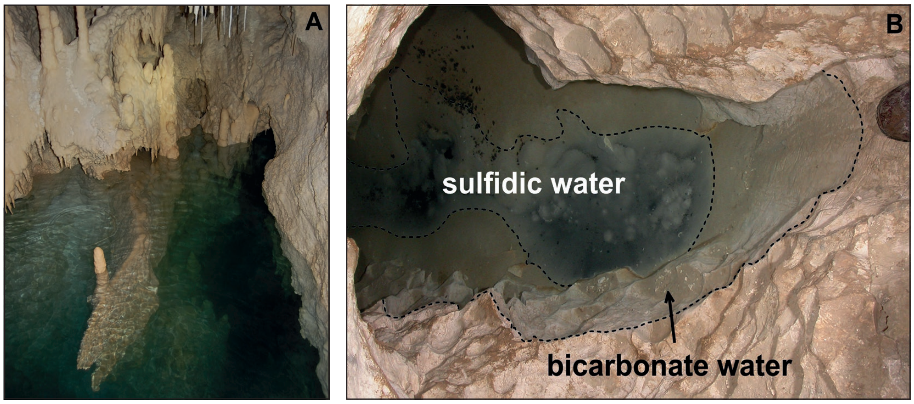


*Figure 8: Cave pools with stratified groundwater. A) Grotta Grande del Vento. One of the pools of the Orsa lakes, accessible only through vertical shafts. The interface between bicarbonate and sulfidic water lies 4.5 m below the surface. Note the submerged dripstones, well preserved in the bicarbonate water up to 4.30 m depth. B) Grotta del Fiume, Pozzo dei Cristalli. Stratified water in a small pool. Note the boot on the right for scale (Photos: S. Galdenzi).*

water table levels are the result of the river entrenchment below the present valley surface. The results of borehole explorations performed for geotechnical purposes confirm the existence of a buried paleovalley bottom ~8 m below the present river bed in the San Vittore village, 500 m downstream from the Frasassi cave system (Figure 6C).

### 4.2 THE ABSOLUTE GROUNDWATER LEVELS

The groundwater measurements performed in the cave pools evidence small altitude differences that never exceeded a few meters. The water level increases moving inwards with a low hydraulic gradient (~3‰), and the highest values were measured in the south-western sector (Figure 7).

The groundwater level in the entire spring area is higher than that of the Sentino River. However, the altimetric relationships between the water levels of the cave and river abruptly reverse, since the slope of the riverbed is ~10‰ (Figure 9). As a consequence, upstream of the entrance to Grotta del Fiume, the riverbed remains permanently above the water table and the gradient between the river and the cave water increases, reaching 25‰ at the GL pool (Figure 7).

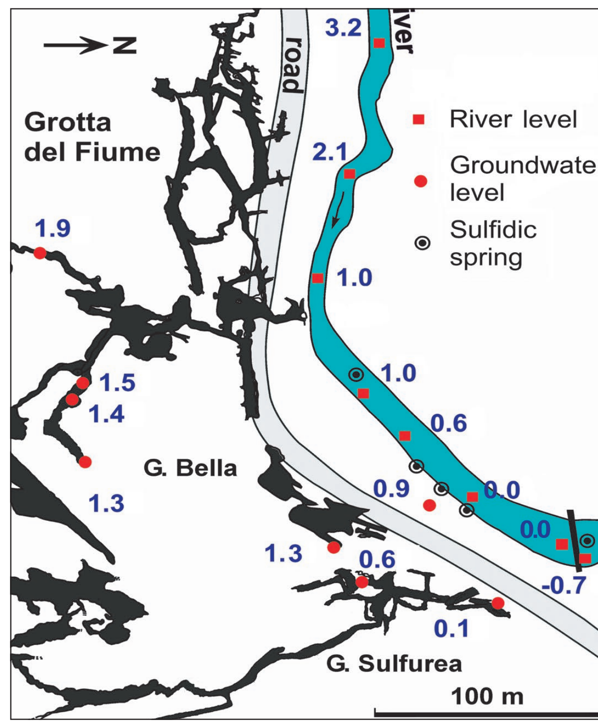


*Figure 9: Detail on the groundwater levels documented in the spring zone (June 2007).*

## 5 THE WATER MONITORING

### 5.1 THE MONITORING STATIONS

Six monitoring stations (Table 1) were selected in the river and throughout the cave to be representative of different draining conditions (Figure 7). Along the Sentino River, a logger was placed in front of the entrance of Grotta del Fiume (ST). Inside the cave, two loggers were placed in flowing sulfidic water: Grotta Bella (BL), near the spring, and Lago del Rinoceronte (RN). Both the places are affected by $H_2S$ degassing which causes active production of slushy gypsum on the walls due to limestone replacement. The BL station is very close to the outside and represents a non-turbulent outflow stream for groundwater towards the river. The other loggers were placed in different types of stagnant pools: i) Lago Verde (LV), that consists of two interconnected sulfidic pools with only weak subaerial SAS; these pools are fed

*Table 1: The monitoring sites.*

| Locality | water dynamic | water type | label | water level | temperature | conductivity |
|---|---|---|---|---|---|---|
| Sentino River | flow | freshwater | ST | X | X | |
| Grotta Bella | flow | sulfidic | BL | X | X | X |
| Lago Verde | stagnant | low-diluted sulfidic | LV | X | X | X |
| Lago della Galleria | stagnant | sulfidic, with surface bicarbonate layer | GL | X | X | |
| Lago del Rinoceronte | flow | sulfidic | RN | X | X | X |
| Budellone Basso | stagnant | sulfidic, thin surface bicarbonate layer | BB | X | X | X |

through a subaqueous shaft by low-diluted sulfidic water coming from a deeper zone of the aquifer (Galdenzi et al., 2008); ii) Lago Galleria (GL), with a surface layer of bicarbonate water; iii) Budellone Basso (BB), with stagnant sulfidic water beneath a few centimeters of mixed bicarbonate water and no subaerial SAS.

The LV pool was chosen to repeat measurements at different depths in 2010. One logger was placed in ~2 m depth, while another remained permanently at ~20 cm below the water surface, attached to a float free to move along a vertical cable. For comparison, the general groundwater characteristics were recorded in the BL stream.

### 5.2 ANNUAL DILUTION CYCLES

The monitoring data evidenced the seasonal cycles (Figure 10), with minor differences in each cave pool due to local factors. The first monitoring period was dry and

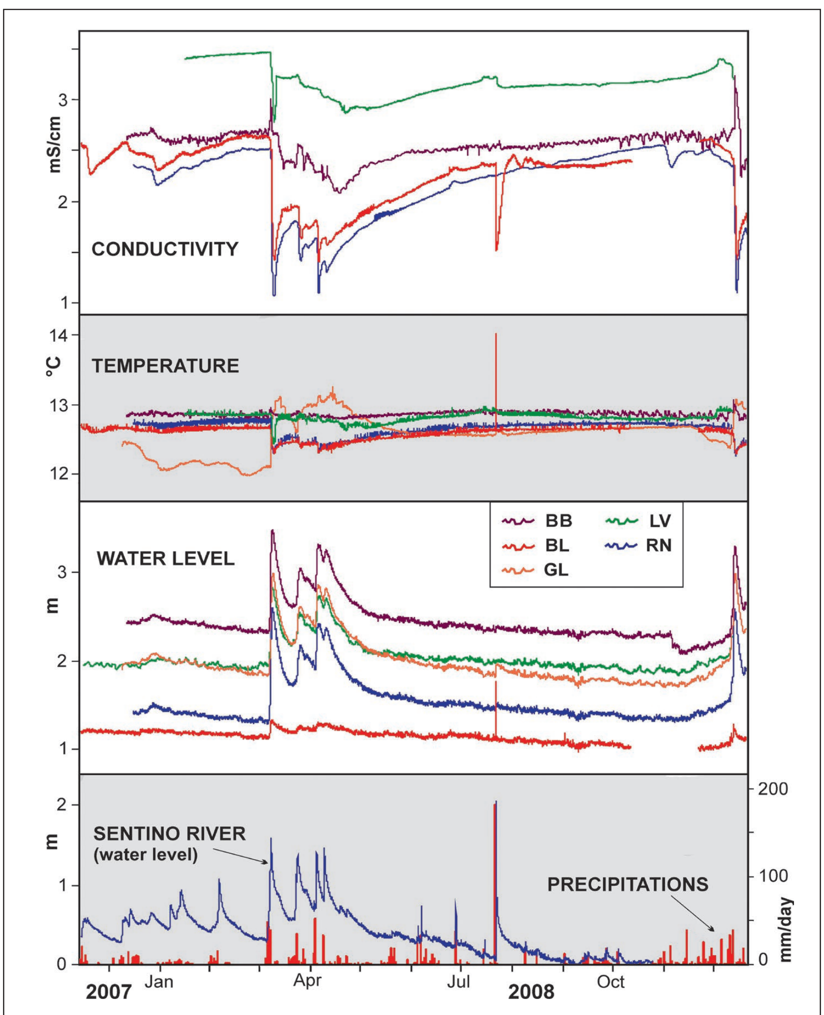


*Figure 10: The hydrographs of the monitored cave pools related to precipitations and water level in the Sentino River. All water levels are referred to the river level in low flow conditions at the main spring. Note the high values of water conductivity in the Lago Verde (LV), fed by low diluted sulfidic groundwater. Legend: BB) Budellone Basso; BL) Grotta Bella; GL) Lago Galleria; LV) Lago Verde; RN) Lago del Rinoceronte.*

high discharge conditions occurred only from March 2008, after significant seasonal precipitation. After the summer dry season, high discharge recurred in December 2008, at the end of the monitoring period. Outside the wet season, precipitations capable of impacting the river discharge had minor or insignificant effects on the groundwater parameters (Figure 10).

The water levels responded to meteoric events simultaneously in all the pools, with almost the same magnitude and timing (Figure 10). The water level increased up to +130 cm during floods, less than reported in previous monitoring periods (i.e. +150 cm, Galdenzi et al., 2008). Only in the BL station, the fluctuation of the water level had a smaller amplitude, less than 40 cm, excluding the peak of 22 July 2008.

The electric conductivity showed an overall opposite trend compared to the water level, as decreasing values were influenced by the meteoric water recharge. Excluding the exceptional event of 22 July 2008, the conductivity of flowing water in the BL and RN stations maintained a very similar trend, well related with water level fluctuations. The conductivity varied from 0.56 up to 2.06 mS cm$^{-1}$ in the RN station. Meanwhile, the BL station close to the spring displayed slightly higher values, from 0.91 up to 2.17 mS cm$^{-1}$. Previous chemistry analysis showed similar differences (Galdenzi et al., 2008).

The conductivity of the stagnant water had more stable values and was less influenced by freshwater dilution. Also, the relationship with water level fluctuations is less evident. The deep sourced sulfidic water of the LV had higher values, from 2.28 and 2.97 mS cm$^{-1}$. The BB showed lower conductivity values, from 1.58 to 2.23 mS cm$^{-1}$, with temporary increases occurring at the beginning of dilution events (Figure 10).

The temperature followed the seasonal trend of the conductivity in the flowing water of the BL and RN stations, varying between 12.5 °C and 13.6 °C, with the lowest values under high discharge conditions. The temperature showed more stable and slightly higher values in the stagnant water of the LV and BB stations. It can be noted that the LV temperature, after the first input of cold water, progressively decreased until the end of the high discharge period (Figure 10). In the GL pool, the temperature maintained lower values for much longer than in all other pools. A fast increase of ~1 °C occurred at the beginning of high discharge periods.

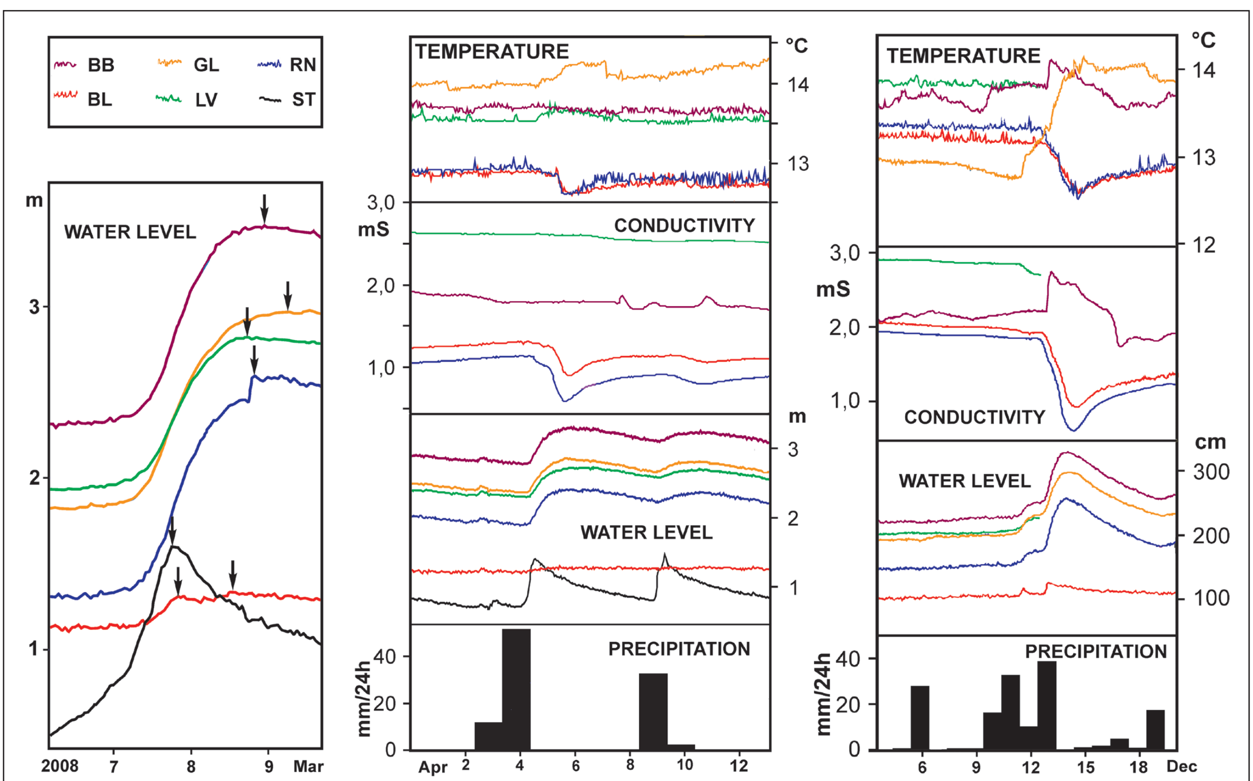


*Figure 11: Detail of hydrographs after flood events. March (left): detail of a flood timing. The arrows mark the delay between the maximum water level in the river and in the cave. April (center): the effect of rain events on the groundwater parameters in high discharge conditions. December (right): these sharp changes represent the beginning of the recharge period, at the end of the 2008 dry season. This last event occurred at the end of the monitoring, when two loggers (LV and Sentino River) had already been retrieved. Legend: BB) Budellone Basso; BL) Grotta Bella; GL) Lago Galleria; LV) Lago Verde; RN) Lago del Rinoceronte; ST) Sentino River.*

### 5.3 THE MAIN METEORIC EVENTS

Only the main meteoric events influenced the groundwater parameters directly, while most minor rainfalls capable of modifying the river discharge did not have any effect on the groundwater (Figure 10). The groundwater level in all the cave pools increased with a significant delay (over 24 hours) after rainfalls. At that time, the river floods were on decline. Detail of the March 2008 flood evidences this delay in the rise of the water. Only in the BL station, in the proximity of the spring, a first maximum was directly caused by the rise of the river level (Figure 11).

The flood events of April 2008 and December 2008 were not influenced by snowfall or snow melting and they represent favorable cases to analyze the influence of surface recharge on the monitored groundwater parameters (Figure 11). The increase of the level was accompanied by a sharp lowering of the temperature and conductivity for the flowing water (BL and RN). In the LV and BB stagnant pools, the April 2008 rains did not trigger an immediate response, but contributed to the progressive seasonal lowering of the temperature and conductivity.

The December 2008 rains represent the termination of a low discharge period. After the sharp, fast changes produced by the flood, the water parameters did not return to previous values, evidencing the change of draining condition. It should be noted that this flood produced an evident sharp temporary uplift of the conductivity and temperature in the stagnant BB pool, and a lasting increase of the temperature in the GL pool.

### 5.4 THE SUMMER FLOOD

A flash flood was caused by the brief and intense storm of 22 July 2008 which directly hit the recharge area of the river, favoring the surface drainage. This event showed the influence of the river on the groundwater during the period of minimal discharge, in the absence of infiltrating water from the karst surface (Figure 12). During the flood, the river water reached the highest water level of the monitoring period, producing a direct invasion of the passages closest to the springs (BL station). A water level rise of ~10 cm occurred also in the GL pool, followed by a slow decrease to the previous level, while the water level remained stable in the other monitoring stations inside the cave.

The flood also caused a sudden increase in temperature and a drop in the conductivity in the BL station. The pre-flood condition of these parameters was restored within a week's time. Similar changes, with a minor range, occurred also in the stagnant water of the LV pool. No changes occurred in the innermost stations, absolutely uninfluenced by the river flood (Figure 12).

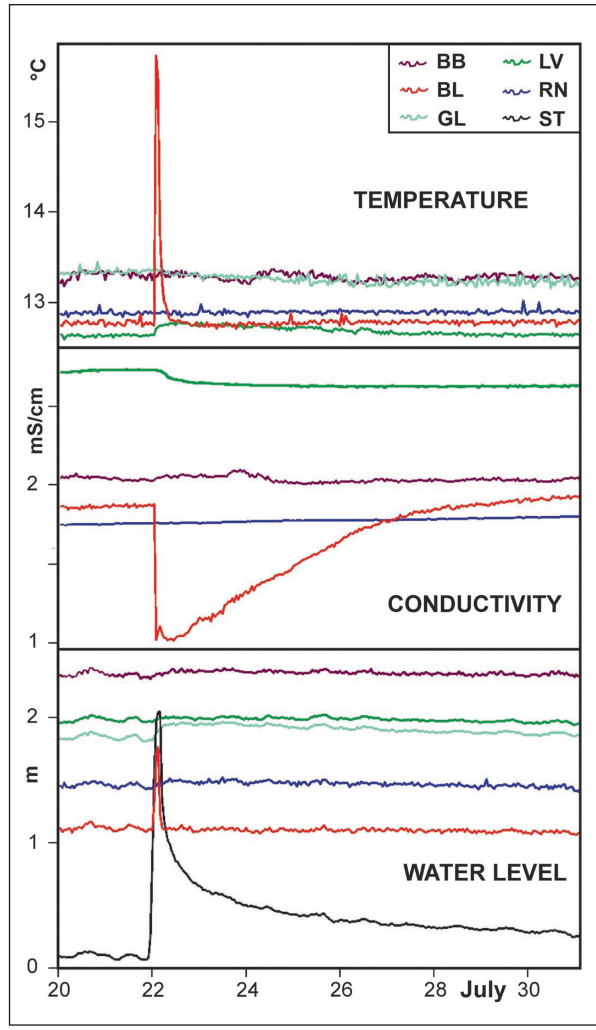


**Figure 12:** *Hydrographs of the isolated summer flood. The peak of water temperature in the BL stream was due to direct invasion of river water. Legend: BB) Budellone Basso; BL) Grotta Bella; GL) Lago Galleria; LV) Lago Verde; RN) Lago del Rinoceronte; ST) Sentino River.*

### 5.5 LAGO VERDE

This water body is fed from the bottom by sulfidic water, but is easily reached by infiltrating water through less than 100 m-thick highly karstified rocks (Figure 7). Descending bicarbonate water does not form a surface layer, but mixes with the sulfidic groundwater causing only a weak surface dilution. Conversely, a surface layer of stratified bicarbonate water was observed during the long drought period of 2006-2007. This surface layer disappeared after seasonal rains restored the normal drainage condition.

During the 2009-2010 monitoring period, the conductivity and temperature under low discharge conditions remained uniform at the surface and in the depth until the heavy precipitation of January 2010 (Figure 13).

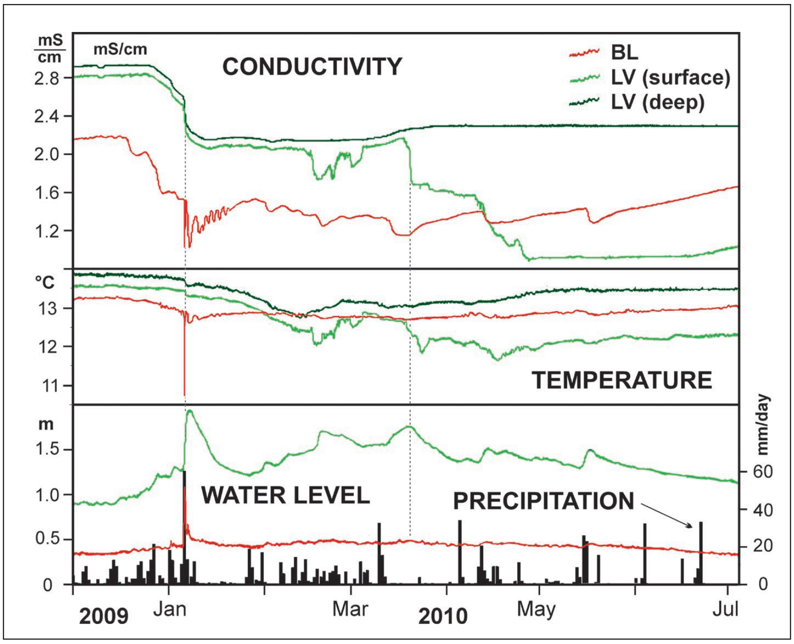


*Figure 13: Hydrographs of Lago Verde (LV, surface and depth) compared to Grotta Bella stream (BL) and precipitation. In the LV pool, a logger was fixed at ~2 m depth, another floated ~20 cm below the water surface.*

This event marked the beginning of the high discharge period and caused the abrupt drop of the conductivity and temperature values in the entire lake. In the following months, only the surface water underwent the influence of the main meteoric events. In March 2010, the increase of the water level due to the infiltrating water caused diverging effects (Figure 13): at depth, temperature and conductivity had a slight increase; at the surface, after the fast drop in the values caused by the inflow of cold meteoric water, a progressive dilution continued for a few weeks until the water parameters stabilized at the end of the high discharge period.

# 6. DISCUSSION

## 6.1 WATER LEVEL AND DRAINAGE CONDITIONS

The low hydraulic gradient in the absence of direct surface connections between most pools implies a very high permeability of the limestone in the cave area, due to the well-developed karst draining system, extended even below the present water table. This condition also justifies the similarity in height and timing of the level changes. These subaqueous passages permit direct connections towards the gravel-filled valley bottom, favoring the drainage of sulfidic groundwater towards the surface and the interaction with the river water (Figure 6).

The lower level fluctuation in the BL station compared to the entire cave results from its role as an outflow stream for groundwater towards the river. In this station, the proximity to the river allowed for the water level to be directly affected by the main river floods. The higher hydraulic gradient between the river and the GL pool (Figure 7) shows that permeability undergoes local variations, possibly due to the degree of karstification or to the occlusion of the phreatic conduits by alluvial fills near the riverbed.

The drainage directions inferred from the piezometric levels are consistent with the geological setting and the cave structure (Figure 7). Minimal levels are documented in the eastern zone, close to the main fault system and the marl aquiclude, where the water converges and moves North, towards the spring. A second drainage direction corresponds to the cave passages developing from SW towards NE in the central part of the cave.

Turbulent flows in the eastern cave sector are not due to higher hydraulic gradients, but can be caused by the convergence of the water flow into the highly karstified zone close to the spring. In this area, overlapping passages of the minor levels just above the water table facilitate the alternation of short free surface streams to subaqueous conduits (Figure 6B). On the contrary, in the inner cave sectors, the isolated pools at the water table are stagnant in the surface and are generally fed by groundwater from below through underwater passages or sumps (Figure 6A).

## 6.2 THE GROUNDWATER DILUTION

### 6.2.1 Flowing water

The monitoring and the spot measurements of the present and past researches (Cocchioni et al., 2003; Galdenzi et al., 2008; Jones et al., 2015) show that the electrical conductivity and chemistry of sulfidic groundwater have similar values under low discharge conditions in most pools and springs. This composition should result from partial dilution of deep-sourced sulfidic water with surface-derived bicarbonate water (Figure 14A). The higher salt content in the Lago Verde (Cocchioni et al., 2003, Galdenzi et al., 2008) is due to the rise of sulfidic groundwater from deeper zones of the aquifer, less affected by the dilution of descending freshwater. This deep-sourced groundwater also emerges in the Pozzo dei Cristalli (Jones et al., 2015) and in a small spring directly from the limestone in the river bed (Fissure spring, Galdenzi et al., 2008; Jones et al., 2015).

A seasonal dilution under high discharge conditions (Figure 14A) clearly results in the almost overlapping hydrographs of the flowing water in the BL and RN pools. This seasonal dilution was already referred to the recharge of meteoric water from the karst surface rather than from the river (Galdenzi et al., 2008). Current monitoring data support this conclusion. The increase of the water level and the lowering of temperature and electrical conductivity after major rainfalls proceeded simultaneously, with peak values reached after a significant delay (over 24 h) with respect to the river flooding. Furthermore, it can be noted that the pulses due to infiltrating water occurred at first in the RN pool, and

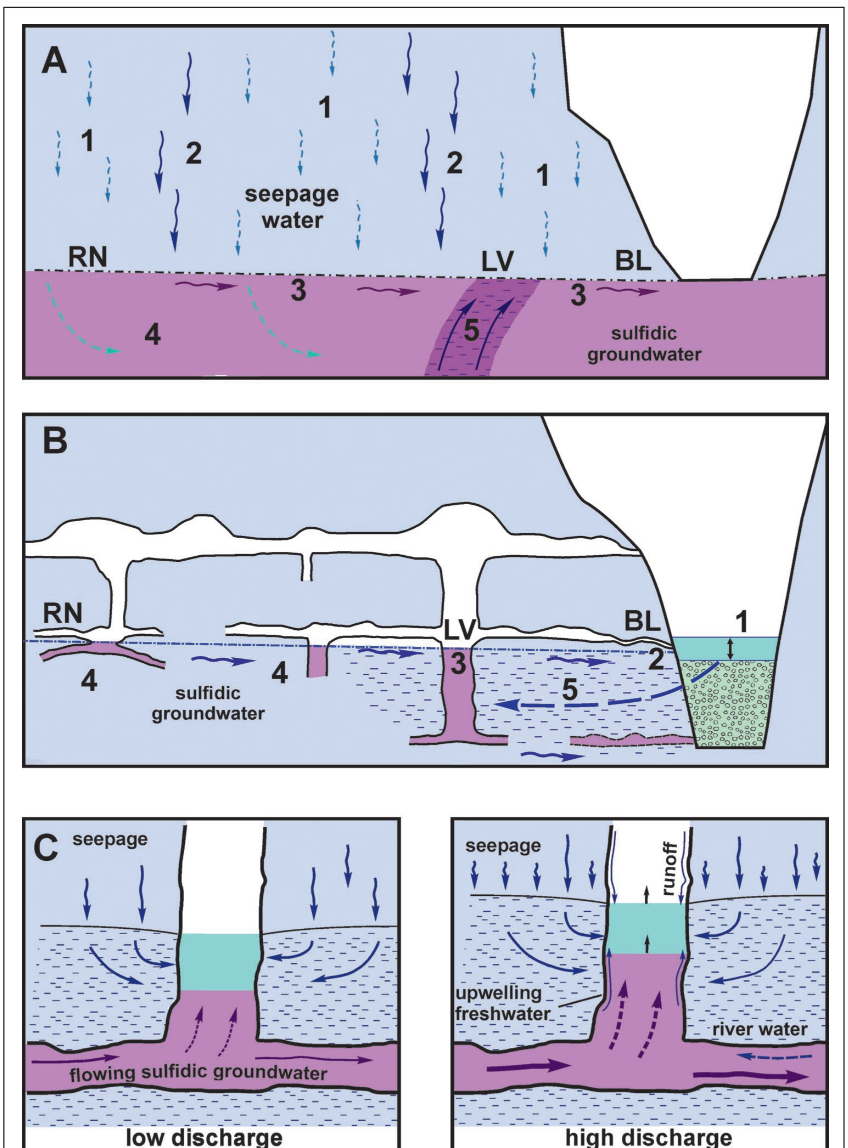


*Figure 14: Schemes of the cave hydrology. A) The groundwater dilution. Legend: 1) slow seepage; 2) seasonal fast seepage through open fissures and karst channels; 3) seasonal surface dilution; 4) long-term dilution; 5) rising low diluted groundwater; BL) Grotta Bella; LV) Lago Verde; RN) Lago del Rinoceronte. B) Effects of the flood of 22 July 2008 on the groundwater at an increasing distance from the river. Drawing not to scale. Legend: 1) flood water level; 2) flow inversion; 3) a few centimeters level increase; 4) uninfluenced groundwater; 5) intrusion zone; BL) Grotta Bella; LV) Lago Verde; RN) Lago del Rinoceronte. C) Scheme for the recharge of the stratified water in the isolated cave pools under different discharge conditions.*

~5 h later at the spring (Figure 11). Meanwhile, minor fluctuations of the river discharge did not influence the groundwater parameters (Figure 10).

This fast response to the meteoric events is evidence of a highly effective drainage of the water in the vadose zone, through small karst channels rarely accessible to man. This draining system is more extensive in the eastern side of the anticline, where well-developed old cave levels produced by SAS coexist with a diffuse karst solution caused by infiltrating water. The consistently slightly higher values of the electric conductivity at the BL spring compared to the RN pool are probably due to the contribution of less diluted, deep-sourced groundwater in the Lago Verde area.

#### 6.2.2 Stagnant pools

In the stagnant pools, only the groundwater level changed synchronously in the entire cave, while local factors interfered with the seasonal evolution for the other parameters. The dilution due to the infiltrating bicarbonate water generally produced less significant changes in temperature and electric conductivity, with minimal values reached late after the increase of the water level (Figure 11). Water stratification, where present, can impede direct dilution by infiltrating water. This lag, therefore, may be the result of a slow seepage of infiltrating water through the overlying rock mass, or of the amount of time necessary for dilution to propagate into groundwater and reach these water bodies not directly involved in a fast drainage.

These effects are evident in the BB pool, located over 500 m below the karst surface in the innermost cave sector. In this pool, the first temporary rise of the conductivity and temperature may have been caused by the upwelling of water from below or by a mobilization of resident groundwater due to the increased hydraulic head (Figures 10 and 11). The dilution of the groundwater occurred only later, and minimal values of electric conductivity were reached a few days later (Figure 11).

Similarly, it is unlikely that the permanent temperature increase in the GL pool at the beginning of the recharge periods was due to the arrival of infiltrating cold water (Figure 11). Instead it was most likely caused by the rise of the chemocline in this stratified water body.

In the LV pool, fast, temporary drops in the electric conductivity and temperature were directly caused by the fast arrival of infiltrating water through the overlying highly karstified rock. The different evolution of the water characteristics at the surface and bottom of the pool shows that the direct surface dilution caused by infiltrating water co-exists with changes caused by the recharge of sulfidic water from below (Figure 13).

### 6.3 THE RIVER INFLUENCE

Although infiltrating water represents the main cause of seasonal dilution, the river flood of 22 July 2008 evidenced the possible influence of the river on the groundwater characteristics, at least in the outermost cave areas (Figure 14B). This isolated pulse in low water regime had an impact on the water parameters only in the vicinity of the riverbed, while it had no influence in the innermost cave sectors (Figure 12). The rise of the water level in the river caused flow inversion in the few karst channels connected to the river and a fast small rise (~20 cm) of water level in the GL pool. It also modified the equilibrium between the sulfidic and the river water in the emergence area, favoring mixing phenomena (Figure 14B). This mixing justifies the slight decrease of electric conductivity in the LV pool and the drop of the electric conductivity values at the spring (BL), where it took a few days to return to the pre-flood condition (Figure 12).

### 6.4 GROUNDWATER STRATIFICATION

Water stratification is a common phenomenon in the stagnant pools and is favored by the present morphological settings, with many isolated pools connected only through submerged passages (Figure 14C). The meteoric water descending from the surface feeds the surface layers remaining above the sulfidic groundwater due to its relatively low density (Nicolini et al., 2022). This event is evidenced by the separation of the electric conductivity lines in the LV pool after rain events, with relatively more diluted water at the surface (Figure 13).

However, bicarbonate seepage water may also feed the surface layers filtering from the limestone walls of the pools (Figure 14C). Diffuse rills produced by ascending fluids on the walls of old phreatic passages suggested that infiltrating $O_2$-rich water descended below the groundwater level inside limestone fissures due to its hydraulic head and seeped from injection points into the sulfidic water (Galdenzi, 2019). The water also caused the incision of rills for SAS corrosion moving toward the surface due to its lower density.

The changes in draining conditions influence the equilibrium between the different layers of water. It is probable that the chemocline follows the water level changes during floods, but during the high recharge periods the inflowing meteoric water also increases the hydraulic gradient and consequently the push of sulfidic water from below, favoring the uplift of the chemocline. The decrease of hydraulic head during the long drought period of 2006-2007 can explain the exceptional presence of a surface stratified layer of $O_2$-rich bicarbonate water in the Lago Verde, a condition which disappeared once normal rainfall resumed.

## 7. MORPHOGENETIC IMPLICATIONS

The influence of surface morphological evolution on the development of Frasassi caves was early recognized by Cattuto (1976) and Bocchini and Coltorti (1990), before the importance of SAS in the cave was understood. These authors related the development of the horizontal levels to the pauses in the river downcutting, and the sub-vertical passages to the periods of fast deepening.

Subsequent research on the SAS did not deny the relationship between cave levels and deepening of the river valley, but considered that SAS occurred both above and below the interface between sulfidic groundwater and oxidizing environment. Most of the shafts and inclined passages were therefore explained as the result of the flow and corrosive action of sulfidic groundwater in the shallow phreatic zone (Galdenzi, 1990; Galdenzi & Maruoka, 2003).

The present research shows that the changes of the river dynamic or surface condition reflect not only on the height of the water table, but also on the groundwater hydrodynamic and, consequently, can influence the speleogenetic conditions.

The river does not directly affect the cave morphogenesis in the present-day setting, as the direct inflow of the river water involves only small areas near the gorge. During the development of the old cave levels the river could be more directly involved in the evolution of the cave. Large water table passages and riverbed stayed long at the same height and direct connections could occur more easily. The allochthonous siliciclastic sands deposited below gypsum deposits during the Eemian interglacial period in the Abisso Ancona area (Montanari et al., 2019) represent evidence of river water invasion during the cave history. Also the abundant clay deposits, which were considered residual by Bertolani et al. (1977), are probably at least in part allochthonous, as suggested by Bocchini and Coltorti (1990), and possibly sourced from the recharge area of Sentino River (Montanari et al., 2019). Cave filling from the surface, however, was also favored by aggradation during cold Pleistocene phases, when abundant debris was sunk from the mountain slopes and fluvial deposits filled passages directly communicating with the surface (Bocchini & Coltorti, 1990).

The changes of morphological and hydrodynamic

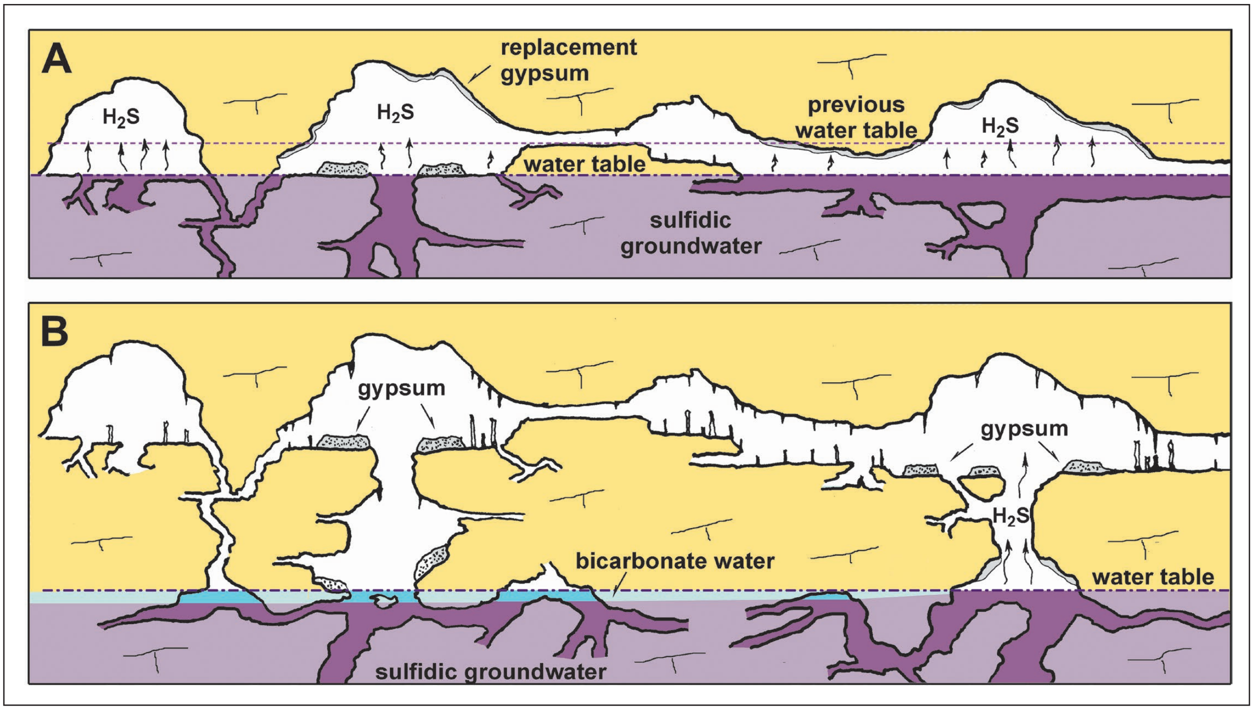


*Figure 15: Scheme of the cave evolution. A) Development of a cave level. A stable water table level favored the development of passages in the shallow phreatic zone. The widening of passages close to the water surface favored subaerial corrosion and gypsum deposition. Repeated minor changes of water level contributed to the widening of cave passages along the water table. B) After a significant lowering of the water table, the corrosion processes moved down in the rock mass. The old passages mainly evolved due to seepage water. The old emptied feeders became the pathway for gases released from groundwater towards the upper levels, where this was not impeded by groundwater stratification.*

condition must also be taken into account to discuss the different extent that subaerial SAS have had throughout the cave history. Subaerial SAS is highly effective (Galdenzi et al., 1997; Jones et al., 2015), but it is currently active only in very few places inside the cave, while the abundant remains of subaerial replacement processes prove that degassing corrosion was widespread during some past periods (Galdenzi, 1990; Galdenzi & Maruoka, 2003).

Favorable conditions for subaerial corrosion occurred more easily during the development of the subhorizontal cave levels, when the water table was stable for extended time periods. Minor fluctuations of the water table and the progressive enlargement of the karst voids produced large interfaces between air and water inside the same passage, favoring the degassing processes (Figure 15A). Wide passages and domes with flat floors were corroded by sulfidic water rising through subaqueous infeeder conduits, while subaerial corrosion enlarged the walls and ceiling, producing the final passage section (Figure 16A). On the walls, the change from rounded to irregularly corroded surfaces often marks the height of the old water table (Figure 16B). Massive gypsum glaciers formed from $H_2S$ oxidation in the cave air (Galdenzi & Maruoka, 2003), indicating a level of gypsum production that far exceeds that of the modern sulfidic zones (Figure 16C).

When the downcutting of the river valley induced the lowering of the water table, the corrosion processes due to the SAS moved downward and the extent of air-water interfaces reduced, occurring mostly in inclined or vertical passages, as in the present setting (Figure 15B). Old, emptied feeder conduits would have provided a pathway for $H_2S$ gas transfer to upper levels. The rise of gas caused periodic corrosion and gypsum production in the upper dry levels, alternating with calcite deposition by seepage water (Figure 16D).

However, the presence of a non-sulfidic surface layer of water could impede the $H_2S$ degassing towards the upper levels in large cave areas (Figure 15B), as it is occurring in the current setting. Some conditions that predispose to the stratification of groundwater can be deduced from the analysis of the present hydrodynamic. Stratification of the groundwater was primarily favored by the lack of direct superficial interconnection among cave pools, as in the present setting. The water stratification may have also been induced by a low recharge of meteoric water from the surface, which reduced the hydrostatic head on the rising sulfidic water. A high gradient along the riverbed may have also represented a favorable condition, as it impeded the drainage of groundwater towards the surface. The river itself, in this condition, might have contributed to fueling the non-sulfidic surface layer of groundwater.

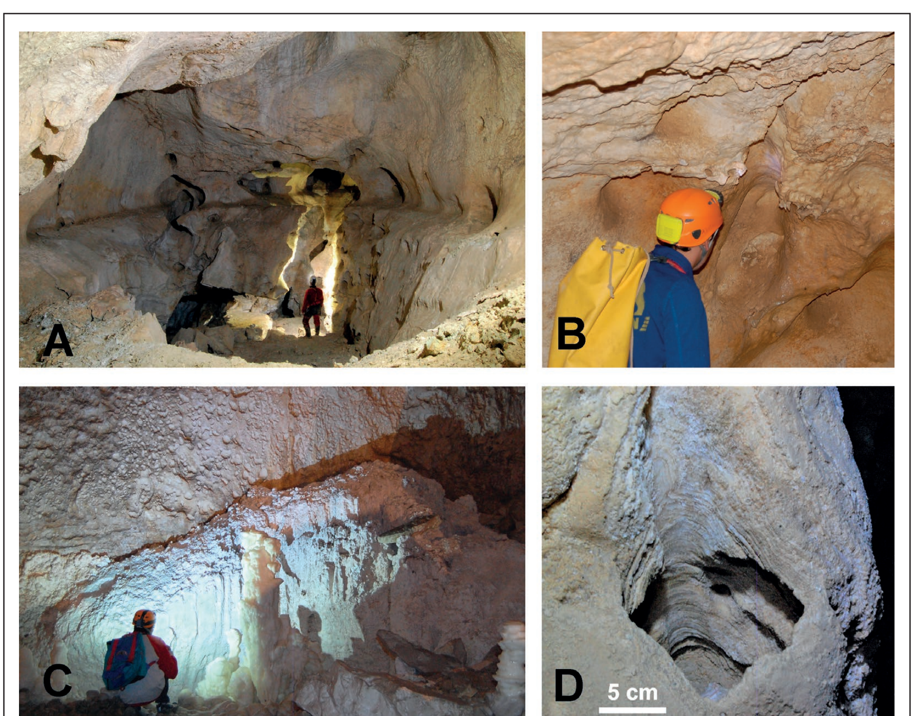


*Figure 16: Subaerial corrosion by sulfidic water. A) Wall notch produced at the interface between the sulfidic water and the cave atmosphere; B) an old water table level marked by the change between smoothed and irregular corrosion; C) massive deposit of replacement gypsum in an old cave level; D) hole produced on a pre-existing stalagmite by $H_2SO_4$ dissolved in the dripwater (Photos: S. Galdenzi).*

## 8. CONCLUSION

The Frasassi caves are an excellent example of a hypogenic cave system with corrosion processes caused predominantly by the rise of sulfidic water towards the oxidizing environment. The groundwater drainage occurs in a highly integrated system of karst conduits, and the water level is directly controlled by the amount of meteoric water infiltrating from the surface. The river represents the local base level, but it is capable of influencing the groundwater only in the outermost cave sectors located near the emergence.

The seasonal dilution of the groundwater by the infiltrating meteoric water clearly results at the spring and in the actively flowing water. In large cave sectors where the groundwater emerges in isolated stagnant pools, the water characteristics are affected by local factors, such as the push and chemistry of rising sulfidic water, the possibility of fast or slow recharge of meteoric water, and the changes in river discharge. Furthermore, bicarbonate water often forms a surface layer that floats on the denser sulfidic groundwater.

The changes in the surface condition of the area turned out to be capable of modifying the morphogenetic processes in the cave throughout time. In particular, the scarce extent of active subaerial SAS contrasts with the widespread relict evidences in the upper cave levels and is the consequence of the lack of wide interfaces between sulfidic groundwater and atmosphere in the present condition. Although the infiltrating water plays a minor role in comparison with the majority of the karst caves, it contributes directly to speleogenesis by enhancing the oxidation processes. Any process which modifies the amount and modality of recharge and drainage, including the possibility of groundwater stratification, can therefore reflect on the cave processes. The amount of sulfidic water rising from depth and of fresh-water descending from the surface, the discharge in the river and the inclination of its bed, the possibility of a direct invasion of river water into the cave, represent all factors which could influence both the intensity of SAS and the contribution of subaerial or subaqueous corrosion to the cave enlargement.

## ACKNOWLEDGMENTS

The present research was conducted by Gruppo Grotte Recanati, G.S. CAI Macerata, C.R.S. “Nottoloni” Macerata e G.A.SP. Civitanova Marche, and was financed by Regione Marche in range of intervention for Speleology (L.R. 12/2000) in the part regarding monitoring of the sulfidic spring and neighboring cave area. I would like to thank Alfredo Campagnoli† for his fundamental support in the organization and field work activities, and the speleologists who participated in the field work. A special gratitude goes to Sandro Mariani, Simone Cerioni, my son Gabriele, who in various periods helped with the field work. A special tank to Fabio Baldoni, who actively contributed to the monitoring and measurements of the water levels. Finally, I thank Danica Jablonska who kindly revised the text.

## REFERENCES

Anelli, L., Gorza, M., Pieri, M., Riva, M., 1994. Subsurface well data in the Northern Apennines (Italy). Memorie Società Geologica Italiana, 48: 461-471.

Audra, P., Mocochain, L., Bigot, J.Y., Nobécourt, J.C., 2009. Morphological indicator of speleogenesis: Hypogenic speleogenesis. In: Klimchouk., A.B., Ford., D.C. (Eds.), Hypogene speleogenesis and karst hydrogeology of artesian basins. Ukrainian Institute of Speleology and Karstology, Special Paper 1, pp. 23-32.

Baldoni, F., 2007. Studio idrogeologico dei complessi carsici di M. Valmontagnana e del M. Frasassi (Genga, Italia Centrale) [Graduation thesis]. Università degli Studi di Perugia, 140 pp.

Bertolani. M., Garuti, G., Rossi, A., Bertolani Marchetti, M., 1977. Motivi di interesse mineralogico e petrografico nel complesso carsico Grotta Grande del Vento-Grotta del Fiume. Le Grotte d’Italia, s. IV, 6: 109-144.

Bocchini, A., Coltorti, M., 1990. Il complesso carsico

Grotta del Fiume Grotta Grande del Vento e l'evoluzione geomorfologica della Gola di Frasassi. In: Galdenzi, S., Menichetti, M. (Eds), Il carsismo della Gola di Frasassi. Memorie Istituto Italiano Speleologia, s. II, 4, pp. 155-180.
Caprari, M., Galdenzi, S., Nanni, T., Ramazzotti, S., Vivalda, P., 2001. La sorgente di Gorgovivo: analisi idrogeologica finalizzata all'individuazione delle zone di tutela, rispetto e protezione. Memorie Società Geologica Italiana, 56: 157-169.
Cattuto, C., 1976. Correlazione tra piani carsici ipogei e terrazzo fluviali nella valle del F. Esino. Bollettino Società Geologica Italiana, 95: 313-326.
Celico, P., 1984. Prospezioni idrogeologiche (V. 1). Liguori Editore, Neaples, 736 pp.
Centamore, E., Catenacci, V., Chiocchini, M., Chiocchini, U., Jacobacci, A., Martelli, G., Micarelli, A., Valletta, M., 1975. Carta Geologica d'Italia alla Scala 1:50.000. Note illustrative del Foglio 291 "Pergola". Servizio Geologico d'Italia, 40 pp.
Ciancetti, G.F., Pennacchioni, E., 1993. Idrologia superficiale ed alimentazione della falda dell'area carsica di Frasassi. Geologia applicata ed idrogeologia, 28: 285-293.
Cocchioni, M., Galdenzi, S., Morichetti, L., Nacciarriti, L., Amici, V., 2003. Studio idrochimico delle acque nel complesso ipogeo di Frasassi. Le Grotte d'Italia, s. V, 4: 49-61.
Coltorti, M., Dramis, F., 1995. The chronology of upper Pleistocene stratified slopewaste deposits in Central Italy. Permafrost and Periglacial Processes, 6: 235–242.
D'Angeli, I., Parise, P., 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
Deiana, G., (Coordinator) 2009. Note Illustrative della Carta Geologica d'Italia alla scala 1:50000. Foglio 302 Tolentino. Servizio Geologico d'Italia, 113 pp.
De Waele, J., Audra, P., Madonia, G., Vattano, M., Plan, L., D'Angeli, I.M., Bigot, J.Y., Nobécourt, J.C., 2016. Sulfuric acid speleogenesis (SAS) close to the water table: examples from southern France, Austria, and Sicily. Geomorphology, 253: 452-467.
Engel, A.S., Stern, L.A., Bennet, P.C., 2004. Microbial contributions to cave formation: new insights into sulfuric acid speleogenesis. Geology, 32(5): 369-372.
Galdenzi, S., 1990. Un modello genetico per la Grotta Grande del Vento. In: Galdenzi, S., Menichetti, M. (Eds.), Il carsismo della Gola di Frasassi. Memorie dell'Istituto Italiano di Speleologia, s. II, 4, pp. 123-142.
Galdenzi, S., 2012. Corrosion of limestone tablets in sulfidic ground-water: measurements and speleogenetic implications. International Journal of Speleology, 41(3): 149-159.
Galdenzi, S., 2019. Barite replacement boxwork in the Frasassi caves (Italy). International Journal of Speleology, 48: 305-310. https://doi.org/10.5038/1827-806X.48.3.2223
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.
Galdenzi, S., Maruoka, T., 2003. Gypsum deposits in the Frasassi Caves, central Italy. Journal of Cave and Karst Studies. 65(2): 111-125.
Galdenzi, S., Maruoka, T., 2019. Sulfuric acid caves in Calabria (South Italy): Cave morphology and sulfate deposits. Geomorphology, 328: 211-221. https://doi.org/10.1016/j.geomorph.2018.12.014
Galdenzi, S., Menichetti, M., 1995. Occurrence of hypogenic caves in a karst region: examples from central Italy. Environmental Geology, 26: 39-47.
Galdenzi, S., Menichetti, M., Forti, P., 1997. La corrosione di placchette calcaree ad opera di acque sulfuree: dati sperimentali in ambiente ipogeo. In: Jeannin, P.Y. (Ed.), Proceedings of the 12th International Congress of Speleology, La Chaux-de-Fonds, Switzerland, 1997, vol. 1, pp. 187-190.
Hill, C.A., 2000. Sulfuric Acid, hypogene karst in the Guadalupe Mountains of New Mexico and West Texas, USA. In: Klimchouk, A.B., Ford, D.C., Palmer, A.N., Dreybrodt, W. (Eds.), Speleogenesis: Evolution of karst aquifers. National Speleological Society, Huntsville, pp. 309-318.
Jagnow, D.H., Hill, C.A., Davis, D.G., DuChene, H.R., Cunningham, K.I., Northup, D.E., Queen, J.M., 2000. History of the sulfuric acid theory of speleogenesis in the Guadalupe Mountains, New Mexico. Journal of Cave and Karst Studies, 62(2): 54-59.
Jones, D.S., Polerecky, L., Galdenzi, S., Dempsey, B.A., Macalady, J.L., 2015. Fate of sulfide in the Frasassi cave system and implications for sulfuric acid speleogenesis. Chemical Geology, 410: 21-27.
Klimchouk, A.B., 2007. Hypogene speleogenesis: hydrogeological and morphometric perspective. Special Paper 1, National Cave and Karst Research Institute, Carlsbad, NM. 106 pp.
Klimchouk, A.B., Palmer, A.N., De Waele, J., Auler, A., Audra, P. (Eds.), 2017. Hypogene karst regions and caves of the world. Springer, 912 pp. DOI 10.1007/978-3-319-53348-3
Longinelli, A., Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. Journal of Hydrology, 270: 75–88.

Montanari, A., Lüthgens, C., Lomax, J., Mainiero, M., Mariani, S., Fiebig, M., 2019. Luminescence geochronology of Pleistocene slack-water deposits in the Frasassi hypogenic cave system, Italy. In: Koeberl, C., Bice, D.M. (Eds.), 250 Million Years of Earth History in Central Italy: Celebrating 25 Years of the Geological Observatory of Coldigioco. The Geological Society of America, Special Paper 542, pp. 411-428. https://doi.org/10 10.1130/2019.2542(23)

Nesci, O., Savelli, D., Troiani, F., 2012. Types and development of stream terraces in the Marche Apennines (central Italy): a review and remarks on recent appraisals. Géomorphologie: relief, processus, environnement, 18(2): 215-238. https://doi.org/10.4000/geomorphologie.9838

Nicolini, R., Di Matteo, L., Galdenzi, S., Baldoni, F., Frondini, F., Valigi, D., 2022. Study of dilution processes of sulfidic aquifer hosted by the Fiume-Vento karstic complex, Frasassi (Central Italy). Acque Sotterranee - Italian Journal of Groundwater, 11(3): 7-17. https://doi.org/10.7343/as-2022-567

Palmer, A.N., 2000. Hydrogeologic control on cave patterns. In: Ford, D.C., Palmer, A.N., Dreybrodt, W., Klimchouk, A.B. (Eds.), Evolution of karst Aquifers. National Speleologic Society, Huntsville (AL), Speleogenesis, pp. 77-99.

Palmer, A.N., 2007. Cave Geology. Cave Books, Dayton, OH. 454 pp.

Palmer, A.N., 2013. Sulfuric acid caves: morphology and evolution. In: Shroder, J. (Ed. in Chief), Frumkin, A. (Ed.), Treatise on Geomorphology. Academic Press, San Diego, CA, vol. 6, Karst Geomorphology, pp. 241–257. https://doi.org/10.1016/B978-0-12-374739-6.00133-0

Perrone, E., 1911. Memorie illustrative della carta idrografica d'Italia. Ministero di agricoltura, industria e commercio, 35, 203 pp.

Sighinolfi, G.P., 1990. Studio chimico delle acque del complesso "Grotta di Frasassi (Ancona)". Implicazioni Speleogenetiche e ambientali. In: Galdenzi, S., Menichetti, M. (Eds), Il carsismo nella Gola di Frasassi. Memorie dell'Istituto Italiano di Speleologia, s. II, 4, pp. 109-122.

Taddeucci, A., Tuccimei, P., Voltaggio, M., 1992. Studio geocronologico del complesso carsico "Grotta del Fiume-Grotta Grande del Vento" (Gola di Frasassi, AN) e indicazioni paleoambientali. Il Quaternario, 5: 213-222.

Tazioli, G.S., Cocchioni, M., Coltorti, M., Dramis, F., Mariani, M., 1990. Circolazione idrica e chimismo delle acque sotterranee dell'area carsica di Frasassi nelle Marche. In: Galdenzi, S., Menichetti, M. (Eds), Il carsismo nella Gola di Frasassi. Memorie dell'Istituto Italiano di Speleologia, s. II, 4, pp. 93-108.