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SULFIDIC GROUND-WATER CHEMISTRY IN THE FRASASSI CAVES, ITALY

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Abstract: A year-long study of the sulfidic aquifer in the Frasassi caves (central Italy) employed chemical analysis of the water and measurements of its level, as well as assessments of the concentration of H_2S, CO_2, and O_2 in the cave air. Bicarbonate water seepage derives from diffuse infiltration of meteoric water into the karst surface, and contributes to sulfidic ground-water dilution, with a percentage that varies between 30% and 60% during the year. Even less diluted sulfidic ground water was found in a localized area of the cave between Lago Verde and nearby springs. This water rises from a deeper phreatic zone, and its chemistry changes only slightly with the seasons with a contribution of seepage water that does not exceed 20%. In order to understand how the H_2S oxidation, which is considered the main cave forming process, is influenced by the seasonal changes in the cave hydrology, the sulfide/total sulfur ratio was related to ground-water dilution and air composition. The data suggest that in the upper phreatic zone, limestone corrosion due to H_2S oxidation is prominent in the wet season because of the high recharge of O_2-rich seepage water, while in the dry season, the H_2S content increases, but the extent of oxidation is lower. In the cave atmosphere, the low H_2S content in ground water during the wet season inhibits the release of this gas, but the H_2S concentration increases in the dry season, favoring its oxidation in the air and the replacement of limestone with gypsum on the cave walls.

Introduction

The Frasassi Caves are one of the best examples of caves with an active flow of H_2S-rich water. Sulfuric acid derived from the oxidation of H_2S is considered the main cave-forming agent, and the oxidation process is enhanced by the supply of oxygen transported in seepage water or directly in the cave atmosphere (Galdenzi, 1990). The active speleogenetic processes can be directly observed in the lower, sulfidic parts of the cave. Experimental measurement using limestone tablets placed in the cave for five years determined the present rate of sulfuric acid speleogenesis (Galdenzi et al., 1997). The weight loss reached values of up to 20 mg cm^{-2} yr^{-1}, both in the tablets exposed to H_2S vapors above the water table and those placed directly in the sulfidic ground water. Sulfide oxidation involves bacterial activity; and organic matter produced by bacteria is the main source of food for the fauna inhabiting the sulfidic sections of the cave (Sarbu et al., 2000).

Detailed study of water chemistry and water-level changes, carried out over the course of a year in different sampling points inside the cave, identified seasonal changes in the ground-water characteristics and formed the basis for assessing their influence on the cave environment and the processes guiding cave development. The purpose of this paper is to document the ground-water characteristics that influence the cave environment and speleogenesis.

Methods

The field work was based on field measurement of environmental parameters and on the chemical analysis of water samples in the laboratory. In order to understand the influences of surface recharge on the sulfidic ground-water characteristics, we identified three sampling points for seepage water and four for sulfidic ground water, two in the cave and two at the emergences. The choice of these sampling points was based on preliminary field analysis of water characteristics in different zones of the cave. The surface water in the Sentino River was sampled in order to ascertain whether the river directly influences the ground-water characteristics. During the period November 2001–December 2002, water was sampled monthly and analyzed in order to identify the most significant seasonal changes. In addition, some further samples coming from other cave lakes were studied.

The water temperature and conductivity were measured *in situ* using probes (Delta OHM, Italy). In the laboratory, chemical and physicochemical parameters of the water samples were measured using the methods shown in Table 1.

To facilitate the interpretation of seasonal changes in water chemistry, temperature, conductivity and water level of sulfidic ground water were measured continuously over the same period. A remote logger for temperature and conductivity (DAS, Italy) was located in a small artificial tunnel near the springs. This probe was exposed to direct contact with the river water during the main floods of the

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Table 1. Chemical and physicochemical parameters of water samples and measurement methods.

Parameter	Method
Temperature	Digital thermometer, Hanna Instruments model HI805
Conductivity	Conductivity meter, Crison model 524
pH	Digital pH-meter, Hanna Instruments model HI 824
Hardness	Titrimetric method, Standard Methods[a] 2340 C
Calcium	Titrimetric method, Standard Methods[a] 3500 B
Magnesium	Calculation method, Standard Methods[a] 3500 B
Sodium, Potassium	Flame photometric method with Perkin Elmer model 3300
Chloride, Sulfate	Ion chromatography with Dionex 120 DX
Carbon dioxide	Titrimetric method and calculation method, Standard Methods[a] 4500 C/D
Bicarbonate	Titrimetric method, Standard Methods[a] 2320 B
Sulfide	Iodometric method, Standard Method[a] 4500 F
Dissolved Oxygen	Iodometric method, Standard Methods[a] 4500 C
Oxygen Saturation %	Calculation method
BOD	Oxygen consumed in a five day SM 5210 B

[a] *Standard Methods for the Examination of Water and Wastewater 20th Edition.*

river itself. Unfortunately, sensor failure compromised the conductivity data for a long period.

Two water-level loggers (Meccatronica, Italy; measurement range: 0–2.5 m) were located inside the cave to monitor changes in ground-water level in different zones of the cave. In the following years, measurements of water-table levels were repeated at different sites to ascertain the timing of water-level changes between the different zones of the cave and the river.

The concentrations of H_2S, CO_2, O_2 and SO_2 in the cave air were measured with a hand pump (Gastec Corporation, Japan) and detector tubes (measurement range: H_2S, 0.1–4 and 0.25–120 ppm; CO_2, 300–5,000 ppm; O_2, 3–24%; SO_2, 0.05–10 ppm). Measurements of H_2S, CO_2, and O_2 were repeated throughout the sampling period at the same time as water chemistry analyses. Sulfur dioxide (SO_2) was not detected in the cave atmosphere, and measurements were repeated occasionally. Two monthly measurements were missed because of difficulties in accessing the sampling sites. Some measurements were also done to verify changes of the air composition in the upper non-sulfidic cave sections.

Geologic Setting

The Frasassi Caves, one of the most famous show caves in central Italy, are located on the eastern slope of the Apennine mountain chain, 40 km from the Adriatic Sea. They are developed in the small area around the Frasassi Gorge, a 500 m deep and 2 km long canyon that the Sentino River cuts in a small anticline ridge. The caves consist of over 25 km of cave passages located at altitudes between 200 (corresponding to the riverbed) and 500 m (Fig. 1).

The cave complex consists of superimposed and interconnected levels, the genesis of which is related to steps in the deepening of the river valley and related base level. The lower levels, present mainly in the Fiume-Vento system, originated during the Middle-Upper Pleistocene, as did the alluvial deposits just outside the Frasassi Gorge (Bocchini and Coltorti, 1990). These lower cave levels host speleothems dating back 200,000 years BP (Taddeucci et al., 1992) and developed under geomorphological and hydrogeological conditions similar to current ones. The upper levels developed mainly in the Buco Cattivo and

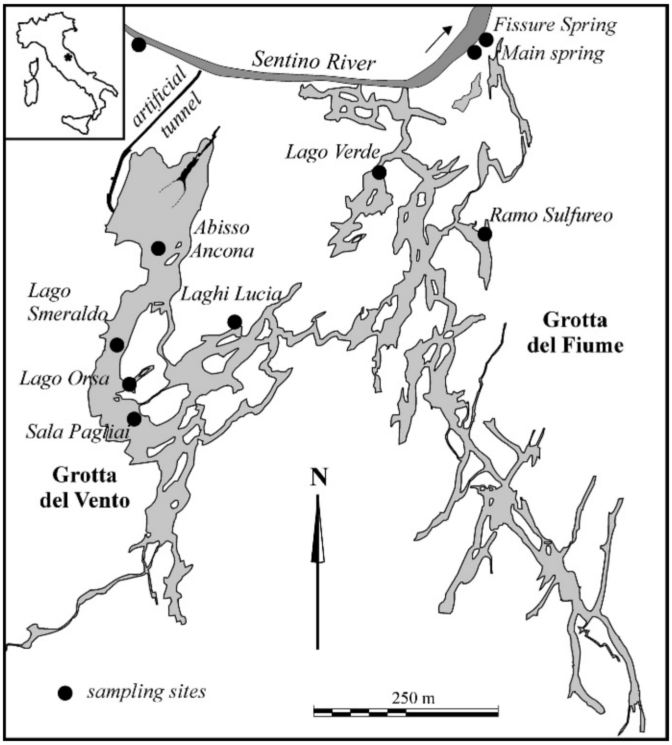

Figure 1. Cave map, with water sampling locations.

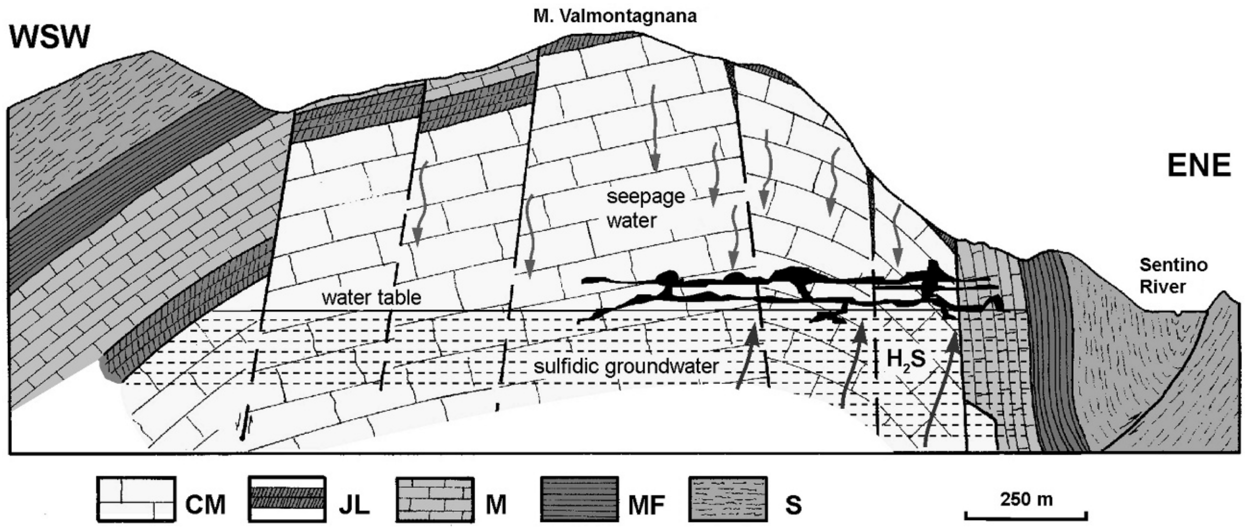

Figure 2. Geologic cross-section of the Frasassi Anticline. The marl layer in the eastern anticline limb causes ground-water flow toward the gorge. CM) Calcare Massiccio Formation; JL) low permeability Jurassic limestones; M) Calcare Maiolica Formation; MF) Marne a Fucoidi Formation; S) Scaglia Bianca and Scaglia Rossa Formations.

Mezzogiorno-Frasassi caves. In these caves, the features originated by sulfidic water near the water table are less common, probably because they evolved under a partly different hydrogeological setting.

The area is mountainous, with altitudes ranging between 200 m at the bottom of the valleys to about 1000 m on the surrounding peaks. The climate is Apenninic subcontinental, and the annual average temperature is ~13 °C, while the annual temperature range reaches 20 °C. The average rainfall is ~1000 mm yr^{-1} with maximum precipitation generally in autumn and spring. Evaporation typically exceeds precipitation in summer. Storms often occur at the end of summer, and sometimes these months can be the rainiest of the year. In the winter, snow often covers the mountain surface for short periods.

The Sentino River reaches the Frasassi gorge 40 km from its source. The recharge area extends ~250 km^2. Limestone outcrops in ~40% of the basin, claystone and sandstone in ~30% of the basin, and the remaining surface is covered by alluvial and detrital deposits (Dramis et al., 1976).

The Karst Aquifer

The steep cliffs of the Frasassi Gorge clearly show the geologic structure of the region (Fig. 2). The Calcare Massiccio Fm., a thick, massively bedded, lower Jurassic limestone, constitutes the core of the anticline and outcrops across the whole gorge. It is a very pure limestone, consisting mainly of wackestone and packstone facies without any significant clay or silica minerals. It is very permeable, due to high syngenetic porosity and a well-developed network of fractures, and it hosts the main aquifer in the area.

Overlying the Calcare Massiccio Fm. is a 60 m thick formation of Jurassic limestone (Bugarone Fm.), containing a marly and a cherty level. This low-permeability formation can influence ground-water drainage locally. In the eastern limb of the anticline, however, a fault permits hydraulic continuity between the Calcare Massiccio and the overlying, permeable Cretaceous limestones (Fig. 2).

The Cretaceous formations are thin-layered, permeable limestones (Maiolica Fm., upper Jurassic – lower Cretaceous, and Scaglia Fm., upper Cretaceous – Eocene) with an interbedded, low-permeability 50 m thick marl formation (Marne a Fucoidi, middle Cretaceous). The Marne a Fucoidi Fm. is the local aquiclude and defines a recharge area of about 5 km^2 feeding the main aquifer hosted in the Calcare Massiccio Fm. and, partly, in the Maiolica Fm. (Fig. 2).

The ground-water drainage is influenced by the geologic setting. In the recharge area, diffuse infiltration prevails, and the drainage network is limited, with only temporary flows in a few channels after major rainstorms. A few low discharge springs originate from small aquifers perched on the Jurassic or Cretaceous marly levels. Most seepage water, however, reaches the main aquifer, whose recharge area corresponds to the core and the eastern limb of the anticline (Fig. 2). Ground water in this aquifer is typically enriched in H_2S and salts due to the rise of mineralized water in the core of the anticline. The spring area is located in the eastern side of the gorge where the down-cutting of the river valley caused the erosion of the marly cover in the limb of the anticline (Fig. 3).

The caves develop in the zone between the core and the eastern side of the anticline in the Calcare Massiccio Fm. and partly in the Maiolica Fm. Here the ground-water

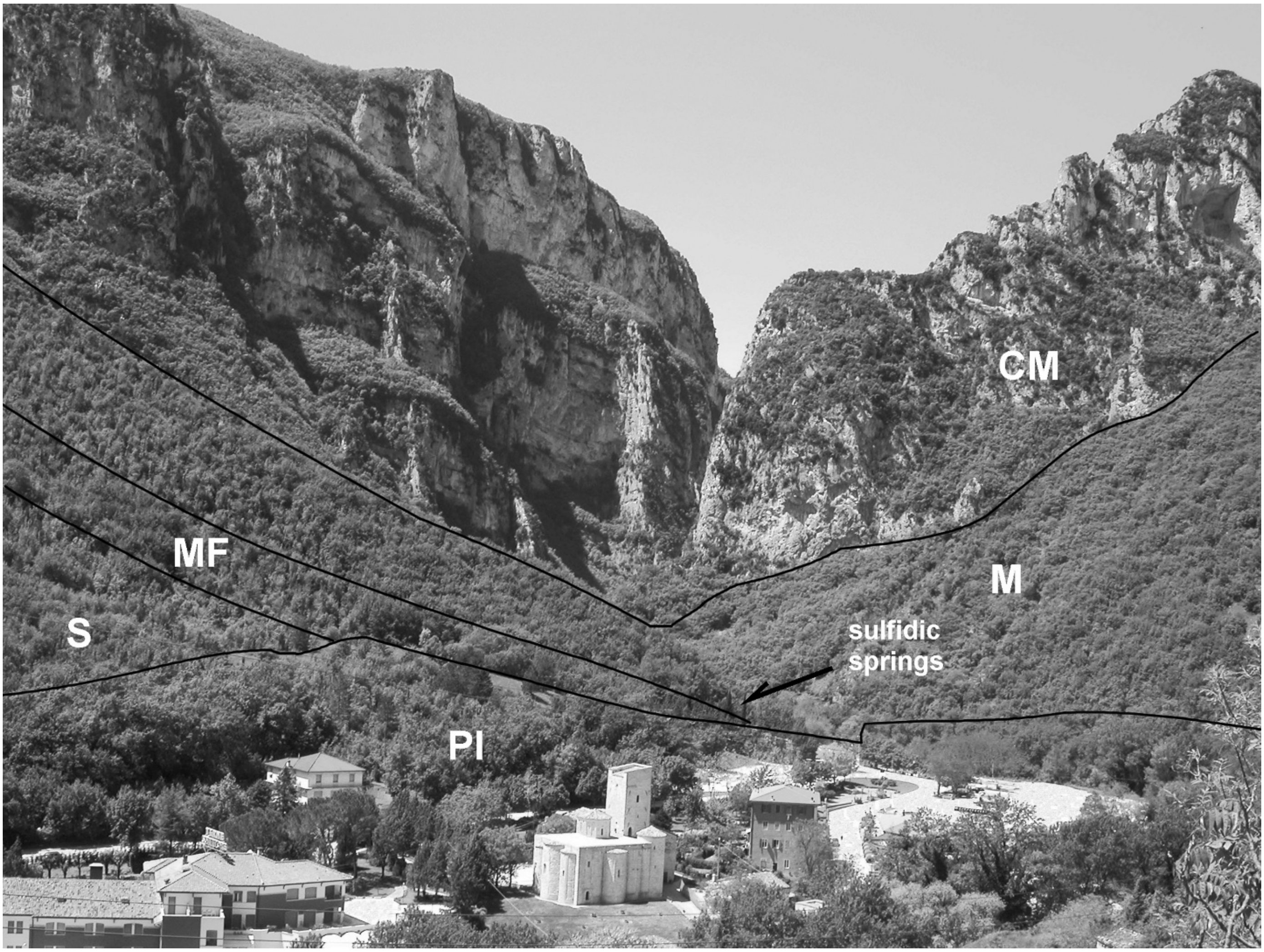

Figure 3. View of the Frasassi Gorge. CM) Calcare Massiccio Formation; M) Calcare Maiolica Formation; MF) Marne a Fucoidi Formation; S) Scaglia Bianca and Scaglia Rossa Formations; Pl) continental Pleistocene deposits.

drainage is concentrated near the large fault dividing the two formations (Fig. 2). The marly cover in the limb of the anticline facilitates drainage toward the springs.

The hydraulic gradient for the ground water is low due to the high permeability of the host rock and water flow is generally very slow. Flowing sulfidic water is only found in the eastern part of the cave. The water table is close to the river level and can be reached in many locations in the lower section of the cave.

Ground Water

General Characteristics of Ground Water

Ground water in the Frasassi area consists of two main types: bicarbonate and sulfidic, which differ in their chemical composition and origin (Tazioli et al., 1990; Sighinolfi, 1990; Cocchioni et al., 2003). The bicarbonate water derives from the diffuse infiltration of surface meteoric water through the limestone, and is found in the vadose zone and in small aquifers perched on interbedded marls. This water has a low salinity (about 200–400 mg L^{-1}), low sulfate, and high dissolved oxygen (about 0.32 mmol L^{-1}).

The sulfidic water is found in the main aquifer. It is cold (about 13 °C), and has a higher salinity than the bicarbonate water, up to 2 g L^{-1}. It is enriched in sodium and chloride, and contains sulfate and hydrogen sulfide. These dissolved components are acquired before the ground water rises upward, and they are generally believed to be a consequence of flow through an underlying Triassic anhydrite formation. Isotopic data on $\delta^{18}O$, $\delta^{2}H$, and tritium discussed by Tazioli et al. (1990) suggested a meteoric origin for the sulfidic ground water. These authors estimated a recharge area located at altitudes of 600–1000 m, with a brief residence time in the aquifer.

The very low water flow in a large part of the cave often leads to ground-water stratification. A surface layer of water stays near the surface of the water table due to its

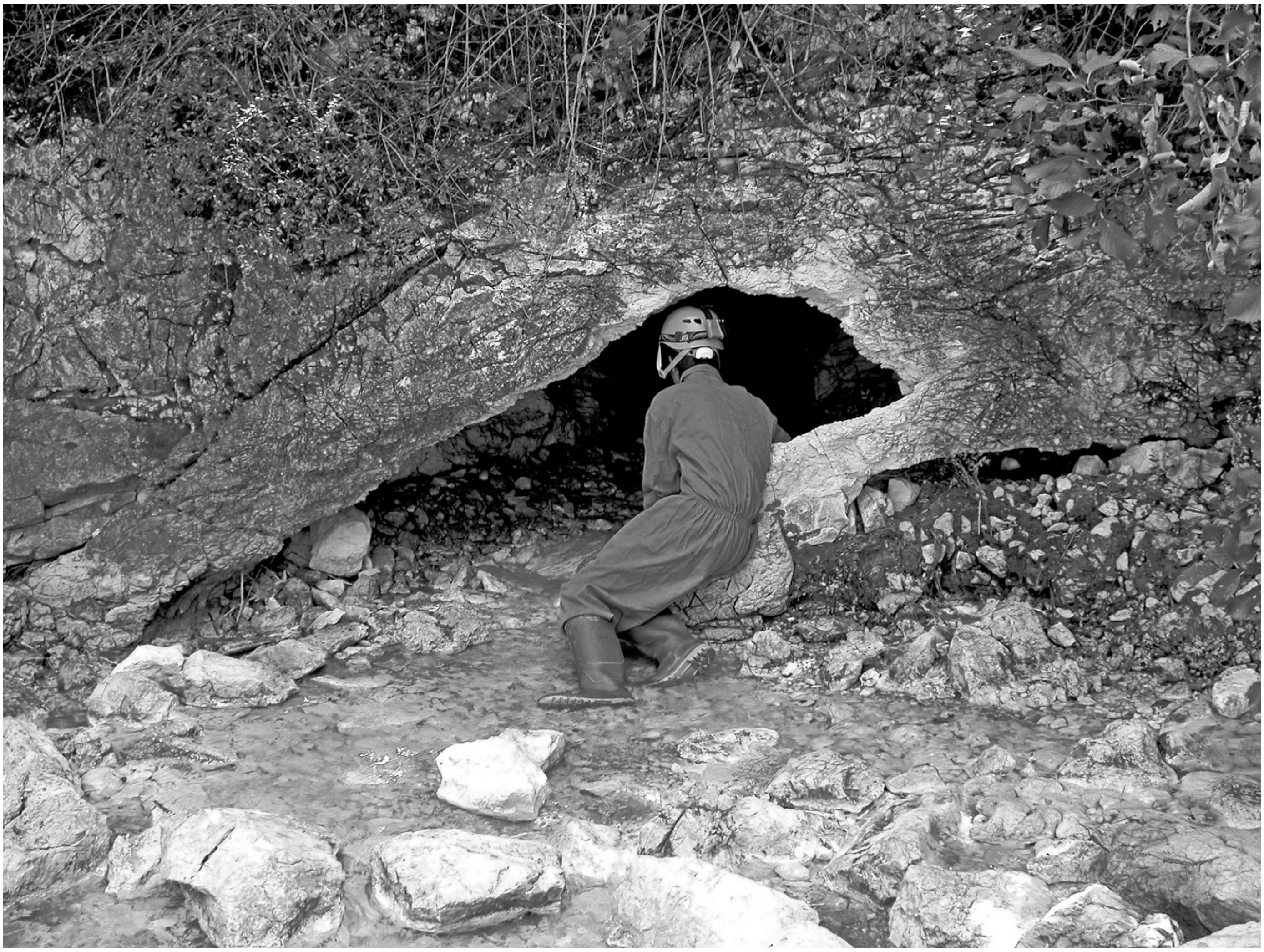

Figure 4. Main Spring. The white color is due to the microbial mats that cover the floor below the running water.

lower salinity. The thickness of this stratified surface layer can reach 5 m (Cocchioni et al., 2003).

The conductivity and temperature of the sulfidic water are correlated with precipitation (Sarbu et al., 2000). These observations indicate that water recharge derived from surface precipitation dilutes the sulfidic ground water (Tazioli et al., 1990; Sighinolfi, 1990). A role of the river in the ground-water dilution, however, has also been hypothesized (Tazioli et al., 1990; Ciancetti and Pennacchioni, 1993; Caprari et al., 2001).

Sampling Sites

The preliminary field analysis of water characteristics was used to identify seven different sampling points, three for seepage water and four for sulfidic ground water (Fig. 1). In addition, the Sentino River water was analyzed upstream from the sulfidic springs. Seepage water was collected inside the touristic part of the cave at three different sampling points (Abisso Ancona, Lago Smeraldo, Sala Pagliai) located at increasing distances from the surface. The sulfidic ground water was sampled both at the springs and at sampling points inside the cave.

The springs discharge along the river bank very close to the river channel. The spring water either flows from the limestone directly to the river or rises through alluvial deposits. Preliminary measurements revealed two different spring water types. Most of the springs have the same conductivity and temperature (13.0–13.5 °C), but a small one rising directly from the limestone (Fissure Spring) had a temperature about 0.5 °C higher and conductivity about 30% higher than the other springs. These differences persist throughout the seasons. For this reason, two springs were sampled: Main Spring (Fig. 4), which is the largest surface spring along the river, and Fissure Spring (Fig. 5). Sampling of the Fissure Spring was not possible on two occasions due to high river levels.

In the cave, sulfidic water was sampled in Lago Verde and Ramo Sulfureo. Lago Verde is a deep stagnant sulfidic pool, fed from the bottom (Fig. 6), where the water has chemical characteristics similar to those of Fissure Spring.

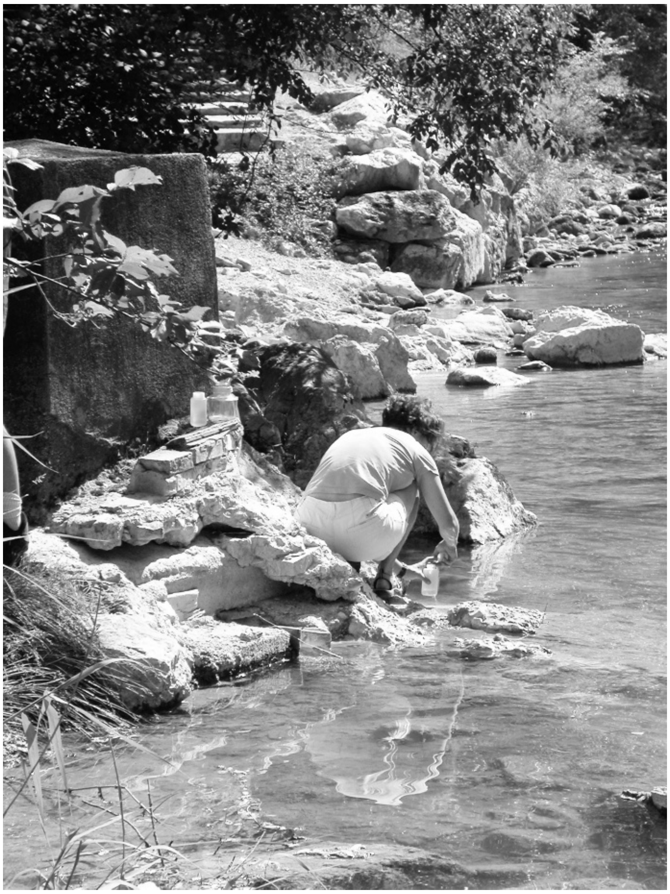

Figure 5. Fissure Spring. This small spring rises in the same limestone outcrop as Main Spring, a few meters away.

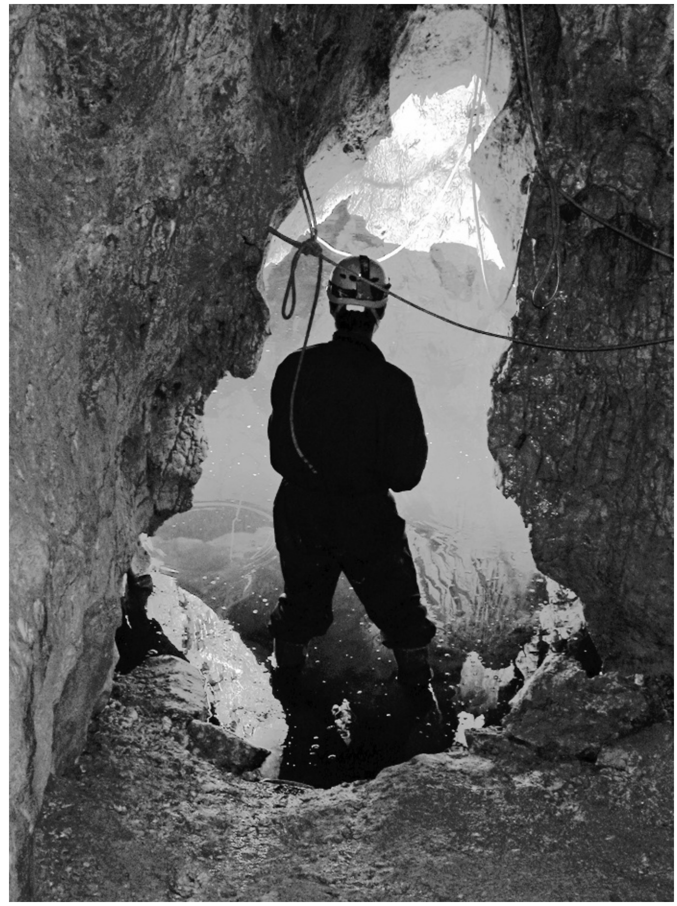

Figure 6. Lago Verde. The water was sampled in the surface of this stagnant deep lake.

Ramo Sulfureo is the most studied cave room (Galdenzi et al., 1997; 1999; Sarbu et al., 2000), with an active flow of sulfidic water. Here the water is similar to that of Main Spring, and the direct influence of meteoric water on its temperature and conductivity has already been documented (Sarbu et al., 2000).

In addition to these sampling sites, samples were collected in other cave lakes. Lago dell'Orsa and Laghi di Lucia proved to be quite interesting and will be described below. A detailed description of the sampling locations is provided in Cocchioni et al. (2003), which also provides the complete set of the data obtained. Data on chemical characteristics of water samples were integrated with the continuous monitoring of the temperature and conductivity of the sulfidic ground water in an artificial tunnel near the springs, and with water-table level monitoring in Lago Verde and Ramo Sulfureo.

Seepage Water

Seepage water at all the sampling points had uniform characteristics with only minor differences. The flow rate of Abisso Ancona dripping water was more variable, while Sala Pagliai dripping water had a constant rate of about 0.2 L min^{-1}. Weak seasonal changes occurred in the chemical parameters examined (Fig. 7).

Water temperature is about 13 °C, like the air temperature in the cave. The pH values in the Abisso Ancona vary between 7.5 and 8.4 and are consistently about 0.4 higher than those of the other sampling points. In April and August, the pH in all the locations shows a small decrease associated with an increase in dissolved CO_2 content. It should be pointed out that during these periods there are more tourists visiting the cave, although the relationship between the number of tourists and the CO_2 concentration in the cave is complex, and is also influenced by the direct arrival of air with low CO_2 from the surface through the artificial tunnel (Galdenzi and Menichetti, 2002). The total dissolved ions and the conductivity are very similar in the Abisso Ancona (average values: 251.3 mg L^{-1} and 359 μS cm^{-1}) and Lago Smeraldo (average values: 247.3 mg L^{-1} and 354 μS cm^{-1}), while they are a little lower in the more interior sampling point of Sala Pagliai (average values: 219.8 mg/L and 314 μS cm^{-1}). There are minor differences in the ion concentrations between Lago Smeraldo and Abisso Ancona. The Abisso Ancona water has a higher concentration of sodium, potassium, chloride

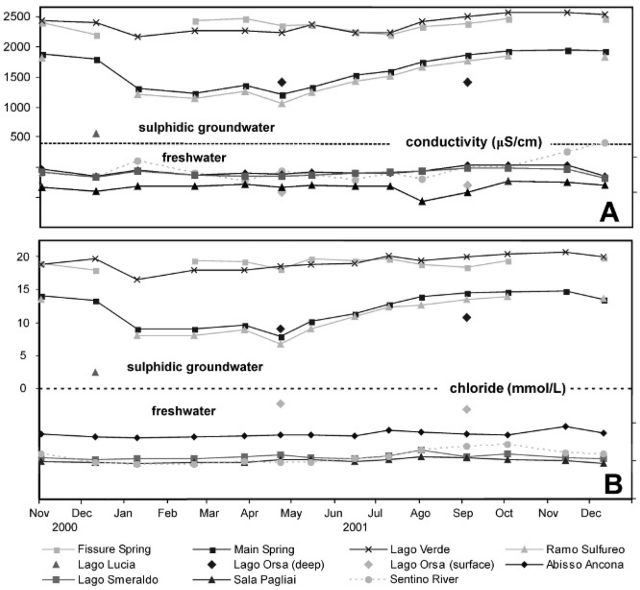

Figure 7. Seasonal changes in conductivity (A) and chloride concentration (B) in the cave waters.

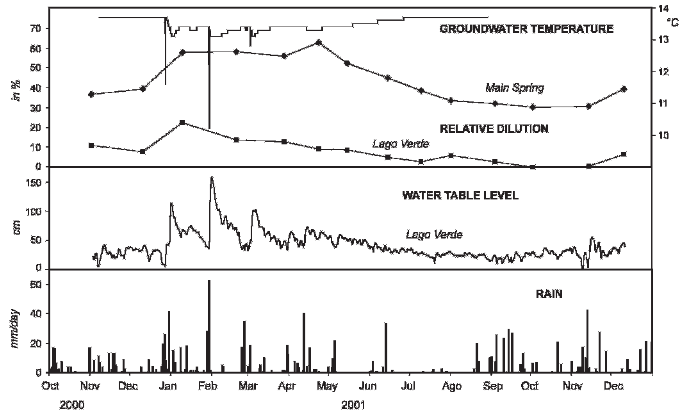

Figure 8. Correlation between rainfall, ground-water level, ground-water temperature, and dilution ratio between rising sulfidic water and descending seepage water. In calculating dilution ratio, the late autumn Lago Verde water was considered not diluted.

and sulfate, while the calcium and bicarbonate content is lower. These ionic variations offset each other and the waters of the two locations have the same salinity. Sala Pagliai water has a lower content of each ion in accordance with the lower salinity. The concentration of O_2 in the water is consistently high in all the samples and during the year the saturation index is between 93–99% (0.31–0.33 mmol L^{-1}).

The water in the Sentino River was sampled upstream from the sulfidic springs. This calcium bicarbonate water has a salinity of 230–300 mg L^{-1} without important seasonal changes. The relative constancy of the chemical composition and the similarity with the characteristics of the dripping water (Fig. 7) make it difficult to use chemical parameters to discuss the river's influence on the sulfidic ground-water composition.

SULFIDIC WATER

Chemical data on sulfidic water confirmed the preliminary observations on the existence of two main types of sulfidic ground water. Water samples from Lago Verde and Fissure Spring had very similar characteristics during the whole year, as did those from Ramo Sulfureo and Main Spring (Fig. 7). The water temperature in Main Spring is almost constant throughout the year, varying between 13.1 and 13.7 °C. The water in Fissure Spring has the same seasonal trend, but is always 0.5–1 °C higher. Sulfidic ground water is slightly warmer than both the seepage water and the cave atmosphere.

Average conductivity values are the same for Lago Verde and Fissure Spring (2360 µS cm^{-1}) and similar for the two other waters (1482–1617 µS cm^{-1}). Sulfidic water in Ramo Sulfureo has slightly lower salinity compared to that of Main Spring. All these relationships remain stable during the year.

Cation and anion compositions confirm the differences between the two types of water. Chloride, sodium and potassium have the same trend described for conductivity (Fig. 7). Average values for chloride in Fissure Spring – Lago Verde are almost identical (19.05–19.12 mmol L^{-1}), while in Main Spring they are a little higher (12.04 mmol L^{-1}) than in Ramo Sulfureo (9.75 mmol L^{-1}). Sodium and potassium concentrations show the same variations. The lower ion concentrations in Ramo Sulfureo can be related to a more significant dilution with seepage water.

The sulfate and sulfide concentrations follow the same trend as other ions, but the range of variability is wider, depending also on the oxidation-reduction processes involving sulfur in the ground water. This subject will be discussed in detail in the following text.

In contrast, the total hardness has a different trend from other parameters. The highest values are reached in Main Spring, with low variations (42–47 °F), while the lowest values are in Ramo Sulfureo (30–39 °F). The water is always undersaturated with respect to gypsum (Saturation Index $\leq$ 1.2 during the whole year in all the sampling sites) while the saturation index for calcite is close to 0. The ground-water temperature in the sulfidic ground water stays a little higher compared with the seepage water and the cave atmosphere. In Ramo Sulfureo, the temperature decrease as a consequence of rapid water recharge after rainfall has been well documented (Sarbu et al., 2000). The data acquired at the springs show a general decrease in ground-water temperature during the rainy winter season (Fig. 8). The sharp temperature decrease in the graph is due to the direct invasion of cold river water during major floods in the artificial tunnel fitted with the temperature logger.

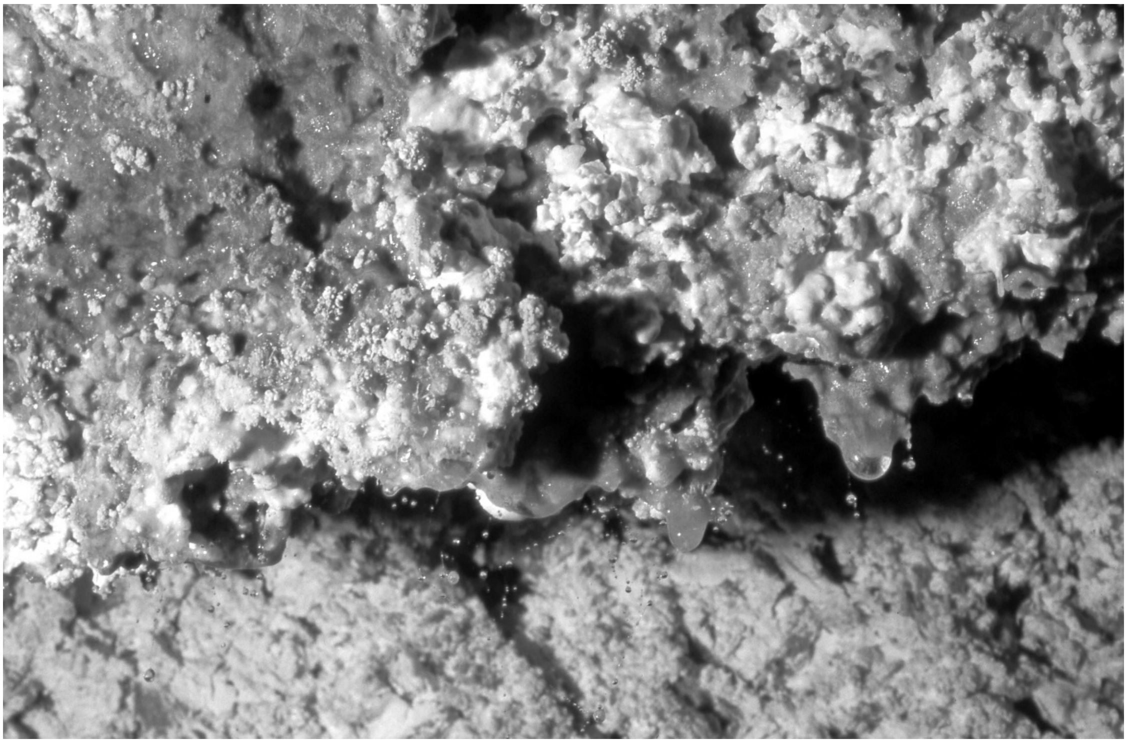

Figure 9. Replacement gypsum on the cave walls. A continuous rim of slushy gypsum covers the cave walls exposed to acidic vapors. The dark color is likely due to a layer of microbially produced organic matter (image width ~10 cm).

Ground-Water Stratification

In many isolated pools of the cave, the water composition is affected by local factors. Because the ground-water flow is generally very slow, ground-water stratification occurs in many places within the cave. The chemistry of the surface layer of water resembles that of seepage water or an intermediate composition between that of sulfidic and seepage water. It stays near the surface of the water table due to its lower salinity, and its thickness differs in each lake. This surface ground water is generally rich in dissolved O_2, although in the Laghi di Lucia H_2S was detected. Brief descriptions of two lakes sampled in this study (Lago dell'Orsa and Laghi di Lucia) follow below.

Lago Dell'Orsa

The Lago dell'Orsa consists of a group of pools interconnected at depth. These pools are inside the show-cave zone, and each pool can be reached by descending through a separate shaft about 20 m deep. We sampled the northern pool, far from the tourist walkway. The water depth is about 8 m and a surface layer of bicarbonate water ~5 m deep overlies the sulfidic water. Samples of sulfidic and bicarbonate water were collected during two different periods (April and September 2001). Sulfidic water showed a composition similar to Main Spring – Ramo Sulfureo water. The composition of the surface layer demonstrated weak, but significant, differences from both the seepage water sampled in the cave and the river water. A small increase in Na^+ and Cl^- content could be attributed to contamination from small amounts of washing water used in the show cave or directly from the sulfidic water. However, the low Ca^{2+} and bicarbonate content correlates well with the characteristics of the seepage water in this area, which has unusually low contents of these ions (Cocchioni et al., 2003).

Laghi Di Lucia

The Laghi di Lucia are two small sulfidic lakes (~20 m^2) that can be reached by descending a 20 m deep shaft. They are fed from the bottom and slow water flow can generally be observed. Widespread corrosion of the limestone above the lakes is due to H_2S vapors that oxidize and produce abundant slushy gypsum on the cave walls and ceilings (Fig. 9). During some periods, however, the H_2S in the air becomes very low or disappears.

In December 2000, the chemical characteristics of the surface water in the lake were intermediate between the sulfidic and bicarbonate water, and the H_2S was low in the water (0.1 mmol L^{-1}) and not detected in the air. This intermediate composition, however, cannot be attributed merely to the dilution of the sulfidic water with a significant amount of seepage water. In fact, while the concentration of the principal ions (K^+, Na^+, Mg^{2+}, Cl^-) was reduced to ~20% of those measured in Main Spring on

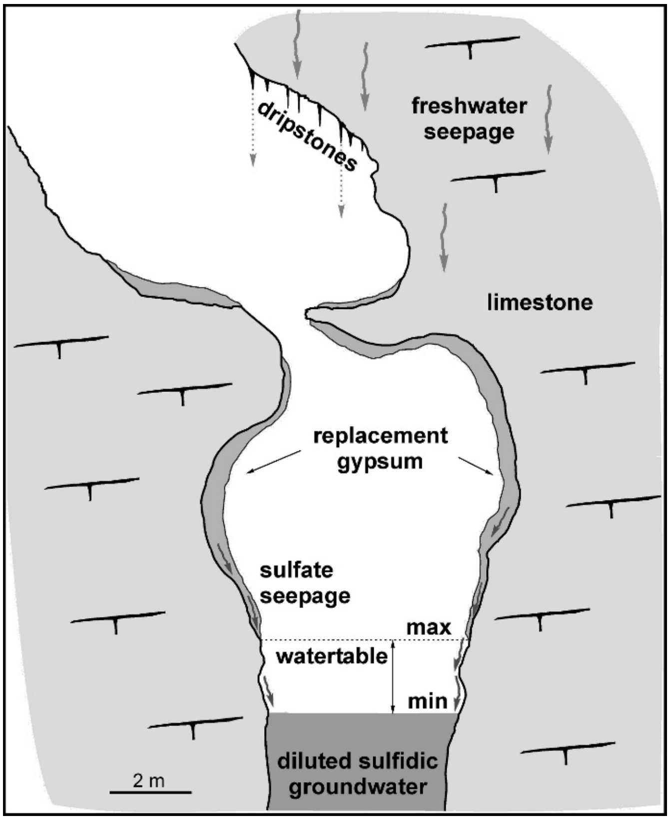

Figure 10. Schematic section of Laghi di Lucia. The high sulfate content in the diluted sulfidic ground water is consistent with seepage water that is sulfate-enriched after flowing through the replacement gypsum crust covering the cave walls above the water table.

the same date, the sulfate concentration in the water maintained values as high as at Main Spring. The anomalous composition of the water might be due to a dilution of the sulfidic ground water with seepage water that has dissolved replacement gypsum as it descends (Fig. 10).

Sulfidic Ground-Water Dilution

Dilution Ratios

The data show that water characteristics vary significantly in the different zones of the cave, and that the surface composition of ground water is often influenced by local factors, including stratification. Furthermore, the water in Ramo Sulfureo is slightly more diluted than in Main Spring (Fig. 7). The water moving from the Ramo Sulfureo to Main Springs mixes with less diluted sulfidic water. These data suggest that the variable recharge of seepage water from the karst surface is the main cause of the dilution of sulfidic ground water in the shallow phreatic zone. The pattern of ground-water dilution we observed is not consistent with river recharge because the dilution ratio is not correlated with the distance to the river.

The ground-water composition in Main Spring is representative of the water in the shallow phreatic zone throughout the cave, as also documented by the similarity of water chemistry in most springs and in Ramo Sulfureo, Lago dell'Orsa, and other cave lakes or streams. On the contrary, water in Lago Verde and Fissure Spring is less diluted sulfidic water, with minor seasonal changes in water chemistry and less influenced by the variable recharge of bicarbonate water. This more concentrated water represents the composition in a lower part of the phreatic zone where the dilution is of lesser importance. This supposed origin is confirmed by its similarity to the water coming from a 30 m deep well drilled for thermal baths, analyzed monthly by one of the authors.

The fairly stable chemical composition of seepage water in the different sampling zones throughout the year made it possible for us to verify by analytical calculation that the concentration of the primary ions in Main Spring – Ramo Sulfureo ground water can derive from the natural mixture of bicarbonate water and high salinity sulfidic water. Since we observed that the river water has a chemical composition similar to that of seepage water (Fig. 7), the calculated dilution ratios are not influenced by the causes of the dilution itself.

To calculate dilution ratios, we compared chloride concentration in each sample with the values measured in the Lago Verde at the end of the summer after a long dry period. This water was considered to be pure deep phreatic water, although there might be a slight dilution by surface water. A comparison of ion concentrations in the studied period shows that the Lago Verde water is diluted with seepage water to a maximum percentage of 20% during the wet season. In Main Spring, the water dilution due to seepage-water recharge varies between 30% in the autumn and 60% during the spring (Fig. 8).

Water-Table Level and Ground-Water Dilution

The elevation of the water table in the cave varies during the year (Fig. 8). Its main range was lower than 50 cm, but during major flooding events in the Sentino River, the level rose quickly up to 1.5 m for short periods. Measurements in Lago Verde and in Ramo Sulfureo showed the same trend, both in the range and in the timing of the water-level changes, and the two curves representing water-level changes can be superimposed (data not shown). The same results were obtained in 2003–2004, comparing water-table levels in Lago Verde and Lago dell'Orsa (data not shown). These uniform variations of water level in the different cave zones after meteoric events reveal the high permeability of the karst aquifer.

Some interesting conclusions can be drawn by comparing seasonal changes in the ground-water temperature, water-table level, and the dilution curve of sulfidic ground water. Periods with a high water-table level correspond with lower temperatures and higher dilution. All these parameters are also related to the distribution of rain events during the year. These data clearly show the influence of seasonal rainfall evolution on the ground-water temperature, level, and chemistry.

The dilution curves of Lago Verde and Main Spring have a similar seasonal trend, but the maximum dilution occurred in different periods (Fig. 8). In Lago Verde, the maximum dilution occurred at the same time as the maximum water-table level. In Main Spring, the maximum dilution was reached in April at the end of the rainy period and at the beginning of the depletion period. In the following months, the water temperature rose slowly, returning to the autumn values in unison with the decrease of dilution.

The differences between the trend of dilution curves in Main Spring and Fissure Spring and their different relations with water temperature and water-table level (Fig. 8) show that Main Spring represents the overall discharge of the shallow phreatic zone, where ground-water dilution varies according to the general hydrologic cycle of the spring. On the contrary, the water in Lago Verde (and in Fissure Spring), rising from deeper zones of the aquifer, is directly diluted by seepage water during the principal rainfalls, but only for short periods and with a lower intensity (Fig. 8).

Flooding Events

A detailed discussion of the relationship between ground water and river levels is not the main focus of the present research. Studies on this subject are currently in progress, including absolute measurements of water levels in the cave. However, the data obtained on the water levels in the cave and water temperature at the springs already give some useful indications about the modality of ground-water dilution.

During the monitoring period (2000–2001) three main flood events occurred (Fig. 8). During these events, the river level increased up to ~2 m near the spring, while in the cave the maximum rise of the water table was ~1.50 m. Detailed analysis of these flooding events shows that they had similar effects on water level and temperature. Figure 11 represents the events of December 27, 2000 and January 31, 2001. In the cave, at the beginning the water level increased without changes in water temperature. In fact, the sharp lowering of the temperature in the spring was due to the cold river water's direct invasion during the flood. The maximum level of ground water was reached after the flood in the river, and it relates to the lowering of water temperature. The water level remained high for some days after the end of the river flood. The rise of the ground-water level is only in part influenced by the increase of the river level, which causes a drainage impediment at the springs. The increased recharge of cold seepage water in the few days following the rainfalls appears to be the main cause of the decreasing temperature and increasing level in the ground water.

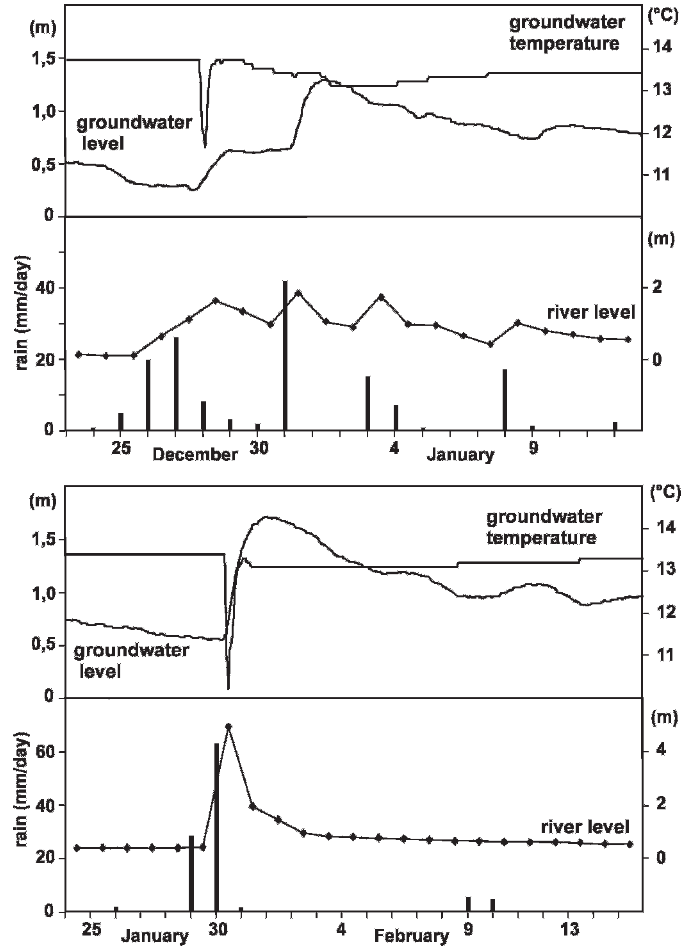

Figure 11. Data on flood events. The sharp lowering of water temperature observed on December 27 and January 31 was due to the direct contact of river water with the thermometer near the sulfidic springs. The river level was registered a few km downstream of the springs. In the Frasassi Gorge, near the springs, the river level increased ~2 m.

Although the river discharge may influence the cave water-table level, the data acquired on flooding events do not suggest a direct invasion of river water or a direct role of the river in the dilution of the ground water in the shallow phreatic zone. Furthermore, the chemical data discussed above suggest that this superficial dilution is mainly due to the variable recharge of seepage water from the karst surface. These data, however, do not exclude the possibility that the river participates in the recharge of the ground water, as already proposed by some authors (Tazioli et al., 1990; Ciancetti and Pennacchioni, 1993; Caprari et al., 2001). This recharge might occur because upstream in the gorge, the river bed is above the sulfidic ground-water level and, consequently, a permanent weak water loss from the river might occur. Measurements of river discharge, however, highlight a constant slight increase of the river discharge from upstream to the

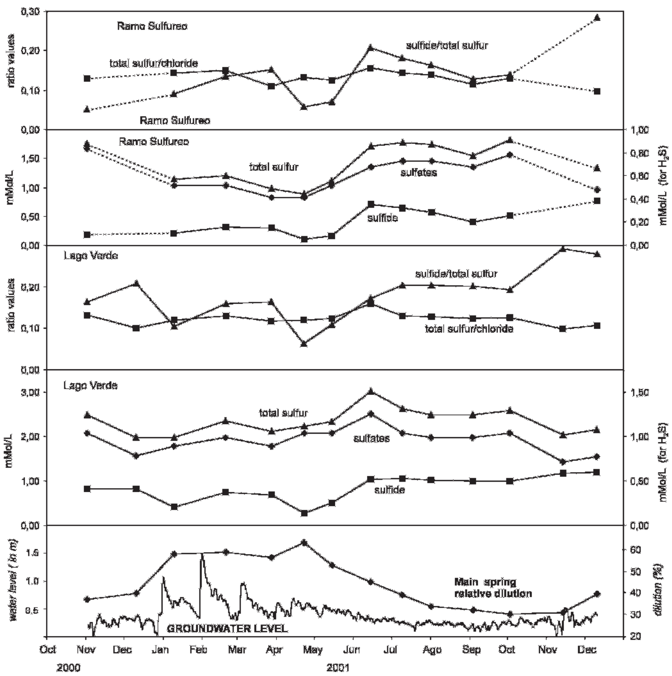

Figure 12. Seasonal changes in sulfide and sulfate concentration in the ground water.

downstream end of the Gorge (Ciancetti and Pennacchioni, 1993) or only minor changes (Caprari et al., 2001).

Sulfate and Sulfide in the Ground Water

The sulfidic ground water contains both oxidized and reduced sulfur with significant variations during the year. The total amount of sulfur species in the water shows a seasonal trend similar to chloride, although the ratio between total sulfur and chloride (in mol) is not constant ($\sim$0.13 $\pm$ 0.03), with a wider range in Main Spring than in the other sampled localities (Fig. 12). The amount of the dissolved sulfur species can be modified by the release of H_2S to the cave atmosphere and by the dissolution of replacement gypsum on the cave walls due to a rise of the water table or to seepage water. The isolated increase of the ratio of total sulfur/chloride observed at Lago Verde in June 2001 is a consequence of increased sulfate in the water. This event occurred two days after a strong rain (Fig. 8), which should have caused the arrival of small amounts of seepage water enriched in sulfate from dissolution of the thin gypsum crystals covering the cave walls (Fig. 13).

The amount of oxidized and reduced sulfur species shows more significant variations because their concentration is not simply controlled by the amount of seepage-water dilution (Fig. 12). Biotic and abiotic oxido-reduction reactions can modify the ratio between sulfate and sulfide in the water. The sulfide concentration undergoes the widest fluctuations on a percentage basis and can increase

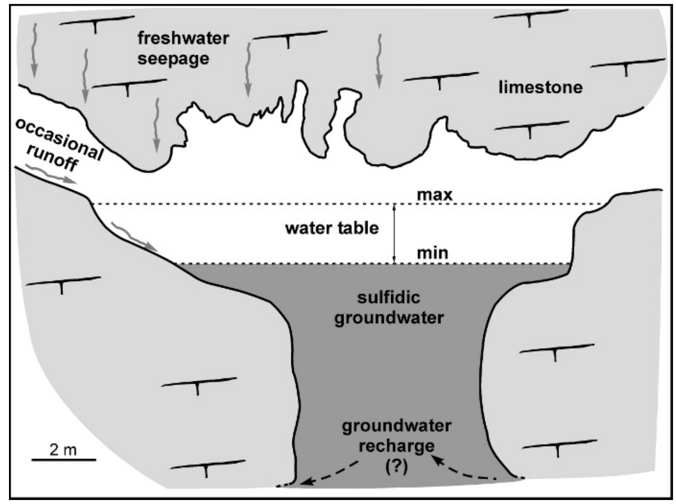

Figure 13. Schematic section of Lago Verde. This lake, near the cave entrance, is fed by rising sulfidic ground water. The irregular recharge of seepage water from the thin, highly karstfied overlying limestone causes a weak dilution at the lake surface only during the wet season or after major storms.

from <0.1 up to 0.5 mmol L^{-1} (Fig. 12). The sulfide/total sulfur ratio varies mainly as a result of changes in the sulfide concentration, which ranges between 5% and 30% seasonally. These changes are correlated with the relative dilution of ground water caused by the amount of seepage-water recharge (Fig. 12). In the wet period, the rapid recharge of water from the surface decreases the total sulfur dissolved in the ground water. Furthermore, the O_2-rich seepage water enhances H_2S oxidation, also reducing the sulfide/total sulfur ratio.

In the dry period, the reduced recharge of water from the surface slackens H_2S oxidation, and both sulfide concentration and sulfide/total sulfur ratios increase. Furthermore, the activity of sulfate-reducing bacteria can contribute to increased H_2S concentrations in the water with more importance during the periods of low oxygen availability. Sulfate reducing bacteria were identified in the ground water (Macalady et al., 2006) where they live closely associated with sulfide oxidizing bacteria in the microbial biofilms that cover walls and floor below the water table (Fig. 14).

Air Composition in the Sulfidic Sections

This first series of gas concentration measurements in the air of sulfidic zones (including H_2S, O_2, CO_2 and, occasionally, SO_2) were made in the Ramo Sulfureo at the same location as water sampling for chemical analyses. The Ramo Sulfureo was chosen because the wide surface of the flowing sulfidic water facilitates gas exchange and enhances active replacement of limestone with gypsum. The first measurement (November 2000) was made at the top of a small pit above a sulfidic lake with the most intense gas rise. All the following measurements were made at a nearby

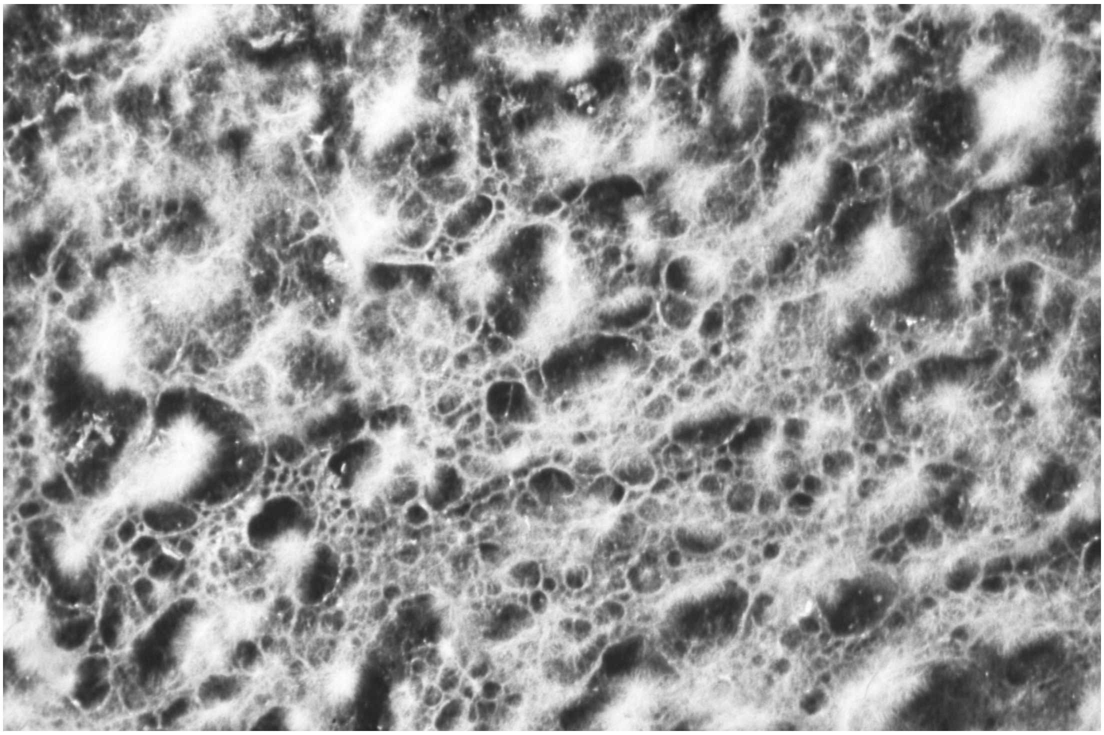

Figure 14. Microbial mats in the sulfidic ground water (image width ~30 cm).

sulfidic lake in the same room as water sampling. This change of gas sampling site was based on the desire to reduce the influence of the rise path on the gas concentration. Measurements for December 2000 and November 2001 are lacking because of difficulties in accessing the room, but the available data cover the entire hydrologic seasonal cycle (Fig. 15).

The oxygen concentration in the air was almost the same as that at the surface (about 20%). The H_2S concentration in the sampled room had seasonal changes, from 1 to 8 ppm. The CO_2 content varied during the year from 1500 to 5600 ppm. SO_2 was not detected.

The air composition in the sulfidic room is strongly influenced by the ease of exchange with the upper non-sulfidic sections. Therefore, the CO_2 content in the air decreases rapidly towards the upper cave levels, a fact that was verified in two different periods (April 9, 2001 (data not shown) and October 7, 2001 (Fig. 16)). The H_2S in the air can only be detected close to the sulfidic sections where it is quickly oxidized (Fig. 16); carbon dioxide, on the

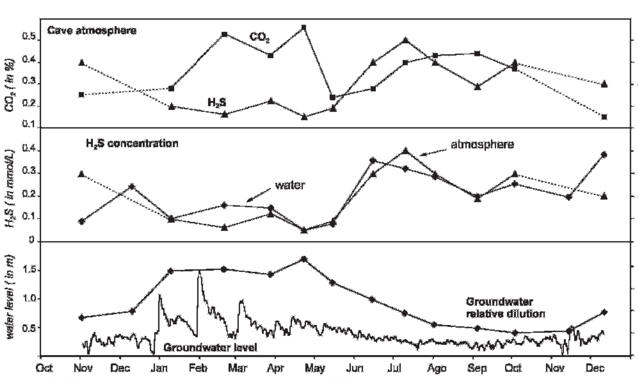

Figure 15. Seasonal changes in the H_2S and CO_2 concentrations in the cave air. The H_2S concentration in the water and in the air has the same seasonal trend, and the lowest values correspond with high ground-water dilution. In the same period, the maximum CO_2 concentration occurs.

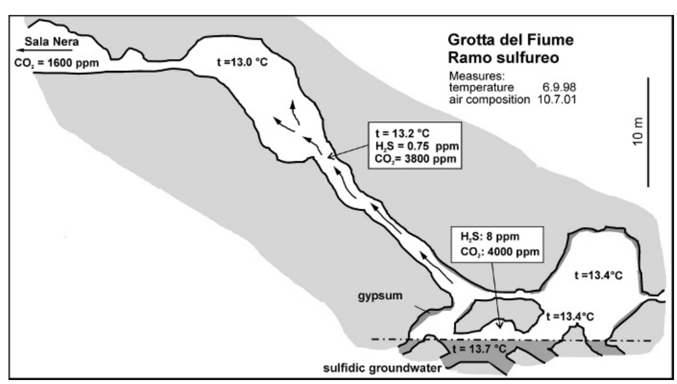

Figure 16. Schematic profile through the sulfidic section of the cave (after Galdenzi, 2001). CO_2 and H_2S can diffuse from the sulfidic lakes to the cave atmosphere. The concentration of H_2S rapidly decreases, because it oxidizes and causes the growth of gypsum replacement crusts on the cave walls.

contrary, can maintain higher values in the surrounding rooms as well. Gas concentrations expected for a room close to air exchange were simulated using an air bell floating on the water table. Here, after a few months, the concentration of H_2S exceeded 120 ppm, while O_2 decreased to 7% (Galdenzi, 2001).

Changes in cave air composition are correlated with seasonal changes in sulfidic-water discharge and chemistry. The concentration of H_2S in the air is related to the dissolved content of the H_2S in the water (Fig. 15). For this reason, there is also a good correlation with ground-water dilution. During the spring, when the ground water is highly diluted by the seepage water, H_2S reaches its lowest values in the cave air.

The CO_2 concentration attains maximum values during the spring when water dilution is greater (Fig. 15). In this case, there is not a clear relationship with the bicarbonate concentration in the water, which fluctuates between 3.9 and 4.6 mmol L^{-1} with higher values in the autumn. This seasonal increase of the CO_2 content probably is not due to atmospheric CO_2 carried in by seepage water during the wet and warm season. In the upper levels, where there is only seepage water, in fact, CO_2 concentration is well known (Galdenzi and Menichetti, 2002) and remains lower than in the Ramo Sulfureo throughout the year. We believe that the air concentration of CO_2 in the sulfidic sections is related to the amount of gas rising from the depths and released from the ground water. An additional source of CO_2 in the shallow phreatic zone may derive from the active speleogenetic processes of the area. In the wet season, while the CO_2 content in the air is increasing, the sulfide in the ground water decreases because of sulfide oxidation (Fig. 15):

$$H_2S + 2O_2 \rightarrow H_2SO_4 \quad (1)$$

$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-} \quad (2)$$

H_2S oxidation (Equation (1)), which reduces the sulfide/total sulfur ratio, also produces H_3O^+ ions that react with limestone (Equations (2) and (3)), increasing the HCO_3^- concentration in the water and consequently, the release of CO_2 into the cave atmosphere (Equations (4) and (5)):

$$H_3O^+ + CaCO_3 \rightarrow Ca^{2+} + HCO_3^- + H_2O \quad (3)$$

$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O \quad (4)$$

$$H_2CO_3 \rightarrow H_2O + CO_2(g) \quad (5)$$

The increase in cave air CO_2 is consistent with a high rate of H_2S oxidation in the ground water during the rainy season compared to the dry season.

Conclusions

The Frasassi aquifer is hosted in highly karstified, permeable limestone where water-level changes are simultaneous at all the monitored sites. The Sentino River forms the base level and can influence the cave water-table level, but the main cause of ground-water dilution in the shallow phreatic zone probably lies with the amount of seepage-water recharge.

Despite high permeability, significant differences were found in water chemistry among sample sites. Water rising from a deep zone of the aquifer directly feeds some pools of the cave, including Lago Verde and Fissure Spring. Low water flow causes seepage water to remain on the surface due to its lower density across a wide zone of the cave,

Seepage-water dilution varies between 30% and 60% during the year in Ramo Sulfureo and in Main Spring. In contrast, water chemistry in Lago Verde and Fissure Spring is more constant and is directly influenced for short periods by the direct arrival of seepage water, causing a dilution of less than 20%.

Seasonal changes in water chemistry interact with speleogenesis in the cave. The recharge of oxygen-rich seepage water promotes H_2S oxidation during the wet season when the sulfide/total sulfur ratio decreases from 30% to 5%. During this period, corrosion in the upper phreatic zone is most intense, promoting the production of CO_2, which is then released into the air. In these wet periods, the low H_2S concentration in the water also reduces H_2S in the cave atmosphere, slowing the growth of the replacement gypsum crusts on the cave walls above the water table. In the dry season, the high H_2S concentration in the water probably testifies to a lower intensity of oxidation processes and limestone corrosion in the ground water, while the higher concentration of this gas in the air likely facilitates limestone corrosion and gypsum production due to H_2S oxidation above the water table.

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