

# Monitoring of percolation water to discriminate surficial inputs in a karst aquifer

S. Covelli · F. Cucchi · R. Mosca

**Abstract** A long-term study on the chemistry of percolating waters in a very large touristic karst cave (Grotta Gigante, northern Italy) was carried out in order to define recharge zones, flowpaths, and possible anthropogenic contamination from the neighboring area. On the basis of a multivariate analysis of the chemical parameters, a discrimination of the dripping points was attempted. Percolation waters whose recharge zone is in the northernmost sector of the cave appeared permanently affected by the anthropic settlements and agricultural activity on the ground surface.

**Key words** Hydrochemistry · Percolation waters · Karst aquifer · Human impact

## Introduction

Research on the identification of the origins of underground waters is carried out basically to provide urban sites with a safe water supply. Natural markers, such as oxygen and hydrogen isotopes (Aires-Barros and others 1995; Ii and Misawa 1994) and artificial tracers (Habic and Kogovsek 1979), are used to date groundwater flows and determine their recharge areas and sampling site at the source. The chemical composition of groundwater and its isotopic ratios depend on natural factors linked to environmental conditions in the recharge zone of aquifers, as well as to permeable rocks and to the course water follows.

The number of cases in which water is contaminated increases with rising population, and the expansion of ur-

ban, agricultural and industrial settlements, and aquifers closer to the ground surface are most susceptible to contamination. Percolation waters in karst caves are underground springs of surficial aquifers, and consequently, chemical variations depend on exchange reactions between water, soil, and rocks.

The Grotta Gigante, in the Trieste Karst, is one of the most important and well-known Italian touristic caves. It is basically formed by a large room that can be reached from a sloping tunnel whose entrance is 265 m a.s.l. Its plan is sub-elliptical and the room, 114 m deep from the ground surface, is 160 m long and 65 m wide; the maximum height of the roof extends up to 107 m and has a volume of about 600 000 m<sup>3</sup>.

Monthly measurements carried out inside the cave over 23 years document 11.57 °C as the average air temperature with a yearly variation of 0.37 °C. The average humidity of the cave reaches 99.7%, with a small fluctuation of 0.7%.

A meteorological station outside the Grotta Gigante cave provides rainfall data between 1980 and 1989: with an average of 1350 mm year<sup>-1</sup>, a maximum of 1494 mm year<sup>-1</sup> and a minimum of 1031 mm year<sup>-1</sup>. The temperature outside the cave ranges from -15 °C to +35 °C, registering 12 °C average.

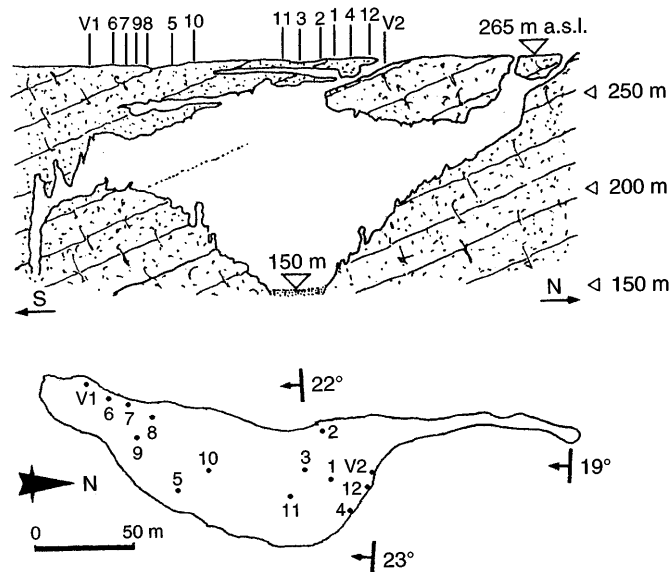
## Geological and geomorphological setting

The cave has developed in very pure limestones of Cretaceous age. Calcite is found in large amounts (92.5–99.5%) along with small quantities of dolomite (0.5–2.5%) and insoluble residues (1.0–5.0%). Geologic units in the cave dip 15°–23° southward (Fig. 1), varying in thickness from 80 to 5 cm. Decimetric strata prevail; fractures are not large and the predominant rocky unitary volume extends up to 1 m<sup>3</sup>. Main discontinuity distribution patterns are subvertical or very sloping (Cucchi and others 1985). Arrangement and frequency of discontinuity surfaces cause a rapid hypogean percolation along sloping (or subvertical) flow lines (permeable thickness ranges from 45 to about 90 m) with limited movements on the horizontal axis due to the disposition of strata and, then, to a weak line southwards. The hypogean percolation catch-

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**Fig. 1**

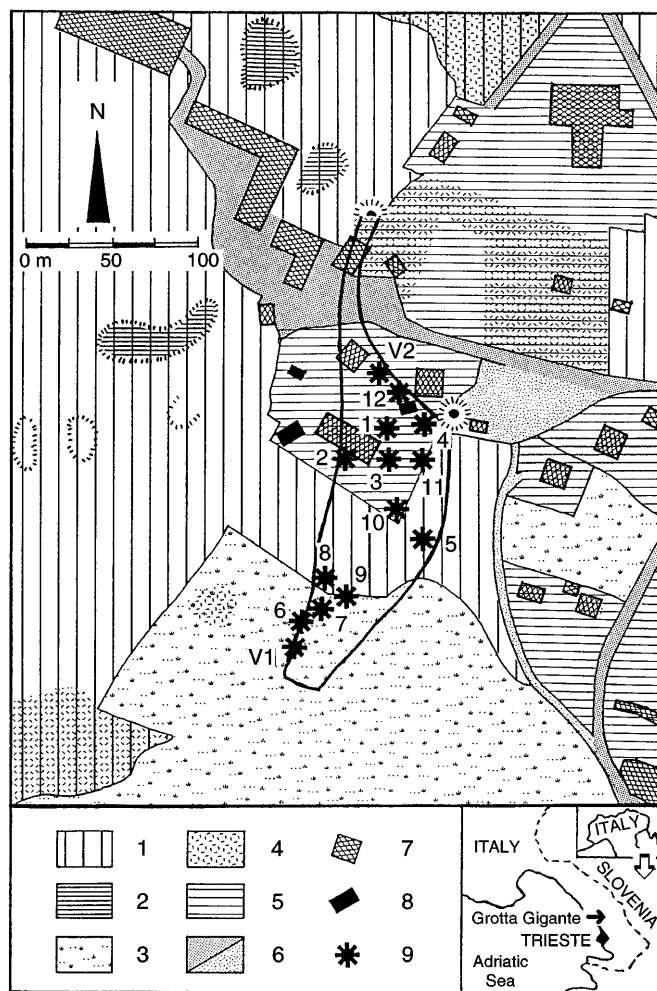
Schematic cross section and planimetric map of the Grotta Gigante cave. Numbers represent dripping points located on the cave roof

ment basin, therefore, is limited to the area surrounding the cave. The morphological features of the area are those typical of the karst, characterized by a tabular, slightly wavy rock surface, and small dolines with steep slopes with red-brown loam at the bottom. The land surface is covered by few centimeters of red karst loam (*terra rossa*), on which shrubs and beeches and oak trees grow. Meadows are characterized by gardens or orchards as well as to areas with houses, concrete roads and asphalted open squares (Fig. 2).

The area around the cave has a discontinuous mixed red soil with rocky fragments, soil thickness ranges from a few centimeters to a couple of decimeters. Petrographical analyses of Trieste Karst (*terra rossa*) (Lenaz and others 1996) have shown the existence of the following mineral associations: illite (6%), kaolinite (2.5%), chlorite (4%), quartz (76%), feldspars (8%), and calcite (3%). Dolomite is not found. The average chemical composition of the oxides of the major elements, obtained from the XRF analysis and expressed in percentages, is: SiO<sub>2</sub> (53%), TiO<sub>2</sub> (1.15%), Al<sub>2</sub>O<sub>3</sub> (18.5%), FeO (7.5%), MnO (0.2%), MgO (1.7%), CaO (1.6%), Na<sub>2</sub>O (0.6%), K<sub>2</sub>O (1.8%), P<sub>2</sub>O<sub>5</sub> (0.15%); the average amount of the organic material is scarce (LOI = 13.5%).

## Sampling and analytical methods

There are numerous dripping points inside the cave, and almost all from the roof from about 10 to 80 m height. There is a good correlation between outer precipitation and percolation and between intensity of precipitation



**Fig. 2**

Utilization map of the ground surface surrounding the cave. 1 Outcropping or suboutcropping bedrock; 2 red karst loam; 3 meadows; 4 trees; 5 gardens, orchards, vineyards; 6 asphalted or country roads; 7 buildings; 8 swimming pools; 9 sampling points

and frequency of dripping. The rock which forms the cave roof reaches a maximum thickness of 90 m (Forti and Gasparo 1981). Samples were collected at 14 sampling sites; 12 of them correspond to percolation waters (S1, S2,...), which cause an increase in the number of stalagmites. Two have been obtained from small pools at the cave floor (V1 and V2). On the basis of surveys on the first four sampling sites, Cucchi and others (1985) calculated, during the 1979–1985 period, the rate of flow in individual dripping points, estimating it at about 2600 l year<sup>-1</sup> with an average 0.12 mm stalagmite growth. Water samples were collected at dripping points with funnels to fill 2-l-capacity containers. Percolation waters collected at S1, S2, S3, S5, S6, S7, S9, S10, S11, S12 were obtained after 1–2 collecting days. Samples procured in 24-h periods are quite rare (at S4, S8), and the samples from the two small pools (V1 and V2) were taken in containers from still water.

Water samples were obtained on 18 occasions from two different surveys; the first field operations began in December 1980 and were irregularly performed until March 1982; the second survey was carried out from January to September 1989. A total of 121 water samples from both surveys were collected and analyzed. The determination of parameters for each water sample was made following some methodologies reported in APHA, AWWA and WPCF (1976).

Ammonia, nitrite, and nitrate were estimated through colorimetric determination, chloride by means of titration involving mercuric oxycyanide, sulfate, and carbon dioxide through, respectively, microtitration and titration methods. Calcium content and hardness were determined directly following the EDTA titrimetric method, whereas magnesium was quantified with the gravimetric method. Phosphates were estimated following the principle involving formation of molybdophosphoric acid, which is reduced by stannous chloride. The Molybdosilicate, the Eriochrome Cyanine R and Phenantroline methods were used to quantify, respectively, silica, aluminium, and iron. Sodium and potassium were determined by atomic absorption spectroscopy. In addition to ionic species, specific conductance at 25 °C and alkalinity, by titration, were defined. The pH values were measured immediately after sample collection in the field. Total residue at 180 °C and 600 °C were also determined. After all, surfactants (MBAS), which could be considered as possible tracers of anthropogenic inputs, were detected by means of the Methylene Blue method.

## Results and discussion

The temperature of the collected water samples varied from 8.9 to 11.2 °C (the average temperature was about 10.5 °C); these variations were related to the outer temperature. As for pH values, they started from 7.08 and elevated to 8.38 (with a mean value of about 7.42 and 8.22) in the survey of 1980–1982, whereas they were lower (5.50–7.30) in the sampling carried out in 1989.

In Tables 1 and 2 the minimum, mean, and maximum amounts of each parameter in every sampling site of the two surveys were observed. The data obtained from the sampling of surfactants (MBAS) have been omitted from the tables as they have appeared only sporadically in some sampling points. Nevertheless, their presence is to be included, since it certainly underlines the existence of anthropogenic inputs. The highest surfactants quantities have been found in percolation waters coming from some sampling sites of the northernmost area, such as S3 (0.09 mg/l), S4 (0.06 mg/l), and S12 (0.05 mg/l). The values regarding specific conductance of waters collected from the northernmost percolation sites (S11 and S12), are richer in salts (between 782 and 642 mg/l in 1980, 566 and 592 mg/l average in 1989) than those from the southernmost area (S6 and S9 have values close to 300 mg/l). Low values are to be explained by the short distance covered by percolating waters before arriving at

the cave roof, thus limiting exchange reactions with rocks and soil.

It can be stated that results regarding alkalinity, hardness, and solid residue are in accordance with specific conductance values.

The representation in Fig. 3 of the mean composition of percolating waters on Piper's diagram (1944), regardless of the sampling period, emphasizes the homogeneity between sources. Waters are very similar, all having approximately the same carbonate-alkaline content as expected as the catchment basin has geological features characterized by the predominance of carbonate rocks. Waters from S1 and S2 constitute an exception. Their average compositions appear slightly richer in Na and SO<sub>4</sub> content, and is explained by the direct influence of the ground above their dripping points, an area of human settlements.

The representation of the same mean data in a Schoeller's diagram (1935) highlights similarities and differences among the contents of both, the main ions and silica in each dripping point better than Piper's diagram. In Figs. 4 and 5 the trends of the spidergrams, although very similar among themselves, stress a more marked variability as well as a greater concentration of nitrate, chloride, calcium, sodium, and phosphate in the northernmost sampling sites of the area (S1, S2, S3, S4, S11, S12) during the first survey (1980–1982). The next survey (1989) presents a greater diversity between the mean data in the southernmost sampling sites as well as an increase in salt contents, as can be observed in some parameters such as nitrate and phosphate.

Examining the mean contents of cations it has been observed that a great part of the sampling sites present re-

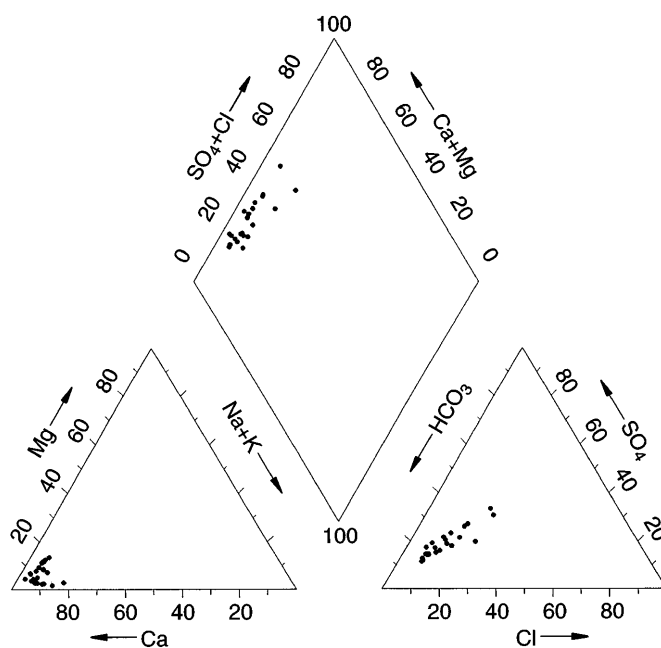


Fig. 3

Piper's diagram of the percolation waters in the Grotta Gigante cave

**Table 1**

Hydrochemical data for the percolation waters in 1980–1982 (Rows: S1 - dripping and sampling sites; (4) - number of sample collections. Columns: Cond - specific conductance; Alk - alkalinity; Hard - hardness; TR - total residue)

		NH <sub>3</sub>	NO <sub>2</sub>	NO <sub>3</sub>	Cl	SO <sub>4</sub>	CO <sub>2</sub>	Ca	Mg	Na	K	SiO <sub>2</sub>	PO <sub>4</sub>	Fe	Al	Cond	Alk	Hard	TR	TR	pH
1980		mg/l															μS/cm	mg/l	180°	600°	
S1 (4)	max.	0.20	0.004	10.7	14.6	32.8	28.2	105.0	6.50	13.30	1.50	3.80	0.010	0.020	0.010	623	216	262	375	262	8.24
	average	0.19	0.003	9.93	11.4	26.7	15.5	84.3	4.45	9.73	1.18	3.60	0.010	0.013	0.010	525	182	210	309	221	7.84
	min.	0.16	0.002	9.10	7.4	14.0	5.1	57.0	2.50	4.60	0.70	3.50	0.010	0.010	0.010	348	153	141	190	162	7.46
S2 (5)	max.	0.25	0.002	12.20	23.8	51.0	20.2	142.0	1.80	20.60	0.31	3.30	0.030	0.016	0.010	769	246	354	500	406	7.91
	average	0.17	0.002	11.24	22.0	49.2	16.4	112.6	1.32	20.43	0.21	3.13	0.014	0.013	0.007	697	211	281	437	353	7.79
	min	0.10	0.002	10.50	20.3	48.0	10.3	98.0	0.60	20.10	0.10	2.80	0.010	0.010	0.002	607	171	246	364	225	7.54
S3 (7)	max	0.46	0.002	6.61	19.7	29.6	26.0	135.0	2.30	13.40	0.14	4.10	0.010	0.080	0.025	783	340	337	385	344	8.14
	average	0.22	0.002	5.23	14.4	26.0	19.1	98.5	1.55	12.17	0.12	2.95	0.010	0.028	0.014	565	239	246	323	277	7.93
	min	0.13	0.002	3.62	5.3	24.0	10.3	78.0	0.70	10.50	0.10	2.20	0.010	0.010	0.002	354	162	194	246	200	7.72
S4 (9)	max	0.47	0.007	8.50	9.0	27.5	22.4	142.0	2.50	7.10	1.90	5.10	0.210	0.070	0.025	696	289	354	419	375	8.36
	average	0.25	0.003	6.52	7.7	26.4	15.2	109.9	1.79	6.65	1.86	4.61	0.139	0.023	0.012	596	238	275	345	271	8.14
	min	0.15	0.002	4.19	5.7	24.0	11.0	96.0	0.60	5.90	1.83	3.90	0.030	0.010	0.002	538	188	241	240	205	7.85
S5 (5)	max	0.36	0.002	1.29	8.0	17.0	16.0	95.0	5.60	4.80	0.54	3.10	0.010	0.010	0.010	498	239	237	273	250	8.18
	average	0.24	0.002	0.96	6.8	15.3	12.6	72.6	4.80	4.67	0.48	2.54	0.010	0.010	0.008	427	197	181	216	192	8.08
	min	0.11	0.002	0.54	5.6	13.9	10.0	58.0	4.30	4.50	0.40	2.20	0.010	0.010	0.003	377	166	144	152	141	7.93
S6 (7)	max	0.33	0.002	1.80	8.8	16.0	13.4	73.0	6.30	5.40	1.10	6.80	0.010	0.150	0.260	401	162	182	217	196	8.38
	average	0.26	0.002	1.40	7.8	14.3	7.0	57.1	5.84	4.82	0.92	3.80	0.010	0.039	0.044	345	143	142	189	157	8.22
	min	0.16	0.002	0.79	6.5	13.0	4.0	46.0	5.30	4.20	0.60	2.50	0.010	0.010	0.001	297	115	114	162	117	7.80
S7 (6)	max	0.57	0.002	1.90	9.0	17.0	15.0	91.0	5.00	4.80	0.63	3.20	0.010	0.048	0.019	468	218	227	267	248	8.26
	average	0.32	0.002	1.46	7.5	14.5	11.3	76.3	4.13	4.58	0.50	2.68	0.010	0.018	0.009	438	201	190	229	190	8.13
	min	0.20	0.002	0.91	6.2	12.9	9.2	67.0	3.20	4.30	0.22	2.40	0.010	0.010	0.002	405	179	168	187	144	7.80
S8 (8)	max	0.42	0.002	3.14	10.6	15.0	17.1	89.0	7.00	5.50	1.26	8.00	0.010	0.010	0.013	474	227	223	271	245	8.29
	average	0.30	0.002	1.53	7.3	14.0	13.6	76.4	6.15	4.82	1.00	3.81	0.010	0.010	0.008	451	203	191	244	207	8.09
	min	0.16	0.002	0.73	5.7	13.0	11.2	66.0	5.10	4.40	0.70	2.70	0.010	0.010	0.002	417	171	164	227	151	7.79
S9 (5)	max	0.35	0.002	1.90	8.3	20.2	15.5	80.0	6.20	4.80	0.90	3.10	0.010	0.030	0.012	448	210	201	240	203	8.12
	average	0.25	0.002	1.44	7.5	16.0	11.1	65.6	5.66	4.80	0.74	2.78	0.010	0.015	0.009	394	177	164	221	174	7.93
	min	0.20	0.002	1.22	6.6	13.0	5.3	56.0	4.90	4.80	0.50	2.40	0.010	0.010	0.006	335	146	140	185	141	7.77
S10 (6)	max	0.32	0.002	1.20	13.3	27.9	18.0	102.0	6.30	13.30	1.50	2.90	0.010	0.020	0.010	512	248	255	309	246	8.25
	average	0.23	0.002	0.81	8.0	17.9	11.7	75.8	4.61	6.68	0.92	2.65	0.010	0.014	0.009	448	193	190	241	200	8.00
	min	0.10	0.002	0.21	6.4	14.0	8.2	61.0	2.10	3.90	0.70	2.40	0.010	0.010	0.004	391	152	153	194	150	7.62
S11 (5)	max	0.47	0.007	9.30	12.4	35.4	25.0	160.0	2.90	8.40	4.47	7.50	0.220	0.070	0.025	790	314	400	482	402	8.36
	average	0.23	0.003	7.26	9.2	30.4	18.2	117.2	1.94	7.19	3.10	5.20	0.120	0.025	0.010	642	252	293	381	319	7.93
	min	0.15	0.002	3.34	5.7	24.0	10.8	84.0	0.60	5.90	1.83	3.90	0.030	0.010	0.002	492	188	210	240	205	7.63
S12 (7)	max	1.80	0.002	12.00	15.8	33.5	76.0	158.0	3.6	15.50	1.36	3.70	0.400	0.060	0.035	813	303	395	485	417	8.31
	average	0.47	0.002	11.03	13.7	32.0	55.3	141.0	2.5	13.63	0.93	3.27	0.066	0.020	0.014	782	281	354	446	347	7.42
	min	0.10	0.002	9.94	12.5	31.0	34.9	132.0	1.7	12.80	0.74	2.00	0.010	0.010	0.002	740	258	331	376	269	7.08
V1 (5)	max	0.41	0.002	0.65	4.9	17.3	26.2	101.0	1.90	2.10	0.14	2.70	0.028	0.020	0.032	482	239	252	276	237	8.34
	average	0.22	0.002	0.45	3.5	14.3	12.8	72.6	1.34	1.87	0.12	2.24	0.014	0.013	0.019	366	173	180	195	176	8.13
	min	0.12	0.002	0.23	2.6	13.0	6.0	62.0	0.70	1.60	0.10	2.00	0.010	0.010	0.010	321	150	154	155	150	7.81
V2 (3)	max	0.75	0.002	10.10	14.3	33.0	320.0	116.0	2.10	13.40	1.00	4.30	0.010	0.030	0.015	635	235	288	380	321	7.95
	average	0.49	0.002	9.25	13.4	31.8	17.4	80.7	1.87	13.00	0.96	3.80	0.010	0.020	0.014	487	128	201	298	224	7.68
	min	0.22	0.002	7.86	12.5	30.5	4.8	63.0	1.50	12.60	0.92	3.30	0.010	0.010	0.014	413	69	157	257	150	7.22

relationships between percentages which keep constant notwithstanding time:  $\text{Ca}^{2+} \gg \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$  or  $\text{Ca}^{2+} \gg \text{Mg}^{2+} \geq \text{Na}^+ > \text{K}^+$ . The last relationship, especially, seems to represent the southernmost sampling sites (S5, S6, S7, S8, S9). Instead, as for relationships between the several anionic components, the following ionic contents  $\text{HCO}_3^- \gg \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$  or  $\text{HCO}_3^- \gg \text{SO}_4^{2-} > \text{Cl}^- \gg \text{NO}_3^-$  have been found, characteristic of

the southernmost sampling points S5, S6, S7, S8, S9, S10, and V1. The increase in the percentage of nitrate in 1989 leads to a radical change in the relationship between nitrate and chloride (i.e.,  $\text{HCO}_3^- \gg \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$ ) mainly in the percolating waters of S4, S11, S8, and S10. The bicarbonate ion, calculated on the basis of alkalinity values, in conjunction with the  $\text{Ca}^{2+}$  ion, which are the main components, define the meteoric origin of waters

**Table 2**

Hydrochemical data for the percolation waters in 1989 (Rows: S1 - dripping and sampling sites; (4) - number of sample collections. Columns: Cond - specific conductance; Alk - alkalinity; Hard - hardness; TR - total residue)

1989	NH <sub>3</sub> mg/l	NO <sub>2</sub>	NO <sub>3</sub>	Cl	SO <sub>4</sub>	CO <sub>2</sub>	Ca	Mg	Na	K	SiO <sub>2</sub>	PO <sub>4</sub>	Fe	Al	Cond	Alk	Hard	TR	TR	pH	
															μS/cm	mg/l		180°	600°		
S1	max.	0.08	0.002	15.00	17.9	31.5	7.5	92.8	3.20	7.40	1.09	1.90	0.020	0.006	0.001	440	96	232	342	263	5.50
(1)	min																				
S2	max.	0.68	0.016	13.20	25.3	52.7	16.0	111.0	2.40	24.00	0.18	2.37	0.038	0.030	0.010	640	174	278	430	379	7.72
(4)	average	0.28	0.005	10.58	24.3	51.5	14.2	94.2	2.05	22.75	0.16	2.00	0.022	0.019	0.005	554	144	235	402	356	6.43
	min	0.08	0.001	8.60	23.5	50.4	11.2	72.6	1.80	21.80	0.13	1.70	0.010	0.010	0.001	505	110	181	381	337	5.30
S3	max	0.56	0.002	12.00	22.1	24.3	29.0	114.0	3.40	8.80	0.31	2.40	0.032	0.030	0.010	620	174	284	392	332	7.86
(4)	average	0.20	0.001	9.88	19.5	22.9	16.0	94.3	2.30	7.55	0.21	1.66	0.020	0.015	0.005	489	138	235	309	257	6.88
	min	0.06	0.001	8.30	17.1	22.0	5.0	69.4	1.40	5.60	0.12	1.24	0.010	0.010	0.001	405	104	173	260	201	6.20
S4	max	0.10	0.003	14.90	14.5	27.9	9.0	106.0	2.55	5.70	2.20	3.87	0.070	0.010	0.005	540	173	265	372	292	6.30
(2)	average	0.08	0.002	14.45	14.0	24.8	7.5	101.6	2.48	5.35	2.13	3.24	0.040	0.010	0.003	505	148	254	367	289	6.20
	min	0.06	0.001	14.00	13.5	21.6	6.0	97.2	2.40	5.00	2.05	2.60	0.010	0.010	0.001	470	123	243	362	286	6.10
S5	max	0.09	3.410	6.10	8.4	15.8	13.0	80.0	2.40	3.00	0.17	1.50	0.010	0.010	0.005	450	168	200	256	222	6.60
(2)	average	0.09	1.706	4.15	5.7	14.1	11.0	79.0	2.29	2.45	0.17	1.25	0.010	0.008	0.003	403	156	197	248	217	6.55
	min	0.08	0.001	2.20	2.9	12.4	9.0	78.0	2.18	1.90	0.17	1.00	0.010	0.006	0.001	355	143	195	240	212	6.50
S7	max	0.55	0.005	2.60	6.3	14.4	8.0	72.5	4.80	4.10	0.40	3.00	0.058	0.030	0.010	360	174	181	214	198	8.10
(5)	average	0.23	0.002	1.88	5.0	11.5	5.5	57.1	2.49	2.55	0.18	1.24	0.026	0.017	0.005	284	128	142	182	169	7.30
	min	0.03	0.001	1.10	3.7	10.6	3.5	41.6	1.85	1.90	0.10	0.43	0.010	0.006	0.001	234	82	104	152	144	6.30
S8	max	0.68	0.630	31.00	17.0	29.9	14.0	116.0	10.20	9.00	0.78	2.10	0.039	0.030	0.010	690	228	289	430	314	7.76
(5)	average	0.27	0.127	15.78	11.7	22.4	10.7	85.5	7.89	6.36	0.69	1.56	0.021	0.019	0.005	486	167	213	333	263	7.00
	min	0.06	0.001	7.00	7.5	17.1	7.8	55.0	6.45	4.60	0.61	0.81	0.010	0.010	0.001	321	115	137	232	200	5.60
S9	max	0.52	0.400	13.00	15.6	19.6	11.0	97.0	7.48	6.80	0.61	2.31	0.080	0.030	0.010	505	174	242	320	253	7.88
(4)	average	0.22	0.101	9.48	10.9	17.3	7.6	71.5	6.12	4.93	0.57	1.51	0.037	0.018	0.005	408	132	178	262	216	6.93
	min	0.03	0.002	4.50	7.1	14.4	5.0	39.6	5.60	3.40	0.46	1.00	0.010	0.007	0.000	280	106	99	184	160	5.80
S10	max	0.08	0.002	19.00	11.4	26.8	20.0	102.0	4.30	3.50	0.51	2.37	0.030	0.010	0.005	505	186	255	349	272	6.55
(2)	average	0.08	0.002	11.95	8.8	24.0	17.0	92.7	4.28	3.48	0.47	1.69	0.020	0.008	0.003	490	155	231	347	262	6.18
	min	0.07	0.001	4.90	6.1	21.2	14.0	83.3	4250	3.45	0.42	1.00	0.010	0.006	0.001	475	123	208	345	252	5.80
S11	max	0.33	0.021	19.00	12.8	36.5	18.0	126.8	3.61	5.90	4.40	5.50	0.210	0.039	0.010	705	232	316	453	364	7.80
(4)	average	0.17	0.007	17.53	12.3	31.2	13.6	112.8	3.30	5.50	4.11	4.60	0.098	0.021	0.005	566	177	282	406	324	6.56
	min	0.04	0.001	16.00	11.5	27.4	9.4	98.4	3.00	5.20	3.70	3.10	0.016	0.006	0.001	520	95	246	371	293	5.10
S12	max	0.48	0.006	10.70	14.0	30.1	28.0	130.0	2.80	10.20	1.00	2.43	0.020	0.010	0.005	625	168	324	379	325	6.60
(3)	average	0.22	0.004	9.58	13.3	29.7	24.3	109.1	2.64	8.60	0.88	2.14	0.013	0.009	0.002	592	136	272	338	289	6.07
	min	0.07	0.001	8.75	12.6	29.3	20.0	95.2	2.53	7.60	0.82	1.70	0.010	0.006	0.001	550	110	238	298	254	5.7
V1	max																				
(1)	average	0.06	0.003	10.40	13.0	37.1	6.0	93.0	2.40	7.60	0.82	1.90	0.010	0.010	0.001	430	114	232	365	300	5.90
	min																				
V2	max	0.73	0.004	10.70	14.7	32.6	6.80	68.0	2.40	12.00	0.62	3.30	0.100	0.010	0.001	345	166	170	292	243	7.77
(2)	average	0.47	0.003	9.00	14.6	29.4	4.90	60.5	2.28	10.40	0.51	2.70	0.055	0.010	0.001	335	121	151	279	228	6.79
	min	0.20	0.001	7.30	14.5	26.1	3.00	53.0	2.15	8.80	0.40	2.10	0.010	0.010	0.001	325	75	133	266	212	5.80

coming from the surface. Diversities in the chemical composition of the different percolation waters can be observed only by examining in detail variations of some minimal components that can be affected contemporarily, either by different courses during percolation or by anthropogenic inputs, being more unlikely, on such a reduced scale, the presence of lithology variations. Some representative ratios have been established from the surveys. The small values obtained from the ratio  $Mg^{2+}/Ca^{2+}$  are typical of waters running in carbonate

reservoirs which were prevalingly calcareous. The northernmost sector shows a variability range with lower values (0.005–0.030) than those of the southernmost sites (0.030–0.100) except for waters collected at V1. It is possible to distinguish the water chemistry of the northernmost area from the southernmost by using a scatterplot diagram between the concentrations of the two mentioned parameters (Fig. 6). Possible explanations could be either the relative impoverishment of  $Ca^{2+}$  favoring other cations, or the existence on the ground surface of red

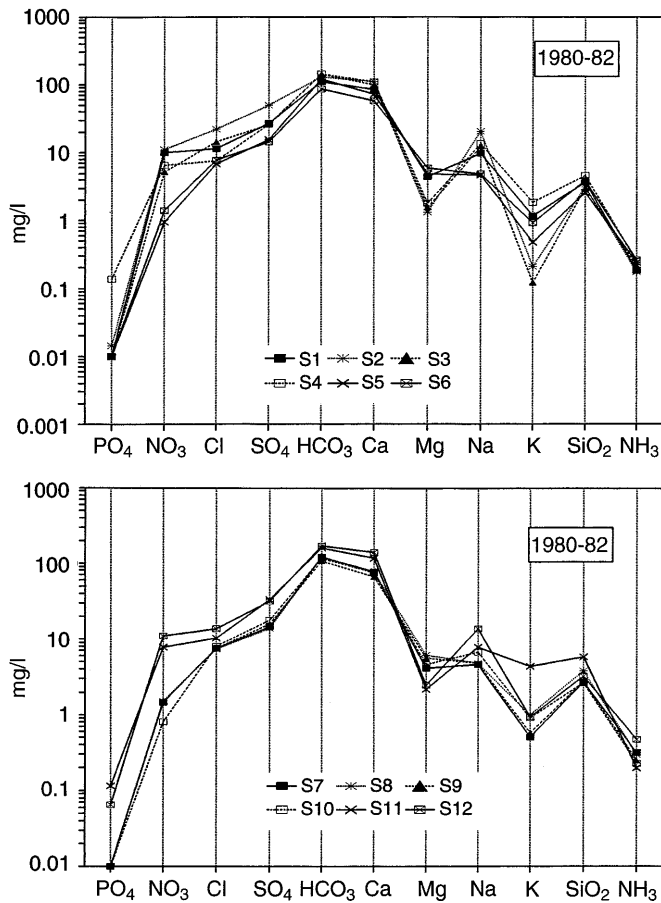


Fig. 4

Schoeller's diagrams considering common and minor constituents of karst waters (1980-1982)

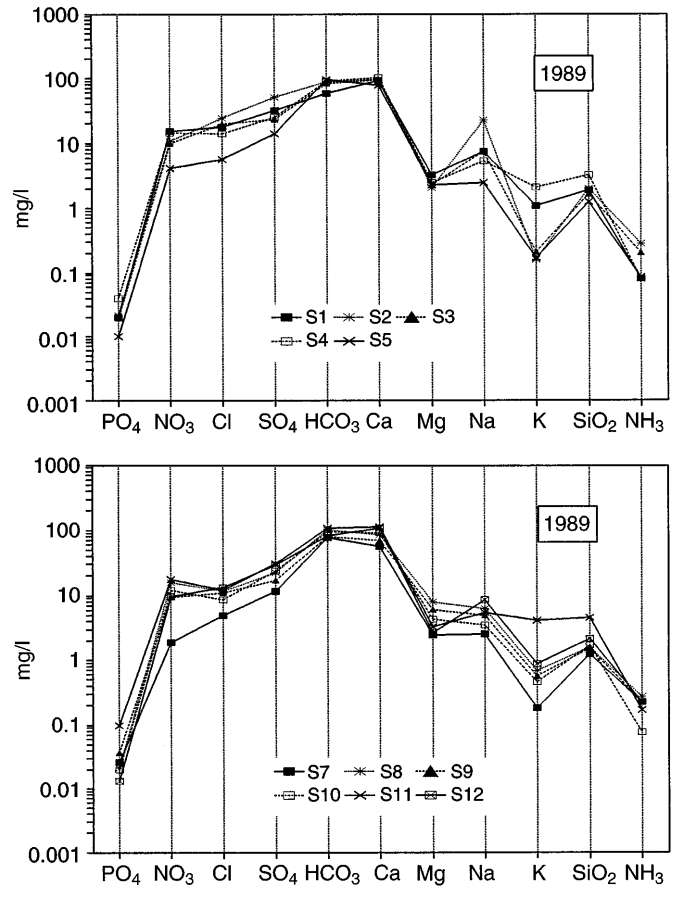


Fig. 5

Schoeller's diagrams considering common and minor constituents of karst waters (1989)

soil with a higher ratio  $Mg^{2+}/Ca^{2+}$  in the southernmost area, which can consequently affect karst dissolution waters.

The higher values of the ratio  $SO_4^{2-}/Cl^-$ , from a 1 to 2 average, are observed in the dripping points S4 (1.10-2.89) and S11 (1.65-2.82) with maximum values corresponding to V1. Those are the richest waters in sulphates which can be contrasted with the lowest values, under 1, found in S3, S8, and S9 where chlorides are of a great importance. Considering the homogeneity of the *terra rossa* soil and of the lithotype where the cave is located plus the absence of pyrites and gypsum, the continuous presence of sulphates in percolation waters beneath cultivated soil or gardens leads to the conclusion that sulphates have to be partially related to organic debris. Sulphured substances derived from this vegetable matter and due to oxidation processes become sulphuric acid which reacts with carbonate rocks and, therefore, produce calcium and magnesium sulphates.

S4 and S11 showed the highest values of the ratio  $K^+/Na^+$ : between 0.154 and 0.254 for the first one and between 0.307 and 0.481 for the second. Usually, in fresh waters these values vary from 0.004 to 0.300 (Zavatti 1984); therefore, in S11, and, to a minor extent, in S4,

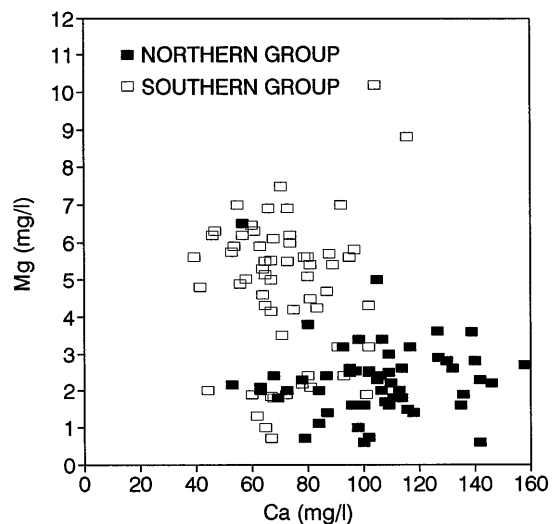


Fig. 6

Scatterplot of alkaline earth contents in percolation waters. All samples are considered

these results would indicate some preferential intake of potassium as observed in the sulphate ion. Waters collected from S2 and S3 have very low ratios between the two  $K^+/Na^+$  cations (from 0.003 to 0.006 for the first one and between 0.004 and 0.025 for the second), an index of the relatively high contents of sodium. In the sampling sites of the southernmost area of the cave as well as in the remaining northernmost sites (S1, S12, V2), ratios are constant in such a way that a linear relationship with a significant coefficient of correlation ( $r=0.66$ ,  $n=58$ ,  $P<0.001$ ) can be established between both parameters (Fig. 7). The comparison between values of sodium and potassium is useful to verify the discrimination of different waters in carbonate aquifers (Christopher 1971). Potassium and sodium concentrations plotting above (S4 and S11) and below (S2 and S3) the positive linear trend, respectively, can be considered anomalous. This may mean that the waters followed a different course during percolation and/or that "not natural" surficial inputs were present, since the dripping points correspond to the soil highly affected by anthropic settlements.

A cluster analysis (Euclidean distance; Ward linkage criterion), with concentrations considered as discriminant variables, helped group together all dripping points with the same compositional features. This procedure has been successfully applied to discriminate between carbonate waters and karst springs (Pulido-Bosch and Ben Sbih 1995; Reisenhofer and others 1996). To get reliable results, standardized concentration data were processed, separating the two surveys and considering each single sampling at each dripping point. Pool sites, V1 and V2, were excluded from the procedure.

Subsequently, the average concentration data were considered. The dendrograms (Fig. 8) resulting from the two procedures are characterized by the same groups. Due to

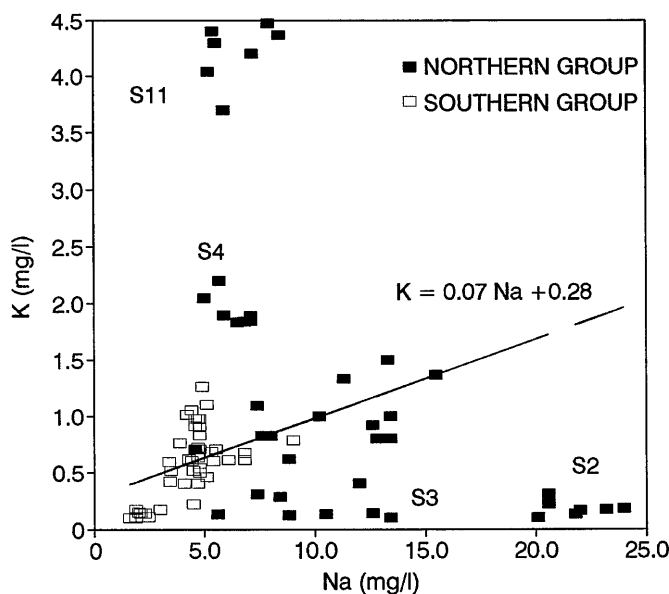


Fig. 7

Correlation of sodium and potassium in percolation waters without sampling distinction

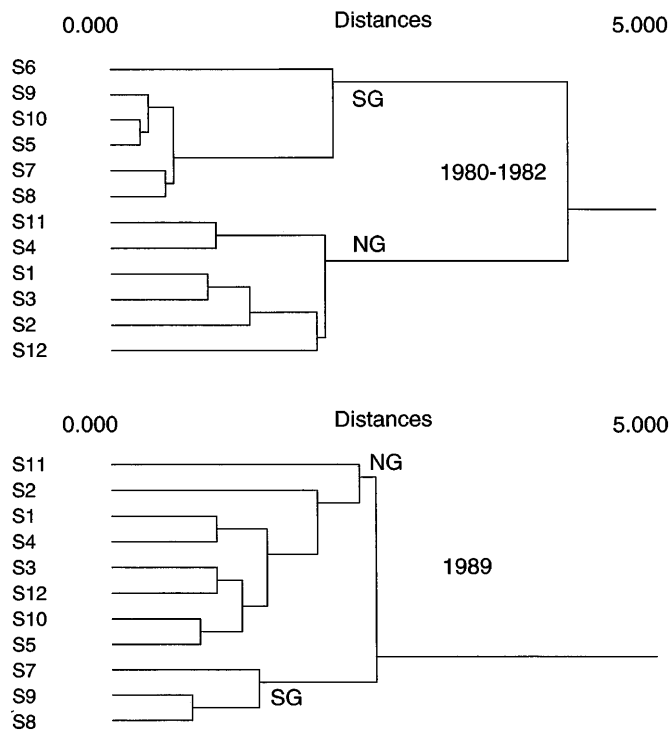
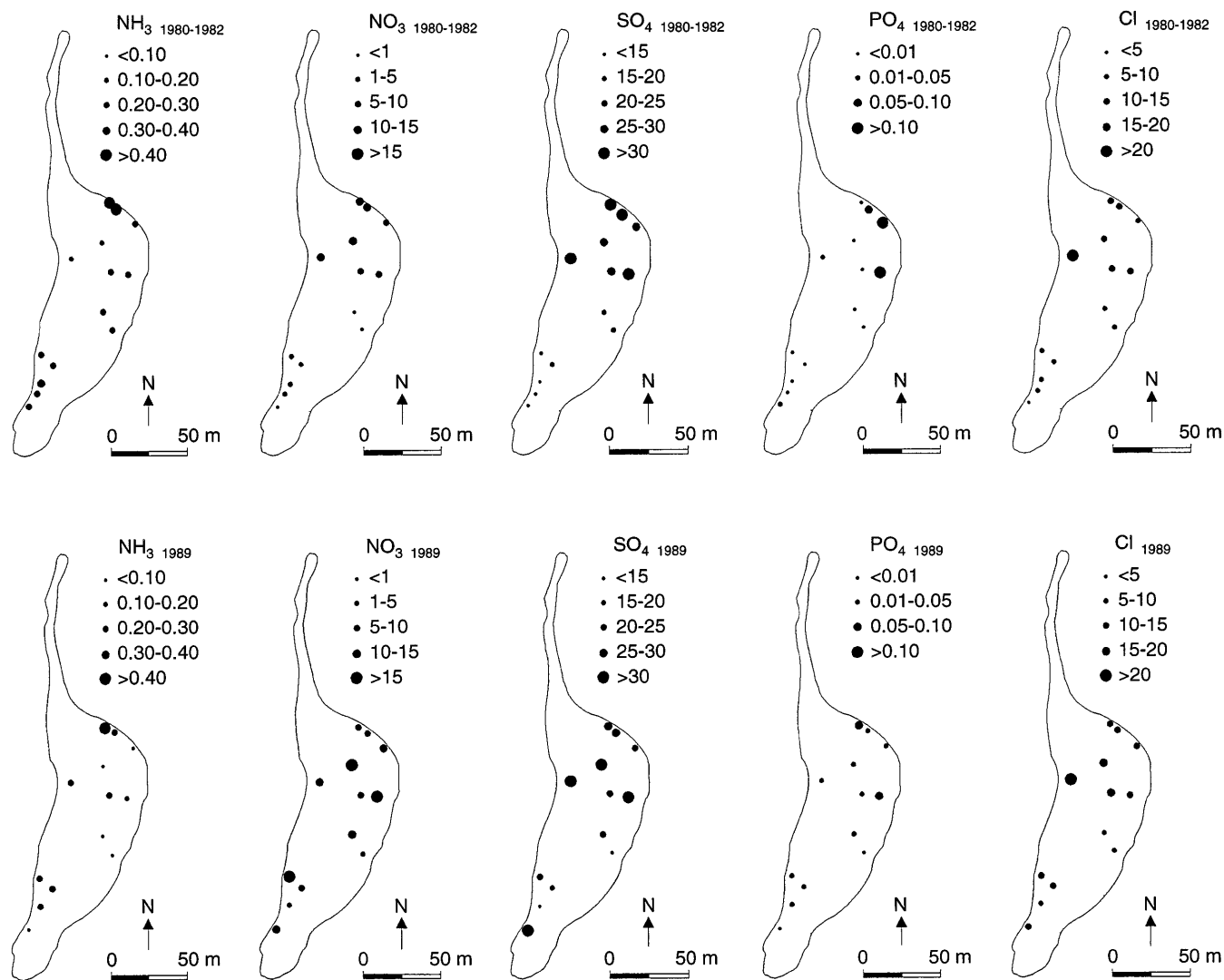


Fig. 8

Dendrogram obtained by cluster analysis. Euclidean distance and Ward linkage criterion between sampling points

space, only clusters calculated on the average values of each parameter are reported. A distinction can be made between the two main groups, the northern (NG) and the southern (SG) one. Meaningful subgroups can be identified in the northern area, which relates dripping points fed by percolation waters through different and well-defined flowpaths. The two main groups remain unchanged throughout the years apart from S10 and S5, which seem to be affected during the survey of 1989 by the characteristics of the ground above the northernmost area of the cave, almost completely inhabited by human beings. The distinction between the 14 percolation sites regarding mean composition, location, and time is presented by a planimetric view of the variability ranges of the elements which are related to anthropogenic alterations (Fig. 9). The values of nitrate, ammonia, chloride, phosphate, and sulphate are higher in the underground dripping points most affected by anthropic concentrations. A slight increase in  $NO_3$ ,  $SO_4$  and  $PO_4$  occurs in the samples from the southernmost area of the cave during the survey of 1989 and is proof of a wider extension of anthropogenic influence on percolation waters through time. Investigation performed on samples collected during the 1980-1982 period have shown the highest significant ( $P<0.001$ ) linear correlations of nonstandardized chemical parameters, first, between Ca versus  $NO_3$  ( $r=0.720$ ,  $n=72$ ),  $HCO_3$  ( $r=0.730$ ,  $n=63$ ) and  $SO_4$  ( $r=0.663$ ,  $n=72$ ). Na appears highly correlated to Cl ( $r=0.948$ ,  $n=47$ ) as well as to  $SO_4$  ( $r=0.896$ ,  $n=47$ ), whereas K varies significantly according to  $PO_4$  ( $r=0.688$ ,  $n=47$ )



**Fig. 9** Areal distribution of some significant chemical parameters in percolation waters and temporal variability. Concentrations are expressed in mg/l

and to SiO<sub>2</sub> ( $r=0.608$ ,  $n=42$ ) increasing contents. It is evident that the human presence is verified by the supply of potassium and sodium salts as well as phosphate, chloride, and sulphate which are related to household wastewaters and fertilizers used in orchards and gardens.

## Conclusions

On the basis of hydrochemical parameters, a northern and a southern group can be distinguished in the location of dripping waters in a large karst cave. Moreover, ratios between some significant elements (such as Na and K) permit the discrimination of some sampling sites inside both groups. The differences between the ratios of

some chemical facies are probably linked to several flow-paths in which underground waters follow along the thin thickness of the cave roof.

Considering the different management of the territory through time, parameters such as sodium, chloride, sulphate, and nitrate existed in higher concentration values in the survey of 1989. Their variations characterize the dripping points beneath swimming-pools in the gardens of small houses, subirrigation from IMHOFF tanks, vineyards, and orchards which have noticeably increased in the 1980s. Therefore, in an area of 2 hectares, percolation waters show distinctive chemical character which is, relatively, homogeneous and constant throughout the years. By examination of several variables, it is possible to identify the location of waters based on the anthropic use of soil rather than on bedrock lithologic variations; for example waters that come from soil which has never been used by humans (ploughed lands, red detrital soil, *terra rossa*), and higher mineralized waters from sampling points related to construction (buildings, concrete and asphalted roads, gardens) and agricultural (vineyards, cultivated fields) areas.



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