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PAPER

Chemical analyses of spring waters and factor analysis to monitor the functioning of a karstic system. The role of precipitations regimen and anthropic pressures

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An approach is presented to study the functioning of a karstic massif and assess the adverse effects of the anthropogenic pressure by monitoring some water chemical and physical parameters of its main springs. The approach has been applied to the Sette Comuni Plateau (Veneto Region, Italy) hosting a well developed karstic system, whose aquifer presents high vulnerability and undergoes a relevant anthropogenic pressure. The Oliero springs, amongst the largest karstic springs in Europe, are the main water output of the plateau. Electrical conductivity, pH, dissolved O_2, hardness, alkalinity, chemical oxygen demand, total suspended solids, ionic species (NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Cl^-, F^-), elements (Cr^{III}, Cr^{VI}, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb), and some chlorinated solvents were monitored for one year. This study presents the application of a factor analysis on the water parameters enabling the identification of the dominant chemical and biological processes and pollution sources affecting the karstic system. Results show four factors which are interpreted as *karstification*, *photosynthesis*, *storm flow pollution* and *anions*. Finally, by associating metals, chemical oxygen demand and total suspended solids with the amount of rainfall in the 48 h before samplings, further detailed information to the fast response of the aquifer to precipitation events was detected and interpreted according to the factor analysis results. The proposed approach, by providing information on the functioning of the aquifer, may help the management of the karstic plateau and is easily adaptable to similar environments.

Introduction

Karst aquifers host large reservoirs of high-quality groundwater and provide about 25–30% of available water for human use worldwide.[1] They mainly occur in carbonate rocks, limestone and dolomite, as a result of the acidic dissolution of rocks.[2] In Europe, carbonate rocks containing karst aquifers are found below 35% of the surface.[3] In Italy, where carbonate and evaporitic rocks cover more than 25% of the surface[4] and meteoric water supply is abundant, karst aquifers are an essential water resource providing about 40% of drinking water. These are also exploited for industrial and agricultural uses and for the production of energy.

Karstic landscapes present characteristic landforms caused by chemical dissolution of surface rocks *i.e.* karren, dolines and

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Environmental impact

The response of a karstic massif to the frequency and intensity of precipitation and to the anthropogenic pressures has been studied by chemically analyzing its waters at two main springs. We assumed that spring waters mirror the events occurring on the massif. To understand the processes "behind" the variations of water parameters, a multidimensional statistical technique, the factor analysis, has been adopted. This powerful tool, originally developed for different studies, mainly in social sciences, has made possible to identify four factors driving the variations of water chemical parameters and establish a link between these variations and the frequency of precipitations on the massif. The proposed approach, by providing information on the functioning of the aquifer may help the management of the karstic plateau. Being definitely multidisciplinary, it can be extended with minor changes to other case studies and therefore may be interesting for other scientists working on the environment.

sinkholes. Streams and rivers sinking underground *via* swallow holes are also frequent. Karstic aquifers are commonly structured as a branching network characterized by a series of well organized, but extremely heterogeneous conduits. This structure allows for rapid and often turbulent water fluxes,[5] in which flow conditions may be identical to those in surface rivers, with free surface flow and high velocity and flow rate.[2] Finally, the whole karst network system generally focuses the water flow to springs situated in the valleys.

These characteristics result in the high potential vulnerability of karst aquifers, in terms of water quality and quantity.[6] Typically thin soil layers, high degree of infiltration points and high permeability of the eroded host rocks frequently result in a fast and direct injection of runoff water into the conduit network following storms.[7,8] The consequences are ineffective attenuation mechanisms and short auto-depuration processes, which normally take place during the permeation in the unsaturated portion of the other aquifers: contaminating substances on the surface are rapidly transported through the aquifer over large distances. Conversely, pollutants can diffuse in the aquifer matrix or micro-fissures resulting in the long-term storage and delivery of contaminants.[9,10] Potential contaminants are not efficiently removed and easily reach the groundwater and eventually springs.

Springs are preferential observation points for karst aquifers, which are very hard to model and protect against pollution because of their heterogeneous distribution of permeability. Frequently the greatest part of groundwater resurfaces through a single spring or a small group of springs. Discharge regime, water quality and parameters' fluctuation after precipitations are indicators of the state of the aquifer and the recharge area.[11,12] For this reason, karstic springs are an ideal measuring and analyzing location for the study of the entire karst system.[5]

For geological features the Oliero springs are amongst the biggest karst springs in Europe,[13] with an annual average flow rate of 13 $m^3 s^{-1}$.[14] These springs drain a catchment area of about 500 km^2 on the Sette Comuni Plateau (Fig. 1). In the last 50–60 years the catchment area land use has seriously changed from an agriculture based economy to livestock farming and small industrial activity like *e.g.* cheese production and decorative limestone extraction. Moreover, rapid urbanization has occurred as well.

This manuscript presents an approach to study the functioning of a karst system and assessing the adverse effects of the anthropogenic pressure. This objective is achieved by monitoring the water quality of its main springs for one year and, subsequently, by applying a multidimensional statistical approach, named *factor analysis* on the water parameters to identify the dominant chemical and biological processes and pollution sources affecting the karstic system. The case study is the Sette Comuni Plateau and springs are located at Oliero (Veneto Region, Italy).

This study is organized in 4 steps: (i) a preliminary anthropogenic pressure assessment to calculate human pressures on the catchment area and estimate the volume of contaminated waters potentially affecting the aquifer; (ii) an evaluation of the quality of spring water by monitoring some chemical and physical parameters and pointing out a possible trend and cycle of considered parameters; (iii) an identification of the main chemical and biological processes and pollution sources affecting the water quality; (iv) an investigation on the chemical response to rain events. The karst system functioning was then interpreted in relation to heavy precipitation periods and anthropogenic pressures.

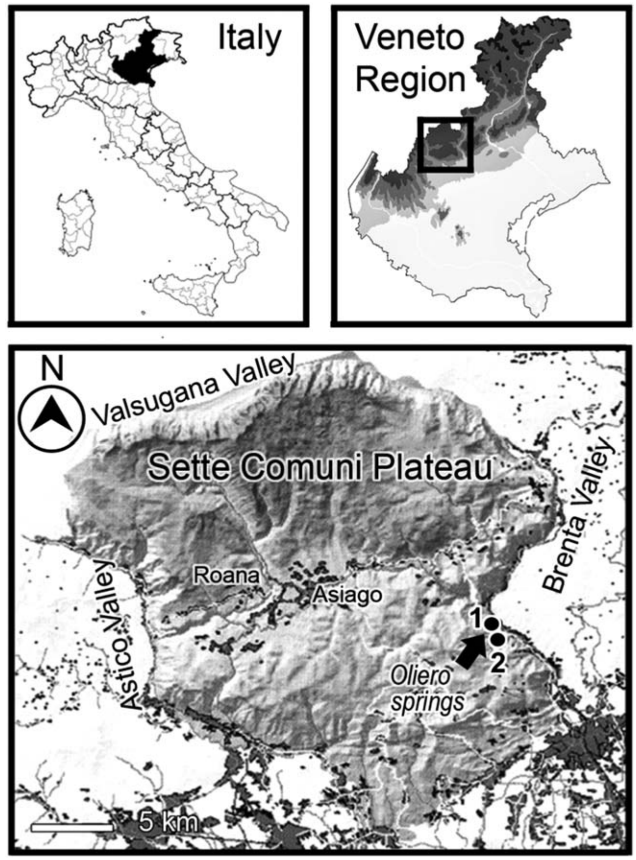

Fig. 1 Study area: (1) Covol dei Veci or Big Cave (BC) and (2) Covol dei Siori or Little Cave (LC).

Study area

Geological and hydrogeological features

The Sette Comuni Plateau (Fig. 1), located in the northeastern part of Italy, in the Veneto Region at the base of the Alps, is bordered by the valleys *Valsugana* to the north, *Astico* to the west and *Brenta* to the east and covers a surface of approximately 500 km^2 with altitudes ranging between 600 and 2300 m above the sea level. The climate is typically alpine with a relatively low annual average temperature (7.4 °C) ranging from −5.4 °C in January to 22 °C in July.[15] Annual precipitation is 1200–1700 mm, with a higher intensity in the middle zone of the table-land.[14] The pluviometric trend shows two distinct peaks, one in spring and one in autumn, whereas the minimum values are recorded in winter. The geology of the plateau is well documented.[16,17] To summarize, a crystalline basement composed of quartz phyllites is overlain by terrigenous–calcareous sediments acting as the lower impermeable boundary of the aquifer. The main aquifer is hosted by marine-carbonaceous series of sedimentary rocks more than 1500 m thick, including Dolomia Principale and Calcari

Grigi, with discontinuities of Rosso Ammonitico formations. Finally, the aquifer is capped by Cretaceous formations, *i.e.* Biancone, Scaglia Rossa formations, Quaternary fluvial and glacial deposits. The dissolution of carbonates has formed a single, large and well-developed karst system.[18,19] Tectonic features have guided the development of the aquifer and the main direction of groundwater to south-southeast, whereas water circulation in a surface hydrographic network is virtually absent.[20]

About two-thirds of rain falling in the plateau is conveyed in four main springs to the Brenta Valley, located at a lower altitude than the Astico Valley. Springs along the northern and southern slopes are almost absent and the water flow from springs in the Astico Valley is negligible.[14] Oliero springs (Fig. 1) represent the main water drain of the entire karst system. Among these springs only two can be considered perennial: *Covol dei Veci* or *Big Cave* (BC) and *Covol dei Siori* or *Little Cave* (LC). Other minor temporary springs are present in the area, but their flow is negligible. The BC spring has an average discharge of 4.3 $m^3 s^{-1}$ with a maximum of 40 $m^3 s^{-1}$ and a minimum of 0.2 $m^3 s^{-1}$. The LC spring has an average discharge of 5.4 $m^3 s^{-1}$ ranging from 27 to 0.8 $m^3 s^{-1}$.[21] Spring hydrographs reveal a single prolonged minimum flow time in winter when precipitations on the plateau are prevalently snowy with only one moderate flow period during the following snow melting. During the rest of the year, the regime is closely connected to rainy periods and very high and fast variations in discharge due to precipitations in the plateau are observed. The spring response to a heavy rainfall generally occurs after 6–12 hours.[21] The two springs feed the Oliero River, 300 m long, flowing into the Brenta River.

Aquifer vulnerability

A recent study has shown that about 80% of the area is highly vulnerable.[15] The northern parts and borders of the plateau are the most vulnerable zones because of the presence of well-developed karst landforms including large dolines, bare rocks and many open cavities with almost no covering vegetation. Lower vulnerability levels are found in the central area, where soils are developed on clastic sediment, which lay prevalently on the Biancone formation. This rock acts both as a filter and a tank by slowly releasing the water of the suspended aquifer towards the cavities of the formation underneath. In this zone a stream named Ghelpach flows for long periods continuously and receives the effluent of the whole plateau. Some sinkholes located aside this course are infiltration points and potential sources of pollution for the underlying aquifer.[22] The lowest vulnerability levels have been recorded in the southeastern part of the plateau.

Human impact

Until the early 20th century, the human impact on the Sette Comuni Plateau was limited to agriculture, mountain pasture and forestry. The increase of deforestation and ovine pasturing in the last century has seriously contributed to soil erosion processes. Moreover, the plateau was the scene of major battles during WWl: the construction of trenches and the intensive bombing have changed considerably the slopes and mountainsides by increasing the drainage capacity of the surface. Between 1960 and 1980, the rapid economic development in Italy accelerated urbanization, a moderate industrialization and a change in the soil use. More recently, tourism has become the main activity on the plateau. Today about 4% of the plateau is covered by buildings, with consequential problems of sewage and garbage disposal. In addition, the sewer system of Asiago feeds the river Ghelpach and may enter the aquifer from some sinkholes. The anthropogenic impact is concentrated in the middle part of the plateau, mainly in the major villages of Asiago and Roana (Fig. 1). The population growth has also caused an increased demand for water. At present, this is *partly recycled* being pumped up from the Oliero springs.

Materials and methods

The anthropogenic pressure on the karst aquifer was estimated by taking into account precipitation rates and Equivalent Inhabitants (EI). Starting data (period: 2000–2002) were supplied by ARPAV, local and Veneto Regional administrations. For the volume of contaminated water potentially influencing the aquifer, an estimation of effective rainfall, total number of equivalent population in the plateau and subsequent water consumption was made. An estimation of additional EI due to animal farming was attempted as well, by using the multiplicative factors proposed by Italian National Research Council.[23]

Physical–chemical parameters of water were measured and samples collected at the BC and LC springs once per week from May 2002 to May 2003. Water temperature and dissolved oxygen were directly analyzed on-site using a portable oximeter (Schott, Milano). Two different samples were collected for subsequent laboratory analyses: a vial of 20 mL for chlorinated solvent analysis (chloroform, methyl chloroform, trichloroethylene, tetrachloroethylene and Total Chlorinated Solvents (TCS)) and a 1 L glass bottle for the analysis of electrical conductivity (EC), pH, hardness (°F), alkalinity, Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), ionic species (NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Cl^-, F^-), metals (Cr, Mn, Fe, Ni, Cu, Zn, Cd, Hg, Pb) and arsenic. Cr^{VI} was analyzed as well. The analytical procedures followed the Italian National Research Council methodology[24] and other methods validated by the Veneto Environmental Protection Agency (ARPAV). EC and pH levels were measured with portable instruments (Mach and Orion Research, respectively). Hardness (calcium and magnesium content) was measured using the ethylenediaminetetracetic acid (EDTA) titrimetric method. Alkalinity expressed as bicarbonate was quantified by acid titration using BDH 4.5 indicator and HCl. The COD was determined following the permanganate Kübel method: oxidation of the organic matter was performed in a boiling mixture of $KMnO_4$ and sulfuric acid. Total suspended solids were obtained by gravimetric determination after filtering 500 mL of sample through 0.45 μm Millipore filters. Ammonium and nitrite were analyzed by a spectrophotometric method. Anions (NO_3^-, PO_4^{3-}, SO_4^{2-}, Cl^- and F^-) were analyzed using a Dionex DX100 ion chromatographic system. Metal concentrations were determined by atomic absorption spectrometry, Hg and As were analyzed using a cold vapors system. No sample filtration was done, samples were acidified (except for Cr(VI)) with suprapur HNO_3 prior to analysis. A colorimetric method using diphenylcarbazide was used to analyze Cr^{VI}. Measurements of chlorinated solvents were performed by Gas Chromatography with an Electron Capture Detector (GC-ECD). The quality and accuracy of quantitative analyses were ensured through careful standardization, procedural blank measurements and duplicate samples.

Microbiological analyses are routinely carried out by the Veneto Environmental Protection Agency for all main streams and springs. As all the microbiological analyses carried out at Oliero springs before this study showed values within the Italian sanitary standards, the authors have focused their analytical efforts on the chemical analyses. Therefore, no data are reported here for fecal indicator bacteria.

As the water chemistry in some karst springs is known to vary considerably over heavy rainfall periods,[25] micro-meteorological parameters (air temperature, rainfall) were concurrently recorded in two station on the Sette Comuni Plateau for all the sampling period and were provided by ARPAV-Osservatorio Meteorologico di Teolo.

Results and discussion

Anthropogenic pressure assessment

The average annual precipitation is 1600 mm. Since the area of the plateau is about 550 km^2, the effective rainfall (1120 mm, 70% of the total, the remaining 30% being lost through evapotranspiration)[14] has been calculated to be 6.2×10^{11} L per year.

About 1.15×10^5 EI are estimated stably living in the plateau,[26] for a total of 4.2×10^7 EI in a whole year. Tourists (holiday makers and day trippers)[27] account for 1.15×10^6 EI. Hence, the total human presence in the plateau can be calculated to be 4.3×10^7 EI, whereas livestock accounts for 8.1×10^7 EI (Table 1).

Table 1 The equivalent inhabitants estimated in the Sette Comuni Plateau for 2000–2003

	Number	Factors	Days	Total
Inhabitants	1.2×10^5	1	365	4.2×10^7
Annual vacation makers	6.9×10^5	1		6.9×10^5
Annual day-trippers	5.0×10^5	1		5.0×10^5
Total human presence				4.3×10^7
Cattle	7508	8.16	365	2.2×10^7
Cattle in alpine pasture	4000	8.16	105	3.4×10^6
Total cattle				2.6×10^7
Sheep and goats	1181	1.78	365	7.7×10^5
Sheep and goats in alpine pasture	6000	1.78	105	1.1×10^6
Total Sheep and goats				1.9×10^6
Horses	325	8.08	365	9.6×10^5
Pigs	200	1.95	365	1.4×10^5
Poultry	8.2×10^4	0.2	365	6.0×10^6
Rabbits	2.5×10^4	0.2	365	1.8×10^6
Minks	1.5×10^4	0.2	356	1.1×10^6
Total zootechnical and alpine pasture				3.8×10^7
Total				8.1×10^7

The average consumption of water for EI was estimated to be 250 L d^{-1}: 20% is lost through evapotranspiration, the remaining 80% represents the load discharged to the aquifer. Additional activities were estimated to discharge 5.6×10^6 L per year.[28]

The total discharge to the aquifer was calculated as *(total EI in the plateau × water discharged) + anthropogenic discharges*. Results show that the karst aquifer receives about 1.6×10^{10} L per year of contaminated water, accounting for 2.6% of the annual effective rainfall. These results reveal a potential anthropogenic pressure to the aquifer and a consequent possible pollution of spring water.

Water physical–chemical data

Table 2 shows the Detection Limits (DL) and some statistics calculated from the analytical results. A total of 53 samples were collected from both BC and LC springs. For seventeen variables (T, O_2, EC, pH, Ca + Mg, HCO_3^-, TSS, COD, Cl^-, NO_3^-, SO_4^{2-}, Mn, Cu, Pb, chloroform, methylchloroform, TCS) the number of determined values was significant, whereas for 14 variables (Cr, Cr^{VI}, Fe, Ni, Zn, As, Cd, Hg, F^-, P_2O_5, NH_4^+, NO_2^-, trichloroethylene and perchloroethylene) only few data above the DL are available. The concentrations of all monitored parameters were largely within the Italian standards for drinking water quality. This represents a positive assessment on the state of the aquifer in relation to the recently increased anthropogenic pressures in the Sette Comuni Plateau. From these data, we concluded that the aquifer is not evidently affected by the anthropogenic pressure exerted by about 8.1×10^7 equivalent inhabitants and the consequent release of about 1.6×10^{10} L per year of contaminated water in the plateau.

Additional considerations on the water physical–chemical parameters

Water temperature shows moderate variations (annual average: 9 °C) with minimum values in spring due to the input of melted snow. Variations in temperature were also recorded as a consequence of a strong rainfall on the plateau due to the piston effect caused by the meteoric water,[29] which pushes warmer and more mineralized water into the springs causing a fast increase followed by a decrease in temperature. Dissolved oxygen ranges from 9 to 17 mg L^{-1} with an average of about 12 mg L^{-1}. Water pH is slightly basic (average pH = 7.7) with more acidic values in summer, probably due to the increase of human presence, organic pollution and biological CO_2 contributions on the plateau. However, the limited variations in pH follow an annual trend linked to precipitation rates.

Positive correlations among EC (mean: 280 μS cm^{-1}), hardness (mean: 15 °F, equivalent to 150 $mg_{(CaCO3)}$ L^{-1}) and alkalinity (mean: 175 $mg_{(HCO_3^-)}$ L^{-1}) were found. In fact, harder water involves higher carbonate and bicarbonate concentrations followed by higher conductivity.[30] These parameters are probably influenced by the melted snow effect,[29] reaching the minimum values in spring time.[13]

TSS range from below 1 to 14 mg L^{-1} with an average value of 3 mg L^{-1}, whereas the COD ranges from 0.3 to 2.5 mg L^{-1}. TSS and COD are positively correlated ($r^2 = 0.6$) and the time series present a synchronism corresponding to abundant

Table 2 Limits of Detection (DL) and statistical parameters of experimental values measured at BC and LC springs

	DL		BC spring			LC spring		
			N	Mean ± St. Dev.	Min–max	N	Mean ± St. Dev.	Min–max
T	°C	0.1	47	9 ± 0.4	8.5–10.4	47	8.9 ± 0.2	8.5–9.3
O_2	mg L^{-1}	0.1	41	11 ± 1	9–15	42	12 ± 1	9 –17
EC	μS cm^{-1}	1	53	280 ± 16	234–328	53	283 ± 17	246–325
pH	—	0.1	53	7.7 ± 0.1	7.5–7.9	53	7.7 ± 0.1	7.4–7.9
Ca + Mg	°F	1	53	15 ± 1	13–16	53	15 ± 1	13–16
HCO_3^-	mg L^{-1}	1	53	174 ± 10	152–195	53	176 ± 20	152–287
TSS	mg L^{-1}	1.0	37	3 ± 3	<1 to 14	33	3 ± 3	<1 to 14
COD (Kubel)	mg L^{-1}	0.1	53	0.9 ± 0.5	0.3–2.6	53	1 ± 0.5	0.3–2.5
Cl^-	mg L^{-1}	0.1	53	2 ± 1	1.6–4.1	53	2 ± 1	1.7–4
NO_3^-	mg L^{-1}	0.1	53	5 ± 1	3.8–8	53	5 ± 1	3.7–7.7
SO_4^{2-}	mg L^{-1}	0.1	53	4 ± 1	2.3–7.1	53	4 ± 1	2.3–5.9
Mn	μg L^{-1}	0.5	34	1.5 ± 2.3	<0.5 to 12.6	34	1.3 ± 2	<0.5 to 9.7
Cu	μg L^{-1}	1.0	9	0.9 ± 0.8	<1 to 3.5	11	0.9 ± 1	<1 to 4.6
Pb	μg L^{-1}	1.0	23	1.3 ± 1.5	<1 to 8.2	23	1 ± 0.8	<1 to 4.2
Chloroform	μg L^{-1}	0.1	6	0.3 ± 0.9	<0.1 to 5.5	9	0.3 ± 0.7	<0.1 to 3.3
Methylchloroform	μg L^{-1}	0.1	14	0.2 ± 0.2	<0.1 to 1	17	0.2 ± 0.2	<0.1 to 1.2
Total Chlor. Solvents	μg L^{-1}	0.4	14	0.5 ± 1	<0.4 to 5.9	17	0.5 ± 0.8	<0.4 to 3.8

precipitations. Whereas TSS are influenced only by precipitations, COD shows an annual trend probably linked to the human presence on the plateau with the lowest values in spring and the highest in summer, respectively.

Chloride (mean: 2 mg L^{-1}), nitrate (mean: 5 mg L^{-1}) and sulfate (mean: 4 mg L^{-1}) are positively correlated one another with relative maximum values in summer and spring. Levels of metals and chlorinated solvents are very low. However, even though only few data are above the DL, a clear correspondence of higher values of metals and TCS with COD and TSS was observed. For metals an increase in winter consequent on abundant precipitations in the month of November was noted, probably because metals can be adsorbed onto clays and other particulates and carried through karst aquifers as suspended particles during storm flow.[25,30] For manganese and lead this increase was almost immediate, whereas for copper it was slightly delayed. This can be due to differences in transport dynamics or sources.

The two springs considered in this work represent the two main destinations of the whole catchment area. Possible differences in analyzed parameters between the two springs could provide information on the structure of the aquifer. However, an analysis of variance (ANOVA) performed on the two datasets indicated that no substantial differences exist. Only for dissolved oxygen and temperature some variations can be observed, but these should probably be ascribed to the different structure of the sampling stations.

Identification of the main sources affecting the water quality

A multidimensional statistical approach (Factor analysis, FA) was used to explore the connections between the considered variables, particularly to highlight relationships which are otherwise difficult to detect. FA transforms the data matrix by extracting few independent variables (factors)—obtained by linearly combining the standardized variables—which account for the highest part of the original dataset variability.[31] Analytical values below the DL were replaced with DL/2, missing data with the median of series, variables with a high percentage of missing data were removed. Hydrogen ion activity [H^+] (mEq L^{-1}) was calculated from pH to obtain a linear variable. Because of the high number of data below the DL, chlorinated solvents were not included in the computations, whereas Mn, Cu and Pb were combined as *metals* because of their positive correlation. Also the amount of rainfall collected in the 48 h period before the sampling date ($rain_{48}$) was included as a variable. Changes in plateau precipitation rates can cause high-flow conditions on the surface[29] and in the aquifer respectively, with the concurrent effect of increasing the amounts of sediments, contaminants and/or nutrients in spring water.[25,30] FA was therefore also used to reveal a generalized response of the karst system to the rainfall.

The resulting factors obtained from the analysis of the 12 variables retained (dissolved O_2, EC, H^+, Ca + Mg, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, COD, metals, TSS and $rain_{48}$) were then orthogonally rotated by the Varimax method, to optimize the distribution of variable weights on the factors.[31]

Results are reported in Table 3: four factors with eigenvalues above 1, accounting for 75% of total variance, were considered significant. The first factor accounts for 24% of the total variance and combines COD, metals, TSS and $rain_{48}$. During precipitation periods, due to the increased flow, the amount of water suspended particles may increase from the remobilization of intra-karstic sediments and from the input of land surface materials due to rapid drainage.[32] The first effect generally occurs shortly after the rain, whereas the second one may arrive from hours to several days later.[33] Also selected metals (Mn, Cu, Pb) can have an intra- and extra-karstic origin. The first one is due to the release of these elements from the crystalline structure of limestone or from clay minerals,[30] whereas a second one is due to the input of surface pollution sources, such as road dust produced by vehicular traffic.[34] The frequency of sampling (one sample per week) resulted probably not adequate to make a hypothesis on this specific pollution source. An extra simulation performed by calculating the Pearson correlation coefficient between each chemical parameter (COD, TSS, metals) and the amount of rainfall in the 24 h ($rain_{24}$), 48 h ($rain_{48}$) and 72 h ($rain_{72}$) before sampling showed the lowest value for $rain_{24}$. These results lead to a greater contribution of land surface materials input than to the intra-karstic sediment re-suspension.

Table 3 Results of factor analysis. The most significant factor loadings (>0.6) are in bold type, whereas loadings ranging from 0.4 to 0.6 are in italics

	Factor 1	Factor 2	Factor 3	Factor 4
	Pollution	Karstification	Anions	Photosynthesis
$Rain_{48}$	**0.77**	0.15	0.07	0.33
O_2	0.10	0.03	−0.05	**0.85**
H^+	0.26	**0.82**	0.04	0.05
EC	−0.02	**0.81**	0.32	0.12
COD	**0.82**	0.01	−0.04	0.16
Ca + Mg	−0.13	**0.88**	−0.07	0.13
HCO_3^-	0.27	*0.43*	−0.04	**0.68**
SO_4^{2-}	0.33	0.02	**0.75**	−0.23
Cl^-	−0.24	0.23	**0.75**	−0.04
NO_3^-	−0.15	−0.03	**0.88**	0.12
TSS	**0.93**	0.09	−0.04	0.07
Metals	**0.66**	−0.20	−0.32	−0.35
% Var	24.4	20.1	17.7	12.8
Cum % Var	24.4	44.5	62.2	75.1

Factor 1 can therefore identify the contamination from both organic substances (COD) and metals due to the injection of the runoff into the aquifer network following rain periods on the plateau ($rain_{48}$).

Other authors[25] have also reported that high-flow conditions due to rainfall may transport increased amounts of sediments and higher concentrations of contaminants absorbed in the suspended solids. Even though chlorinated solvents were not included in the model, it was observed that some concentration peaks can be observed following heavy rain periods.

The second factor (20%) mainly links (factor loadings > 0.6) EC, H^+, Ca + Mg, and secondarily (factor loadings 0.6–0.4) bicarbonate. This factor derives from rock weathering and identifies the limestone dissolution effect due to the karstic phenomenon following the chemical reaction:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

As no correlation of EC, Ca + Mg and HCO_3 with $rain_{24}$, $rain_{48}$ and $rain_{72}$ was observed, thus the probability that the influence of precipitation on rock weathering processes works on a much longer time scale than those considered for correlations is high.

The third factor (18%) is made up of three anions (Cl^-, NO_3^- and SO_4^{2-}). Anions show relatively high values in summer and spring, but no correlation with precipitations was found. The interpretation of this factor is not straightforward. Chloride can derive from different sources, such as road salts during winter, fertilization during spring and summer, but also contamination of waters due to domestic and industrial use during the whole year. Nitrate contamination has been extensively assessed and documented.[10,30] In karst aquifers contaminated by agricultural runoff, NO_3^- concentrations vary seasonally as a direct response to land use and fertilizers.[35] Sulfate is a ubiquitous ion in natural waters being released by a variety of natural and anthropogenic sources and processes. Sulfate can derive from fertilizers, pollution and also from the dissolution of minerals (*e.g.* gypsum: $CaSO_4 \cdot 2H_2O$) which can be present in a karstic massif. Moreover, these ions may also derive from atmospheric depositions.[36,37]

The absence of any correlation between the anions and $rain_{48}$ likely exclude the soil use/release and the atmospheric deposition origins. This factor was then interpreted as the anthropogenic pressure on the plateau due to water use and pollution deriving from livestock farming.

The fourth factor (13%) shows an association between dissolved O_2 and HCO_3^-, by identifying the influence of the photosynthetic activity on the aquifer. In fact, bicarbonate is the main inorganic carbon source for photosynthetic organisms in water, and oxygen is one main product. Photosynthesis is therefore the natural positive link between these two parameters.

Chemical response to rain periods

Depending on the rainfall amount and recharge conditions, water chemistry of karst springs represents a variable mixture of both groundwater and surface water in accordance with the karst system's vulnerability. To check the interpretation of these sources extracted from FA, a combination of samples with similar rainfall conditions in the two days before, *i.e.* no rain, moderate rain and heavy rain storm were collected. These results are shown in Table 4. As expected, TSS, COD, metals and

Table 4 Average values of monitored water parameters obtained by grouping samples with similar rainfall conditions and seasons of the year

		Heavy $rain_{48}$ > 50 mm	Moderate $rain_{48}$ 5–50 mm	No $rain_{48}$ < 5 mm	Spring	Summer	Autumn	Winter
		n = 5	*n* = 8	*n* = 40	*n* = 14	*n* = 13	*n* = 13	*n* = 13
$Rain_{48}$	mm	—	—	—	1.8	20.9	18.4	2.2
T	°C	8.8	8.8	8.9	8.9	8.8	8.9	8.8
O_2	mg L^{-1}	12.4	12.0	11.5	11.4	11.9	12.2	11.2
EC	μS cm^{-1}	286	285	283	274	288	290	282
pH	—	7.6	7.7	7.7	7.8	7.7	7.7	7.7
Hardness	°F	14.6	14.5	14.5	13.9	14.6	15.0	14.7
HCO_3^-	mg L^{-1}	**212**	176	172	164	186	185	173
TSS	mg L^{-1}	**9**	3	2	2	3	4	2
COD	mg L^{-1}	**1.8**	1.1	0.8	0.7	1.3	1.1	0.7
Cl^-	mg L^{-1}	2.4	2.5	2.4	2.6	2.4	2.3	2.3
NO_3^-	mg L^{-1}	4.7	5.0	4.8	5.0	4.9	4.9	4.6
SO_4^{2-}	mg L^{-1}	4.5	4.4	4.3	4.3	4.5	4.3	4.3
Metals	μg L^{-1}	**6**	3	3	3	2	4	4
TS	μg L^{-1}	**0.8**	0.2	0.6	0.5	0.2	0.9	0.6

chlorinated solvents strongly increase during intense rainfall together with HCO_3^-, whereas other variables are almost constant. This way, for these pollutants the response to a rain storm is almost immediate, revealing a fast and direct injection of runoff into the aquifer with minimal filtering by soil and rocks. In contrast, precipitation has no direct effects on the ionic composition of waters (chloride, nitrate and sulfate) and the process of karstic erosion (EC and Ca + Mg).

A time difference between winter skiing activities and the chemical effects in the spring waters ascertained some time later may be caused by the retaining effect of snow. Water contaminants may be kept on the plateau and released into the karst system during the spring snow melting period. Possible changes of water composition in different seasons were investigated, and the results are reported in Table 4. No significant differences were found. This confirms that changes in spring water quality occur mainly after rainfall periods.

Conclusions

The Oliero springs are the main focus of a vulnerable catchment area of about 550 km^2. Recently, the plateau was assessed to be highly vulnerable to water contamination due to the presence of well-developed karstic structures that facilitate water percolation and groundwater contamination risk.[15] The water quality at two karst springs was monitored once a week for a whole year and an estimation of anthropogenic pressure in the catchment area was made. The concentrations of all monitored parameters were largely within the Italian standards for water quality, thus confirming that probably the aquifer is not significantly affected by the anthropogenic pressure on the plateau.

A factor analysis was performed to explore the relationships between all the variables and identify the most probable processes affecting the water characteristics. Results reveal four processes, two natural and two linked to the anthropogenic pressure in the plateau: (i) karstification due to dissolution of rocks; (ii) photosynthesis; (iii) pollution due to the injection of runoff into the aquifer network following rain periods in the plateau, and (iv) anions, ascribed to human water use and livestock farming.

In this study, the response of the aquifer to the contaminant input was also investigated. Concentrations of pollutants (metals and chlorinated solvents), organic matter *e.g.* COD, and total suspended solids result strongly affected by the amount of rain falling in the catchment area. The chemical response to a rainstorm is almost immediate, highlighting a fast and direct injection of runoff into the aquifer with limited filtering by soil and rocks.

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