ORIGINAL ARTICLE

Hydrogeological and geochemical characterisation of the Rock of Orvieto

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Abstract The town of Orvieto, located on the Rock of the same name, is an example of "vulnerable town"; problems of slope instability connected with the lithological and morphological characteristics of the Rock have been thoroughly examined and discussed during previous research studies. Hydrogeochemical data about groundwater recharging the springs present in the area were never taken into account. Pollution of the springs is well known but still occurs for unclear reasons. The aim of this work is therefore to present the results of a hydrogeological and geochemical investigation of all the springs along the slopes of Orvieto hill and at the foot of the tuffaceous Rock, to characterize the groundwater flow paths and to suggest a possible source of contamination. The research study was carried out during three hydrogeochemical surveys in the years 1998–1999, 2003–2004, and 2007–2008.

Introduction

Following a Special National Law (Law 05.25.1978 n. 230 "Urgent measures for the consolidation of the Cliff of Orvieto and the Hill of Todi to protect the landscape, historical, archaeological and artistic heritage, of the two Cities"), consolidation work started on the Rock of Orvieto in order to deal with the instability phenomena along the walls of the tuffaceous cliff. The mineralogical composition of the tuffaceous cliff was very important for the hydrogeochemical remarks presented here. In fact the presence of zeolite minerals in the tuffaceous cliff had a great influence on the chemical composition of the groundwater. This investigation started in the period 1998–1999, when all the springs of Orvieto hill and at the foot of the tuffaceous Rock were studied, with monthly measurements of discharge, temperature and electrical conductivity. Springs were characterized by high contents of nitrates, chlorides and sulphates. The chemical composition of groundwater was initially considered the consequence of recent and ongoing pollution phenomena.

Further investigations were started in 2004 and completed in 2008, in order to confirm the isotopic and chemical parameters previously found, and to investigate a possible source of pollution. The isotopic data now available, together with several laboratory experiences and mineralogical observations, favour the hypothesis that groundwater chemistry is due to a peculiar geochemistry and antropogenic history of the Orvieto Rock. These rocks are likely to have absorbed pollutants in the past and then

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slowly release them by leaching into the groundwater after saturation of the crystalline sites of the zeolite.

Geomorphological and geological description

The town of Orvieto, situated in the south west of Umbria (Central Italy), stands on the summit of a tuffaceous cliff with a surface area of 866,000 m^2. The cliff has an irregular elliptical shape and a sub-horizontal position and rises with vertical walls on the summit of a gently sloping hill (Fig. 1). The present morphological structure of the hill and the Rock of Orvieto is the result of erosion which has furrowed and fractured a large pyroclastic plateau produced by the magmatic activity of the nearby Bolsena volcano, which is part of the even greater "Vulsin Apparatus" (Conversini et al. 1977; Cencetti et al. 2005). The tuffaceous Rock of Orvieto is between 40 and 70 m thick, with vertical walls which are higher on the south-western side than on the north side. On the contrary, the hill has gently inclined slopes (between 15° and 18°), which are

furrowed by gullies called *Salto del Livio*, *Civetta*, *St. Zero*, *St. Benedetto* and *Cavaiene*.

The stratigraphical sequence (Figs. 1, 2, 3) is characterised, from the lower layers upwards, by marine clays, followed by a sequence known as the "Albornoz series" and finally by the tuffaceous plateau, which is covered on the eastern edge by a limited outcrop of travertine; variously distributed layers of detrital deposits can be found almost along the whole perimeter of the hill (Conversini et al. 1977; Faraone and Stoppa 1988; Cencetti et al. 2005).

The basal layer of clays, dating from the middle Pliocene, is a massive seam with a sub-horizontal position; the clays have a dark bluish colour and contain a relatively high amount of calcite. Following the clays there is an "Albornoz series" of limited thickness (maximum about 8 m), made up of overlapping layers which include, from the bottom upwards, a sandy conglomerate with blocks of balsaltic lava, nut-brown calcareous silts, a layer of white pulverulent calcareous material with diatoms, black scoriae and cineritic material and finally a layer of pumicious clasts which marks the transition to the tuffaceous rock.

Fig. 1 Photograph of the Rock of Orvieto; geological map of the Orvieto area (from CENCETTI et al. 2005). *1* Talus (Holocene), *2* recent and present alluvial sediments (Holocene–Upper Pleistocene), *3* volcanic rocks of the Alfina Plateau (Middle Pleistocene), *4* gravels, sands and clays (marine clastic sediments, Lower Pleistocene–Pliocene), *5* Marls and sandstones (pre-Pliocenic bedrock), *6* River Paglia and its main tributaries
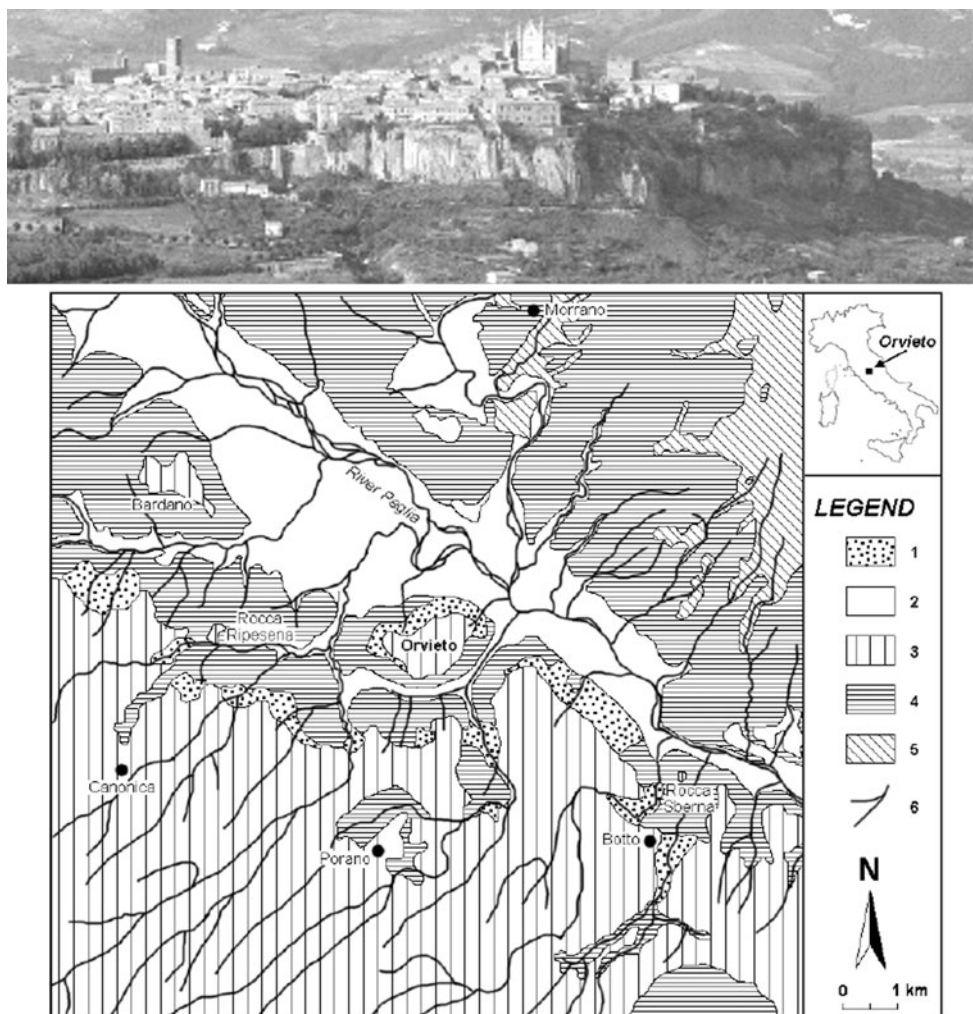
Fig. 2 Location of the analysed springs (*squares*) and outline of the cross-section of Fig. 3. Map of the isophreatic lines in the area of the cliff (the values are related to the sea level). The boreholes carried out for the geotechnical characterisation of the cliff are also indicated (*small circles*)
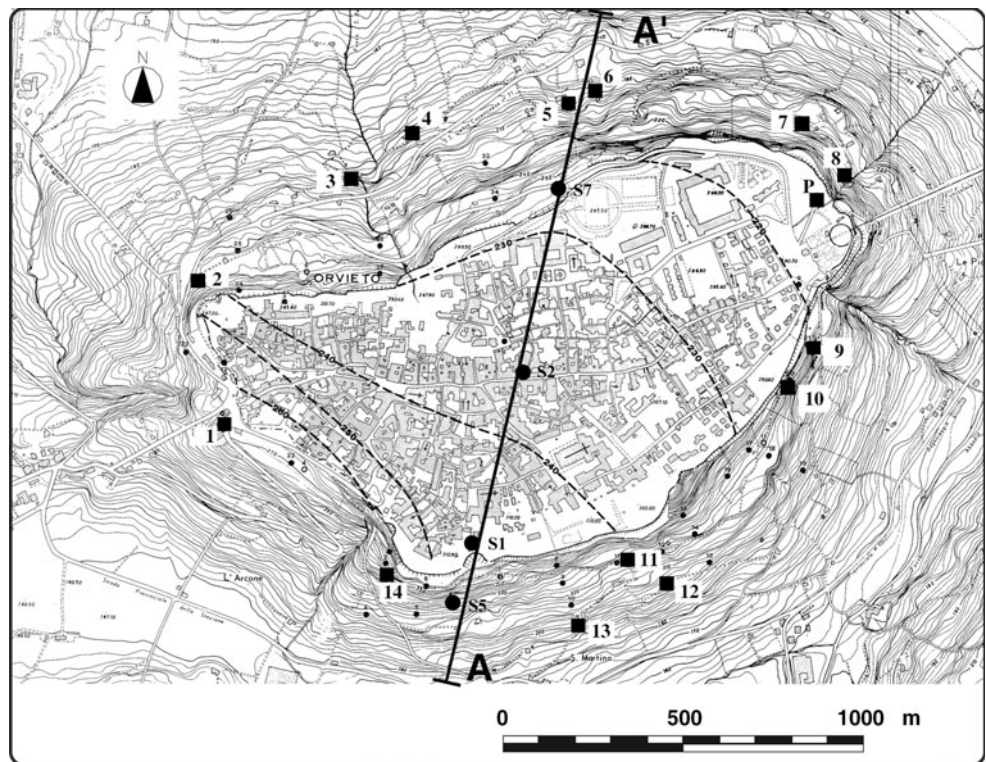
Fig. 3 Geological cross section of the Rock of Orvieto. *1* Orvieto Tuff (pumice facies and Zeolite facies, Holocene), *2* Albornoz formation (silty sand sediments characteristic of a swampy pre-volcanic environment; at the top of the formation there are the first heterogeneous volcanic clasts, Pleistocene), *3* Pliocenic clays, *4* Debris and loose material from translational landslides and rock falls
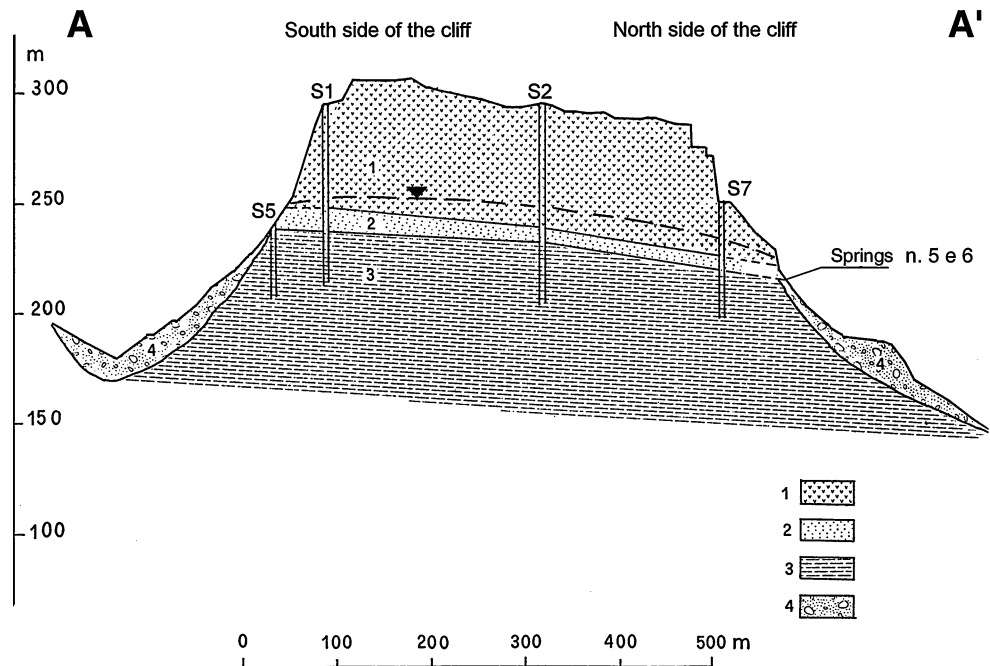
The presence of diatoms and fossils groundwater indicates a lacustrine environment. The succession of calcareous silt and conglomerates proves that in the area of Orvieto, after the regional plio-pleistocene uplift, a river system which, formed left conglomerates and sandy deposits. This was contemporary with the eruption of lava and other volcanic products. The river system subsequently evolved into a lake system, as shown by the calcareous silt deposits.

The tuffaceous cliff is the result of the cooling of a high temperature pyroclastic flow, which partially hardened immediately after being deposited. This process gave rise to two clearly distinct facies which characterise the Rock;

the first has a marked stony appearance (facies *sillar*), with sub-vertical fissures and a reddish-yellow colour; the other is made up of an incoherent mass of grey-black pyroclastic material of varying composition and granulometry with no clear fissures. The first facies is known as "*red tuff with black pumice clasts*", the second as "*pozzolana*" (Zanon et al. 2007).

Detrital deposits, produced by the weathering of the Rock, are found at the bottom of the walls. This detritus is variously distributed and made up of blocks of variable size immersed in a pozzolana and ash matrix.

General hydrogeological properties

The tuffaceous plate of the Rock of Orvieto, the Albornoz series and the detrital deposits are permeable by single porosity and double porosity (fracturing); the basal clays are practically impermeable. The permeability of the lithotypes and their stratigraphical arrangement affect the circulation of the meteoric water, which seeps through the tuffaceous plateau and the Albornoz series. When the water reaches the basal clays, its vertical movement is stopped and a watertable is formed. Numerous springs along the cliff (very close to the tuffaceous wall) indicate the presence of groundwater flow inside the cliff. Some springs are localized where the basal clays contact the Albornoz layer, other springs are scattered along the slopes, close to the interface between debris and clays, or where the ground forms hollows in the lower morphologic part of the cliff. In a previous investigation (Conversini et al. 1977), 31 springs were counted and their discharge was measured over a period of 2 months (May and June). The overall flow was approximately 8 l/s. The main groundwater direction seemed to go from SW to NE (only few hydrogeologic data were available). Our study takes into account 14 springs along the cliff sides and 30 geological drillings and some piezometers used in a previous survey for geotechnical purpose (Conversini et al. 1995). Data collected from boreholes, geological drillings (going to a maximum depth of 100 m from ground level) and experimental tracer, endorse such flow direction. In fact, as shown in the map of

the isophreatic lines (Fig. 2), the groundwater run-off direction is going from SW to NE.

These findings are in agreement with the placement of the basal clay layer (Fig. 3) which slopes from W to E. The high discharge measured in the springs n. 7 and n. 9 (located at NE and E side of the Rock) is also consistent with this observation.

The tracer dilution tests (performed with radioactive and electrolytical tracers in some boreholes located within the town perimeter as illustrated in Fig. 2) show long residence time and very low water infiltration rates. Data regarding the discharge and the position of each spring were also collected.

Climate in the Orvieto area

Rainfall

The annals of the National Hydrographic Service (http://www.idrografico.roma.it/), show that in the period between 1921 and 2002 there was a total annual average rainfall of 815 mm, with an annual maximum value of 1,433 mm in 1928 and a minimum of 245 mm in 1931. The maximum monthly rainfall occurred in September 1965 with 314 mm, while the minimum rainfall was found in June 1952, August 1962 and October 1965 with values of 0 mm.

In 1998, when the present research study began, the total annual average rainfall was 651 mm, with a maximum of 95 mm in September and a minimum of 7 mm in July; in 1999 the total annual rainfall was 993 mm, with a maximum of 188 mm in November and a minimum of 17 mm in August (Table 1).

Temperature

According to Giaquinto et al. (1982), who collected thermometric data for the period 1921–1970 at five climate stations, including Orvieto (Fig. 4), the average annual temperature of the Orvieto area was about 14.5°C. The same authors calculated an evapotranspiration of 622 mm/year, equivalent to 58% of the rainfall. The thermometric

Table 1 Summary data on rainfall, temperature and evapotranspiration in Orvieto area

	Average value	Max value (year 1928)	Min value (year 1931)	Max monthly rainfall	Min monthly rainfall
Total annual rainfall (mm of rain)	815	1,433	215	314	0
Annual temperature (°C) 1921–1970	14.5	–	–	–	–
Annual temperature (°C) 1995–2005	13.4	–	–	–	–
Evapotranspiration rate (mm/year) 1921–1970	622	–	–	–	–

Fig. 4 Ubication of climatic stations (*bold circles*) used in the present study

data provided by the Regional Authority of Umbria taken from a climate station located in Orvieto Scalo, show an average annual temperature of 13.4°C in the period 1995–2005 (Table 1).

Physical and chemical properties of the springs

This study investigates the springs located at the foot of the Rock and along the slopes. These springs are tapped and

Table 2 Names of the investigated springs

N	Name
1	St.Lucia
2	Le Conce
3	Baffone
4	Pescara
5	Pettinacci 1
6	Pettinacci 2
7	Spring with no name
8	St.Zero
9	Leone
10	Barlocio
11	Cannicella alta
12	Cannicella bassa
13	Casa Maggi
14	Livio

exploited mainly for agricultural use; they are listed and briefly described in Table 2.

Together with the springs, the so called *St Patrick's Well*, situated within the town perimeter a few meters from the eastern edge of the Rock, was also considered. The Well bores through the entire thickness of the tuffaceous Rock through to the basal clay layer.

All the springs were analysed in the period June 1998– May 1999 (in some cases till December 1999). Discharge, temperature and electrical conductivity were measured with monthly intervals.

Discharge

All the springs, except for spring n. 7, have a perennial regime, although the discharge is generally limited: 6 out of 14 may be classified as "sub-variable" (*St. Lucia, Le Conce, Baffone, Pettinacci 1, Leone, Livio* and *Casa Maggi springs*), while the others can be considered "variable" (*Pettinacci 2, St. Zero* and *Barlocio springs*), as suggested by the Meinzer classification (Meinzer 1932). The maximum discharge was measured in *Fonte del Leone* spring with an annual average of 28 l/min and a total annual discharge of 16,300 m^3, while the minimum value was found in *Fonte di St. Lucia* spring with an annual average of 0.43 l/min and a total annual discharge of 225 m^3 (Table 3).

In the period between June 1998 and May 1999 the springs delivered an overall water amount of 91,000 m^3, equivalent to 18% of the rainfall in the area of the Rock of Orvieto.

Temperature of the waters

The average temperature of the waters remained within the range of 13–15°C; the seasonal temperature range was restricted, except for *Fonte di St. Lucia* spring, which showed a considerable variation in values (ranging between 8 and 16°C) due to its prevalently detritic aquifer (Table 3). Nevertheless, the observed seasonal variation of the temperature was relatively small as compared to the size of spring basins. This may be attributed to the particular configuration of the Orvieto hydrogeological system, with the formation of a water table at the foot of the Rock and a slow run-off which results in a uniform temperature of the groundwater.

Electrical conductivity and chemical properties

The electrical conductivity of groundwater was measured using a multi-parametric probe which is able to simultaneously measure the temperature (t°C) and the electrical conductivity (EC μS/cm). The maximum values were

Table 3 Summary data on spring discharge and temperature

Springs	Discharge (l/min)			Temperature (°C)		
	Mean value	Min value	Max value	Mean value	Min value	Max value
1	0.3	0.6	0.4	13.5	8.4	18.4
2	17.4	36.0	22.2	13.0	11.7	13.8
3	23.0	45.0	32.8	13.7	12.1	15.6
4	4.3	19.0	6.8	13.6	12.8	14.1
5	6.1	13.8	9.2	13.1	11.8	13.8
6	3.0	7.5	4.4	13.3	10.1	16.3
8	7.5	25.0	16.1	13.6	11.7	14.8
9	28.6	37.5	32.8	13.8	12.2	14.7
10	0.5	3.3	2.2	14.3	13.2	15.4
11	2.6	5.3	4.2	14.4	13.1	15.7
12	0.0	1.6	0.9	13.7	13.0	14.2
13	10.0	15.8	12.8	15.4	12.4	16.3
14	4.9	14.0	7.7	14.5	12.4	16.0
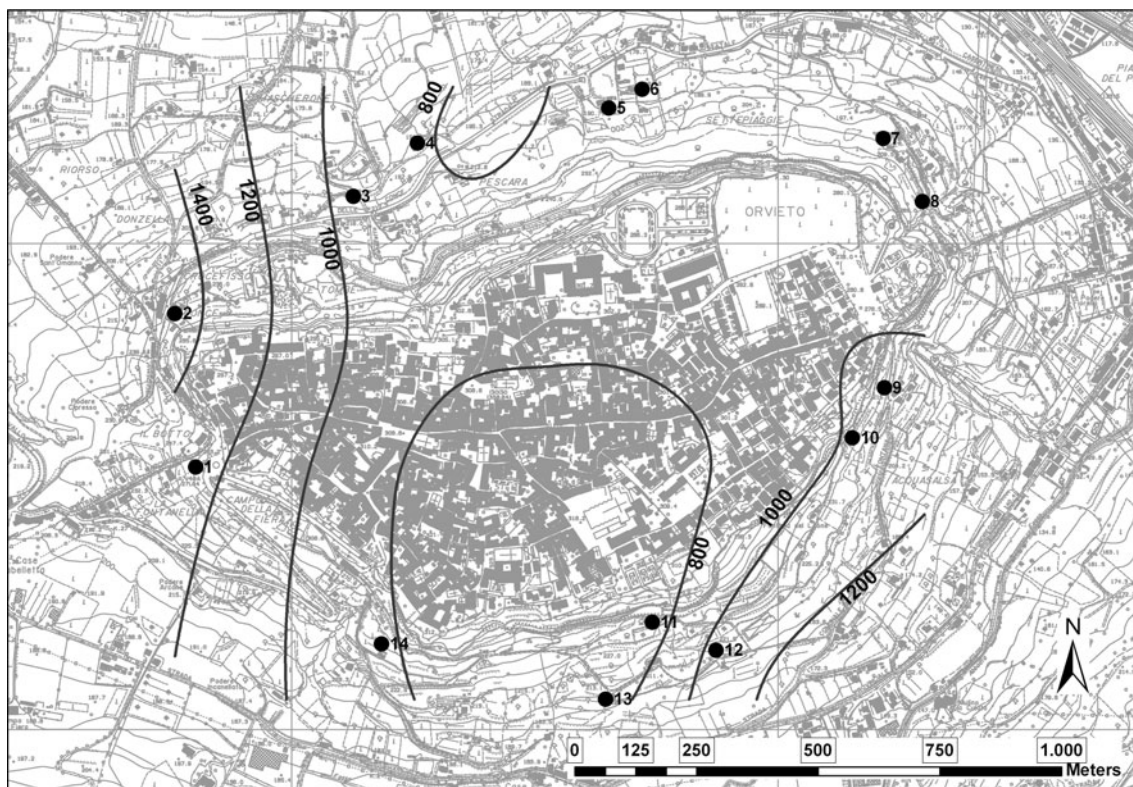
Fig. 5 Trend of the electrical conductivity (μS/cm) of the springs; interpolation with Spline method

measured in *Le Conce* (spring n. 2) with a seasonal variation ranging between 1,400 and 1,550 μS/cm, and the minimum values were found in *Casa Maggi* spring (n. 13), with values ranging between 700 and 850 μS/cm (Fig. 5). Total salinity ranged from a minimum of 520 mg/l (spring n. 13) to a maximum of 1010 mg/l (spring n. 1), with most of the values falling within the range of 600–700 mg/l.

The salinity measures suggested a differential release of chemical elements by the minerals of the cliff. In general, the increase in salinity observed during the hottest period of the year was probably due to a lower infiltration.

The spring chemical composition allowed most of the waters to be classified as bicarbonate-calcium rich-alkaline waters (Fig. 6) with $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$ and
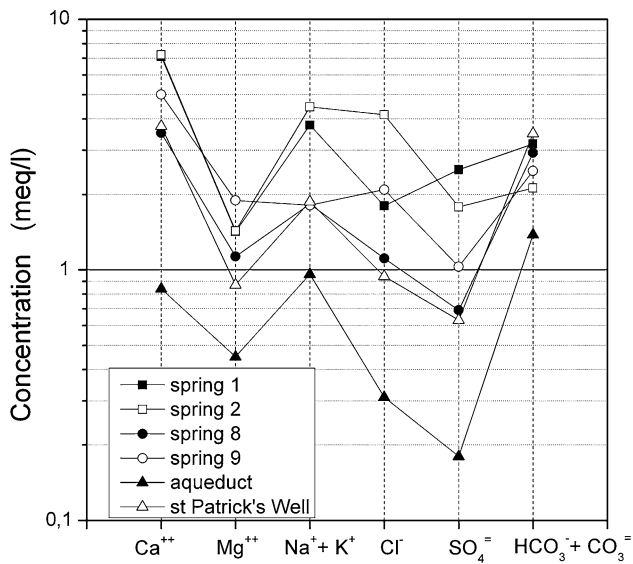
Fig. 6 Schöeller-Berkaloff diagram showing the chemical composition of the springs waters. The *bold triangles* are relative to aqueduct water

$HCO_3^- > NO_3^- > Cl^- > SO_4^{2-}$ as regarding the ionic formula.

In all the springs, the chemical element with the highest equivalent concentration is calcium, as shown the Fig. 6; in some springs the Ca^{2+} concentration was greater than 100 mg/l and the NO_3^- value was higher than 300 mg/l. The Schöeller–Berkaloff diagram clearly showed the variations of chemical elements in some springs; in particular, springs n. 2 had the highest content of chloride, calcium, sodium and potassium, the spring n.1 had the highest content of sulphate.

Correlations among the different chemical elements and the rNa/rCl, rMg/rCa, rCa/r(SO_4 + HCO_3) ratios may then be indicative of the water behaviour in the subsoil, and provide useful information on the type of rock the water passes through (Bowen 1979; Celico 2003; Freeze and Cherry 1979; Hem 1985).

The Cl-TDS (Total Dissolved Solids) diagram showed that the amount of Cl^- may be connected, with remarkable accuracy ($R^2 = 0.91$), to the overall saline content, except in the springs of *St. Lucia* (n. 1) and *Le Conce* (n. 2), where very high values were found (Fig. 7a). The same was true for the rSO_4–rCl values, which were fairly well-aligned except the value of *Le Conce* (n. 2) and *St. Lucia* (n. 1), located on the west side of the cliff (Fig. 7b).

The high regression coefficient indicated that the chemical composition of the spring water is closely related to leaching phenomena coming from rocks belonging to the same type. On the contrary, the higher Cl^- and SO_4^{2-} contents of the two above mentioned springs likely indicate the presence of areas where pollutants preferentially accumulate.

Notes on lithological properties and contamination mechanism

The facies "red tuff with black pumice clasts" (with a thickness up to 100 m), covers an overall area of about 2,000 km^2 (Passaglia et al. 1990). In the past this formation underwent zeolitisation processes which occurred at high temperatures connected with its ignimbritic nature (Alvarez et al. 1975; Passaglia et al. 1997).

Zeolite properties, such as high cation exchange capacity and high selective sorption (Snellings et al. 2008), are particularly important when considering the Orvieto area, since the red tuff with black pumice clasts is highly zeolitised (Lenzi and Passaglia 1974; Passaglia et al. 1997). Therefore it greatly affects the release of nitrogen compounds into the groundwater. In fact, high concentrations of nitrates, potassium, sodium, calcium and magnesium

Fig. 7 a The chloride content and total dissolved solids ratio. **b** The sulphate content and dissolved chloride ratio expressed in milliequivalents per liter
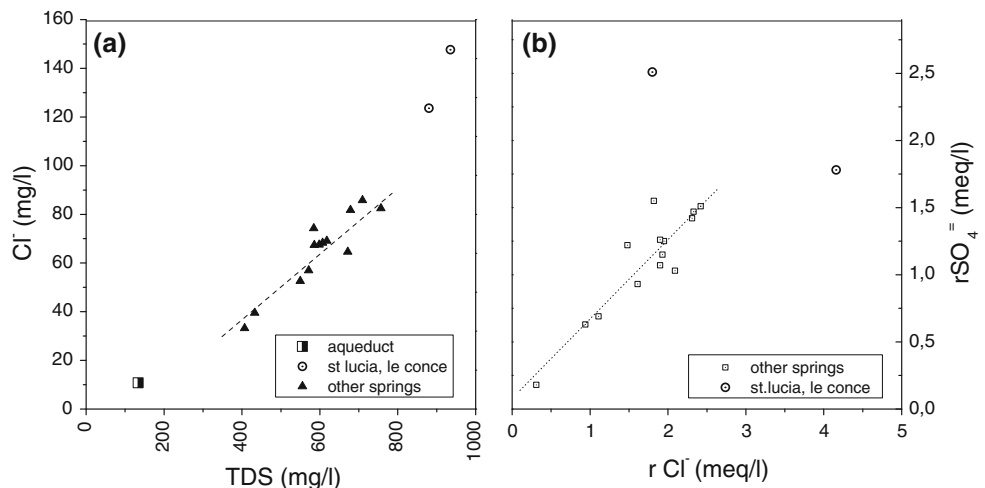
were found in the springs during the first investigation; such concentrations were considered as a consequence of recent and direct pollution of anthropic origin (current leakages from pipes and sewers). Observing the composition of the tuffaceous rock and taking into account the zeolitisation process (Lenzi and Passaglia. 1974; Langella et al. 1995), another possible explanation may be considered: anthropic and animal pollution which occurred thousands of years ago (there is evidence of pre-Roman settlements in the area, as reported by Cencetti et al. 2005) led to the accumulation of pollutants in the tuffaceous rock. After the crystalline sites of the zeolite saturated, nitrogen compounds started to be released into the groundwater.

Due to the zeolite feature to act as a sponge, the high concentration of chemical compounds is the evidence of pollution phenomena which occurred thousands of years ago.

In order to test if the zeolite properties are maintained by the Orvieto tuff, some release tests were performed. Leaching tests are often used to determine chemicals release from rocks in laboratory environment (Bradley et al. 1980; Latham and Schwarcz 1987; Zhou et al. 2005); in the present study, long-term release tests (using bidistilled water and dry tuff samples) were performed. The rock samples were collected in different zones of the cliff; the overall duration of the test was of 268 h. The leaching test procedure consisted of a continuous contact between the dried rock sample (previously reduced in dust) and a certain volume of liquid (bidistilled water). The final result is to "extract" the chemical elements bounded on the surface of the rock.

Such tests have been performed by using a standard apparatus for batch tests (ASTM D4646 2008) consisting of a set of HDPE bottles filled with the rock samples and the bidistilled water, kept flurry by a mechanical stirrer for the entire duration of the test. The amount of rock sample used in the test were equal to 5 g, with 100 ml of water each sample. Measurements of the chemical concentrations were carried out on the outflow liquid after 55, 74, 99 and 268 h; concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-} and NO_3^- were determined (Table 4). The results reported in Table 4 stressed that high content of chemical compounds can be released into the groundwater by rocks of the cliff. For example, up to 35 mg/l of nitrates were found in the leachate water at the end of the test. Probably the slightly acidic nature of some rains contributed to increase the leaching of these ions over the time.

Isotopic data

The isotopic composition of groundwater throughout the experimental surveys are shown in Fig 8. The $\delta^{18}O$ values
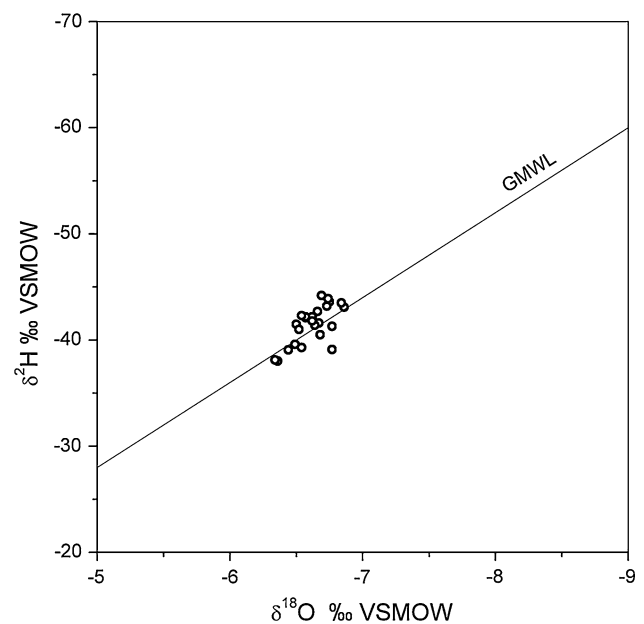

Fig. 8 Deuterium and oxygen-18 ratio measured in the springs. Global Meteoric Water Line (GMWL) refers to the rainfall in whole the world

Table 4 Leaching tests on samples of tuffaceous rock. Results of chemical composition of the leachate expressed in mg per litre per gram of rock

Sample	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)
ORV-1c	2.38	0.47	1.75	2.26	3.34	34.46	0.41
ORV-3c-light	0.16	0.12	2.12	0.07	1.64	1.69	0.50
ORV-3c-dark	0.53	0.19	1.11	0.67	2.16	1.65	0.65
ORV-1°	0.20	0.06	2.60	0.95	2.04	3.04	0.39
ORV-2°	1.18	0.25	6.42	1.28	0.45	16.04	4.68
ORV-3°	0.09	0.04	0.49	0.10	0.10	0.86	0.46
ORV-1b	4.32	0.49	1.57	0.81	3.58	23.92	2.12
ORV-2b	1.85	0.14	0.72	0.67	2.28	15.28	0.44
ORV-3b	1.68	0.45	1.26	0.44	6.18	1.05	0.20
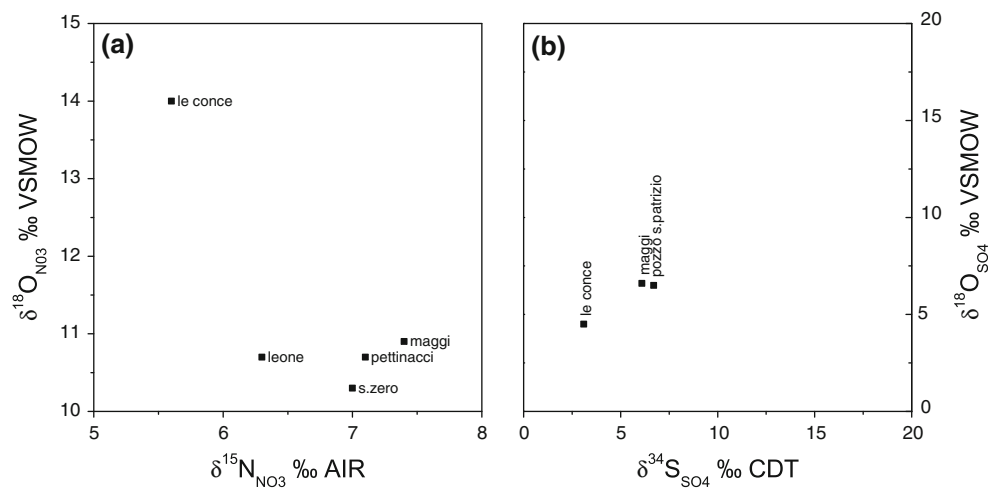
ranged between −6.34 and −6.48‰ VSMOW with a mean
value of −6.40‰ and a standard deviation of 0.12; the δ^2H
values ranged between −38.9 and −44.2‰ VSMOW (data
referred to the last survey), with a mean value of −41.4‰
and a standard deviation of 1.77. These values indicated
that all the groundwater circulating in the tuffaceous cliff
were similar and came from local rain water. Therefore all
the springs belonged to the same system.

According to the isotopic values the estimated infiltra-
tion altitude ranged between 200 and 300 m a.s.l., consis-
tent with the morphology of the cliff.

In the years 1999, 2000, 2004 and 2008 tritium (^3H)
levels were measured in a few springs, with values ranging
between 2 TU (Tritium Unit) and 8 TU. The lowest values
(2–3.5 TU), generally found in the south and south-east
side of the cliff, indicated longer residence time and/or
slower circuits; slightly higher values were measured in the
west side of the cliff (*St. Lucia* and *Le Conce* springs). The
low seasonal variability of the ^3H values indicated that
groundwater was homogeneous and presented a slow run-
off through the tuffaceous plateau and the Albornoz series.
The difference in ^3H values among sampled springs high-
lighted different contact times between the rock and the
water, and allowed us to identify the main area of infil-
tration which was situated in the NW side of the cliff.

In the year 2000 the contents of $\delta^{34}S$-(SO_4^{2-}), $\delta^{18}O$-
(SO_4^{2-}), $\delta^{15}N$-(NO_3^-) and $\delta^{18}O$-(NO_3^-) were measured.
The NO_3^- data (Fig. 9a), only slightly enriched in $\delta^{15}N$,
seemed to exclude current pollution, which is otherwise
attested by $\delta^{15}N$ values of 20–30 ‰, according to Clark
and Fritz (1997); Fukada et al. (2004); Mariotti (1984);
Pitcairn et al. (2005); Tandia et al. (1998).

The results obtained for sulphates are reported in
Fig. 9b, with $\delta^{34}S$ between +3.1 and +6.7 ‰, and $\delta^{18}O$-
(SO_4^{2-}) values ranging between +4.5 and +6.6 ‰.
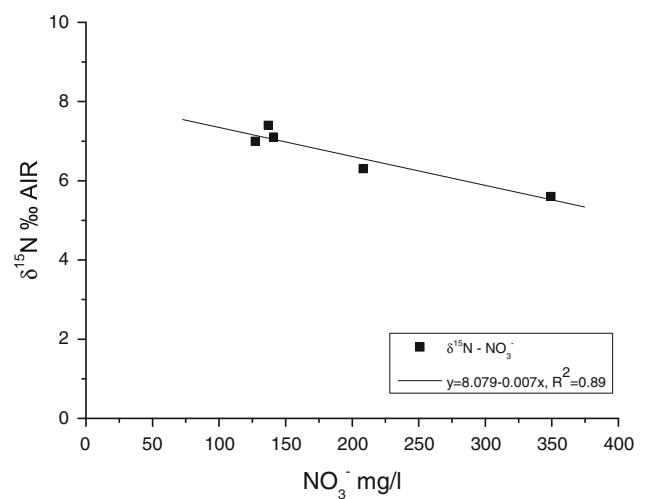Figure 9a clearly showed the difference between the

Fig. 10 Diagram of $\delta^{15}N$ as a function of NO_3^- concentration

isotopic composition and chemical composition amounts
between Le Conce spring (situated in the W side of the cliff)
and all the other springs on the south and east sides. More-
over, when comparing Le Conce spring with other west side
springs, the isotopic composition was similar but Le Conce
spring presented much higher amounts of nitrates (Fig. 10).

Conclusion on hydrogeochemistry

Hydrogeological considerations

Chemical and isotopic data together with discharge values
contributed to understand the groundwater circulation. It is
also important to understand where the discharge area of
the springs was: debris deposit, tuffaceous cliff, transition
between the Albornoz series and the basal clays, etc. In
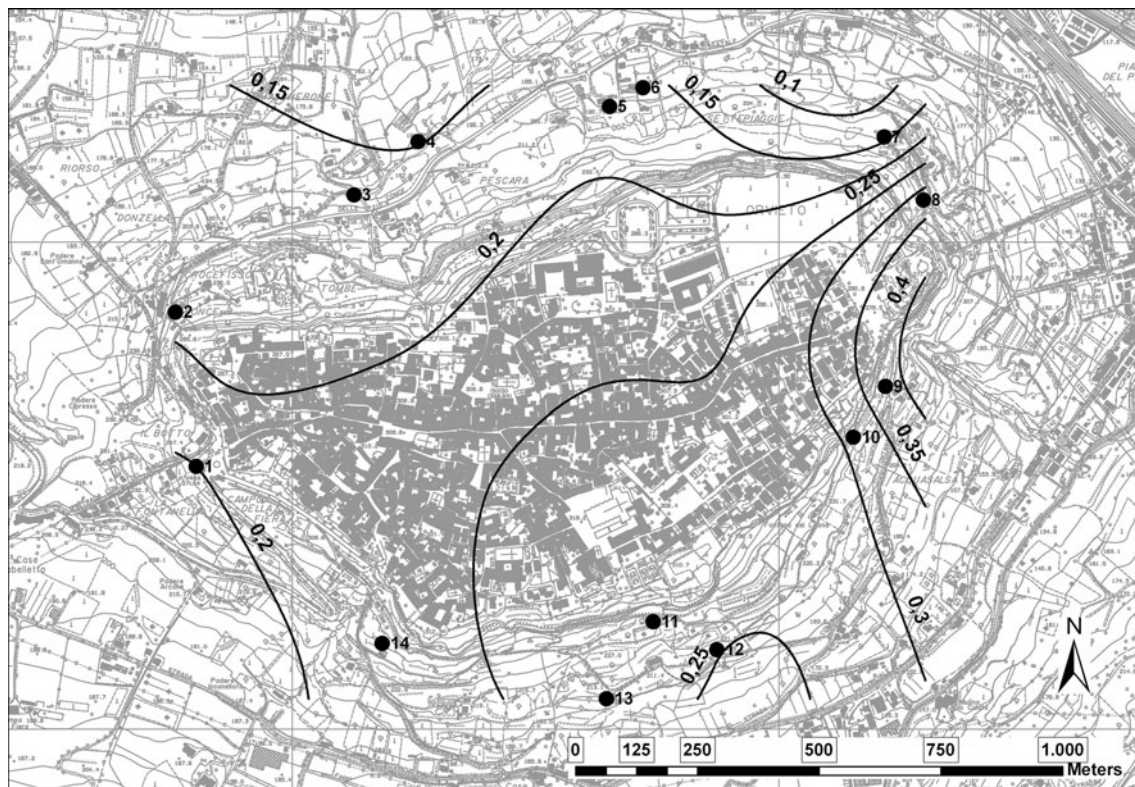fact, the lythological and morphological features of the

Fig. 11 Trend of the rMg/rCa ratio of the springs. Interpolation with Spline method

area may influence the chemical properties of the ground-water. The N and NW springs showed the lowest rMg/rCa ratio (Fig. 11), and this is consistent with an area of relatively fast groundwater circulation; the springs in the west side of the cliff had a ratio between 0.25 and 0.4, suggesting the presence of an area characterized by slower groundwater flow.

Both the study of the lithological features and the hydrogeological findings allowed us to identify a main groundwater flow direction, from SW to NE.

The main area of infiltration was situated in the NW side of the cliff, where higher concentration of pollutants were measured. Most likely the infiltrated water then moved towards E-NE, after reaching the watertable. During the flow the infiltrated water mixed with the rainwater coming from intermediate zones.

Geochemical considerations

On the base of isotopic data, laboratory tests on tuff samples, literature findings on zeolisation of volcanic tuff, we concluded that the chemical pollutants were not a direct result of ongoing processes of contamination (mainly due to sewers), but were caused by leaching mechanism involving water and tuffaceous rock

containing zeolite. The minerals of the rock were indeed progressively releasing chemical compounds (such as NO_3^-) which were present in concentrations greater than 300 mg/l.

Both the isotopic data of $\delta^{15}N$ and $\delta^{18}O$ (NO_3^-) and the high chemical concentrations of NO_3^- were consistent with an organic origin due to pre-roman settlements; the past pollution phenomena was then reactivated by the saturation of zeolite crystalline sites.

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