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HYDROGEOCHEMISTRY OF THE CORSAGLIA VALLEY, MARITIME ALPS, PIEDMONT, ITALY

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ABSTRACT

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This study presents the results of hydrogeochemical investigations in the drainage basin of the Corsaglia Valley (Piedmont, Italy). This small catchment area (110 km²) is located on the northern side of the Maritime Alps and shows different lithologic types (crystalline and carbonate rocks). It is thus possible to find zones with important karstic systems adjacent to very impermeable rocks in which local groundwater flow can occur through fracture systems. Because of the complex geology, all karstic systems and their respective catchment areas are independent. 36 sampling stations were selected throughout the basin and sampling was carried out during two different climatic periods: during April 1976 and October 1974.

The problems considered in this investigation are:

(1) Chemical compositions of rain waters as a function of geographic locations and climatic conditions.

(2) Crystalline rock hydrogeochemistry.

(3) Rock–water interactions in karstic systems.

(4) Water flow in carbonate rocks and related fluctuations of chemical contents. Two principal flow systems can be recognized for the karst: the first, deep and chemically homogeneous, represents the base flow; the second, shallow and characterized by rapid flow, has a low and variable salt content. In the crystalline rocks only one flow system can be recognized: it is characterized by rapid flow and a remarkable variation of the ionic species.

INTRODUCTION

The River Corsaglia Valley with a surface drainage area of 110 km², is the most easterly of a series of parallel valleys of similar dimension and lithologic characteristics. It is cut into the Maritime Alps and drains to the north towards the Po Valley (Fig. 1). A detailed geographical description was presented by Susella (1976), therefore, only the dominant features are summarized here.

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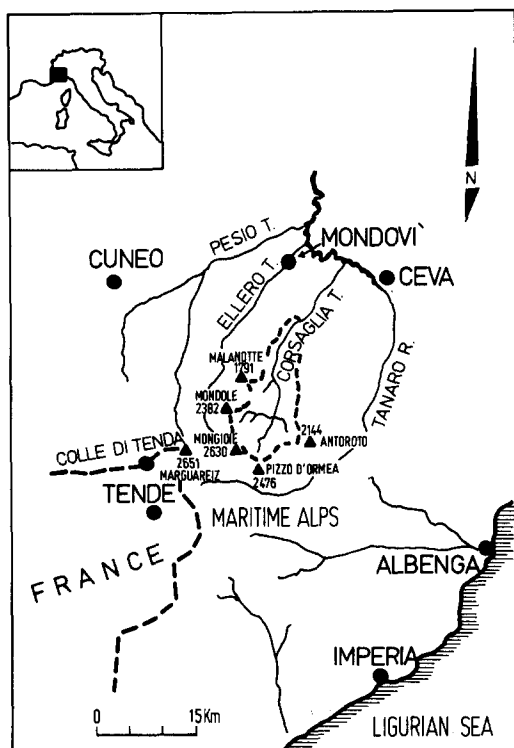


Fig. 1. Location of study area.

The Corsaglia Valley borders on France and Liguria and is characterized by unusual "mixed weather conditions" on the basis of the stable-isotope content of precipitation (Bortolami et al., 1979). It receives primarily Atlantic precipitation during the summer months whereas winter precipitation generally originates in the Mediterranean basin. Because of their dissimilar origin, summer and winter precipitation carry different chemical loads which are useful as a natural tracer in hydrogeological investigations.

Hydrogeological paths

Three principal lithologies characterise the Corsaglia basin (Fig. 2):

- (a) The highest side of the valley consists of Mesozoic carbonate rocks (limestones and dolomitic limestones) which are karstified to a considerable degree.
- (b) The middle zone is dominated by Permian porphyroids (epimetamorphic rocks from original rhyodacitic volcanic deposits) and Eotriassic quartzites which include several main tectonic slices of Mesozoic carbonate.
- (c) The area in the northern part of the basin at low altitude is composed of Mesozoic calcareous schist.

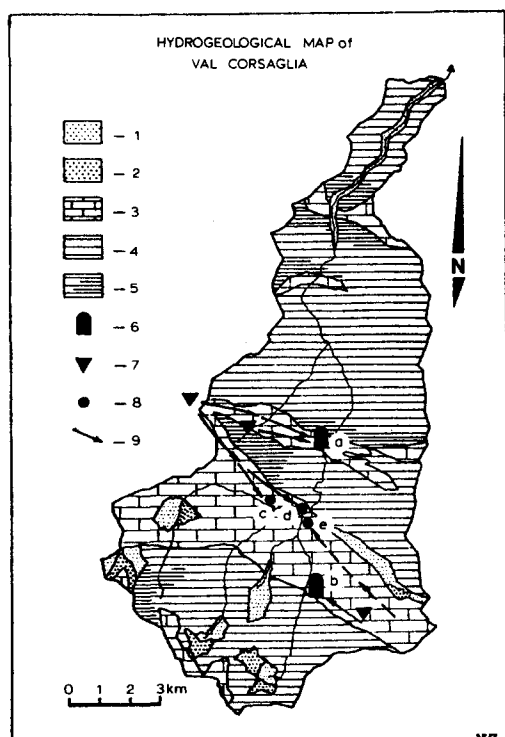


Fig. 2. Geologic sketch and locations of sampling sites in the Corsaglia Valley.

1 = tills and fluvial deposits: high to medium intergranular permeability; 2 = scree deposits: high intergranular permeability; 3 = Mesozoic limestones: very high karst permeability; 4 = Mesozoic calc-schists and Permian metaporphyries: generally impermeable; 5 = Mesozoic calc-schists and Permian metaporphyries: low fracture permeability; 6 = most important karstic caves; 7 = shallow hole (doline); 8 = springs with an average flow greater than 50 l/s: (a) Bossea Cave, (b) Mottera Cave, (c) Stalla Buorch, (d) Ponte Murao, and (e) Captazione Borello; and 9 = underground flow directions determined by colorimetric method.

The karstic system of Bossea, one of the principal study areas, is tectonically wedged into the crystalline rocks in the central zone.

The principal tectonic features extended NW—SE and the intensity of tectonic deformation increases towards the north and the inner part of the Alpine arc. Thus, from simple monoclinic lithostratigraphic sequences in the most southern and highest parts of the basin, one passes into compressed and strongly folded tectonic units toward the north. The resulting relationship between tectonics and stratigraphy accounts for the special geohydrological situation in the River Corsaglia Valley, where highly karstic zones alternate with very impermeable layers. Within the karstic terrain, there are a number of independent groundwater systems fed by small, well-defined, separate recharge areas.

METHODOLOGY

The geochemistry of the groundwater systems within different lithological zones of the Corsaglia Valley is discussed and related to the physical characteristics of the recharge zone and aquifer lithology.

The chemical characteristics of groundwater are compared with the chemical data obtained on local precipitation. In order to obtain a reasonable assessment of the precipitation input, a number of integrating pluviometers have been installed in a N—S axis in addition to the regular rain-water samplers operated by the Italian National Meteorological Network. At both types of sampling station, the rain samples were collected in a simple funnel-type pluviometer which contained a layer of about 3 cm of liquid paraffin in order to avoid evaporation of the samples. The collection took place over two periods of one month: October 1974 and April 1976. The chemical analyses of rain water thus represent the weighted averages of dry and wet fallout during each month. These two sampling periods were chosen because they coincide with the maximum runoff during snow melt and minimum discharge during late summer and fall.

The principal measurements made on all water samples were: conductivity, field pH, temperature (of groundwaters) and analyses of major ions. Analyses were made in the Geological Institute at the University of Turin, following the standard procedures of APHA (1965). These included the titrimetric determination of alkalinity, chloride, calcium and magnesium (statistical error of 3–4%), emission analyses for sodium and potassium (statistical error of 3%), and the turbidimetric determination of sulphate (statistical error of 4%). All analyses of waters from karst systems have been treated by the computer programme WATEQ (Truesdell and Jones, 1973).

Rain-water chemistry and its seasonal variation have been studied in order to identify the best natural tracers in the hydrogeological investigations including studies of: (1) hydrogeochemistry of crystalline rocks; (2) rock—water interactions in karstic systems; and (3) water flow in reservoir rocks and fluctuations of chemical contents as a function of the hydrogeological behaviour.

This hydrogeochemical study is a part of a detailed hydrogeological and hydrogeochemical investigation in which the environmental isotopes (deuterium and ^{18}O) variations in spring waters are related to the origin of water (Bortolami et al., 1979).

RAIN-WATER CHEMISTRY

In general the chemistry of precipitation is related to the origin of vapour masses although it is usually modified during circulation over the continent. However, one notes that the greater the distance from the origin the more constant is the chemical load of humid air. Furthermore, several ions inherited from seawater are lost and sometimes replaced by compounds originating from the continent (Junge, 1963).

TABLE I

Chemical data in Corsaglia Valley precipitation waters

Pluviometer	Altitude (m.a.s.l.)	Conductivity ($\mu\text{S cm}^{-1}$)	pH	HCO_3^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^+ (ppm)	K^+ (ppm)	SO_4^{2-} (mar) (%)
<i>October 1974:</i>											
Mondovi	400	28	5.6	6.1	0.9	5.8	2.2	0.8	0.7	0.4	2.0
Corsagliola	620	23	5.7	6.1	1.1	2.9	2.0	0.6	0.7	0.4	5.0
Prea	830	21	5.8	6.1	0.4	3.4	1.5	0.7	0.5	0.4	2.0
Distretti	1,080	18	6.0	3.8	1.2	3.9	1.7	0.6	0.5	0.4	4.0
Case Mommo	1,380	19	5.8	3.3	1.5	4.2	2.0	0.2	0.6	0.4	5.0
M. Malanotte	1,780	17	5.5	2.4	1.3	3.0	1.6	0.2	0.5	0.4	6.0
R. Garelli	2,000	16	5.8	4.4	0.8	1.5	1.4	0.2	0.5	0.4	7.0
<i>April 1976:</i>											
Mondovi	400	56	5.4	9.2	2.5	9.2	3.6	1.7	2.1	1.0	4.0
Corsagliola	620	46	5.7	9.2	2.0	6.4	3.6	1.7	1.0	0.6	4.0
Prea	830	47	5.8	10.4	1.9	7.9	3.5	1.6	1.8	0.8	3.0
Distretti	1,080	35	6.0	3.1	2.9	4.5	1.2	0.5	2.6	1.0	9.0
M. Malanotte	1,780	18	6.1	1.2	2.2	1.4	0.4	0.4	1.7	0.6	22.0
R. Garelli	2,000	17	6.2	3.1	2.4	1.4	0.5	0.6	1.5	1.0	24.0

The percentage of sulphate derived from marine dust is calculated on the basis of the following equation:
 $100 [\text{Cl}^- (\text{ppm})] / 7.1 [\text{SO}_4^{2-} (\text{ppm})]$.

The chemistry of precipitation may vary with altitude, for the concentration of salts, as aerosols, or in solution, decreases with altitude. The conductivity of the rain water in the Maritime Alps shows a good correlation with altitude, h . In October conductivity follows an exponential relationship of the form:

$$C \text{ (}\mu\text{S cm}^{-1}\text{)} = 37.2 \exp [-0.34 \cdot 10^{-3} h \text{ (m)}] \quad (1)$$

but is relatively constant above 1200 m (Fig. 3). In April, however, one observes the following relationship:

$$C \text{ (}\mu\text{S cm}^{-1}\text{)} = 80.1 \exp [-0.79 \cdot 10^{-3} h \text{ (m)}] \quad (2)$$

This seasonal change is caused by the origin of air masses. The rainfall with an "Atlantic origin" reaches the area highly depleted in "dissolved marine salts" and has apparently reached a steady-state composition.

Chloride concentrations are of special interest in this respect because Cl^- is essentially all of marine origin (Eriksson, 1958). In the Corsaglia Valley area air masses from the Mediterranean Sea have higher chemical load and Cl^- contents than those from the Atlantic Ocean (Table I). The uniform Cl^- contents at different elevations in the same months with varying conductivity, can be explained by a steady-state concentration of marine origin with a variable continental component. Turbulence and vertical mixing over land surfaces tend to homogenize through a great thickness of atmospheric chlorine and HCl (Junge, 1963) which could be produced by hydrolysis and photolysis of chlorides and are present in precipitation in the form of NH_4Cl . Once dispersed they produce a constant background of Cl^- of Atlantic origin in the precipitation over Piedmont.

Sulphate present in precipitation is thought to have both a marine and continental origin. The rise of SO_4^{2-} content during April may be explained by entrainment of S of terrestrial origin by raindrops during their downward passage (Nakai and Jensen, 1967; Cortecchi and Longinelli, 1970). If one considers that all Cl^- originates from seawater, and assumes that no fractionation occurs during aerosol formation and dry fallout, one can calculate the percentage of SO_4^{2-} of marine and continental origin dissolved in rain water by the following ratio which equals unity for seawater (Mizutani and Rafter, 1969):

$$\frac{[\text{Cl}^- \text{ (ppm)}]}{7.1 [\text{SO}_4^{2-} \text{ (ppm)}]} \times 100 \quad (3)$$

Table I shows that the calculated percentage of continental SO_4^{2-} ranges between 95 and 100% in October rainfall, whereas in April precipitation, the percentage ranges between 70 and 95%. The decrease in $\text{Cl}^-/\text{SO}_4^{2-}$ ratio during April at lower elevations is due to relatively more efficient washing out of sulphur pollutants which enter the atmospheric circulation. During spring the atmospheric situation does not permit prompt renewal of the air and, frequently, large air masses stagnate over the area for periods often exceeding 4

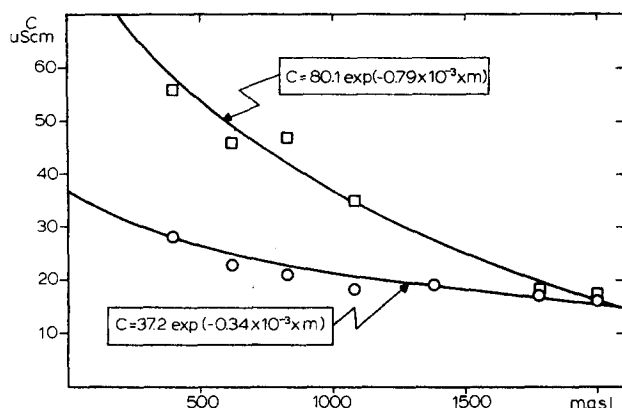


Fig. 3. Chemistry of precipitation: conductivity vs. altitude gradient. The coefficients of determination (r^2) are 0.99 and 0.97 respectively for October 1974 and April 1976. The standard errors of estimate ($\sigma_{y,x}$) are 0.32 (October) and 0.28 (April).

or 5 days. Weak air circulation and thermally stable conditions in the lower layer (up to about 1000 m) of such air masses favour buildup of fairly large pollutant concentrations. Fig. 4 shows that about 95% of the sulphates present in precipitation below 1000 m is of non-marine origin. Therefore, the conductivity gives a fairly good indication of pollution within the industrial Po Valley which adds contaminants from below and therefore is in part responsible for the observed altitude gradient.

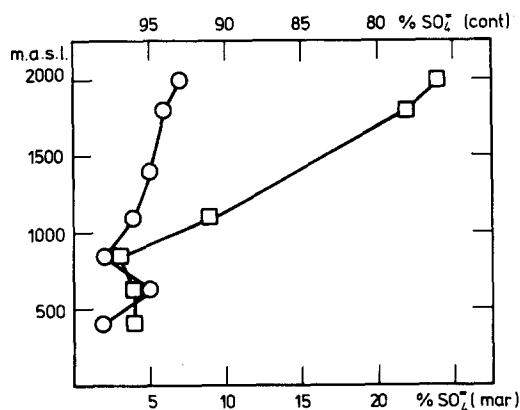


Fig. 4. Chemistry of precipitation: altitude vs. percentage of continental sulphate. The rapid decrease of the percentage of continental sulphate in spring precipitation (*squares*) is due to the better washout of sulphur from human activities during this period. One can consider that the stagnating air mass in the lower atmospheric layers (up to approx. 1000 m) favours the dissolution of pollutant sulphur compounds. The uniform content of man-made sulphate in October precipitation (*circles*) gives an index of atmospheric pollution over the Po Valley.

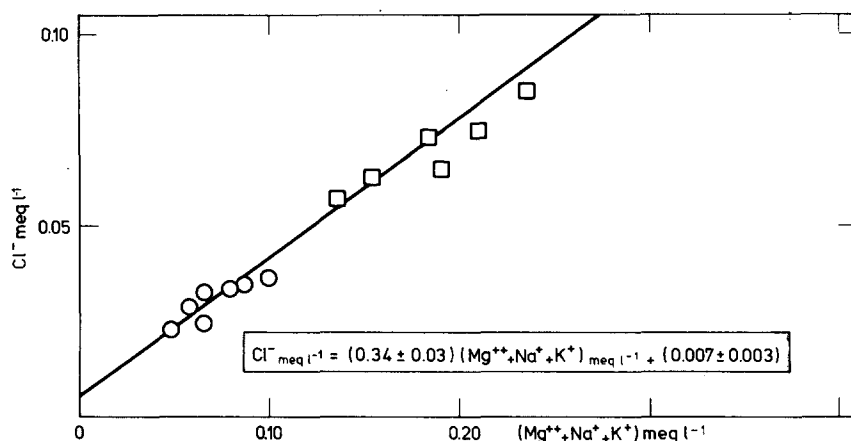


Fig. 5. Chemistry of precipitation: chloride content (in meq. l^{-1}) vs. the sum of the millequivalents per liter of magnesium, sodium and potassium in the precipitation samples. Circles and squares refer to October and April precipitations, respectively. The coefficient of determination (r^2) is 0.95 and the standard error of estimate ($\sigma_{y,x}$) is 0.005. The correlation indicates the marine origin of these cations.

Bicarbonate as well as calcium primarily result of reactions between atmospheric CO_2 and Ca compounds present as dust. The extent of these reactions depends on the pH of rain water which is controlled, not only by the formation of carbonic acid, but probably more by SO_2 oxidation which takes place in solution in the droplets; indeed the gas is soluble in water to a considerable degree (Junge, 1963). An increase of S compounds in the atmosphere and successive formation of H_2SO_4 is thus often responsible for conditions known as "acid rain" where pH values may drop as low as 3.

Magnesium, sodium and potassium are closely correlated with Cl^- (Fig. 5) and show the same seasonal evolution. A similar relationship has been observed on precipitation samples from central Italy (G.M. Zuppi, unpublished data, 1973):

$$[Cl^- \text{ (meq. } l^{-1})] = (0.34 \pm 0.03) [Mg^{2+} + Na^+ + K^+ \text{ (meq. } l^{-1})] + (0.007 \pm 0.003) \quad (4)$$

The seasonal and altitude changes in the chemical content of precipitation have been used as geochemical tracers in the study of underground hydrological paths. If no significant geochemical processes affect the water chemistry during its underground passage, the input "signal" may occur with some delay where it discharges if the system has only a low dispersivity.

Water—crystalline rock interactions

The Corsaglia basin contains extensive impermeable layers composed of crystalline rocks but the intensive tectonic fractures produce local permeability and local groundwater circulations can occur.

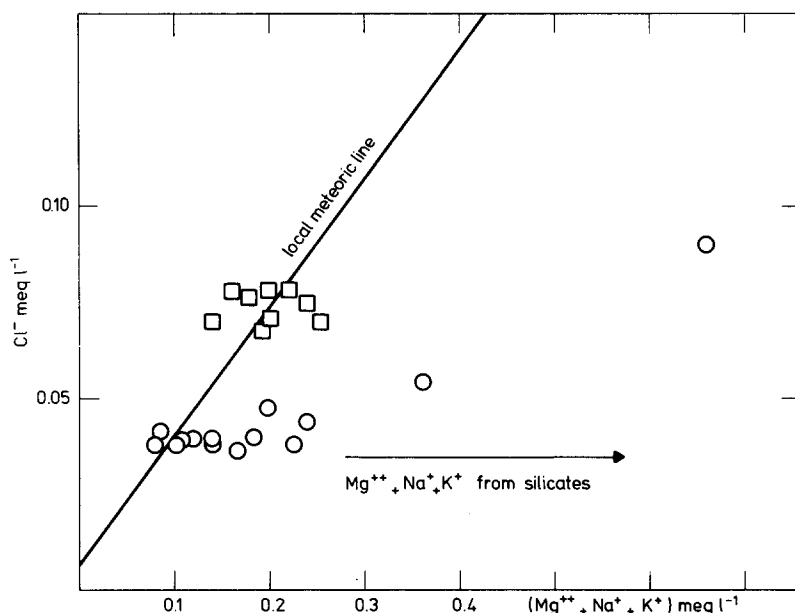


Fig. 6. Chloride plotted vs. the sum of magnesium, sodium and potassium for the waters from crystalline rock reservoirs. All samples fall on the local meteoric line (see Fig. 5). However, only in a few cases (Prato Nevoso, Seccata, etc.) is the chemical load higher than in precipitation. This fact is due to the lower water yield from precipitation. The underground residence time increases and the water-rock contact consequently increases too.

The chemical load of the springs discharging from crystalline rock generally follows the chemical composition of rain water; this suggests that the subterranean flow paths are very short and similar to subterranean runoff with little chemical interaction between water and rocks, particularly during the snow melt (spring season and April precipitation).

The pH values of waters from crystalline rocks generally approach 6.5 which is common for silicate — carbon-dioxide — water systems for these environments in an open and shallow system where low-temperature silicates are involved (Garrels and Christ, 1965). The total salt content is low and bicarbonate plays a dominant role. HCO_3^- content is independent of month which could be explained by the uniform partial pressure of CO_2 , p_{CO_2} , control by the soil and the weathering which takes place within the uppermost crystalline rocks during infiltration. In fact, as shown in Table II, the calculated p_{CO_2} ($= -\log p_{\text{CO}_2}$) is rather constant (p_{CO_2} equals to 2.65 ± 0.40) and greater by about a factor of 10 with respect of the p_{CO_2} in water in equilibrium with the atmosphere (Garrels and Christ, 1965).

Variations in Cl^- as well as SO_4^{2-} concentrations generally reflect their seasonal variations in precipitation. Fig. 6 shows that virtually no addition of Cl^- occurs from dissolution of silicate minerals in shallow groundwater systems with the only exception as given by the spring of Prato Nevoso, where-

as at times (e.g., Lanza Serra, Seccata, Prato Nevoso) a slight addition of SO_4^{2-} from oxidation of sulphide present in the aquifer may occur.

The concentrations of dissolved cations reflect their abundance in the minerals of the silicate rocks, especially the feldspars. Hence, in these crystalline rocks in which feldspars are abundant, Ca^{2+} dominates over Na^+ and K^+ , followed by Mg^{2+} from minerals of the pyroxene and mica groups. Because of the reactions with silicates during underground flow the cation contents increase by about factor of 2 with respect to their original concentration in precipitation. This chemical load is higher during the last part of the summer season when the water yield from the precipitation is minimal (Seccata and

TABLE II

Chemical data of waters from crystalline rock reservoirs

Reservoir	Altitude, h_c * ¹ (m.a.s.l.)	Period	Flow (l s^{-1})	Conductivity ($\mu\text{S cm}^{-1}$)	TDS (ppm)	pH	pCO_2 * ²
Bassi	885	Oct. 74	0.20	24	19.3	6.4	2.40
		Apr. 76	0.30	27	27.0	6.5	2.46
Bottero	720	Oct. 74	0.05	32	26.2	7.2	3.03
		Apr. 76	0.10	40	36.5	6.4	2.16
Case Bertoni	1,108	Oct. 74	0.20	25	19.6	6.6	2.64
		Apr. 76	0.40	27	21.0	6.3	2.42
Case Torno	1,060	Oct. 74	0.06	16.5	14.9	6.8	3.02
		Apr. 76	0.09	20.0	24.6	6.5	2.50
Celle Stanti	2,000	Oct. 74	0.04	16.5	12.1	6.5	3.20
Croce Cardini	1,222	Oct. 74	15	26.5	17.7	6.8	3.02
		Apr. 76	25	32.0	36.6	6.7	2.50
Fontana Gioia	700	Apr. 76	0.10	17.5	15.6	6.0	2.30
Gias Brana	1,270	Oct. 74	0.90	36.0	34.4	6.5	2.26
		Apr. 76	1.60	44.0	43.0	7.6	3.30
Lanza Serra	1,022	Oct. 74	0.15	39.0	26.0	6.7	2.66
		Apr. 76	0.20	50.0	19.6	6.5	2.80
Navonera	1,145	Oct. 74	0.3	12.0	14.0	6.0	2.30
		Apr. 76	0.5	19.0	13.8	6.0	2.38
Pizzo	2,200	Oct. 74	0.04	32.0	26.5	6.8	2.62
Potitta	1,180	Oct. 74	0.1	26.0	16.2	6.7	2.82
Prato Nevoso	1,930	Oct. 74	12	68.0	84.9	7.3	2.71
Seccata	1,040	Oct. 74	0.2	50.0	64.7	7.4	2.89
Zucco	2,200	Oct. 74	0.02	14.2	11.5	6.0	2.61

*¹ h_c is the "conductivity altitude" of recharge (eqs. 1 and 2).

*² pCO_2 is the negative logarithm, base 10, of the partial pressure of carbon dioxide, $p\text{CO}_2$.

Prato Nevoso). In that case residence and also the potential for water—rock interaction time increases.

The low salt load in the waters from crystalline rocks reflects the short and rapid circulation. The springs of Prato Nevoso and Seccata are exceptions. Because of complex structure the groundwater movement occurs through geologically heterogenous rocks. In this case the higher total salt load, still reflecting the lithological and geochemical patterns, stems from greater dissolution of silicates and the subsequent formation of clay. There, the waters would circulate in an aquifer of lower permeability with resulting longer residence time.

HCO ₃ ⁻ (ppm)	Cl ⁻ (ppm)	SO ₄ ²⁻ (ppm)	Ca ²⁺ (ppm)	Mg ²⁺ (ppm)	Na ⁺ (ppm)	K ⁺ (ppm)	<i>h_c</i> ^(*) (m.a.s.l.)	Reservoir
12.2	1.4	0.6	3.0	0.5	1.2	0.4	1,100	Bassi
13.4	2.8	3.8	4.8	0.9	1.1	0.2	1,210	
18.1	1.4	<0.1	4.4	1.0	0.7	0.5	200	Bottero
21.4	2.5	3.3	6.4	0.9	1.2	0.8	1,030	
11.0	1.1	2.0	2.2	0.5	1.6	1.2	880	Case Bertoni
9.2	2.1	3.8	2.0	0.6	2.3	1.0	1,210	
7.3	1.1	2.4	2.2	0.6	0.5	0.8	1,500	Case Torno
12.2	2.5	2.4	2.0	0.7	2.8	2.0	1,280	
2.4	1.4	3.4	2.8	0.1	0.8	1.2	2,200	Celle Stanti
7.3	1.4	3.0	2.6	0.1	1.4	1.9	500	Croce Cardini
19.5	2.8	3.4	7.2	0.5	1.5	1.7	1,130	
6.1	2.8	1.9	1.6	0.5	1.9	0.8	1,500	Fontana Gioia
21.3	0.7	3.4	6.4	0.6	1.2	0.8	800	Gias Brana
24.5	1.8	5.2	6.4	1.2	2.3	1.6	—	
13.4	1.4	3.3	2.6	0.5	2.3	2.5	—	Lanza Serra
6.1	2.8	5.3	3.4	0.7	0.9	0.4	600	
6.1	1.4	2.2	1.8	0.4	0.9	1.2	2,500	Navonera
5.0	2.5	1.9	1.6	0.2	1.4	1.2	1,320	
18.3	1.4	<0.01	5.2	0.5	0.6	0.5	100	Pizzo
9.1	1.4	1.0	2.2	0.4	0.9	1.2	700	Potitta
48.8	3.5	2.9	18.0	5.2	3.5	3.0	—	Prato Nevoso
40.0	2.1	4.8	9.2	1.5	2.8	4.3	600	Seccata
3.0	1.1	4.8	1.0	0.6	0.5	0.5	2,450	Zucco

ROCK—WATER INTERACTIONS IN KARSTIC SYSTEMS

Most of the springs in the Corsaglia drainage basin tap karstic systems and therefore were in contact with carbonate rocks which results in somewhat higher dissolved solids contents. Similarly, high mineral contents are observed in water discharging from calcareous schists in which, however, the residence time must be somewhat longer because these rocks have moderate to low permeabilities (Jamier, 1975; Bortolami et al., 1979).

The chemistry of these waters is dominated by carbonate dissolution and small, or no, seasonal variations are observed in HCO_3^- contents because times of reaction are short compared with groundwater residence times. Significant seasonal variations occur in calculated pCO_2 . These variations could be explained by the scarce soil at the surface of carbonate rocks ($\text{pCO}_2 \approx 2.9$).

The Cl^- content does not increase during subterranean residence and is close to that of precipitation, which shows a maximum of about 1.5 mg l^{-1} during October 1974 at Case Mommo, where the elevation is close to the average altitude of the basin. One karstic flow system with a higher content than that value has been found with 2.5 mg l^{-1} , at Case Milano. This could be explained as a fast response to a local meteoric event by the spring (Miserez, 1973; Bakalowicz, 1976).

In April, the maximum Cl^- content in rain waters is 2.9 mg l^{-1} (Distretti) whereas in spring waters the Cl^- content is generally higher. This could signify that the waters collected during this time originate from the melting of winter precipitation more enriched in chlorides (Bortolami et al., 1979). This phenomenon can be explained as due to the Mediterranean origin of the air masses during winter, or to the evaporation effect from the snow cover or during infiltration (Fontes et al., 1979).

In Fig. 7 one thus observes that the Cl^- content is related to the concentration of the alkaline ions by the relation:

$$[\text{Cl}^- (\text{meq. l}^{-1})] = (0.36 \pm 0.03) [(\text{Na}^+ + \text{K}^+) (\text{meq. l}^{-1})] + (0.22 \pm 0.002) \quad (5)$$

This relation is practically the same as eq. 4 calculated for precipitation where Cl^- content had been reported to be a function of the sum of alkali metals and Mg^{2+} . This indicates that Na^+ and K^+ as well as Cl^- are fingerprints of the input from precipitation recharging this karst. The positive value of "intercept" is due to the Mg^{2+} content in precipitation, especially for those originating in the western Mediterranean basin. Fig. 7 permits two important observations: (1) in the winter time when the underground flow is rapid and no dissolution of silicate minerals takes place all the points fall on the relationship observed for meteoric waters; and (2) during summer, at low discharge, some springs show an increasing content of the alkali metals evidently due to a greater reaction time with the silicates locally present in the rocks.

Sulphate contents show a general small increase during subterranean circula-

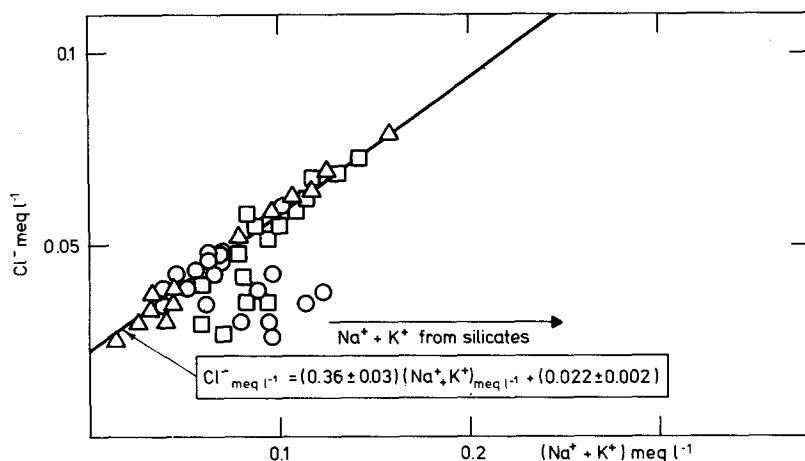


Fig. 7. Chloride as function of the alkaline contents in the karstic systems. For the karst springs, sodium and potassium as well as chloride are also good meteorological indices. The positive value of "intercept" is due to the magnesium content in precipitation. *Triangles* refer to the precipitation, whereas *circles* and *squares* refer to October and April groundwater samples, respectively. The coefficient of determination (r^2) is 0.89 and the standard error of estimate ($\sigma_{y,x}$) is 0.002.

tion. However, for some springs, one notes that a lithological change in the rock reservoir results in the higher SO_4^{2-} content in the spring water (i.e. Case Lardini, Costa Lumenda). This increase is more visible in the base flow during summer and occurs especially in aquifers which include Triassic carbonate rocks.

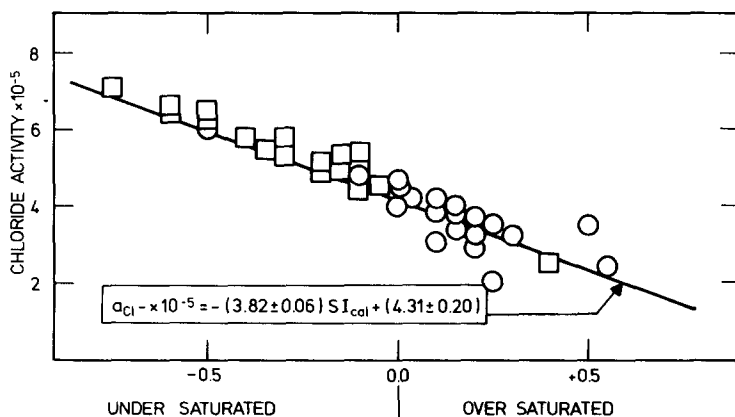


Fig. 8. Hydrogeochemistry of karstic systems: chloride activity plotted vs. calcite saturation index. The coefficient of determination (r^2) is 0.90 and the standard error of estimate ($\sigma_{y,x}$) is 0.39. The *squares* refer to the April samples originating from snow melt. The *circles* refer to October samples of base flow.

Ca^{2+} , Mg^{2+} and HCO_3^- are the most important ions and their presence as dissolved species is controlled by the reaction of CO_3^{2-} (solid), CO_2 (aqueous) and H_2O . This carbonate reaction could reflect indirectly the length of the underground circulation of the waters.

In plotting the calcite saturation index vs. chloride activity ($\text{SI}_{\text{cal}} - a_{\text{Cl}^-}$) (Fig. 8) the best regression line has a negative slope; water samples range between two poles indicating melting of snow from Mediterranean precipitation (left-hand side) and base flow (right-hand side), respectively. During winter, the surface of the basin is frozen and little or no infiltration can occur. At the end of the winter, snow melt occurs at progressively increasing altitude and the spring precipitation can infiltrate only in those areas where snow melt has already occurred.

After spring runoff, saturation with respect to calcite may be gradually approached in the different karstic systems due to increasing contribution of geochemically homogeneous base flow to the discharge.

In May the karst system of Mottera shows a great oversaturation with respect to calcite and low Cl^- activity; whereas, in October the opposite effect occurs. This is explained by a "phase displacement" of about six months as compared to the other springs.

A plot of dolomite saturation index vs. chloride activity ($\text{SI}_{\text{dol}} - a_{\text{Cl}^-}$) (Fig. 9) describes the same hydrological regime: mixing of spring runoff with a base flow component.

The variations in time of several chemical parameters are reported for Bossea Spring since this spring is the only one for which continuous discharge measurements were made. Fig. 10 shows a similar variation between discharge and conductivity. Furthermore, calcite and dolomite saturation indices and chloride and sodium activities are independent of discharge but tend to in-

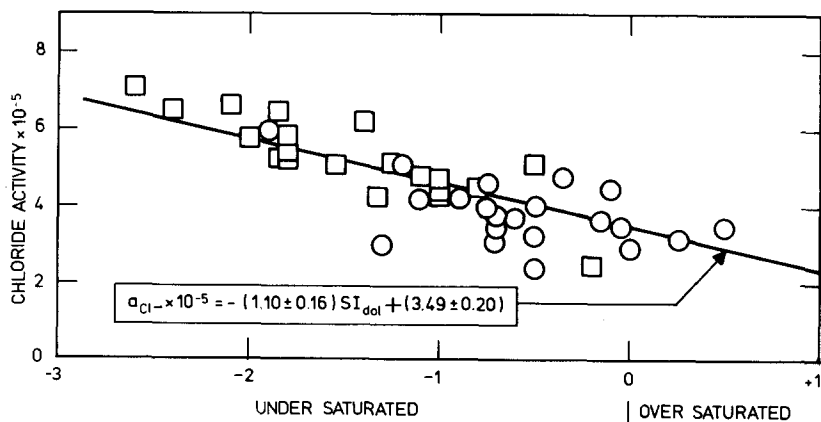


Fig. 9. Chloride activity plotted vs. dolomite saturation index. The coefficient of determination (r^2) is 0.52 and the standard error of estimate ($\sigma_{y,x}$) is 0.85. The mixing or at least the contribution of snow melt waters (squares) with a base flow component (circles) is identifiable as in the Fig. 8.

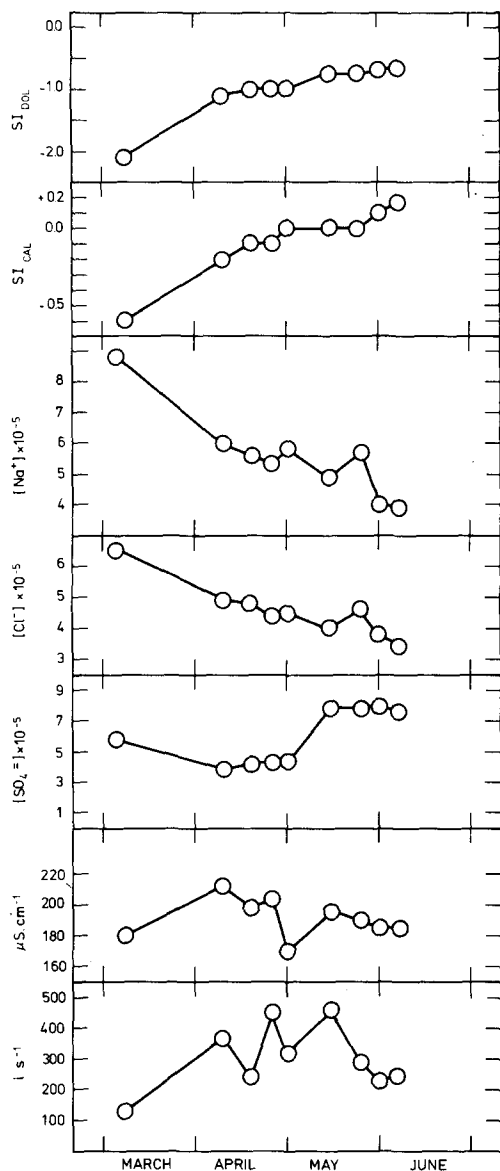


Fig. 10. Seasonal evolution of discharge, conductivity, sulphate, chloride and sodium activities, and calcite and dolomite saturation indices in Bossea Cave during spring 1976. (Only Bossea, of the caves and springs of this basin is equipped with discharge gauge.)

crease during the period from March to June. Variations of the sulphate activity indicate a relative increase of the influence of dissolution of evaporite deposits of Triassic gypsum or anhydrite present in the reservoir when the discharge is decreasing.

TABLE III

Chemical data of karstic waters

	Altitude (m.a.s.l.)	Date	Flow (l s ⁻¹)	Conductivity (μS cm ⁻¹)	pH	pCO ₂ *	HCO ₃ ⁻ (ppm) 10 ⁻³ × α
Bocche Roccon	735	10-10-74	0.5	162	7.9	2.80	166 2.45
		09-04-76	1.0	235	7.5	2.45	143 2.20
Borello (Captazione)	945	08-10-74	100	124	7.9	2.71	200 3.1
		09-04-76	250	184	7.5	2.46	134 2.1
Borello (Inferiore)	930	08-10-74	50	125	7.9	2.70	202 3.1
Brunenghi	910	12-10-74	0.05	200	8.0	2.91	164 2.4
		18-04-76	0.10	270	7.4	2.28	166 2.5
		13-10-74	72	137	8.3	3.28	132 2.2
		07-03-76	132	180	7.6	2.67	111 1.6
		09-04-76	368	212	7.8	2.73	151 2.3
		18-04-76	238	200	7.9	2.83	156 2.3
		25-04-76	446	204	7.9	2.83	151 2.3
		01-05-76	316	170	7.8	2.66	177 2.7
Bossea	810	14-05-76	464	195	8.0	2.93	148 2.3
		23-05-76	291	190	8.0	2.93	150 2.3
		30-05-76	225	185	7.9	2.75	180 2.5
		06-06-76	243	185	8.0	2.93	148 2.3
Buorch II	1,065	20-10-74	0.10	203	8.1	3.04	146 2.2
Buorch (Stalla)	1,056	20-10-74	50	180	7.6	2.26	285 4.3
		02-05-76	100	204	8.1	3.11	126 1.9
Case Lardini	6,45	10-10-74	1	420	7.7	2.35	293 4.4
		18-04-76	1	360	7.8	2.62	198 3.0

						SI _{cal}	SI _{dol}
Cl ⁻ (ppm) 10 ⁻⁵ × a	SO ₄ ²⁻ (ppm) 10 ^{-4.5} × a	Ca ²⁺ (ppm) 10 ⁻³ × a	Mg ²⁺ (ppm) 10 ⁻⁵ × a	Na ⁺ (ppm) 10 ⁻⁵ × a	K ⁺ (ppm) 10 ⁻⁵ × a		
1.6	4.6	51.5	2.4	0.9	0.5		
4.2	3.7	1.0	7.6	3.3	0.9	+0.05	-1.10
2.2	10.0	44.1	3.7	1.9	1.0		
6.5	8.0	0.8	11	8.3	2.4	-0.60	-1.85
0.7	6.4	66.6	1.0	0.9	0.4		
2.0	5.0	1.2	3.1	3.6	0.9	+0.25	-1.20
2.1	5.4	38.4	4.9	1.7	0.8		
5.8	4.4	0.7	15	3.9	1.9	-0.40	-1.80
1.2	4.8	63.9	2.9	0.7	0.4		
3.1	3.7	1.2	8.9	2.8	0.9	+0.10	-0.70
1.8	9.7	50.1	3.6	1.6	0.9		
3.8	7.7	0.9	11	6.5	2.1	+0.15	-0.70
2.0	4.3	57.0	1.0	1.3	0.7		
6.5	3.4	1.1	3.1	5.3	1.7	-0.50	-2.40
1.3	7.0	43.5	2.1	0.6	0.4		
3.2	5.7	1.0	6.7	2.5	1.0	+0.30	-0.50
2.6	6.9	33.5	3.0	2.8	0.4		
6.6	5.7	0.8	9.8	8.9	1.0	-0.60	-2.08
2.0	4.8	44.9	3.8	1.7	0.5		
4.9	3.9	0.9	12	6.0	1.0	-0.20	-1.10
2.0	5.2	45.5	4.0	1.5	0.5		
4.8	4.2	0.9	13	5.6	1.0	-0.10	-1.00
1.7	5.3	46.5	3.1	1.4	0.4		
4.4	4.3	0.9	10	5.3	1.0	-0.10	-1.00
1.9	5.4	56.1	2.4	1.6	0.5		
4.5	4.3	1.1	7.9	5.8	0.7	0.00	-1.00
1.6	9.6	46.0	3.9	1.2	0.8		
4.0	7.7	0.9	12	4.9	0.9	0.00	-0.75
1.9	9.6	47.0	3.4	1.4	0.6		
4.6	7.7	1.0	11	5.7	0.9	0.00	-0.75
1.6	10.1	59.8	3.1	1.0	0.8		
3.8	7.9	1.2	9.5	4.0	0.9	+0.10	-0.70
1.5	9.5	47.0	3.5	1.0	0.5		
3.4	7.6	1.0	12	3.9	0.7	+0.15	-0.70
1.6	11.5	49.7	1.8	1.1	0.9		
4.2	9.2	1.0	5.7	4.8	2.1	+0.10	-0.90
1.5	9.2	85.7	7.1	1.5	0.2		
3.7	6.8	1.5	21	5.8	0.5	+0.20	-0.60
1.8	18.8	43.0	3.7	1.5	0.2		
4.5	15	0.9	12	6.0	0.5	-0.05	-0.80
1.2	60.0	95.2	15.2	1.7	1.2		
2.9	42	1.6	43	6.7	2.8	+0.20	0.00
2.0	18.7	56.2	9.5	1.4	0.8		
5.4	14	1.0	29	5.6	1.9	-0.10	-0.50

TABLE III (continued)

	Altitude (m.a.s.l.)	Date	Flow (l s ⁻¹)	Conductivity (μ S cm ⁻¹)	pH	pCO ₂ *	HCO ₃ ⁻ (ppm) $10^{-3} \times a$
Case Milano	1,200	15-10-74	1	142	7.2	1.98	220 3.3
		14-05-76	1	130	7.2	2.11	164 2.5
Case Roatta	720	18-04-76	0.5	220	8.0	2.92	152 2.4
Costa Lumenda	730	10-10-74	1	279	7.9	2.60	255 3.8
		18-04-76	1	320	7.3	2.06	224 3.4
Molline	495	27-10-74	1	375	7.9	2.50	338 5.0
		25-04-76	1	425	7.3	1.93	306 4.6
Mottera	1,350	20-10-74	300	125	8.4	3.53	93.1 1.4
		01-05-76	100	165	8.4	3.35	146 2.3
Murao (Ante)	960	08-10-74	2	215	8.1	3.06	143 2.2
		09-10-76	10	264	7.8	2.84	116 1.8
Murao (Ponte)	966	12-11-74	80	160	8.0	2.72	246 3.7
		09-04-76	90	100	7.7	2.63	151 2.3
Piano	500	27-10-74	0.5	162	8.0	2.83	187 2.9
		25-04-76	1	160	7.7	2.68	135 2.0
Presa Mondini	910	17-11-74	50	92	8.3	3.26	138 2.1
		07-03-76	100	155	7.6	2.54	150 2.3
Presa Mondini (Ante)	910	14-05-76	10	126	7.6	2.46	180 2.7
Stalla Rossa	1,050	01-05-76	1	213	7.9	2.89	130 2.0
Tetti Peironi	630	27-10-74	1	330	7.8	2.46	280 4.2
Valloni	580	27-10-74	1	290	7.8	2.43	303 4.6

SI_{cal} and SI_{dol} = saturation index for calcite and dolomite, respectively. SI = log IAP · log K_S with IAP = $a_{\text{cation}} \cdot a_{\text{CO}_3^{2-}}$ and K_S = solubility product.

*pCO₂ is the negative logarithm, base 10, of the partial pressure of carbon dioxide, pCO₂.

						SI _{cal}	SI _{dol}
Cl ⁻ (ppm) 10 ⁻⁵ × a	SO ₄ ²⁻ (ppm) 10 ⁻⁵ × a	Ca ²⁺ (ppm) 10 ⁻³ × a	Mg ²⁺ (ppm) 10 ⁻⁵ × a	Na ⁺ (ppm) 10 ⁻⁵ × a	K ⁺ (ppm) 10 ⁻⁵ × a		
2.5	2.1	62.7	4.9	2.6	0.6	-0.50	-1.90
6.0	1.6	1.2	15	8.4	1.4		
2.7	2.5	50.4	1.8	2.8	0.9	-0.75	-2.60
7.1	2.0	1.0	5.7	3.2	2.1		
1.6	7.2	51.6	0.9	1.4	0.6	+0.05	-1.34
4.2	5.8	1.1	2.9	5.7	1.4		
1.6	17.7	80.0	6.0	2.3	1.3	+0.20	-0.15
3.7	1.3	1.4	18	9.2	3.0		
2.1	7.2	74.0	1.2	1.5	1.3	-0.30	-2.00
5.8	5.5	1.3	3.6	6.0	3.1		
1.5	9.4	91.6	13.5	2.6	0.6	+0.50	+0.50
3.5	6.8	1.6	39	10	1.4		
2.0	10.1	96.0	4.8	2.1	0.4	-0.15	-1.24
5.1	7.4	1.7	14	8.3	0.9		
1.6	7.5	31.8	1.3	1.1	0.4	+0.05	-0.95
4.2	6.3	0.7	4.3	4.2	1.0		
1.1	1.0	45.0	2.4	0.7	0.5	+0.40	-0.20
2.5	0.8	0.9	7.7	2.9	1.2		
1.8	8.0	33.8	9.8	1.4	0.5	-0.10	-0.35
4.8	6.4	0.7	31	5.3	0.9		
2.4	4.8	32.0	5.3	1.8	0.8	-0.50	-1.40
6.3	3.9	0.6	17	7.7	1.9		
0.8	4.0	79.8	1.6	1.0	0.4	+0.55	-0.50
2.4	3.0	1.4	4.8	4.0	0.9		
2.0	5.4	47.4	2.2	1.7	0.4	-0.20	-1.55
5.1	4.3	0.9	7.0	6.7	1.0		
1.8	3.4	41.3	12.7	2.1	0.4	0.00	-0.10
4.5	2.7	0.8	39	8.5	1.0		
2.1	0.9	42.6	1.7	2.1	0.3	-0.30	-1.85
5.3	7.4	0.8	5.5	8.5	0.7		
1.5	2.0	43.0	1.9	1.3	0.8	+0.15	-0.50
4.0	1.6	0.8	6.1	5.3	1.9		
2.1	5.8	47.1	2.4	1.9	0.6	-0.35	-1.80
5.5	4.7	0.9	7.6	7.7	1.4		
2.0	7.7	60.0	1.2	1.6	0.4	-0.15	-1.80
5.3	6.0	1.1	3.7	5.6	1.0		
1.9	2.0	37.0	3.7	1.5	0.6	-0.20	-1.20
5.1	1.6	0.7	12	5.2	1.4		
1.5	7.2	79.7	9.3	1.1	0.4	+0.25	-0.05
3.5	5.4	1.4	27	4.4	0.9		
1.1	5.8	57.0	26.7	1.8	0.8	+0.20	+0.25
3.2	4.3	1.0	78	7.2	1.9		

HYDROLOGICAL BEHAVIOUR IN THE CORSAGLIA BASIN DEDUCED FROM HYDROGEOCHEMISTRY

The most suitable chemical characteristics to describe the origin and the underground history of flow systems are:

(1) Chloride and alkaline ions which reflect seasonal variations in the input of meteoric waters (i.e. differentiation between contribution: direct from rainfall and indirect from snow melt in the spring.

(2) Conductivity, calcite and dolomite saturation indices and sulphate activity which describe the water-rock interactions (i.e. indirect length of the circuits).

These parameters suggest two different groundwater flows within the karst:

(a) A shallow rapid groundwater circulation, mainly due to snow melt and varying chemically according to the meteorological event on the catchment area.

(b) A deeper chemically homogeneous system that represents base flow.

For the first type which is little mixed the "precipitation signal" is preserved and the chemical composition of the water indicates low water-rock interaction (saturation in carbonate minerals is not reached). Variations of the input show that waters circulate mainly by piston flow (March and April). During this time, the conductivity follows the discharge: variations of Cl^- , SO_4^{2-} , Na^+ and K^+ contents show values close to that of the precipitation as snow melt or falling during that time in the basin.

During the latter part of the spring and during summer, the underground flows become better mixed; meteoric input variations are no longer recognizable. The conductivity becomes rather constant and independent of discharge variations. Cl^- and Na^+ contents move away from spring values and reach, during October, values corresponding to a weighted annual mean of the input value (minimum discharge occurs at this time). Calcite saturation index indicates that equilibrium with calcite is reached, whereas the dolomite saturation index and sulphate activity reach their highest value. One thus observes in the annual cycle of the geochemical evolution of these karst waters, a transition from non-dispersive flow with maximum discharge to a dispersive low flow condition. The latter homogenizes input variations and permits prolonged contact between water and aquifer rocks. Similar conclusions have been reached (Bortolami et al., 1979) using stable isotopes in this karstic area. If deuterium excess* is plotted vs. chloride activity (Fig. 11) one can compare two different meteoric "signals". The behaviour of these two parameters during the season indicates that during summer and fall mixing is at a maximum and a complete homogenization of the different components is reached; during spring time, deuterium excess and chloride activity indicate

*The deuterium excess, d , of waters of meteoric origin, defined as $\delta D - 8 \delta^{18}O$ is fixed mainly during the evaporation of water from the ocean and is considered to roughly depend upon the prevailing climatic conditions. Deuterium excess d is usually close to $+10\text{‰}$ especially at ocean stations (Craig, 1961). However, if a significant part of vapour mass has originated in a closed basin, as the Mediterranean Sea, the parameter d may be larger.

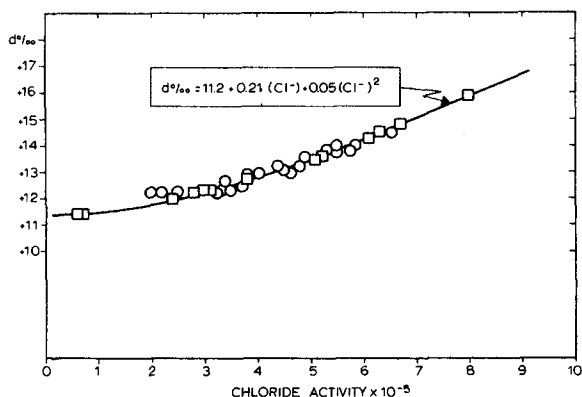


Fig. 11. Deuterium excess plotted vs. chloride activity. Circles indicate groundwater samples, squares precipitation samples. The coefficient of determination (r^2) for this correlation is 0.98 and the estimated standard error ($\sigma_{y,x}$) is 0.03 (after Bortolami et al., 1979).

that the underground flow is essentially non-dispersive. In the same way the mixing or at least the contribution of spring runoff is suggested by Fig. 12 where the deuterium excess is plotted vs. calcite saturation index.

The crystalline rocks show, in general, only one type of underground flow. An exception are the Prato Nevoso and Seccata springs where the circulation is shallow and rapid and chemically variable. In general, the low dissolved mineral content of the springs is due to the low water—silicate interactions which closely reflects the altitude of the recharge area (Table II). In this connection, the conductivity of the spring samples can be compared to that of precipitation at different altitude in order to determine the average altitudes of the recharge areas. This assumes that in the recharge area meteoric waters infiltrate and circulate through the subsurface without saline contributions from the dissolution of rocks and subsequent modification of their chemical

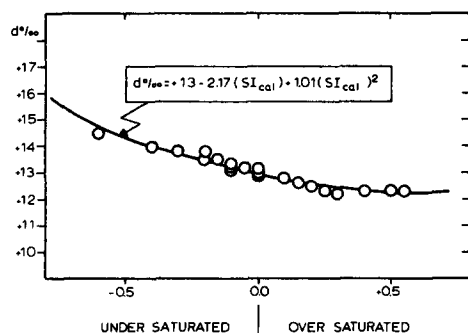


Fig. 12. Deuterium excess, d , in per mil plotted vs. calcite saturation index. The coefficient of determination (r^2) is 0.98 and the estimated standard error ($\sigma_{x,y}$) is 0.25 (after Bortolami et al., 1979).

composition. This assumption can be considered quite valid here because particularly in crystalline rocks, rapid infiltration of rain water, fast underground flow and a shallow circulation occur. The altitudes of recharge areas computed from conductivity gradients are very close to those computed from isotope gradients (Bortolami et al., 1979) and agree with hydrogeological observations (Table II). One also notes that because flow paths are sometimes extremely short, the conductivity of the spring waters cannot be compared to an average monthly chemical composition of the precipitation, but rather reflects single precipitation events (Bottero, Case Bertoni, Navonera, Pizzo, Potitta, during October 1974).

CONCLUSIONS

This study demonstrates the use of geochemical analyses in hydrogeological studies. The information that chemistry of precipitation waters can provide about air masses and the seasonal variation of the input can be combined with the geochemical parameters to interpretate the history of groundwaters.

The following can be pointed out: generally the groundwater flow patterns are short and circulation is rapid. In crystalline rocks the response to meteorological events is much faster than in carbonate rocks. In the first case there is only one type of groundwater circulation, which is a very fast, chemically variable, and characterized by low chemical reactions with the rocks. For the karstic aquifers two different types of groundwater circulation are recognized:

(1) A deep flow system, chemically homogeneous and in chemical equilibrium with the reservoir, representing the base flow.

(2) A shallow and faster circulation chemically variable according to the meteorological situation on the catchment area, and with a low content of dissolved salts.

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