

# Estimation of quantitative descriptors of northeastern Mediterranean karst behavior: multiparametric study and local validation of the Siou-Blanc massif (Toulon, France)

Stéphane Binet & Jacques Mudry & Catherine Bertrand & Yves Guglielmi & René Cova

S. Binet ( ) : J. Mudry : C. Bertrand EA2642 Géosciences, Déformation, Ecoulement, Transfert, Université of Franche-Comté, 16 route de Gray, 25030, Besançon, France e-mail: [stephane.binet@univ-fcomte.fr](mailto:stephane.binet@univ-fcomte.fr) e-mail: [jacques.mudry@univ-fcomte.fr](mailto:jacques.mudry@univ-fcomte.fr) e-mail: [Catherine.Bertrand@univ-fcomte.fr](mailto:Catherine.Bertrand@univ-fcomte.fr) Y. Guglielmi Géosciences Azur, Centre National de la Recherche Scientifique, Université Nice Sophia-Antipolis, 250 rue Albert Einstein, 06560, Valbonne, France e-mail: [guglielmi@geoazur.fr](mailto:guglielmi@geoazur.fr) R. Cova Direction départementale de l'Agriculture et de la Forêt du Var, 80 avenue Paul Arène, 83300, Draguignan, France

## Abstract :

Key parameters controlling the recharge and behavior of Mediterranean karsts were selected in order to make a quantitative description of northeastern Mediterranean karsts on a regional scale. The methodology was applied to an actual karstic aquifer on the Siou-Blanc Plateau (France). For the recharge study, it was observed that the average yearly rainfall value and  $\delta_{18}\text{O}$  measurements in springs can be considered as good descriptors of climatic variations observed in the Mediterranean area.

They can be used to estimate the intake area and the infiltration coefficient. A comparison with a numerical (double permeability) flow model (MODFLOW) on the Siou-Blanc karst improves these exponential relations between effective rainfall and  $\delta_{18}\text{O}$  measurements. Infiltrated water, which flows through different rock types, induces contrasts in the water chemistry. An instantaneous physical and chemical analysis of all the springs of the Siou-Blanc aquifer displays the same expected functioning and variations as had been forecast using the conceptual scheme. Thus, it can be applied to wide areas associated with a northeastern Mediterranean climate for a first approach of a karst study; such a model enables a useful estimation of recharge and behavior with few simple data.

Keywords Karst . Mediterranean climate . Groundwater recharge . Water chemistry . Toulon

## Introduction

Over a wide area, the Mediterranean hydrogeological context involves similar characteristics: (1) similar geologic alpine structures, (2) typical low vegetation prevailing on the carbonate substratum, (3) a dry season with scarce but intense rainfall episodes (700–800 mm/year), (4) mountainous terrain inducing rainfall that increases rapidly with elevation. Karst aquifers are subjected to parameters that are fairly similar, therefore the determination of relevant factors could enable a conceptual model to be built of the northeastern Mediterranean karst. Among a broad choice of parameters (input and output), the problem is to choose the relevant parameters. The choice of parameters is realized with the aim of characterizing karst recharge and behavior. The study aims to show how simple climatic parameters and water chemistry measurements of karst springs contribute to a quantitative estimate of northeastern Mediterranean karst recharge, behavior, and residence time. Each estimation will be tested on a well-constrained Mediterranean karst: the Siou-Blanc karst aquifer, France. The infiltration coefficient and its spatial variability were defined with numerical modeling, calibrated with spring hydrographs and  $\delta_{18}\text{O}$  (stable isotope of oxygen) measurements. Fast/ slow infiltration and rock/water interactions are discriminated from the descriptor variations through a statistical comparison.

## Construction of a conceptual model of the Karst behavior

The model was based on a regional scale (Fig. 1), with data from Bakalowicz 1979; Laty 1981; Vernet and Vernet 1981; Mudry 1987; Puig 1987; Lastennet 1994; Chalumeau 2000; Emily 2000; Plagnes 2000; Reynaud 2000. These studies involved multi-parameter analyses, with recording of many input/output data, topographic data (elevation, latitude, slope, soil type, etc.), climatic parameters (air temperature, rainfall values, sun radiation, etc.), and output data (spring outflows, water chemistry, isotopes measurements, etc.). This model selects relevant parameters, with few measurements, to describe the karst functioning. The selection of the key parameters was realized with intercorrelations which show redundancy between recorded parameters. The functioning model was built in three different steps: (1) infiltration characterization, (2) understanding fluid/rock interactions, and (3) residence time estimation. The first step

involves delimiting the intake area to attain a hydrogeological water balance, and then estimating the effective rainfall. Comparison of temperature and rainfall gradients versus elevation (Mudry 1987; Puig 1987; Lastennet 1994; Andreo 1996; Fairchild et al. 2000; Reynaud 2000; Table 1) shows that the spatial variability around the Mediterranean Sea can be wide at about one order of magnitude.

These gradients improve the water balance estimation on a regional scale because they take better account of both a contrasted elevation and a contrasted Mediterranean climate. As a matter of fact, it appears that the rainfall value, temperature and elevation are correlated to each other with gradients. So only one of these values can be a relevant factor of the peculiarities of the area. Another relevant factor, correlated with climatic factors, is the  $\delta_{18}\text{O}$  measurement of spring water which gives us information about the recharge area that supplements climatic observation (this concept will be developed later in the paper).

The second step is a quantification of infiltrated water (volume) and flow paths using water chemical measurements (Bakalowicz 1995; White 2002). Measurements of major ion concentrations,  $\delta_{18}\text{O}$  and the few data about the soil thickness and exokarstification, enable an estimate to be derived for effective infiltration and for flow paths.

The third step consists of isolating the two major drainage components in karst aquifers - the quick infiltration component that is flowing through conduits with a low chemical content (Mudry et al. 1994; Martin and Dean 2001), as opposed to the slow infiltration component, flowing through fractured rocks with a higher chemical content (Mudry 1987). The flows in saturated or unsaturated zones can be marked with  $\delta_{13}\text{C}$  (stable isotope of carbon) measurements (Emblanch, 1997). The epikarstic aquifer can have a storage role, as demonstrated by  $\delta_{18}\text{O}$  data during a flood (Perrin et al. 2003). Isotopic measurements like tritium or oxygen isotopes provide information about residence time that can be quantified with a simple model (Blavoux and Letolle 1995). Other residence time markers are magnesium, 13-carbon (Mudry et al. 2002) and Total Organic Carbon (TOC; Celle-Jeanton et al. 2003). The concentrations of these elements in water evolve with time (Batiot 2002; Batiot et al. 2003); the measurement is simpler than isotopic measurements and enables inter-area comparison.

Thus, the tritium repartition in the air is complex and evolves in time (Fontes 1976; Blavoux and Letolle 1995); therefore, inter-area comparison, with measurements taken at different times, will not give regional information.

The regional relationships between rainfall, infiltration, karst functioning, and residence time presented in the first part of the study show that they are all connected to each other. The conceptual diagram (Fig. 2) shows the water flow from rainfall to spring discharge, the principal steps which influence the water chemistry, and the descriptors which characterize the flow in a northeastern Mediterranean karst aquifer. The next quantitative approach will define the forecasted value of the relevant parameters, with statistical correlations between the key parameters.

## Methodology to test the conceptual model: application to the Siou-Blanc Karst aquifer The Siou-Blanc Plateau

The Siou-Blanc massif is a limestone plateau, 826 (m a.s.l.) at its highest point in the Toulon hinterland (Var region). It is bounded by the Gapeau (to the northeast) and the Reppe (to the west) valleys. The mountain range alignment (Coudon, Combes, Caumes) determines the southern boundary of this massif. It is covered by low vegetation and is subjected to a typical Mediterranean climate. The study area is about 30 km from the Mediterranean Sea. The karst, about 110 km<sup>2</sup> wide, is drained by springs described in Table 2. Tracer tests have confirmed the boundaries of some sub-systems (Fig. 3 and Table 3), but water balance is deficient and it seems that a significant part of water flows under the sea in the "Rade de Toulon" through a submarine spring (Lamarque and Maurel 2000).

The general structure corresponds to limestone and dolomite aquifers that belong to the calcareous Provence region (Blanc et al. 1974) outcropping over the Triassic evaporites (Fig. 3). The stratigraphic series ranges from Muschelkalk to Turonian. The tectonic partition of the Siou-Blanc Plateau divides it into three units—Morieres, Ragas, and Tete du Cade—which give it an internally complex structure (Gouvernet 1963, 1969).

### Adopted methodology

An 'instantaneous' physical and chemical analysis of all the springs that drain the Siou-Blanc aquifer was performed during a long, low groundwater-level period in June 2002 (810 mm of rain fell in 2001, but the first 6 months of 2002 were without any effective rain). The major ion composition of springs (Table 2) were compared with the conceptual model of karst functioning. Observing concentration variations of appropriate factors defined in the conceptual model would permit the testing of the previous descriptors.

The analyses were undertaken at the Geosciences Laboratory (University of Franche-Comté). Cation measurements were made with the atomic absorption spectrophotometer PerkinElmer A analyst 100 and the anion measurement with a high-pressure ionic chromatograph Dionex DX 100 (precision is about 5% maximum, according to the dilution coefficient). Bicarbonate was measured volumetrically. The stable isotope of oxygen,  $\delta_{18}\text{O}$ , was determined with a mass spectrometer MAT 250 Hausverfahren ( $\pm 0.15 \delta_{18}\text{O}$ ) by Hydroisotop GmbH; the unit of measurement corresponds to a normalized value referred to as the seawater value. The TOC was analyzed with a Bioritech TOC analyzer ( $\pm 0.05 \text{ mg/L}$ ) by the University of Avignon. Flow rate measurements at the Rampins spring and rainfall measurements on the Pilon Saint Clement Massif were collected by Chanut (1976). These measurements enable a comparison of actual data with regional quantification of flow using two approaches: (1) numerical calculation to test repartition of flow with elevation, and (2) statistical test to improve the chemical descriptors choice of flow paths, and using organic carbon to study an actual residence time problem.

### Aquifer recharge: a quantitative approach In situ recharge assessment

A graph displaying evolution of infiltration in the area (Fig. 4) was derived from data from Mont Ventoux in the Vaucluse region (Puig 1987; Emblanch et al. 1998), Mont Vial and Nice ranges (Maritime Alps; Emily 2000 and Reynaud 2000), from eight weather stations in the Bouches-du-Rhône region (Vernet and Vernet 1981), seven areas in the Var region (Cova and Durozoy 1980), four sites in the Hérault region (Laty 1981) and one site in Malaga, Spain (Andreo 1996).

As a link had been observed between rainfall value, elevation, and temperature (Table 1), the average yearly rainfall value should characterize the climatic variations from one place to another. The average yearly rainfall value, which is easy to obtain, incorporates variations of several parameters (temperature, altitude, watershed exposition) which are necessary for infiltration estimation.

The infiltration coefficient is a descriptor that enables karst systems to be compared. It corresponds to the ratio of infiltrated water volume against rainfall volume and quantifies the effect of evapotranspiration. The coefficients used here are all derived from rainfall/ flow rate studies. A graph of the log of average yearly rainfall value versus infiltration coefficient (Fig. 4) shows a point repartition between two extreme curves. The dispersion of the infiltration coefficient (intercept to origin) is caused by the soil type. Gdalia (1980) had used analytic modeling on several Mediterranean karsts to attest that the soil thickness is one of the most relevant inter-area infiltration parameters. The karst aquifers, situated near the highest curve (high infiltration coefficient), display important exokarstic forms, with thin soils and no important runoff. In the opposite case, the karsts with low infiltration coefficients present a situation where soil with high vegetative content covers the epikarst fractures. The inter-annual climatic variations are represented by the lines drawn on Fig. 4. This graph is a tool to estimate infiltration with yearly rainfall values and few observed data.

Another parameter for estimating the infiltration water volume is  $\delta_{18}\text{O}$  measurements during low rainfall periods (Blavoux and Mudry 1990).  $\delta_{18}\text{O}$ , which is thermodependent and stable during infiltration time, is an excellent infiltration tracer (Razafindrakoto 1988).

Guglielmi et al. (1998) give a relationship between  $\delta_{18}\text{O}$  and recharge altitude (Table 1) that is valid for Southeastern France. As infiltration is related to climate and soil type, and as it is one of the more important parameters used for hydrogeological studies, a scatterplot of yearly effective rainfall and  $\delta_{18}\text{O}$  measurements was prepared (Fig. 5). The volume of infiltration water estimate can be confirmed by a comparison between these two different approaches.

$\delta_{18}\text{O}$  is controlled by climatic conditions and evapotranspiration (Fontes 1976). Locally, the origin of air masses, seasonal variations, and local microclimatic difference between sunny or shady mountain slopes influence the  $\delta_{18}\text{O}$  rain content (Guglielmi et al. 1998). However,  $\delta_{18}\text{O}$  remains an interesting descriptor of infiltration. Taking into account the low groundwater level, the correlation (Fig. 5) between  $\delta_{18}\text{O}$  measurements and effective rainfall is another tool for flux estimation. On this scale, the isotopic gradient is marked by the high contrast in elevation, which takes precedence over the local variability (Guglielmi et al. 1998). The  $\delta_{18}\text{O}$  values represent recharge by infiltration only if the measurements have been taken during low groundwater level periods. The  $\delta_{18}\text{O}$  values during flood periods are controlled by more complex phenomena not described here, like partitioning evolution during the flood (Vandenschrick et al. 2002; Lee and Krothe 2001). This correlation is an interpolation between data from Nice to Malaga, so one can consider that these relations are valid on the northeastern Mediterranean karsts. Estimation of the rainfall value and recharge altitude gradients gives a better understanding of rainfall and integrates the spatial variability of a massif. Thus, the volume of infiltrated water can be estimated with a precision of about

$\pm 10\%$  (calculated with residue of the linear correlation in Fig. 4) and this resolution enables inter-annual variations and inter-area differences to be distinguished.

## Numerical parametric study of recharge variation

### Objectives

Yearly rainfall values and  $\delta_{18}\text{O}$  values, used to describe infiltration, record the influence of elevation in the estimation of the volume of water input in the karst. The non-linear correlation between these parameters and infiltrated water suggests that an infiltration gradient exists with the elevation. A numerical model of a karstic spring flow was set up in order to estimate the infiltration coefficient during a flood. This method should take account of spatial variability, and allow for the study of the relative importance of a gradient of infiltration water versus elevation. Thus, the variability observed in Fig. 4 can be discussed.

### Method

The numerical model applies to the Pilon Saint Clement area (Fig. 3) studied by Chanut (1976). It is a simple hydrogeological sub-system which presents an interesting elevation variation (ranging between 350 and 700 m a.s.l.) within the watershed. This elevation can be considered as representative of the average elevation of the Mediterranean recharge area. The geological structure is a syncline and the springs are located along the watershed boundary, emerging on the impermeable layer. Rainfall is the only input in the hydrogeologic system. Spring outflow and rainfall were monitored for 4 years between 1974 and 1976, comprising three average years and one exceptionally rainy year (1976). The recharge area of the three springs draining the massif will be defined with the MODFLOW model. The outflow of the Rampins spring (spring 3 in Fig. 6a) ranges between 4 and 7,500 L/s. Numerical tests were undertaken with MODFLOW (McDonald and Harbaugh 1988), which simulates underground water flows using a finite difference method in a porous saturated media (Scanlon et al. 2003). The model enables the assessment of infiltration with a rainfall value and outflow data. Infiltration flow rate is spatialized with the three-dimensional calculation. Tests aim to show and quantify the connection between elevation and increase in infiltration.

Many parametric tests were performed to adjust the flow in the massif with the measured flows at the springs. The mountain is cut in vertical blocks with a permeability of  $10^{-6}$  m/s and an effective porosity of 0.05%, separated by fractures. Fracture permeability is represented by a 1 m/s permeability and an effective porosity of 0.01%, and assimilated to vertical continuous layers with a width of 10 m (Mangin 1975 and Eisenlohr 1997). The density of fractures and their orientation were estimated with the geological setting (Fig. 6).

The spring is modeled using a drain boundary condition, equivalent to the cave observed at the site (Dufresne and Drake 1999). The recharge area of the Rampins spring is defined with a steady-state calculation. The limits of the recharge area can be precisely defined (Fig. 6) with a fixed geometry, and the discharges during low rainfall periods can be measured at springs 1, 2, and 3. This model does not aim to demonstrate flow paths in a karst system, but it enables the determination of a recharge area with such a geometry and is, therefore, appropriate for the Rampins spring. Evapotranspiration estimates can then be tested in this recharge area.

### Parametric tests on infiltration

The main objective of the parametric tests is to test which parameters (using recorded data) influence the intra-area variability in infiltration and rainfall (shown in Fig. 4) in the Pilon Saint Clement area. The main factors of the variability between infiltration ratio and yearly rain value seem to be elevation and inter-annual climatic variations, and two types of parametric analysis were undertaken to test and compare these observations. First, on a yearly scale, several infiltration coefficients were calculated for 4 years, where rainfall conditions were different. Only climatic conditions were varying. The first year was the reference calculation and the three other years were used to study the annual variability. This will show if the yearly rainfall value correctly describes these variations. It will confirm that the line, in Fig. 3, represents intra-area variations. Secondly, with a rainfall scale in the order of a few days, applied to the numerical model, several gradients of evapotranspiration were applied to test elevation influence on infiltrated water volume. The first calculation was undertaken without an infiltration gradient value to calibrate the model and estimate the average infiltration coefficient (Fig. 6b). Then, the same calculation was undertaken with different infiltration gradients applied to water input. This test does not significantly modify the numerical calibration of water volume. The second calibration step involves parametric tests of the repartition of infiltrated volumes in space in order to compare its effects on calculated  $\delta_{18}\text{O}$  at the spring. The  $\delta_{18}\text{O}$

variability is linked to elevation variability on the recharge area and an actual gradient was defined with field data ( $\delta_{18}\text{O} = -0.0055 \times \text{elevation} - 4$ ;  $n = 12$ ,  $r =$  correlation coefficient  $= -0.96$ ). An increase of infiltration coefficient versus elevation means that the infiltrated water originates from the highest elevation area, which depletes the  $\delta_{18}\text{O}$  value. The calculated  $\delta_{18}\text{O}$  value at the Rampins spring incorporates a mixture of waters coming from different elevations with different  $\delta_{18}\text{O}$  values (Table 4). The  $\delta_{18}\text{O}$  adjustment is realized with a comparison of  $\delta_{18}\text{O}$  measurements and calculations. It will show if the rainfall value gradient and the  $\delta_{18}\text{O}$  measurements, estimated with the conceptual model, correctly describes the influence of elevation.

## Results

The results of parametric tests on a yearly scale (Fig. 4) show that under various yearly climatic conditions, the evolution of infiltration coefficient versus yearly rainfall value can be fitted with this logarithmic statistic expression:

Infiltration coefficient  $\ln(\text{yearly rainfall}) = 2.85; r = 0.96; n = 4$ :

This regression supplements the regional quantitative model and proves, by calculation, that the line in the graph describes intra-area variations mainly linked to soil effects. With the rainfall scale in the order of weeks and internal parameters fixed, for an optimum calibration of the water volume mobilized during a flood without elevation gradient, the average infiltration coefficient needs to be fixed at 0.21% (Fig. 6b). This calibration establishes the gradient of the infiltration coefficient as being equal to 10 mm per 100 m, including the rainfall gradient monitored at the site (7 mm per 100 m).

Now, estimation of the infiltrated water volume is undertaken with the regional model to compare both approaches. The measurements of the Siou-Blanc  $\delta_{18}\text{O}$  values range between  $-5.8$  and  $-7.5\text{‰}$  and the mean is about  $-6.58\text{‰}$   $\delta_{18}\text{O}$ . The  $\delta_{18}\text{O}$  variability of the measurements can be used to estimate (with Fig. 5) an infiltration gradient with elevation. A gradient of 11 mm per 100 m was obtained for an average effective rainfall of 300 mm.

These gradients, estimated with a numeric calculation and the conceptual model, give a value of 10 mm per 100 m, which is coherent and proves the existence of an infiltration gradient independent of the rainfall value gradient (7 mm per 100 m).

The comparison between the regional  $\delta_{18}\text{O}$  approach and the numerical approach, calibrated with local measurements, confirms the importance of elevation in assessing the infiltration coefficient under a Mediterranean climate. The numerical approach enables assessment of infiltrated water on an area with an excellent resolution, since the exact spatial variability is taken into account.

Here, it was proved that the regional model, with  $\delta_{18}\text{O}$  gradient, is a good method of calibrating infiltration using a numerical modeling approach. The calibration of the gradient has the same precision, whether undertaken with numerous meteorological data or with the  $\delta_{18}\text{O}$  gradient, but the second is easier to obtain. Thus, water chemistry is a calibration tool for flow modeling.

## Behavior based on chemical descriptors Karst water content of Mediterranean karst systems and water-rock interactions

Water chemistry variation in springs of the Mediterranean karst aquifer is mainly controlled by lithology (Mudry 1987). Rainwater has a lower concentration compared to spring water, and human-induced pollution (for example  $\text{NO}_3^-$ ) is generally low in a karst area, which often constitutes the mountainous areas of the Mediterranean region. Water chemistry provides, then, a set of natural tracers that enables flow paths to be identified, using a lithologic and chemical comparison. Major ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations are controlled by dolomite, calcite and evaporitic minerals. A threecomponent

diagram of the chemical ratios  $(\text{SO}_4^{2-} + \text{Cl}^-) / \text{HCO}_3^-$  and  $\text{Mg}^{2+} / \text{Ca}^{2+}$  variations (Fig. 7) was built, using data from various karst aquifers of the Mediterranean area. The clusters that represent the aquifer lithology were defined means of small springs with well-known water pathways. The measured ratio shows (1) the preferential flow path, and (2) an intermediate value of a mixture of different waters. This scattergram is useful in collecting information from inside the system. The chemistry can reveal structural elements by comparison of the geological map and the chemical data. For example, an indication of the location of evaporites provides information on the location of the bottom of the aquifer. The variability caused by the variation of residence time is tiny compared to inter-area variability. Residence time increases the water concentrations but does not significantly affect the ratio at this scale, as illustrated in the chemographs of a karst spring in Fig. 7.

## Statistical test applied on Siou-Blanc

In the Siou-Blanc area, a principal component analysis (PCA) was undertaken on chemical data to test the factors that control the chemical water composition (Olivier 1997; Lopez-Chicano et al. 2001) and validate the rock clusters presented in Fig. 8. PCA validates the choice of descriptive parameters. This classic hydrogeological method displays correlations between variables, placing the factors responsible for observed variations in hierarchical order. Thirty-five samples and 15 variables were used. The three major factor axes were studied. The variance explained by the two major factors is high (49%) and shows that the lithology explains the major ion scaling. The ions used to describe flow paths are improved by PCA; however, other processes such as anthropic pollution, control a part of the variations (axis 2). For the particular case of  $Mg^{2+}$ , its slow dissolution kinetics and its presence in dolomitic rocks creates confusion between residence time and presence of dolomite. The other descriptors of the PCA, like TOC, are not sufficient for differentiating an axis of residence time and an axis of presence of dolomite. However, residence time effect on chemical acquisition is statistically less important than rock mineralogy. Thus, axis 3 mainly represents the variations between limestone and dolomite interaction. The chemical measurements of the Siou-Blanc karst are plotted in Fig. 8 and they fit with the regional forecast.

The regional clusters enable reference water contents to be correlated to lithology. Thus, the ratio  $Mg^{2+}/Ca^{2+}$  evolves from 0.015 ( $\pm 0.005$ ) in a limestone rock to 0.5 ( $\pm 0.1$ ) in a 100% dolomitic rock. The  $(SO_4^{2-}+Cl^-)/HCO_3^-$  variations scale from 0.03 ( $\pm 0.005$ ) in a non-evaporitic rock, to 50 ( $\pm 15$ ) in halite. The Siou-Blanc test improves the quality of these ratios for describing water content variations. The data of this area are well distributed between these clusters and enable water types with very similar flow paths to be distinguished.

## Estimation of the residence time: An interesting descriptor: total organic carbon (TOC)

When the dolomite proportion remains constant (within the same lithologic formation), the  $Mg^{2+}$  concentration increases with residence time (Blavoux and Mudry 1983). Another interesting tracer of the residence time is the total organic carbon (TOC), especially for short residence times (Batiot et al. 2003). Water dissolves TOC in the soil cover. It is then oxidized in the unsaturated and saturated zones by bacterial activities (Emblanch et al. 1998). The TOC measurements, in all the springs of a given area, can give information about the relative residence time of spring water (Batiot et al. 2003). Compared to an isotopic marker of the residence time, the TOC records the very fast infiltration; in contrast, magnesium content records long residence time. The evolution in time of these elements is always observed, but the initial concentration is variable, meaning that regional correlation is not possible.

## TOC contents on the Siou-Blanc springs

Total organic carbon (TOC) and  $Mg^{2+}$  concentration variations were compared (Fig. 9) for the springs draining the Siou-Blanc karst. The decrease of TOC is correlated to the increase of the magnesium content and with the remoteness of the spring from its mean infiltration zone (cross section, Fig. 9b). These five springs drain the same aquifer water coming from the Siou-Blanc Plateau. The  $\delta_{18}O$  values are similar for these five springs ( $-6.5 \delta_{18}O\text{‰} \pm 0.5$ ) and prove that the water recharge area of these five springs is the same. Tracer tests have confirmed that during low groundwater flow, the greater the infiltration zone, the greater the residence time (Table 3). All these data explain the decrease of TOC compared to the increase of magnesium and are linked to increasing residence time. Experiments with tracer tests yield interesting results used to calibrate the TOC decreases under a given climate (Fig. 9a). TOC, as a residence time marker, has excellent potential in work associated with short residence time and may quantify average residence time of water of this system.

## Discussion: relevance of the selected parameters

The parameters used to describe the Mediterranean karst aquifers are climatic data, major ions,  $\delta_{18}O$  and TOC measurements. The major ions are compared on all the Mediterranean area samples. As the climate is similar for all of them, we can estimate that dissolution kinetics is fairly similar, and concentration has the same order of magnitude. Nevertheless, as chemical concentrations in rainwaters are lower than spring water concentrations by about two orders of magnitude, variations in water chemistry observed in the rainwater measurements were discounted.

The yearly mean rainfall value can be discussed if it is a parameter used for the estimation of infiltration. In a very irregular climatic area characterized by intense and irregular rainfall, yearly parameters are not very

appropriate. However, yearly mean rainfall was used in this study due to the following advantages: (1) it is an easy access parameter, which indirectly describes elevation, exposition, and temperature variations; (2) it is a simple means for describing the climatic difference between waters in Mediterranean aquifers. The dispersion observed in Fig. 4 can be explained by a complex interaction between soil, slope, and rock type (limestone or dolomite) that cannot be quantified with the presented descriptors.

The use of  $\delta_{18}\text{O}$  measurements to estimate recharge needs care. Since  $\delta_{18}\text{O}$  water content is a function of temperature on the infiltration area, and of the rainfall intensity, a correlation of  $\delta_{18}\text{O}$  with the effective rainfall value requires several precautions. Thus,  $\delta_{18}\text{O}$  values must be measured during a long, low-groundwater period, in order to be representative of evaporation in the average infiltration zone.

## Conclusion

The model, built and tested here, provides some methods of quantifying the recharge and functioning of a Mediterranean karst aquifer using water chemistry and few meteorological data. One of the strong features of water chemistry data in this study is the possibility of comparing different areas. This work proves that water chemistry is controlled by three mechanisms: infiltration, geology and residence time. The dynamics of these mechanisms is similar over the whole Mediterranean climatic area. One can, thus, realize a scale-change and build a regional conceptual model with quantitative data to allow the use of this quantitative model over the whole area. This model is appropriate to the northern part of the Mediterranean area (from Malaga to Nice). For a first approach to studying an aquifer, applying this model requires few data and technical instrumentation and can thus be easily carried out. The chemical measurements give this model an interesting sense of the parameters in relation to the topography. The precision of the quantitative approach of this model enables water budget and water flow studies to be undertaken, which are useful for calibrating a numerical flow model or evaluating water supply in a Mediterranean karst. This model can be improved by including the evolution of water chemistry over time at the main spring outlet of the karst study area, thereby integrating a time dimension within this spatial approach.

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FIGURES AND TABLES



Fig. 1 Geographical location of the karsts used to build a conceptual model of Mediterranean karst  
 Table 1 Atmospheric parameters versus elevation in a Mediterranean climate

Atmospheric parameters in Mediterranean locations	Slope	Intercept	Correlation $r$	Number of measurements	References
Temperature					
Provence	-0.00641	14.53	-0.993	28	Mudry 1987
Maritime Alps	-0.0053	15.2508	-0.99	7	Reynaud 2000
Ventoux	-0.0052	13.95	-0.92	14	Puig 1987
Rainfall value					
Provence, Maritimes Alps, Var, Bouches du Rhone	0.498	713.8	0.686	28	Mudry 1987
Provence	0.55				Blavoux and Mudry 1990
Var, Herault, Bouches du Rhone, Maritime Alps, Provence	0.57	683.9	0.89	33	Vernet and Vemet 1981; Fairchild et al. 2000; Lastennet 1994; Laty 1981; Reynaud 2000; Emily 2000
Malaga (Spain)	0.43	582.1	0.43		Andreo 1996
$\delta^{18}O$					
Maritime Alps, log (elevation)	-3.62	1.923	0.92	34	Guglielmi et al. 1998

Table 1 Atmospheric parameters versus elevation in a Mediterranean climate

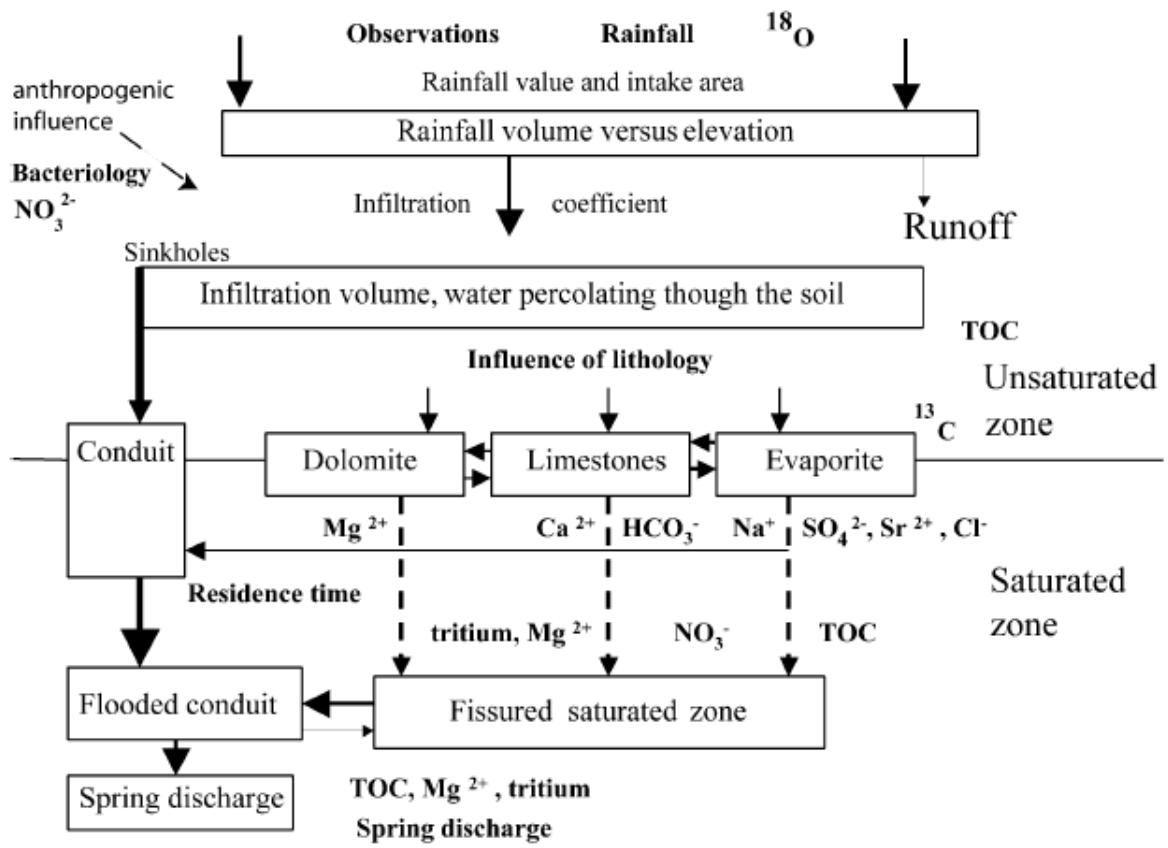


Fig. 2 Conceptual model of a Mediterranean karst system shows functioning of karst components and appropriate model descriptors (shown in bold) useful for understanding the system. Text in black is for the description

Site number	Spring name	Elevation m a.s.l.	Q low water (L/s)	Q flood (L/s)	Temp. °C	Cond. uS/cm	pH	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	mg/L					TOC	<sup>18</sup> O ‰	B ‰
													Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Se <sup>2+</sup>	Ca <sup>2+</sup>			
1	Trians	335	0.5		12.2	512	7.6	318	0.5	7.5	1.8	6.0	10.6	3.9	0.5	0.1	95.6	1.0	-6.75	1.5
2	Font Gayou	330	5.6		12.4	591	7.5	378	0.5	7.4	1.6	7.0	28.0	4.1	0.4	0.0	86.8	0.9	-6.98	0.6
3	Rampins	250	4.1	7,300	11.0	522	8.1	310	0.1	8.7	6.7	19.3	25.0	5.1	0.7	0.1	77.0	1.0	-6.70	1.6
4	Gavaudan 1	290	1	100	12.5	530	8.0	355	0.1	6.7	0.3	6.6	30.5	3.7	0.3	0.0	65.2	0.7	-6.98	-3.2
5	Gavaudan 2	220	3		12.4	567	7.6	373	0.1	7.1	0.0	9.1	34.5	3.9	0.4	0.0	77.8	0.7	-6.93	1.6
6	Saint Manhieu	145			14.1	781	7.7	316	0.4	10.7	1.8	16.41	27.5	5.8	1.1	1.0	159.0	0.8	-6.82	7.2
7	Lacanal	180	1	120	13.8	550	7.6	332	0.1	8.9	0.6	13.3	29.5	6.0	0.7	0.2	79.2	0.9	-7.13	4.2
8	Rouvière	170	0	130	14.7	560	7.5	364	0.1	10.4	2.4	16.0	23.0	4.8	0.6	0.1	84.4	0.9	-6.61	-3.2
9	Font du Thôn	104	5	115	14.8	622	7.5	303	0.3	11.4	2.7	7.14	23.5	6.1	1.0	0.5	97.8	0.7	-6.71	1.2
10	Valaur	200	5	500	10.7	550	7.5	325	0.1	13.2	2.9	19.7	18.5	6.4	0.9	0.1	89.0		-5.83	0.2
11	Les Genets	83	4		13.4	833	7.7	289	0.4	23.2	3.1	200.7	29.0	15.1	1.4	1.0	159.0	0.5	-7.05	6.0
12	Werotte	110	0.5	5	14.2	568	7.5	337	0.5	14.0	2.2	43.7	20.5	9.0	1.0	0.9	85.6	0.6	-7.16	-4.6
13	Foux	160			12.6	947	7.6	289	0.3	25.5	9.5	260.7	23.8	14.0	4.8	1.0	194.0	0.7	-7.09	5.3
14	d'Avauou Reganus	145	0.25	10	15.5	676	7.4	305	0.0	26.5	3.9	84.3	20.8	11.2	1.1	1.3	137.0	0.8	-7.37	8.5
15	Maire des eaux	130	10	500	15.6	627	7.5	346	0.6	7.8	4.0	19.1	18.8	7.6	0.9	0.2	105.8	0.8	-6.65	5.3
16	Manteoli obs. borehole	120			16.9	958	7.7	377	0.8	30.1	18.5	168.2	25.0	13.9	1.3	1.2	190.0		-6.54	5.4
17	La Ripelle	250	0.25	3	14.3	572	7.7	337	0.1	12.4	5.7	17.2	2.8	5.4	0.6	0.1	147.0	0.7	-6.49	10.7
18	Rodeillac obs.	5		35	18.8	938	7.5	316	0.0	78.2	37.9	94.1	20.7	40.5	3.9	0.4	158.0	0.6	-6.58	7.1
19	Borehole Saint Antoine	20	50	1250	15.3	578	7.8	284	0.4	18.5	9.5	45.8	14.9	10.5	1.3	0.3	96.6	0.7	-6.72	1.5
20	CEO's drilling	90			15.8	434	7.8	224	0.2	10.6	2.4	23.8	10.5	4.7	1.3	0.1	73.4	2.3	-5.78	2.2
21	Ragas	90	1	115	14.2	422	8.2	249	0.1	8.8	3.7	13.7	10.2	4.7	0.3	0.1	82.4	0.9	-6.80	4.6
22	Baumes de dardennes	24	4	31	16.0	637	7.9	307	0.3	23.6	13.6	46.2	15.9	12.4	1.2	0.3	110.0	0.7	-6.44	3.1
23	Captage d'Evenos	260			13.3	733	7.2	420	0.0	24.1	3.9	25.2	6.5	12.5	0.7	0.4	173.0		-6.73	8.8
24	Sia Reppe	75			14.8	504	7.2	290	0.1	21.4	1.9	25.9	4.0	13.7	1.2	0.5	197.0	1.0	-7.78	29.0
25	Daniel's Spring	290	0.25	5	13.0	715	7.8	406	0.0	24.5	3.9	25.8	6.5	12.5	0.7	0.4	169.0	0.7	-6.70	9.1
26	Trou de la Bombe	100	0	48	14.6	525	7.4	270	0.6	24.7	1.6	27.0	5.1	15.9	1.0	0.3	95.4	1.0	-8.37	1.3
27	Mascaron	61	23	152	16.1	529	7.6	277	0.5	20.9	1.5	23.1	4.4	13.3	0.8	0.3	99.4	0.9	-7.77	2.2
28	Maire des Fontaines	50	1	30	14.1	563	7.2	312	0.1	14.7	4.7	21.5	6.6	0.8	0.9	0.2	108.2	0.9	-6.69	-0.6
29	Bonnefont	60	0	15	15.3	721	7.4	364	0.2	31.3	13.8	34.6	23.5	20.7	0.8	0.3	107.6	0.6	-6.81	2.3
30	Messonier drilling	20			19.5	2040	7.3	407	0.0	47.9	8.3	646.0	32.0	26.5	1.1	3.8	509.0	0.8	-6.25	14.8
31	Gapeau	315	2	5	13.4	430	7.7	251	0.1	7.0	1.3	10.8	26.0	4.1	0.5	0.1	52.4	0.4	-7.71	2.6
32	Font de l'Ecove	320	0	1	11.4	616	7.4	359	0.1	6.3	0.1	40.6	22.9	3.4	0.4	0.3	106.0	0.6	-7.05	2.2
33	Montrieux le vieux	280		5 to 7	12.2	510	7.6	317	0.1	5.8	0.5	9.4	28.5	3.2	0.4	0.0	66.4	0.5	-7.52	0.8
34	Montrieux le Jeune 1	340	1	24	11.9	468	7.8	295	0.1	5.6	0.4	6.6	27.0	3.2	0.3	0.0	59.8	0.4	-7.37	0.6

Q low water is flow rate during low water period; Q flood is flow rate during flood event; B% is the water ionic balance

Table 2 Natural chemical tests undertaken on the Siou-Blanc Plateau springs in June 2002 (analyzed at the Geosciences Laboratory, Besançon). Spring sites are located in Fig. 3

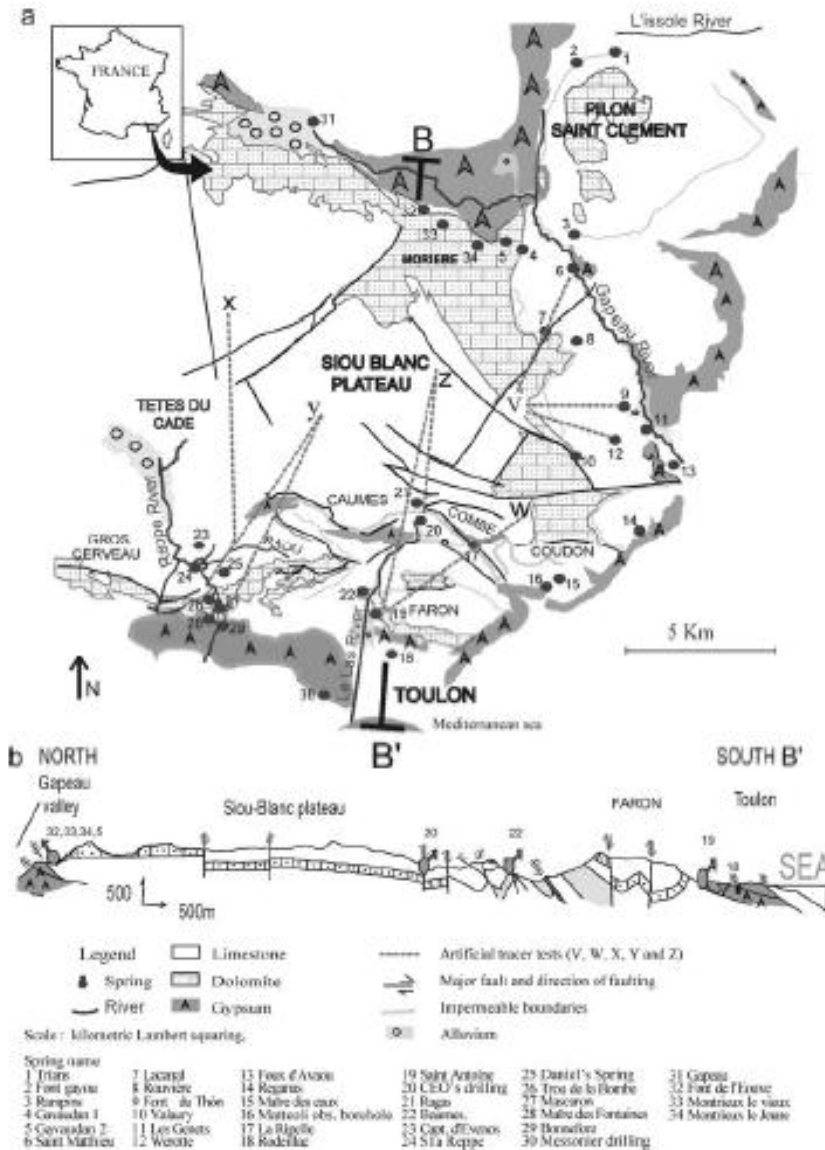


Fig. 3 a Hydrogeological map and b cross section of the Siou-Blanc Plateau and b cross section of the Siou-Blanc Plateau

Input locations	Map code Fig. 3	Mean velocity (v m/h)	Tracer type	Output springs
Aven de La solitude	Z	15<v<20	Fluorescence	Ragas 21, St Antoine 19
Abime de Maramoye	X	3<v<4	Rhodamine	Bonnefont 29, Trou de la Bombe 26, Mascaron 27, Maire des Fontaines 28
Aven des Polonais	V	10<v<18	Rhodamine	Rouviere 8, Font du Thon 9, St Mathieu 6
Aven Gauthier	Y	3.4<v<4.1	Fluorescence	Bonnefont 29, Trou de la Bombe 26, Mascaron 27, Maire des Fontaines 28
Aven du Caniveau	W	7	Lithium	St Antoine 19

Table 3 Artificial tracer tests undertaken by Lamarque et al. (2000). Tracer test identifiers are shown in Fig. 3  
Input locations Map code

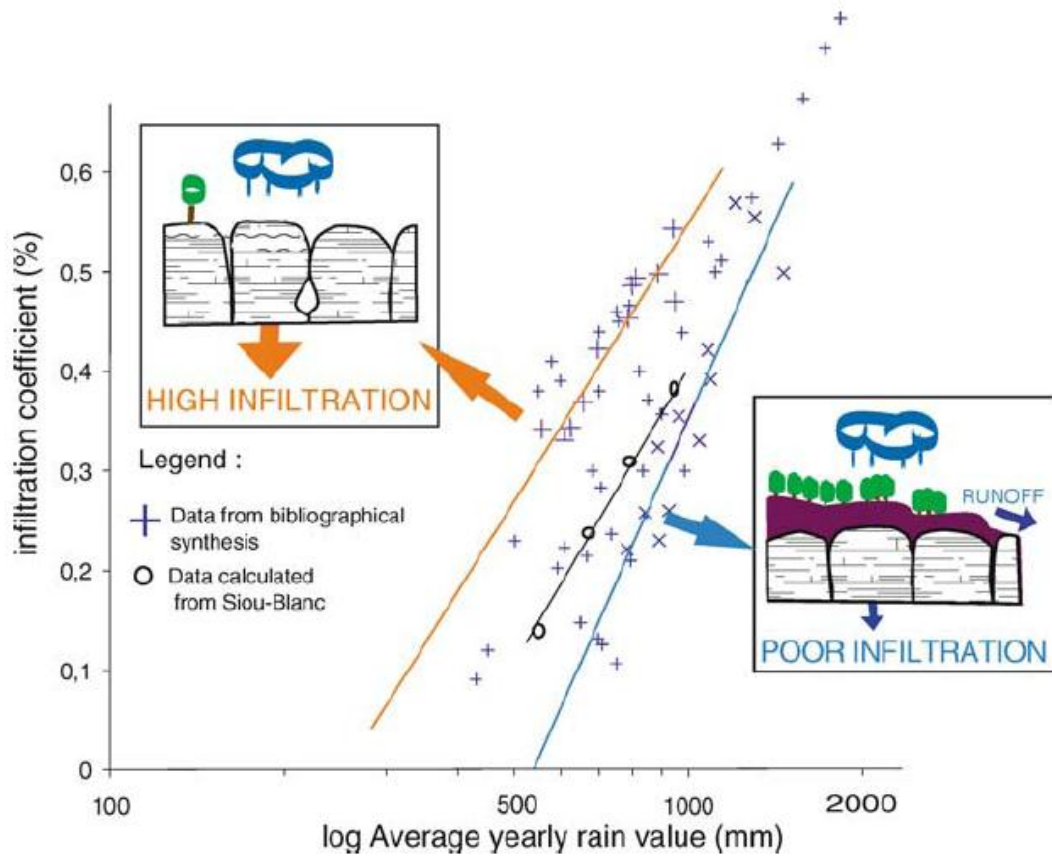


Fig. 4 Infiltration coefficient versus rainfall value. Data are from Cova and Durozoy (1980), Laty 1981, Vernet and Vernet (1981), Puig (1987), Andreo (1996) and Reynaud (2000) and calculations are from the Pilon Saint Clément recharge area

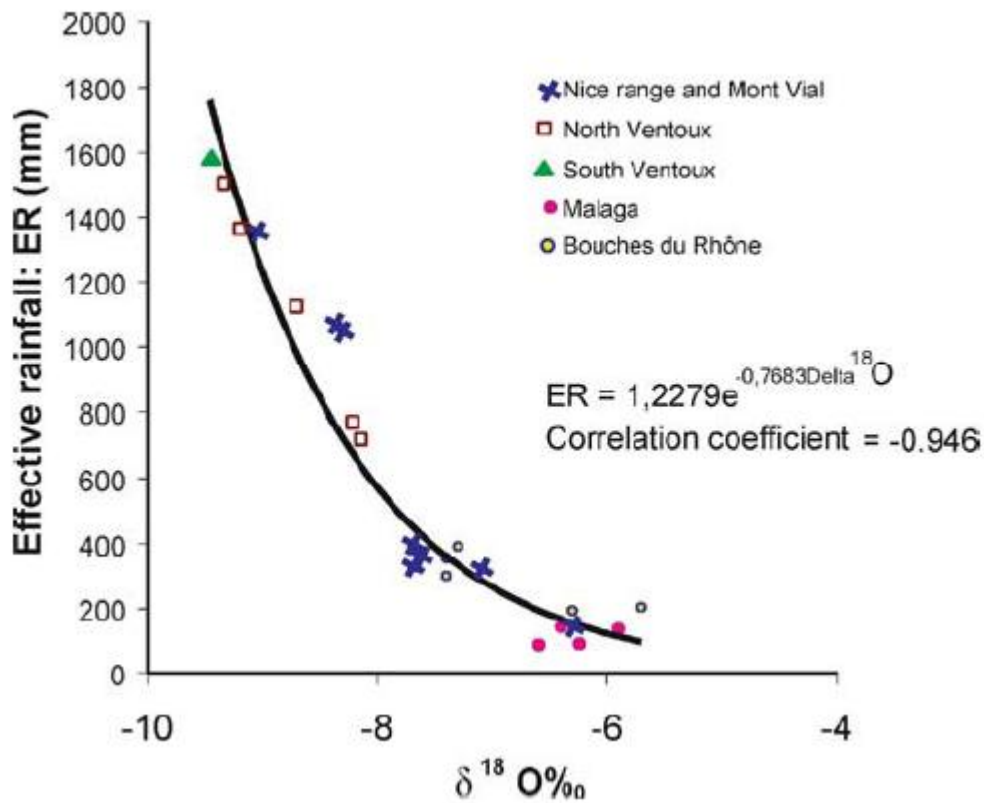


Fig. 5 Effective rainfall versus  $\delta^{18}\text{O}$  content in rainfall. Data are from Vernet and Vernet (1981), Puig (1987), Andreo (1996) and Reynaud (2000)

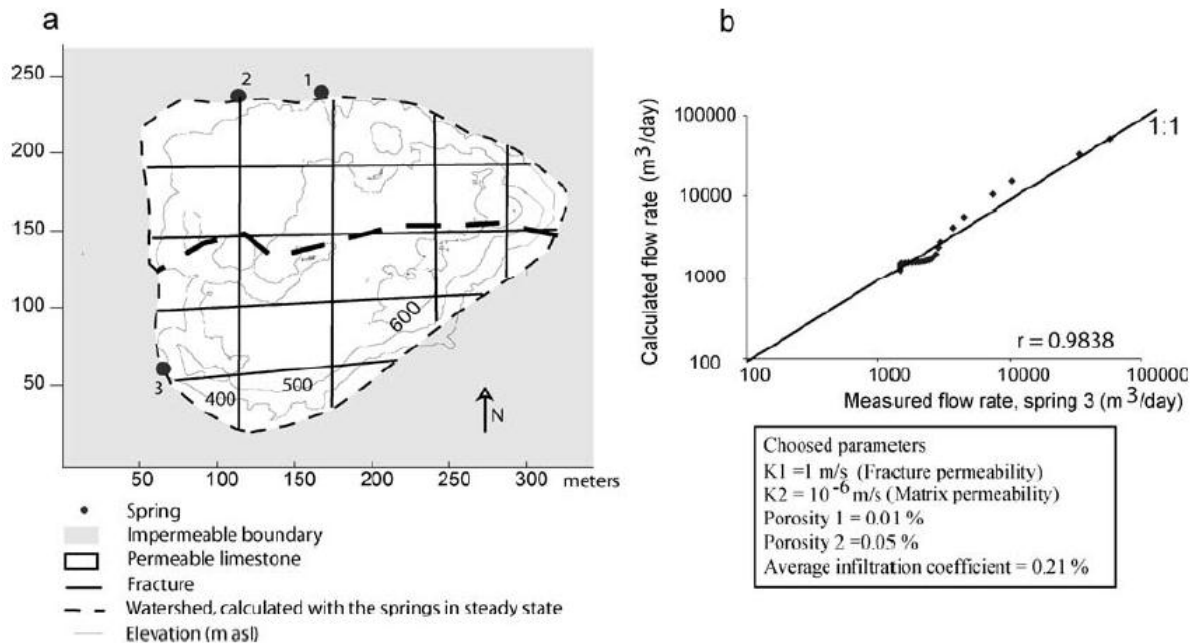


Fig. 6 The Pilon Saint Clement model: a numerical determination of the watershed (steady state calculation, calibrated with low flow rate at the spring), and b chosen model parameters

$\delta^{18}\text{O} = 0.0053 \times \text{elevation} - 3.25$ (estimated with field data)	
Infiltration gradient	Calculated $\delta^{18}\text{O}$ ‰
0 mm/100 m	-6.05
2 mm/100 m	-6.08
5 mm/100 m	-6.36
10 mm/100 m	-6.72
15 mm/100 m	-7.05
$\delta^{18}\text{O}$ measured at the Rampins spring no. 3	-6.7

Table 4 Calibration of the numerical model with  $\delta^{18}\text{O}$  values calculated for different infiltration gradients  $\delta^{18}\text{O} = 0.0053 \times \text{elevation} - 3.25$  (estimated with field data) Infiltration gradient Calculated  $\delta^{18}\text{O}$  ‰

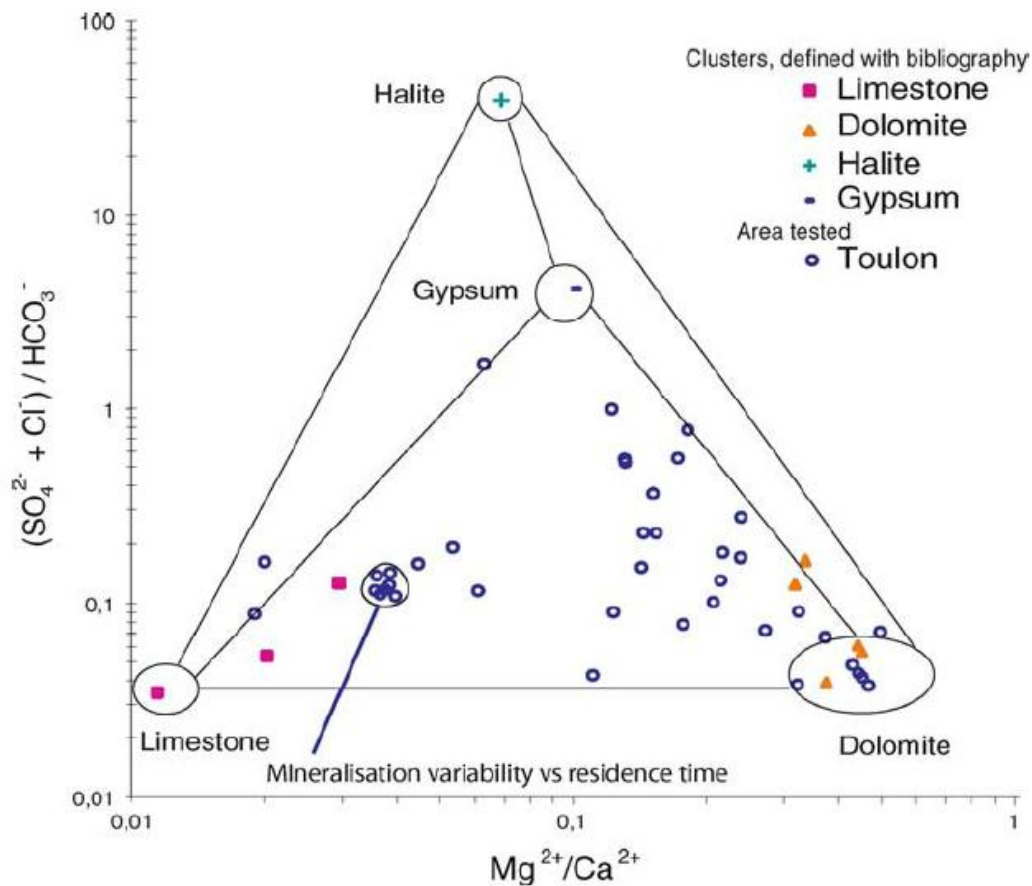
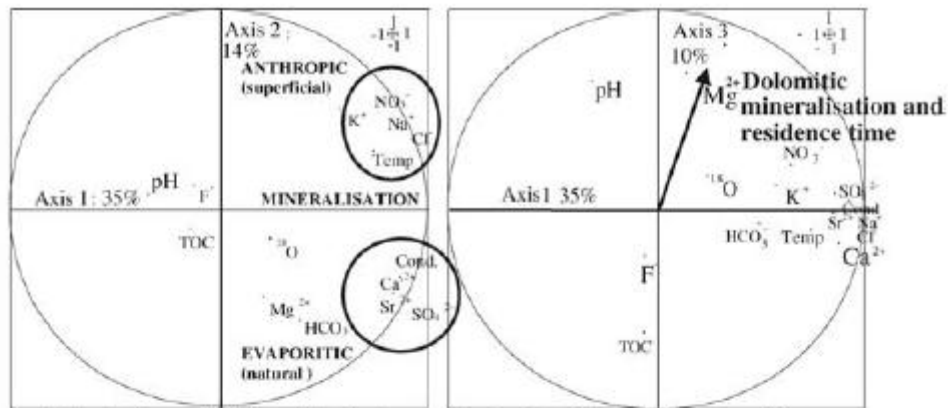
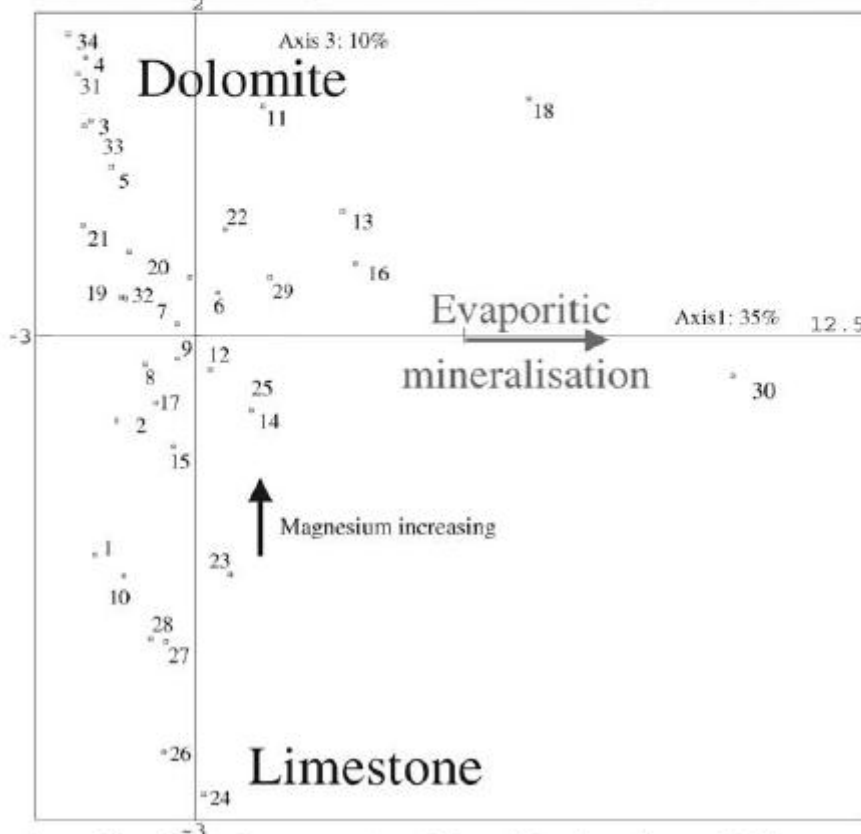


Fig. 7 Component mixture of karst water chemistry. Evolution of the ratio  $\text{Mg}^{2+}/\text{Ca}^{2+}$  and  $(\text{SO}_4^{2-} + \text{Cl}^-)/\text{HCO}_3^-$ . The clusters were built with data from Cova and Durozoy (1980), Laty (1981), Vernet and Vernet (1981), Puig (1987), Petelet et al. (1998), Emily (2000), Fairchild et al. (2000) and Reynaud (2000). The plotted data correspond to the Siou-Blanc spring measurements





Correlation circle axes 1 and 2, explained variance 49% Axes 1 and 3, explained variance 45%



Sampling data along axes 1 and 3 explained variance 45%

Fig. 8 Principal component analysis of water chemistry measurements at the Siou-Blanc springs

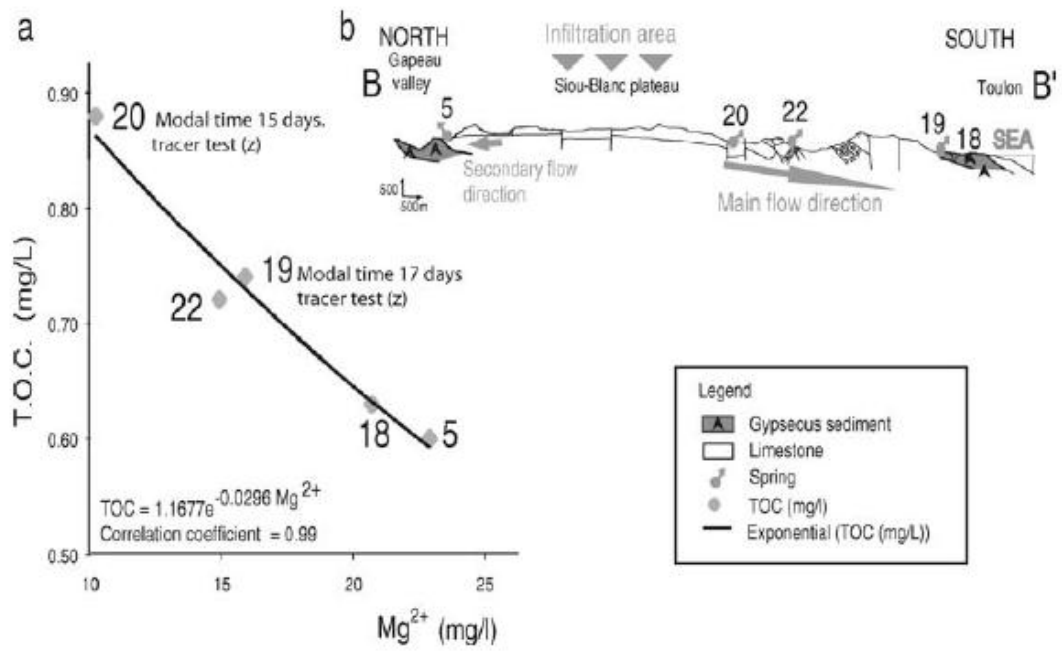


Fig. 9 a Total organic carbon measurements versus magnesium contents of the Siou-Blanc karst springs. b A schematic cross section shows the relationship between measurements and residence time across the Siou-Blanc Plateau