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# Implications of the spatial variability of infiltration-water chemistry for the investigation of a karst aquifer: a field study at Milandre test site, Swiss Jura

J. Perrin · P.-Y. Jeannin · F. Zwahlen

**Abstract** The Milandre test site is an ideal karstic aquifer for studying the spatial heterogeneity of groundwater chemistry. Numerous observation points can be sampled: the spring, the underground river and its tributaries, and boreholes at different depths. The main causes of the spatial variability of the chemical parameters are: nature and localisation of the input, the structure of the infiltration zone, chemical reactions (transit time vs. reaction kinetics) and mixing of different waters. Physico-chemical data on springs discharging from the karstic system represent the sum of this spatial heterogeneity. Therefore, it is difficult to interpret the global-chemical response with a simple mixing model of the aquifer subsystems (runoff, matrix reservoir, epikarst). Chemical constituents related to agricultural inputs show important seasonal variations (coefficient of variation approximately 15%) and parameters linked to rainfall ( $\delta^{18}\text{O}$ ) and to the aquifer ( $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ) present variations of less than 5%. This result indicates the importance of water storage in the epikarstic aquifer for periods of a few months.

**Résumé** Le site test de Milandre est un aquifère karstique idéal pour étudier l'hétérogénéité spatiale des éléments chimiques majeurs car de nombreux points d'observation sont accessibles : source, rivière souterraine et affluents, forages à différentes profondeurs. Les principales causes de la variabilité spatiale des paramètres chimiques sont : nature et localisation des intrants, la structure de la zone d'infiltration, la réactivité des paramètres (temps de transit vs. cinétique de réaction) et le mélange des eaux. Les chimiogrammes observés à la source du système karstique représentent la somme de cette hétérogénéité spatiale. Il est de fait difficile, pour un tel aquifère,

d'interpréter la réponse chimique globale en termes de mélanges d'eau des différents sous-systèmes de l'aquifère (ruissellement, réservoir matriciel, épikarst). Les éléments chimiques correspondant aux intrants agricoles montrent des variations saisonnières relativement importantes (Coefficient de variation d'environ 15%) alors que les paramètres liés à la pluie ( $\delta^{18}\text{O}$ ) et à l'aquifère ( $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ) présentent des variations de quelques pour cents. Un tel résultat indique un stockage d'eau d'au minimum quelques mois dans l'épikarst.

**Resumen** La zona de ensayos de Milandre (Suiza) es un acuífero kárstico ideal para estudiar la heterogeneidad especial de la química de las aguas subterráneas. Se puede muestrear numerosos puntos de observación, incluyendo manantiales, ríos subterráneos y sus tributarios, y sondeos a diferentes profundidades. Las causas principales de la variabilidad espacial de los parámetros químicos son las siguientes: naturaleza y localización de la entrada, estructura de la zona de infiltración, reacciones químicas (tiempo de tránsito versus la cinética de las reacciones), y mezcla de aguas diferentes. Los gráficos hidroquímicos de los manantiales en el sistema kárstico representan la suma de esta heterogeneidad espacial. Por tanto, es difícil interpretar la respuesta química global con un modelo de mezcla simple de los subsistemas acuíferos (escorrentía, reservorio de la matriz, epikarst). Los parámetros asociados a aportaciones de origen agrícola muestran variaciones estacionales importantes, con un coeficiente de variación en torno al 5%, mientras que los parámetros vinculados a la precipitación ( $\delta^{18}\text{O}$ ) y al acuífero (calcio, bicarbonato) presentan variaciones inferiores al 5%. Este resultado indica que se produce un almacenamiento importante de agua durante un par de meses en el acuífero epikárstico.

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## Introduction

Groundwater physico-chemical parameters are increasingly used for obtaining information on the structure and behaviour of karstic aquifers. Combined with hydraulic observations, they are used to estimate water-transit

times, percentage of water issued from different parts of the aquifer, reactivity within the aquifer, vulnerability, and transport processes. Parameters recorded during flood events have been interpreted in terms of proportions of diffuse and point recharge (Scanlon and Thraikill 1987; Wicks 1997; Mayer 1999; Lakey and Krothe 1996; Hess and White 1988; Vervier 1990; Worthington et al. 1992), existence and importance of subsurface storage (Williams 1983, Lastennet and Mudry 1997, Bakalowicz et al. 1974), and percentage of quick and matrix flow (Blavoux and Mudry 1983, Kiraly and Müller 1979). Hydrochemistry can also be used for testing conceptual models of the hydraulic behaviour of karst aquifers (Kiraly and Müller 1979, Grasso and Jeannin 1998).

Often these studies try to extrapolate observations at the spring to the basin scale. Such an upscaling can cause some limitations in the validation of the interpretation. In order to avoid this, several researchers recorded chemical parameters inside the karstic aquifer. These studies consider several topics such as the chemical evolution and kinetic processes along drains (Wicks and Engeln 1997, Groves 1992), residence times of waters issuing from different tributaries (Wicks 1997), and description of the spatial and temporal variability in the water chemistry (Perrin 1997, Mayer 1999, Liñan et al. 1999).

The current project enters this second category of hydrochemical studies in which observations are made at different points in the aquifer. The first step, presented in this paper, considers the spatial variability of groundwater chemistry. The second step, which will be published later, aims at describing the temporal variability of some points selected from the observations made in the first phase. The main objectives are as follows:

- Characterisation of the spatial variability of the parameters by sampling different tributaries within the aquifer
- Determination of the causes that control the spatial variability
- Evaluation of the information that can be inferred from the different types of natural tracers at the spring of a karstic system

Such an empirical approach should improve the interpretation of karstic spring chemical responses and bring new ideas on solute transport and vulnerability of karst groundwater. The Milandre test site has been chosen for its accessibility and its well-documented hydrodynamic behaviour (Jeannin 1996), which plays a prominent role in the chemistry of karstic aquifers (Kiraly and Müller 1979, Grasso 1999).

## Study Area

The Milandre test site is a karstic aquifer located in the Swiss tabular Jura in the vicinity of Basle (Fig. 1). Figure 2 presents a geological cross section of the area illustrating the structure of the aquifer, and the diffuse

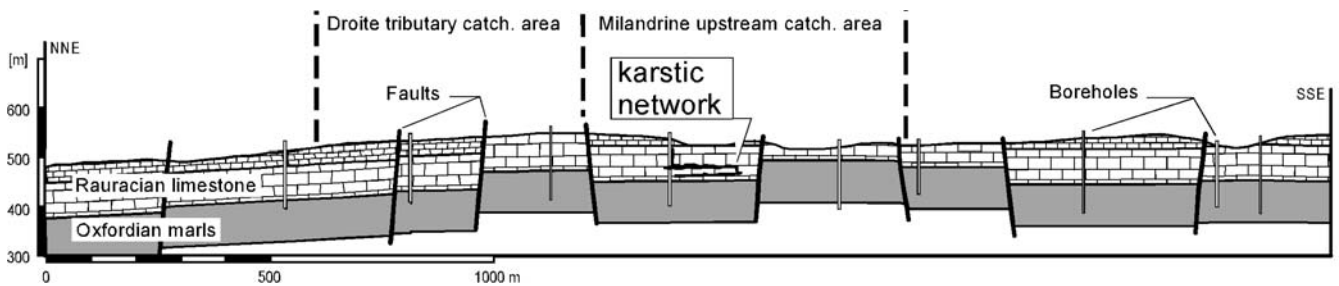
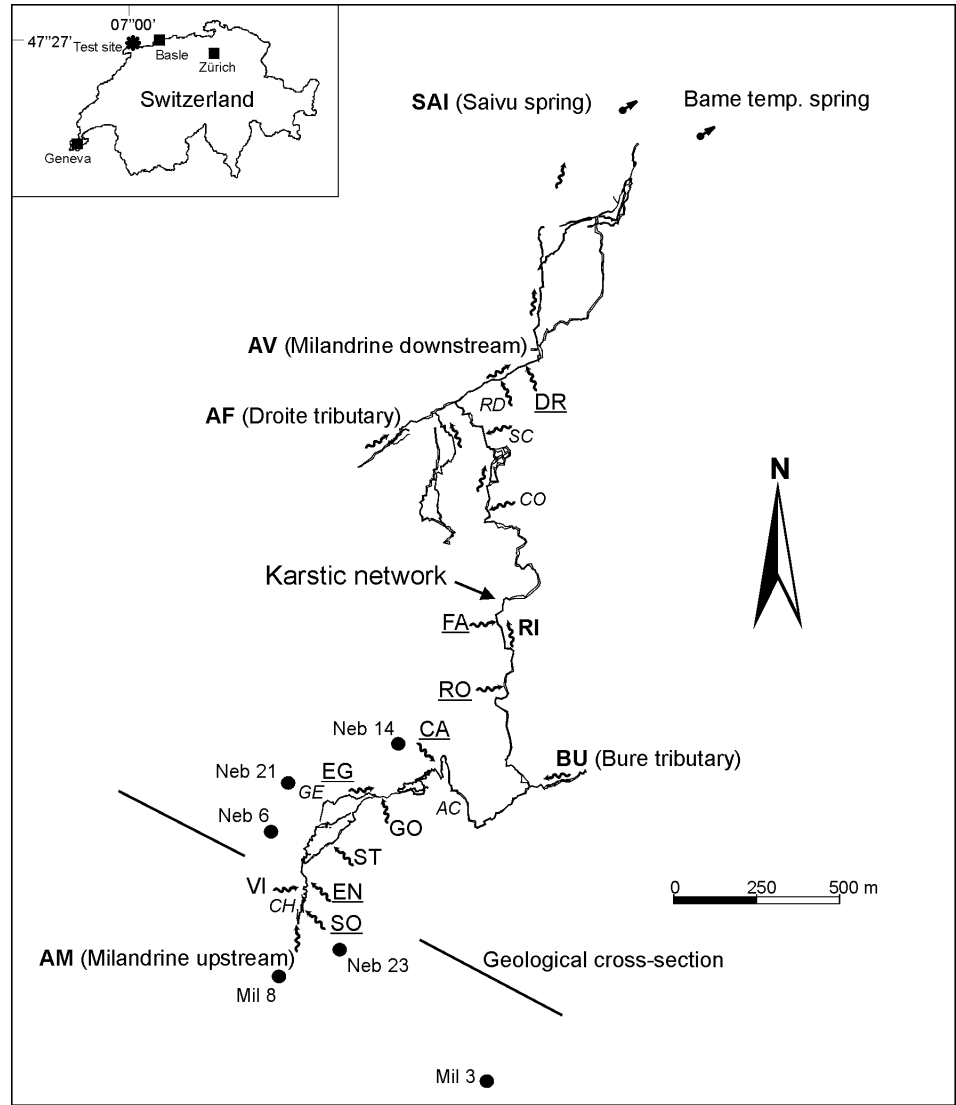
infiltration which recharges the Rauracian limestone overlying the Oxfordian marls and limits the downward flow. Piezometric levels are highly variable (Jeannin 1996), but the unsaturated zone is about 40–80 m thick and the saturated zone is limited to a few tens of metres. A well-developed karstic network drains the aquifer towards Saivu spring (Fig. 1). Sampling points are located along the drain and include the spring, the underground river, and several tributaries.

The area receives approximately 1,000 mm of annual precipitation, which recharges the karst aquifer mainly by diffuse infiltration. The springs of the system are the Saivu, with a discharge varying between 20 and 150 l/s, and the Bame intermittent spring with a discharge reaching up to 1,500 l/s (overflow of the system).

The regional-flow system is mainly controlled by the karst-conduit network and the dip direction of the Oxfordian marls aquiclude. The faulting appears to have a limited effect on flow paths. The catchment area of the Milandre karst system has a common limit to the west with the catchments of Val and Doux karst springs located farther to the west (Fig. 3). To the east, Oxfordian marls plunge eastwards, directing groundwater towards several small karst springs located along the Allaine alluvial plain. This plain limits the basin to the north, and controls the position of the discharge area. To the south, a change in the dip direction directs flow to the important Beuchire karst spring situated 5 km to the southeast. The groundwater divides have been specified by numerous tracing experiments and piezometric measurements (Gretillat 1996, Jeannin 1995, 1996). The surface area of the whole catchment area is 13 km<sup>2</sup>, which corresponds to an estimate made from water-budget calculations. It can be further divided into four sub-basins (Fig. 3).

1. Milandrine upstream sub-basin, surface area 4.6 km<sup>2</sup>, is occupied by 30% cultivated land, 30% forests, and 40% meadows. The small farming village of Villars le Sec (France) is located entirely in this sub-basin. Several tracing experiments were used to determine the precise limits of the catchment (Favre 2001).
2. Bure tributary sub-basin, surface 3.6 km<sup>2</sup> is occupied by 10% cultivated land, 20% forests, and 50% meadows. The Bure village and a military camp are partly located within the catchment. Its limits have been approximated by tracing experiments (Favre 2001).
3. Droite tributary sub-basin, surface area 3.8 km<sup>2</sup> is occupied by 10% cultivated land, 80% forests, and 10% meadows. Tracer tests were not conducted in the catchment, and the limits are based on the geology and a water-budget calculation.
4. Small tributaries and percolation waters comprise a basin which includes all the water inlets encountered along the Milandre cave system. The surfaces of the different subbasins have been estimated by water-budget calculations, and the basins have been located directly above the respective inlets, as no tracing tests were available. The catchment is mainly cultivated in

**Fig. 1** Map of the karstic network showing location of the sampling points. Sites in *bold* (e.g. **RI**) correspond to main tributaries and the underground river, sites *underlined* (e.g. CA) correspond to secondary tributaries, and other sites (e.g. *GO*) correspond to percolation water. Sites in *italics* were sampled once. *Dots* indicate the location of the sampled boreholes



**Fig. 2** Geological cross section showing the aquifer in the Rauracian limestone, the location of the karstic network, and selected boreholes

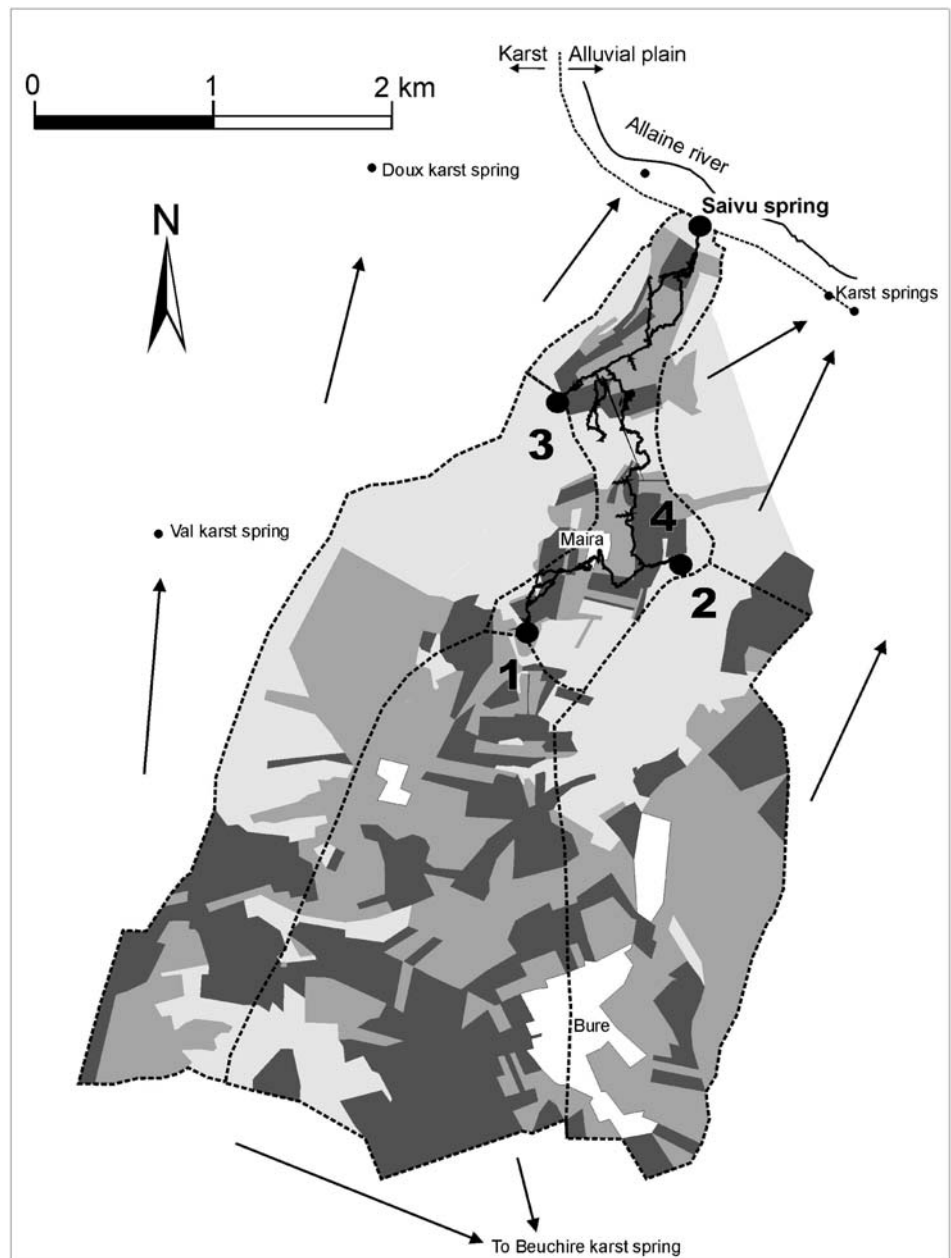
the upstream part, and occupied by forests and pasture in the downstream part.

The underground river, as well as several tributaries, have been equipped with continuous recording stations measuring parameters such as water levels that have been

converted to discharge with a rating curve, specific conductance, and temperature.

The discharge rates of individual tributaries react differently to flood pulses: the drainage axis is very sensitive and shows repeated flooding, whereas some tributaries have delayed responses and others show completely dampened hydraulic responses.

**Fig. 3** Simplified land-use map of the Saivu catchment area. *Pale grey* represents forests, *grey* meadows, and *dark grey* cultivated areas. Villages are represented in *white* and the Milandre cave system is indicated by the *thick irregular line*. The four main subcatchments are delineated by *dashed lines*: 1 is Milandrine upstream (AM), 2 is Bure tributary (BU), 3 is Droite tributary (AF), and 4 corresponds to the catchment of all the secondary tributaries encountered along the cave (i.e. SO, EN, EG, RO, FA, etc.). *Arrows* indicate flow direction



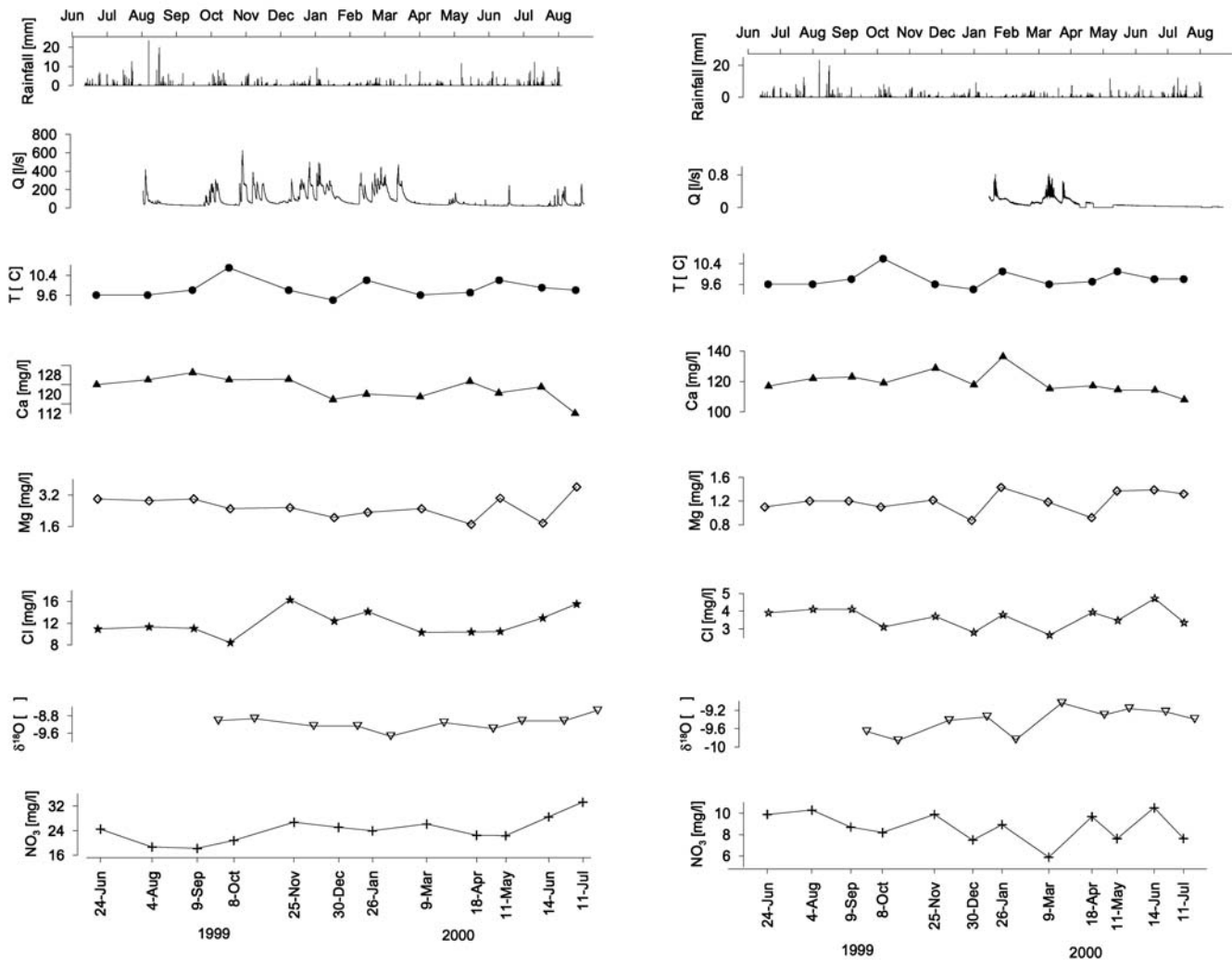
## Methods and Analyses

A preliminary study on the spatial variability of the chemical parameters has shown the adequacy of the site for illustrating the prominent role of land use, mixing processes and structure of the infiltration zone on the groundwater chemistry.

Sampling was done monthly from June 1999 to July 2000. The day of sampling was chosen to represent stable hydraulic conditions in the aquifer. This choice was made in order to get a sample set which was representative of the spatial variability of the infiltration conditions, and the least influenced by concentration changes occurring during flood events (e.g., dilution by fresh infiltrated water). Each time, 15 samples were collected, i.e. three

along the main drain (SAI, AV, AM), two on the main tributaries (AF, BU), seven on secondary tributaries (DR, FA, RO, CA, EG, EN, SO) and three of percolation water (VI, GO ST; Fig. 1). Specific conductance and temperature were measured directly on site, pH was determined within 12 h at sampling temperature, bicarbonate within 24 h by titration, and the other parameters were analysed by ionic chromatography after a 0.45- $\mu\text{m}$  filtration. For cation preservation, filtered samples were acidified to pH < 2 with  $\text{HNO}_3$ . Nitrate concentrations in samples with or without formol were equivalent; therefore, most samples were taken without it.

The quality of the analyses was checked by ionic balances, with acceptable results between 0 and 5%, and by comparing calculated conductivity vs. measured



**Fig. 4** Temporal variation of the physico-chemical parameters for two differing tributaries: site AM (river upstream) on the *left* and site SO (secondary tributary) on the *right*

conductivity. Oxygen-18 analyses were made by the laboratory Hydroisotop GmbH (Schweitenkirchen, Germany) with the standard method of  $\text{CO}_2$  equilibration and purification. The analytical precision is  $\pm 0.15\%$ . Raw data are available on the web under the research topic karst hydrogeology.

## Data Processing

Spatial variability of the water chemistry can be assessed only if the temporal variability of the available data is known and can be removed. The physico-chemical and hydraulic parameters are illustrated in Fig. 4 for sites AM and SO tributaries. The first site (AM) is the underground river in the upstream part whose discharge varies sharply in a short period of time, while other parameters appear to be stable throughout the year. The main reason is that sampling campaigns were carried out under base-flow conditions. The second site (SO) is a secondary tributary

with a stable discharge during the dry season and marked floods in winter. It is less contaminated by nitrates and chloride than at site AM. The physico-chemical parameters also appear to be stable, similar to other sampling sites. Therefore, it can be hypothesised that average concentrations should give a good approximation of the representative chemistry of each outlet under base-flow conditions. This hypothesis has been tested by estimating the importance of the temporal variability.

In order to determine the spatial variability of a constituent, it is necessary to quantify the temporal variability of the data, and to reduce it if necessary. A simple way to characterise the temporal variability of a constituent is via the coefficient of variation (CV, the standard deviation divided by the mean and expressed as a percent). The CV values are given in Table 1. It appears that the most sensitive sites are RO, FA and to a lesser extent the underground river (AM, AV, SAI). The first is an outlet fed partly by sewage water from the Maira



**Table 1** Water-analysis data from the 15 sites located in Fig. 1. Means (a) and coefficient of variation (b) were calculated based on 12 measurements for the physico-chemical parameters and 10

measurements for  $\delta^{18}\text{O}$ . Sampling points are classified in three categories of decreasing flow rate: *Mr* Milandrine River, *Tr* tributary, *Pw* percolation water

Sites	Flow (l/s)	pH	Temp (°C)	Cond ( $\mu\text{S/cm}$ )	Na <sup>+</sup> (mg/l)	K <sup>+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	HCO <sub>3</sub> <sup>-</sup> (mg/l)	$\delta^{18}\text{O}$ (‰)	
(a) Means														
AM	Mr	69.55	7.17	9.78	610.4	3.71	2.38	2.58	122.4	12.00	8.84	24.22	351.9	-9.14
BU	Tr	44.16	7.27	9.84	586.9	3.67	2.30	2.61	114.6	8.71	9.69	17.08	344.1	-9.01
AF	Tr	39.10	7.24	9.51	571.2	1.87	0.44	1.27	116.8	7.42	8.75	16.14	340.8	-9.19
AV	Mr	140.25	7.25	9.86	598.6	3.17	1.87	2.25	117.3	10.20	9.31	21.01	347.8	-9.07
SAI	Mr	140.25	7.26	9.90	598.7	3.42	1.94	2.34	119.5	10.50	9.62	21.55	349.0	-9.10
SO	Tr	0.16	7.23	9.77	554.7	1.95	0.32	1.19	119.4	3.63	8.37	8.73	352.7	-9.36
VI	Pw	0.001	7.27	9.98	610.9	3.21	0.27	2.62	125.9	13.33	11.27	43.50	324.6	-9.02
EN	Pw	0.04	7.30	9.71	576.7	2.34	0.31	1.51	123.2	5.85	11.35	18.21	360.5	-9.37
ST	Pw	0.02	7.26	9.98	663.0	2.46	0.40	1.37	137.3	9.79	16.55	55.93	357.6	-9.32
GO	Pw	0.01	7.34	10.13	711.3	2.41	4.32	2.08	147.4	5.62	12.32	41.92	414.1	-9.51
EG	Tr	0.98	7.29	9.65	636.6	2.21	0.84	1.75	133.5	8.37	13.06	30.06	373.0	-9.24
CA	Tr	0.74	7.14	9.81	671.2	2.51	1.12	2.05	139.1	11.96	12.47	46.47	367.9	-9.10
RO	Tr	0.43	7.28	10.35	683.1	4.72	25.24	3.80	118.5	14.66	10.92	27.60	371.8	-8.64
FA	Tr	0.38	7.26	10.07	564.7	1.51	1.37	1.70	115.8	5.80	6.07	13.52	349.9	-9.27
DR	Tr	1.02	7.24	9.97	585.7	1.77	0.99	2.92	119.3	7.72	8.15	13.00	353.5	-8.97
(b) Coefficient of variation (%)														
AM	Mr	79.08	1.68	3.60	5.77	28.59	46.48	21.90	3.87	19.47	11.44	17.45	5.09	3.39
BU	Tr	75.00	2.24	3.01	5.72	18.13	24.07	34.15	7.91	14.79	6.99	17.36	7.52	1.65
AF	Tr	86.45	1.40	1.58	2.46	9.83	14.38	17.32	3.82	15.38	12.69	22.98	2.97	0.58
AV	Mr	65.07	2.08	2.05	3.85	21.90	47.38	23.11	6.14	20.60	9.51	17.43	6.31	1.50
SAI	Mr	65.07	2.12	1.86	3.94	35.00	51.90	14.86	6.14	22.87	13.42	19.19	6.73	3.51
SO	Tr	156.32	1.29	3.30	5.08	14.25	20.08	14.73	6.21	16.27	17.41	16.07	3.32	2.95
VI	Pw	18.75	2.38	3.81	4.52	18.61	33.80	16.46	5.64	5.87	7.56	9.75	1.72	1.29
EN	Pw	158.97	2.57	3.57	6.18	13.06	28.55	16.90	4.20	9.48	14.18	14.30	1.90	1.38
ST	Pw	158.47	1.40	3.61	5.26	13.30	23.09	16.28	4.73	8.07	7.55	6.64	2.31	1.24
GO	Pw	117.89	2.60	3.12	5.59	12.82	6.74	13.39	2.58	10.08	9.17	10.61	1.74	1.09
EG	Tr	65.21	1.40	3.83	5.49	12.18	13.10	15.52	3.48	12.35	7.87	17.44	2.21	1.39
CA	Tr	60.97	1.06	1.76	7.63	12.33	8.59	17.09	2.43	8.41	7.74	6.91	1.74	1.66
RO	Tr	110.47	2.04	1.32	7.41	39.03	52.64	23.84	5.85	38.43	24.82	32.14	5.96	3.28
FA	Tr	220.29	2.26	1.60	4.19	27.37	68.79	20.80	4.41	36.15	36.91	43.61	5.56	3.30
DR	Tr	101.61	1.61	1.44	3.64	18.31	22.15	29.18	4.68	16.26	24.47	27.59	5.33	2.26

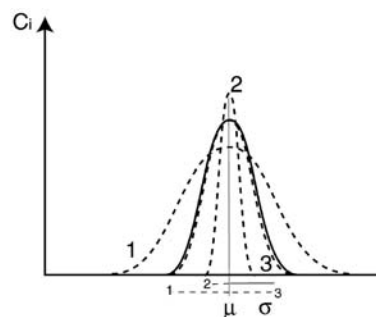
village, the second is an outlet very sensitive to rain events. Other sites have a low temporal variability.

An objective approach for testing the importance of the temporal variability is to compare the standard deviation for intrasites (temporal variability) and the standard deviation for intersites (spatial variability). The principle is illustrated in Fig. 5 with a theoretical example of frequency-distribution curves. Three categories can be distinguished:

1. The standard deviation (SD) intrasite is lower than the SD inter-site
2. The SD intrasite is higher than the SD intersite
3. Both are comparable

The first category means that the temporal variability of the considered site is less important than the spatial variability, the second illustrates the opposite, and the third indicates that the temporal variability of a site is comparable to the spatial variability.

Results are compiled in Table 2, and it appears that the intersite SD is generally higher than the intrasite SD: the temporal variability of the samples is limited and the spatial variability is important for the data of Milandre test site (category 1). The parameters that best illustrate



**Fig. 5** Theoretical frequency distribution curves for a parameter. The solid black curve represents the distribution of the intrasite concentrations. Dashed curves represent the three cases of intersite distribution.  $\mu$  represents the mean and  $\sigma$  the corresponding standard deviations

the spatial variability are nitrate, potassium, sulfate, chloride, and magnesium. In contrast, temperature and  $\delta^{18}\text{O}$ , bicarbonate, and even calcium show close intrasite and intersite SD (category 3).

In karst systems, flood water can present a very different chemistry than base-flow water. As an example, at site AM specific conductance can decrease to 520  $\mu\text{S}/$

**Table 2** Comparison of the standard deviation intersite and intrasite in order to evaluate the importance of the temporal variability of the parameters. The corrected data column gives the standard deviation computed after suppression of the values, which are the most distant from the mean in both directions. *Number in parentheses* indicates the quantity of values removed. Site RO is not considered due to its specific chemistry

	Temp.		Na <sup>+</sup>		K <sup>+</sup>		Mg <sup>2+</sup>		Ca <sup>2+</sup>		Cl <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		NO <sub>3</sub> <sup>-</sup>		HCO <sub>3</sub> <sup>-</sup>		δ <sup>18</sup> O		
	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	Raw data	Corr. data	
Standard deviation intersite																					
AM	0.21	0.21	0.91	0.87	6.26	0.71	0.72	9.97	3.14	2.54	14.13	20.06	20.01	0.21							
BU	0.36	0.19 (3)	1.13	0.73 (1)	1.11	0.56		4.73	2.34	1.01	4.23	17.90		0.31							
AF	0.30	0.18 (1)	0.67		0.55	0.97	0.55 (1)	9.06	1.29	0.68	2.97	25.86	15.90 (1)	0.15							
AV	0.15		0.18		0.06	0.22		4.45	1.14	1.11	3.71	10.14		0.05							
AV	0.20		0.70		0.88	0.52		7.20	2.10	0.89	3.66	21.84	18.56 (1)	0.14							
Standard deviation intrasite																					
SAI	0.18		1.20	0.50 (2)	1.01	0.35		7.34	2.40	1.29	4.14	23.47	16.98 (2)	0.32							
SO	0.32	0.19 (2)	0.28		0.06	0.18		7.42	0.59	1.46	1.40	11.70		0.28							
VI	0.39	0.20 (4)	0.60		0.09	0.43		7.10	0.78	0.85	4.24	5.57		0.12							
EN	0.35	0.18 (3)	0.31		0.09	0.26		5.18	0.55	1.61	2.60	6.86		0.13							
ST	0.36	0.21 (4)	0.33		0.09	0.22		6.49	0.79	1.25	3.72	8.25		0.12							
GO	0.32	0.21 (4)	0.31		0.29	0.28		3.80	0.57	1.13	4.45	7.19		0.10							
EG	0.38	0.19 (2)	0.27		0.11	0.27		4.65	1.03	1.03	5.24	8.24		0.13							
CA	0.17		0.31		0.10	0.35		3.38	1.01	0.97	3.21	6.41		0.15							
FA	0.16		0.41		0.94	0.35		5.11	2.10	2.24	5.90	19.47		0.30							
DR	0.14		0.32		0.22	0.87	0.68 (2)	5.59	1.25	1.99	3.59	18.86		0.20							

cm, Ca<sup>2+</sup> to 94 mg/l, or HCO<sub>3</sub><sup>-</sup> to 300 mg/l (data not used in the present study). These values are far from the average values presented in Table 1. Hence the temporal variability of the data set has to be tested in order to keep only the data which represent the base-flow chemistry of the sampling site.

The following procedure was applied: analyses, which were out of the interval delimited by the standard deviation around the mean, were discarded and thus the intrasite SD was strongly reduced. Corrected mean values have been compared to raw values in Table 1. The difference is systematically lower than 5%. It demonstrates that the raw data are little affected by temporal variations and can be used for the study of spatial variability.

Mean values are given in Table 1. They can be considered as representative of base-flow conditions at each station. The waters are all calcium-bicarbonate types with the exception of site RO, which has anomalously high concentrations of sodium, potassium, and chloride. This outlet is partly fed by sewage effluent from the small village of Maira. Major ion concentrations of sewage water are the following according to Dubreucq (1987): K<sup>+</sup>: 44 mg/l, Na<sup>+</sup>: 91 mg/l, Mg<sup>2+</sup>: 8.5 mg/l, Ca<sup>2+</sup>: 107 mg/l, SO<sub>4</sub><sup>2-</sup>: 51 mg/l, Cl<sup>-</sup>: 57 mg/l, NO<sub>3</sub><sup>-</sup>: 11 mg/l. These values confirm the influence of sewage on the chemistry of the RO tributary site. Owing to its peculiar chemistry, site RO has been discarded in the statistical analysis presented in the following section.

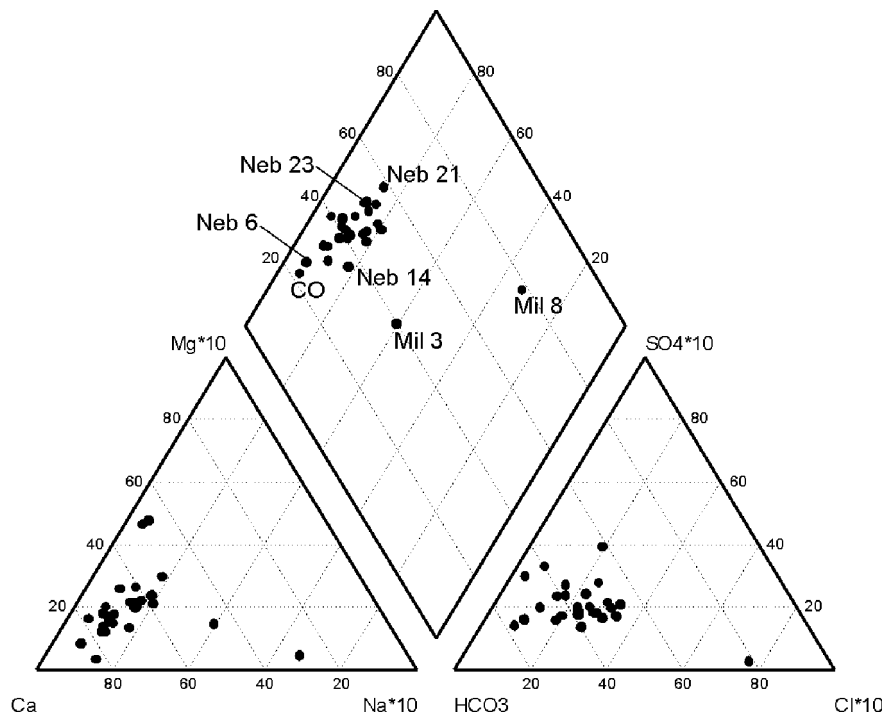
Measured parameters can be split into two groups: the first, comprising nitrates, sodium, potassium, magnesium, chloride, and even sulfates, is characterised by significant spatial variability and high CV. The second includes parameters with a more homogeneous distribution and low CV: pH, oxygen isotopic ratio, temperature, calcium, and bicarbonates.

### Illustration of the Spatial Variability

The Piper diagram (Fig. 6) represents average values obtained for the 15 sites and additional single measurements taken from six boreholes and six tributaries (Table 3). The boreholes are located in forested areas (Neb 6, Neb 23), in meadows (Neb 21, Mil 8) and in cultivated land (Neb 14, Mil 3). Additional tributaries are distributed along the underground river. The spatial variability of the water chemistry is clearly illustrated by the elongated cluster of sampling points. It is possible to distinguish several groups and boreholes Mil 3 and Mil 8 are contaminated by NaCl inherited from former salt-tracing experiments. These tracer tests were carried out in order to test the relation between the boreholes and the Milandrine upstream (Maréchal 1995).

Sewage water at site RO deviates in the direction of the NaCl pole. The points near the Ca<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup> pole represent waters not influenced by human activities (CO, Neb 23, SC, Neb 6, SO). The points approaching the Mg<sup>2+</sup>-NO<sub>3</sub><sup>-</sup> pole are the most influenced (Neb 21, Neb 14, ST, CA, VI, GE) and the points in between seem to be

**Fig. 6** Piper diagram showing the spatial variability of the data set. Concentrations of  $Mg^{2+}$ ,  $Na^+$ ,  $SO_4^{2-}$ ,  $Cl^-$  are multiplied by a factor 10 in order to improve the readability of the graph



**Table 3** Data for samples collected once on one tributary (Tr), five percolation waters (Pw), and six boreholes (Bor)

Site	Flow (l/s)	pH	Temp. (°C)	Cond. ( $\mu S/cm$ )	$Na^+$ (mg/l)	$K^+$ (mg/l)	$Mg^{2+}$ (mg/l)	$Ca^{2+}$ (mg/l)	$Cl^-$ (mg/l)	$SO_4^{2-}$ (mg/l)	$NO_3^-$ (mg/l)	$HCO_3^-$ (mg/l)	
RD	Tr	0.2	7.19	9.9	570	1.57	0.78	2.08	122.6	5.58	13.2	8.3	356
CH	Pw	0.003	7.16	9.8	496	2.20	0.20	2.40	91.0	6.60	8.2	12.0	298
AC	Pw	0.1	7.18	9.8	633	1.97	0.81	1.87	115.8	7.51	9.0	27.3	364
SC	Pw	0.01	7.29	10.1	566	1.47	0.94	6.79	110.0	2.81	6.0	2.7	351
CO	Pw	0.05	7.11	9.6	587	0.96	0.54	1.54	120.0	2.39	5.3	0.1	372
GE	Pw	0.08	7.16	10.0	770	3.49	5.24	2.88	144.0	14.50	12.4	55.6	394
Mil 3	Bor		7.12	9.3	543	10.61	1.89	2.10	109.1	8.64	6.0	17.2	337
Mil 8	Bor		7.22	9.3	824	36.67	0.62	1.30	137.9	75.33	3.5	15.4	367
Neb 6	Bor		7.11	8.5	563	1.24	0.00	0.75	125.8	1.07	12.7	13.2	359
Neb 14	Bor		7.12	8.8	779	4.56	0.03	1.86	158.4	6.71	8.1	112.9	377
Neb 21	Bor		7.26	9.5	624	2.39	0.00	0.31	125.4	7.70	21.7	67.8	289
Neb 23	Bor		7.20	8.4	563	1.20	0.09	6.58	113.6	2.42	15.4	3.0	356

the result of mixing of these tendencies (Milandre underground river and its main tributaries BU and AF).

### Main Causes of the Spatial Variability

#### Land Use

Man-induced impacts are highly variable at the basin scale with large amounts of fertilisers used in cultivated areas to none in forested land. At the Milandre test site, about 20% of the catchment is cultivated, 40% is grazing pasture, and 40% forest (Fig. 3). The most contaminated sampling points drain only cultivated catchments (ST, EN, VI, Neb 14, Neb 23), whereas slightly contaminated tributaries are fed by a mixing of pristine and contaminated waters.

Solute inputs from agriculture can be estimated with the help of Table 4, which summarises data found in the

literature and obtained from this study data. The values from Milandre are based on quantities of fertilisers used by the farmers and on two analyses of rainwater. Missing information has been supplemented with data presented by Pedersen et al. (1991). Their data are a compilation from several agricultural statistical tables.

The theoretical leachate chemistry is computed with the following equations:

$$M_{pi}(\text{leachate}) = M_{pi}(\text{rain}) + M_{pi}(\text{fertilizer}) + M_{pi}(\text{manure}) - M_{pi}(\text{plant}) \quad (1)$$

$$V_w = I_a S \quad (2)$$

$$C_{pi}(\text{leachate}) = \frac{M_{pi}(\text{leachate})}{V_w} 10^3 \quad (3)$$

where



**Table 4** Origin and quantification of the chemical constituents issued from agricultural activities based on the literature and data from this study. The last column gives an approximation of leachate concentration based on a mean actual infiltration of 500 mm (Jeannin and Grasso 1995). Values taken from Pedersen et al. (1991) and accepted for this study are shown in italics

		Rain (kg ha <sup>-1</sup> year <sup>-1</sup> )	Fertilizer (kg ha <sup>-1</sup> year <sup>-1</sup> )	Manure (kg ha <sup>-1</sup> year <sup>-1</sup> )	Plant removal (kg ha <sup>-1</sup> year <sup>-1</sup> )	Available for leaching	
						(kg ha <sup>-1</sup> year <sup>-1</sup> )	(mg/l)
K <sup>+</sup>	This study	5	50	37	80	12	2.4
	Dubreucq (1987)	1.9	5		50		
	Pedersen et al. (1991)	3	45	85	80	53	
Na <sup>+</sup>	This study	3	1	15	6	13	2.6
	Dubreucq (1987)	2.6					
	Pedersen et al. (1991)	2	1	15	6	30	
Mg <sup>2+</sup>	This study	0	4	6	6	4	0.8
	Dubreucq (1987)	0.7	2.5		10		
	Pedersen et al. (1991)	3	4	10	6	11	
Ca <sup>2+</sup>	This study	10	29	20	25	34	6.8
	Dubreucq (1987)	18	25		25		
	Pedersen et al. (1991)	3	29	30	25	40	
SO <sub>4</sub> <sup>2-</sup>	This study	16	33	45	21	73	14.6
	Dubreucq (1987)	35	8.5		12		
	Pedersen et al. (1991)	39	33	45	21	96	
Cl <sup>-</sup>	This study	6	38	30	35	39	7.8
	Dubreucq (1987)	19	3				
	Pedersen et al. (1991)	37	38	30	35	70	
NO <sub>3</sub> <sup>-</sup>	This study	10	340	320	330	330	66
	Dubreucq (1987)	20	62		530		
	Pedersen et al. (1991)	75	550	528	330	823	

$M_{pi}$  = mass of parameter  $p_i$  (kg ha<sup>-1</sup> year<sup>-1</sup>)

$C_{pi}$  = concentration of parameter  $p_i$  (mg/l)

$V_w$  = yearly water volume infiltrated on one hectare (m<sup>3</sup> ha<sup>-1</sup> year<sup>-1</sup>)

$I_a$  = actual infiltration (m year<sup>-1</sup>)

$S$  = surface (m<sup>2</sup>)

Equation (1) gives the mass of fertiliser available for leaching per hectare and per year. This mass is converted to a concentration by Eqs. (2) and (3) using an actual yearly infiltration value of 500 mm.

The results (Table 4) are in agreement with concentrations measured in Milandre (Table 1) except for calcium. The results indicate that the source of the ions K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> is mainly due to fertilisers. Farmers use mainly combined chemical fertilisers containing nitrogen, phosphorus, potassium, and magnesium. Manure and liquid manure are used as complementary sources, which contain all the pollution-related constituents. Thus, land use in the subcatchment plays a key role in the spatial variability of groundwater chemistry, at least for these constituents.

Inputs are also dependent on the actual infiltration, knowing that evapotranspiration processes act in a completely different manner depending on whether the area is cultivated or forested. This process can increase concentrations of the ions, influence the temperature of the infiltrated water, or even change isotopic ratios. Evapotranspiration can cause a  $\delta^{18}\text{O}$  enrichment of around 1.2‰ in rain compared to the water collected in lysimeters (Blavoux 1978). This process should be a determinant for the differences of isotopic ratios at the

sampling sites (from -8.64‰ for site RO to -9.51‰ for site EG), as the altitude effect on precipitation isotopic composition is negligible at the Milandre site.

### Chemical Reactions

In case of limestone dissolution along the drainage axis, dissolution-related physico-chemical parameters (calcium, bicarbonate and specific conductance) concentrations should increase from AM to AV and SAI. The contrary occurs due to dilution by less mineralised waters issued from the major tributaries BU and AF.

Even if pH has not been measured in the field, qualitative values of calcite saturation indices could be calculated by the Phreeqe software with an accuracy of  $\pm 0.15$ . Calcite-saturation indices range between 0.12 to 0.25 (unpublished data). Highest values are obtained for seepage waters issued from speleothems located at the base of the unsaturated zone (sites EN, ST, GO). Other samples are close to equilibrium with respect to calcite. However, dissolution-related constituents show a clear spatial variability. As dissolution processes occur mainly in the unsaturated zone, the observed spatial variability is acquired in this subsystem. It is well known that water gets its acidity by dissolution of soil CO<sub>2</sub> (White 1988). Unpublished measurements on the Milandre site show that soil pCO<sub>2</sub> is spatially heterogeneous with generally more CO<sub>2</sub> in thicker soils; at 90 cm depth on the same day pCO<sub>2</sub> changes from 1.2% under a forested area, and to 3.6% under tillage. This variability is likely to directly influence the differences observed in Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations.

Nitrates and sulfates are subject to redox reactions under certain conditions. At the Milandre test site, oxidation processes are limited to the soil zone and the epikarst. Below, the concentrations of constituents are stable during their transit to the spring. During flood events, the underground river can show traces of nitrites, but in concentrations lower than 1 mg/l.

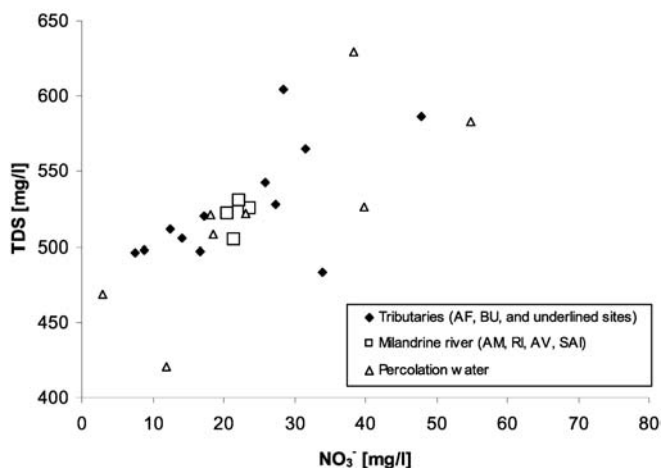
**Mixing Processes**

The role of mixing is illustrated in Fig. 7. The drainage axis (Milandre River) is located in the middle of the plot, as the water is mixed with tributary waters of contrasting solute concentrations. Nitrates can be less than 10 mg/l in some outlets and over 50 mg/l in others. The underground river concentrations are stable at around 21 mg/l.

Mixing processes are often described in the literature but generally only two or three end members have been considered: matrix-reservoir water and direct infiltration (Blavoux and Mudry 1983); rainwater and pre-storm water (Lakey and Krothe 1996); concentrated infiltration, diffuse infiltration, and water issued from low permeability materials (Vervier 1990); conduit storage, subcutaneous storage, and fresh water (Williams 1983, Sauter 1992); and rain, soil, epikarst, and phreatic water (Lee and Krothe 2001).

On the Milandre test site, a more complex image of mixing processes occurs, as chemistry is heterogeneous even at the low stage where only one end member (storage) should be present. However, it has to be kept in mind that the site is probably more heterogeneous than other “better preserved” aquifers due to the impact of agricultural seepage on groundwater chemistry.

The prominent role of mixing on the water chemistry of the main drain has been tested by a simple mixing model given by the following equation:



**Fig. 7** Correlation between mineralisation (TDS) and nitrates, and illustration of the mixed origin of the spring water. The correlation is attributed to changes in the soil thickness in the respective catchment. Forested catchments have thin unfertilised soils with a low production of CO<sub>2</sub>, and thus produce less mineralised waters. On the other hand, cultivated catchments have thick fertilised soils with an elevated production of CO<sub>2</sub>, giving more mineralised waters

$$C = \frac{\sum_i C_i Q_i}{\sum_i Q_i} \tag{4}$$

where

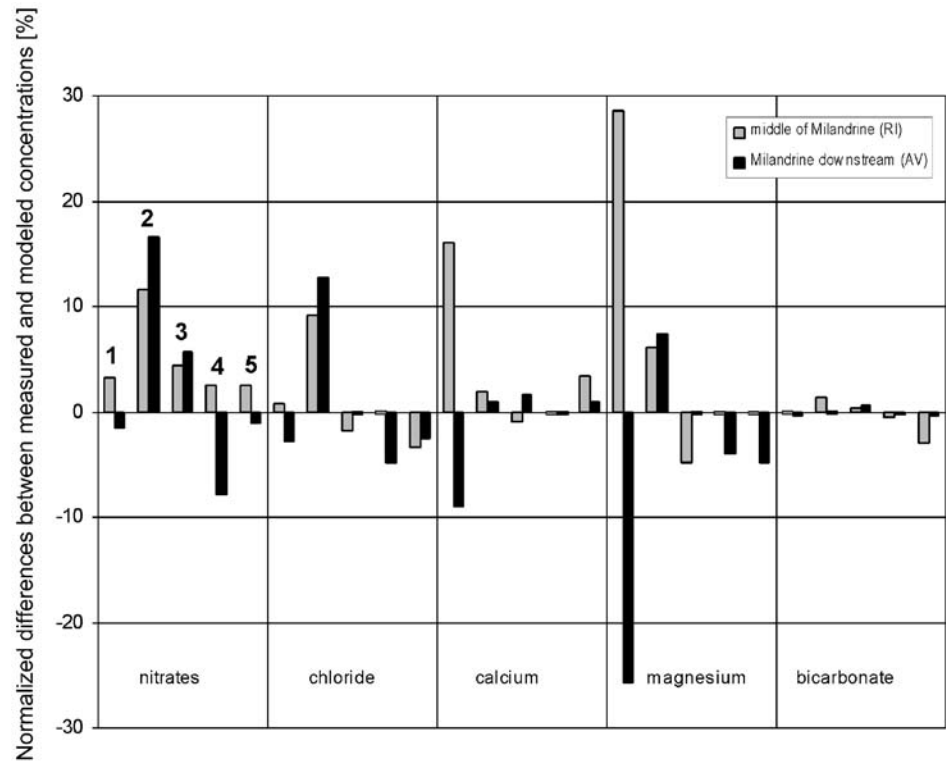
- C = modelled concentration
- C<sub>i</sub> = measured concentration at site i
- Q<sub>i</sub> = discharge at site i

Sampling sites with low discharge was not considered, as their impact on the modelled concentration is not significant. Thus, the concentration at site RI (middle part

**Table 5** Results of the mixing-model calculation for 11 July 2000 sampling campaign

Site	AM	SO	CA	EG	BU	RO	AF	DR
Q (l/s)	32	0.02	0.41	0.78	29	0.14	30	0.26
NO <sub>3</sub> <sup>-</sup>	33.3	7.6	43.2	21.7	12.8	30.7	12.1	21.6
Flux (mg/s)	1,065.6	0.2	17.7	16.9	371.2	4.3	363.0	5.6
c <sub>calc</sub> (mg/l)		33.3	33.4	33.1	23.7	23.7	19.9	19.9
c <sub>meas</sub> (mg/l)						26.6		23.5
Cl <sup>-</sup>	15.5	3.3	11.6	7.1	6.9	20.9	6.4	5.5
Flux (mg/s)	496.0	0.1	4.8	5.5	200.1	2.9	192.0	1.4
c <sub>calc</sub> (mg/l)		15.5	15.4	15.2	11.4	11.4	9.8	9.7
c <sub>meas</sub> (mg/l)						12.5		10.9
Ca <sup>2+</sup>	112.0	108.0	134.0	127.0	95.0	107.0	112.0	109.0
Flux (mg/s)	3,584.0	2.2	54.9	99.1	2,755.0	15.0	3,360.0	28.3
c <sub>calc</sub> (mg/l)		112.0	112.3	112.6	104.4	104.4	106.9	106.9
c <sub>meas</sub> (mg/l)						106.0		108.0
Mg <sup>2+</sup>	3.6	1.3	2.5	1.8	2.7	4.4	1.3	3.4
Flux (mg/s)	115.20	0.03	1.03	1.40	78.30	0.62	39.00	0.88
c <sub>calc</sub> (mg/l)		3.6	3.6	3.5	3.1	3.2	2.6	2.6
c <sub>meas</sub> (mg/l)						3.4		2.8
HCO <sub>3</sub> <sup>-</sup>	326	346	362	368	281	349	323	314
Flux (mg/s)	10,432	7	148	287	8,149	49	9,690	82
c <sub>calc</sub> (mg/l)		326	326	327	306	306	311	311
c <sub>meas</sub> (mg/l)						310		311

**Fig. 8** Comparison of the concentrations calculated by a simple mixing model and the measured concentrations in the middle part of Milandrine (site *RI*) and on Milandrine downstream (site *AV*). The calculation is based on the results of five sampling campaigns: 26-Jan-00 (1), 11-July-00 (2), 30-Dec-99 (3), 11-May-00 (4), 09-March-00 (5)



of the main drain) has been computed with data from sites AM, SO, EG, CA, BU and RO. The concentration at site AV (downstream part of the drain) has been calculated with the same sites as mentioned above, including the AF and DR sites.

Measurements taken on July 11, 2000, are given in Table 5 for chloride (conservative ion), nitrate (sensitive to redox processes), and ion indicators of calcite dissolution or precipitation (calcite, magnesium, bicarbonate). Five sets of measurements are summarised in Fig. 8. Normalised differences between modelled and measured values are comparable to the conservative ion chloride, except for the magnesium sampled on January 26, 2000. This exception is probably due to inaccurate analyses on samples from sites RI and AV. The normalised difference between modelled magnesium concentration at site AV and the measured concentration at the SAI spring is only 4%.

The consistency of the mixing model pinpoints the absence of significant chemical reactions (dissolution, redox) in the aquifer during stable hydraulic conditions. Changes in the water composition by mixing are mainly caused by the high-discharge tributaries sites (BU and AF). The other outlets account for less than 1 mg/l variation even if their chemistry is clearly distinct compared to that of the underground river.

**Table 6** Classification of the physico-chemical parameters by their statistical and chemical characteristics. *SV* Spatial variability; *CV* coefficient of variation

	High SV and CV	Low SV and CV
Non-reactive	K <sup>+</sup> , Na <sup>+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	T, δ <sup>18</sup> O
Reactive		pH, HCO <sub>3</sub> <sup>-</sup> , Ca <sup>2+</sup>

## Discussion

### Specific Characteristics of the Parameters

The measured physico-chemical parameters can be classified in order to establish the types of information they supply. This classification is based on the discussion in the preceding paragraphs and is summarised in Table 6. Three groups can easily be distinguished: land-use related parameters, dissolution parameters, and parameters dependent on physical processes. The same type of classification can be extended to karstic aquifers with the following characteristics: agriculture on the catchment, oxygen-saturated groundwater, rapid flow, and the occurrence of a shallow saturated zone (50 m or less).

The next step is to see what kind of information can be obtained from these groups using spatial and temporal (on a seasonal and on a flood scale) observations.

### Land-Use Related Parameters

Spatial variability will denote a contrasted land use in the catchment with cultivated land, pasture, forests, and/or urbanised areas. Temporal variability on a seasonal scale will indicate changes in the input rate and/or low storage.

**Table 7** Calculated residence time following the equation of Ternan (1972). Values range between 15 and 163 days. The 30 days obtained for Saivu spring illustrates the mixing of waters with different ages. The highest residence times are obtained for tributaries draining catchments located in cultivated areas with thick soils

Site	Ca hardness CV (%)	Residence time (day)
AM	3.63	75
BU	8.35	15
AF	3.15	99
AV	6.02	29
SAI	5.88	30
SO	6.02	29
VI	5.55	33
EN	3.88	66
ST	4.52	49
GO	2.62	140
EG	3.18	97
CA	2.42	163
RO	5.08	40
FA	4.15	58
DR	4.22	56

For a flood event, it will indicate changes in the respective contribution of the subcatchments.

### Dissolution Parameters

Spatial variability will be an indicator of contrasting soil CO<sub>2</sub> availability (dependent on soil thickness, altitude, and vegetation type). Temporal variability on a seasonal scale should denote climatically related changes in CO<sub>2</sub> production. For a flood event, it will be an indication of transit times, as dissolution kinetics will compete with flow velocity. This assertion has been developed by Ternan (1972) and Wicks (1997) for computing groundwater residence time using the CV of calcium hardness. In both cases, the waters issued partly from a point recharge with high temporal variability and low residence time. In Milandre (Table 7), residence times vary widely, and it appears that shorter times occur in tributaries draining forested or urbanised areas, whereas longer times are characteristic for drainage of cultivated land. Reservoirs in the unsaturated zone seem larger under cultivated areas with thicker soils. However, the calculated residence times for such reservoirs have to be considered as qualitative as the data set is too reduced to have strong statistical validity.

### Parameters Dependent on Physical Processes

Spatial variability of physico-chemical parameters are mainly related to altitude differences of the subcatchments (not the case in Milandre), but could also denote contrasts in evapotranspiration rates due to differences in land use and vegetation. Temporal variability on a seasonal scale will give an idea of residence times in the aquifer. For a flood event, it will indicate the occurrence of rapid infiltration of fresh water.

These distinctions will be helpful for the interpretation of the data collected during flood events and should allow a better interpretation of physico-chemical data.

### Conceptual Model of Solute Transport

To summarise the observed spatial variability of infiltration-water chemistry, a conceptual model of solute transport is presented in Fig. 9 showing the physical and chemical processes which play a role in the groundwater chemistry of the Milandre test site. Rainwater is a major source of ions in natural areas, especially for sulfate, chloride, nitrate and potassium (Table 2). In cultivated or inhabited areas, fertilisers, sewage, and salt for road management release large amounts of ions into the system. Evapotranspiration, plant consumption, ion exchange, oxidation, and CO<sub>2</sub> hydration occur mainly in the soil zone. These processes lead to important solute-concentration changes. Soil is therefore the subsystem of major importance, as its thickness governs land use (thick soils are cultivated whereas thin soils are forested) and its physical properties control many biochemical processes.

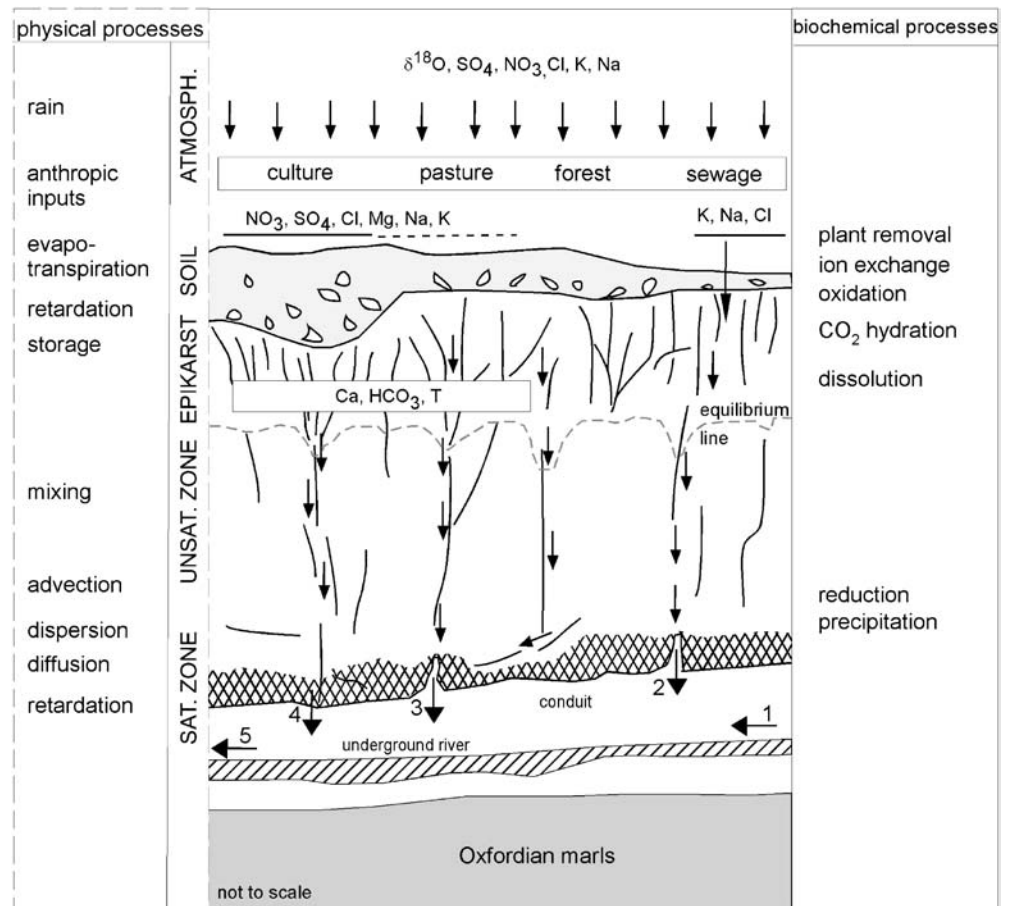
Below the soil, a significant part of the water is stored in the epikarst subsystem or circulates slowly in the unsaturated zone, as indicated by the low temporal variability of  $\delta^{18}\text{O}$ , which is the sole non-reactive parameter with an evenly distributed input (Table 1). Transit times in the epikarst seem in most cases sufficient for reaching equilibrium with respect to calcite. Water then discharges to the drains and the saturated zone. No chemical reactions (reduction, precipitation) could be observed under normal hydraulic conditions along the drainage axis. Water chemistry variations are essentially caused by a mixing of waters derived from different infiltration zones.

Graphs of physico-chemical properties at the springs represent the integration of the contrasts in the chemistry of the tributaries. For this type of karst aquifer, application of a mixing model with two end members (e.g., runoff and matrix reservoir) would be a dangerous approximation. Such models do not take into account the existing spatial variability of the physico-chemical parameters. However, the chemistry of the tributaries will give information on the prevailing land use for each catchment, CO<sub>2</sub> production, and storage as outlets fed by a large reservoir (e.g., in the epikarst) should have a relatively constant chemistry throughout the year. In contrast, outlets draining zones of rapid infiltration will show significant variations in physico-chemical properties.

The use of mixing models is correct below the so called "equilibrium line" (Fig. 8). This line represents the trace of the surface below which groundwater becomes chemically equilibrated with respect to a given constituent. Each chemical reaction will have its own surface depending on the reaction kinetics. This surface is dependent on the transit time and therefore on the hydraulic conditions in the aquifer. During flood events, the line will move downstream and could reach the spring for some dissolved species (e.g., HCO<sub>3</sub><sup>-</sup>).



**Fig. 9** Conceptual model of solute transport at Milandre test site. Observation points (i.e. groundwater samples) are located in the conduit. Some waters come directly from the epikarst (2), others from the saturated zone symbolised by the *cross-hatched* surface (4); most of them are a mixing of different origins (3). The chemistry of drain water (1) is changed by the arrival of tributaries (2, 3, 4) and mixing gives drain water (5) a different chemistry



### Comparison with Models from the Literature

Conventional studies (Bakalowicz 1979, Blavoux and Mudry 1983, Lastennet and Mudry 1997) define natural tracers for the aquifer subsystems. They separate waters moving from the soil epikarst containing high chloride and sodium concentrations, from waters in low permeability materials of the saturated zone with high magnesium and sulfates concentrations. For the Milandre aquifer, this separation is not possible due to the importance of the man-induced sources of these constituents. Natural tracers of the aquifer subsystems have to be defined after a preliminary study to determine the spatial variability and the true origin of the chemical constituents.

End-member mixing models (Lee and Krothe 2001) cannot be applied to aquifers such as those at Milandre because within each subsystem the water chemistry is too heterogeneous. The main drawbacks of these models are that they need a unique chemical composition for each system and that they do not take into account possible chemical changes due to reactions during flood events.

These mixing models seem to be most appropriate for karst aquifers with a dual recharge mode, i.e., point recharge and diffuse recharge. Generally, point recharge has a chemistry inherited from another geological context, which clearly contrasts with diffuse recharge chemistry (Vervier 1990, Scanlon and Thraikill 1987, Worthington et al. 1992).

### Conclusions

The major conclusions of this study are:

1. The spatial variability of the groundwater chemistry of the Milandre test site has been clearly established. Land use controls to a large extent the concentrations of pollution-related constituents in the tributaries of the karst system. The less contaminated tributaries are fed by basins which are mainly forested, whereas the more contaminated ones drain basins which are cultivated. The mixing of waters of contrasting chemistry can modify notably the final water composition. Chemical reactions have a limited effect on the observed spatial variability of the infiltration-water chemistry, at least in normal flow conditions.
2. The soil zone plays a prominent role in the spatial variability of the groundwater chemistry. Its properties control land use and  $\text{CO}_2$  production.
3. Generally the sampling points show the occurrence of saturated waters with respect to calcite and oxygen. In normal flow-conditions, chemical reactions (dissolution, oxidation-reduction) are limited to the soil and the epikarst zone. Downstream, changes in groundwater chemical composition are mainly due to mixing processes.



4. Different types of tracers can be distinguished: non-reactive, spatially heterogeneous tracers such as nitrate, which are directly related to land use; reactive tracers such as bicarbonate, which are mainly dependent on dissolution processes; and conservative tracers represented by oxygen isotopes, which have a spatially homogeneous character. These tracers do not have the same time-dependency. Therefore, temporal measurements should be made to draw inferences about transit times and the geometry of the aquifer flow system.

In the future, detailed investigations of the epikarst and the soil should be carried out in order to better understand the reactivity of these subsystems. Sampling during flood events will allow for estimations about storage and transit times in the unsaturated zone. The importance of mixing compared to chemical reactions should be assessed. The objective is to develop a conceptual model consistent with the observed hydraulics and transport characteristics of the infiltration zone. The resulting model should help to improve existing aquifer-protection methods for application to karst aquifers.

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