

Using turbidity dynamics and geochemical variability as a tool for understanding the behavior and vulnerability of a karst aquifer

M. Fournier · N. Massei · M. Bakalowicz ·
L. Dussart-Baptista · J. Rodet · J. P. Dupont

Abstract In a karst system, the characterization of transport properties is based on the comparison of natural tracers observed at the inlet (a swallow hole on the karst plateau) and the outlets of the system (a spring and a well). At Norville, northwest France, electrical conductivity (EC) and turbidity (T) were used as natural tracers for characterizing dissolved elements (surface water geochemistry) and particulate matter transport, respectively. Two methods were used for this study: (1) a comparison of the relations between EC, T and spring discharge (Q) by means of normalized EC– T – Q curves, and (2) a principal component analysis (PCA) including water geochemistry data in addition to EC, T and Q . Three different characteristic flood events have been chosen for the analyses. EC– T – Q curves highlighted the direct transfer, resuspension and deposition of particles during their transport in the karst network. Transport from the swallow hole to both the spring and the well appeared to be dominated by karst-conduit flow. On the other hand, PCA results showed a diffuse source of contamination of groundwaters by nitrate and a point-source contamination of groundwaters by streaming/runoff surface waters with high turbidity and phosphate concentration infiltrated at the swallow hole.

Résumé Dans un système karstique, la caractérisation des propriétés de transport est basée sur la comparaison des traceurs naturels observés à l'entrée (une dépression sur le plateau karstique) et à la sortie du système (une source et un puits). A Norville, Nord-Ouest de la France, la conductivité électrique (EC) et la turbidité (T) ont été

utilisées comme traceurs naturels pour caractériser les éléments dissous (géochimie des eaux de surface) et le transport des particules en suspension, respectivement. Deux méthodes ont été utilisées dans cette étude: (1) une comparaison des relations entre EC, T et le débit de la source (Q) au moyen de courbes EC– T – Q normalisées, et (2) une analyse en composante principale (ACP) incluant les données géochimiques de l'eau en complément de EC, T et Q . Trois différents événements de crues caractéristiques ont été choisis pour les analyses. Les courbes EC– T – Q ont mis en évidence le transfert direct, la remise en suspension et le dépôt des particules durant leur transport dans le réseau karstique. Le transport de la dépression vers la source et le puits apparaît comme dominé par l'écoulement en conduit karstique. D'un autre côté, les résultats de l'ACP ont montré une source diffuse de la contamination des eaux souterraines par les nitrates et une contamination ponctuelle des eaux souterraines par des eaux de surface de ruissellement et de cours d'eau présentant une turbidité et une concentration en phosphate élevées, infiltrées dans la dépression.

Resumen En un sistema kárstico, la caracterización de las propiedades de transporte se basa en la comparación de trazadores naturales observados en la entrada (una sima somera en una superficie kástica) y la salida del sistema (un manantial y un pozo). En Norville, al Noroeste de Francia, la conductividad eléctrica (EC) y la turbidez (T) se usaron como trazadores naturales para caracterizar los elementos disueltos (geoquímica de aguas superficiales) y transporte de material particulado, respectivamente. Para este estudio, fueron utilizados dos métodos: (1) una comparación entre las relaciones de EC, T y descarga del manantial (Q) mediante curvas normalizadas EC– T – Q , y (2) un análisis de componentes principales (PCA) que incluye datos geoquímicos además de EC, T y Q . Para el análisis, se seleccionaron tres eventos de flujo característicos. Las curvas EC– T – Q pusieron de manifiesto la transferencia directa, resuspensión y sedimentación de las partículas durante su transporte en el sistema kárstico. El transporte desde la sima somera al manantial y al pozo parece estar dominado por el flujo por los conductos kársticos. Por otro lado, los resultados de PCA muestran una fuente difusa de contaminación de aguas subterráneas por nitratos y una contaminación puntual de aguas

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M. Fournier (✉) · N. Massei · L. Dussart-Baptista · J. Rodet ·
J. P. Dupont
Department of Geology,
University of Rouen, 76821, Mont-Saint-Aignan Cedex, France
e-mail: matthieu.fournier@etu.univ-rouen.fr

M. Bakalowicz
CREEN-ESIB,
Riad El Solh BP 11-514, Beirut, 1107 2050, Lebanon

subterráneas por aguas superficiales con alta turbidez y concentraciones de fosfatos infiltradas en la sima somera.

Keywords Karst · Hydrochemistry · Groundwater statistics · Contamination · Conceptual models

Introduction

Karst hydrosystems are well known for their vulnerability to contamination due to their complex and unique characteristics which make them very different from other aquifers: high heterogeneity created and structured by groundwater flow, i.e., large voids, high flow velocities up to several hundreds of m.h^{-1} , high flow rate springs up to some tens of $\text{m}^3.\text{s}^{-1}$ and most of all, a strong connection with surface watersheds. Karst systems can be affected by either rapid, delayed or slow infiltration processes through surficial formations, swallow holes or epikarst, and on the other hand by rapid horizontal flows (high groundwater flow velocity in conduits, sometimes underground runoff; Ford and Williams 1989; Vaute et al. 1997; Bertrand-Krajewski et al. 1998; Beaudreau et al. 1999; Mahler et al. 1999, 2000; Katz et al. 2001; Panno et al. 2001; Plagnes and Bakalowicz 2002; Dussart-Baptista 2003; Vesper and White 2003; Bakalowicz 2005). The great complexity of their functioning makes the characterization of their vulnerability difficult. Depending on rainfall/recharge conditions, karst spring-water chemistry represents variable mixtures of groundwater and surface water (Massei 2001; Nebbache et al. 2001; Panno et al. 2001; Massei et al. 2003). Nitrate and phosphate can contaminate karst aquifers by infiltration of surface waters which flow in

agricultural watersheds (Igbal and Krothe 1995; Katz et al. 2001; Nebbache et al. 2001; Panno et al. 2001). They are recognized as two of the most important sources of groundwater contamination in the northwest of France (Nebbache et al. 2001). The determination of the sources of nitrate in groundwater is an important first step in the process of improving groundwater quality, and perhaps reducing the amount of nitrate discharging to water bodies downstream. Among the huge amount of recent works that have addressed the problem of groundwater flowpaths and karst aquifer functioning, the most noticeable are those of: Herczeg et al. 1997; Labat et al. 2000a,b; Lee and Krothe 2001; Pinault et al. 2001; Desmarais and Rojstaczer 2002; Denic-Jukic and Jukic 2003; Emblanch et al. 2003; Lee and Krothe 2003. These studies are mostly based on natural geochemical tracers or time series analyses. Full deterministic approaches for investigating and modelling karst aquifer transport properties are sometimes possible (Hauns et al. 2001; Jeannin 2001; Cornaton and Perrochet 2002; Grasso et al. 2003) but they usually require quite a good knowledge of the geomorphologic features of the system and are mainly designed to describe specific quantitative behaviors.

Actually, the use of turbidity and electrical conductivity has already been extensively used by many authors (Bakalowicz 1979; Plagnes 1997; Mahler and Lynch 1999; Mahler et al. 1999; Reynaud et al. 1999; Massei et al. 2002a,b, 2003; Alessandro Grasso et al. 2003; Birk et al. 2004; Valdes et al. 2005; Massei et al. 2006; Valdes et al. 2006). However, lots of these works still remain rather descriptive, as they are, most of the time, based on the description of the time series. Additionally, hysteresis curves have been used in a couple of studies (Valdes et al. 2005; Valdes et al. 2006) using only conductivity and

Fig. 1 Location of the study site at Norville in the lower Seine Valley, France (modified from Massei et al. (2002b), with permission from Elsevier)

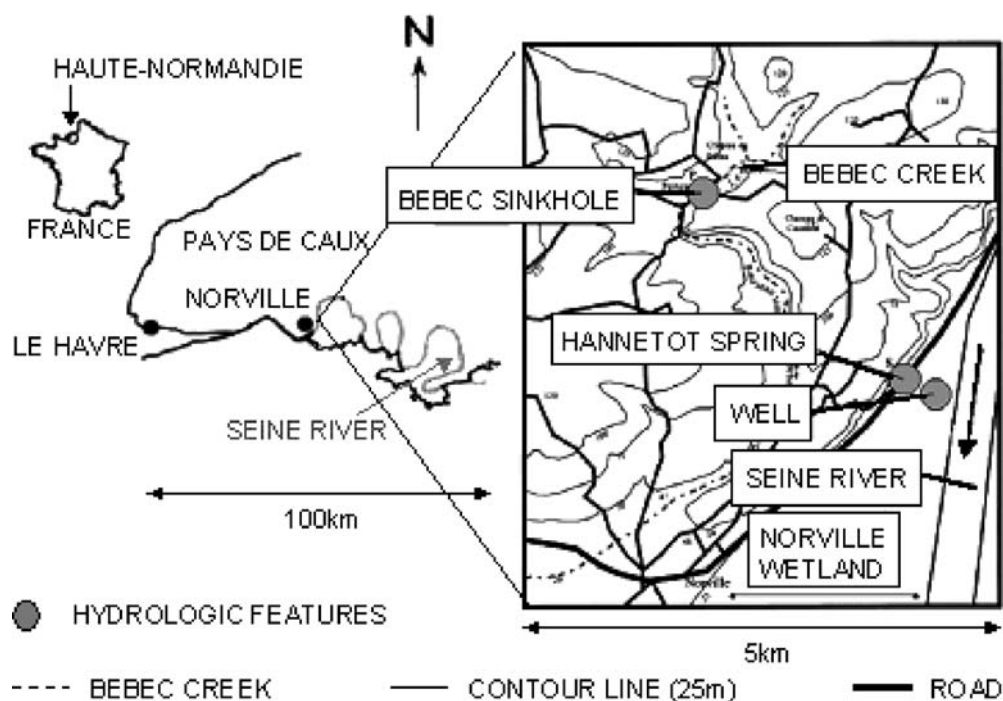
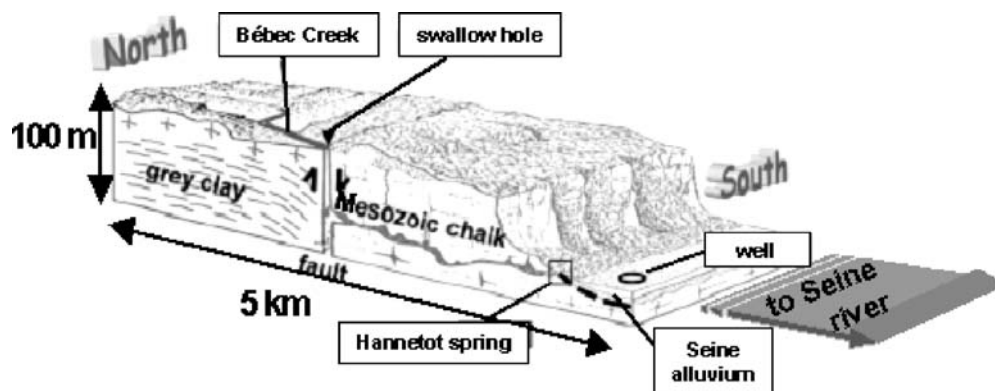


Fig. 2 Geomorphological three-dimensional diagram of the Bébéc-Hannetot karstic system; the well is located in the alluvial plain of the Seine River, which flows 300 m to the south (reprinted from Massei et al. (2002b), with permission from Elsevier)



turbidity, and other authors have already used principal component analysis (PCA) to describe the geochemical variations at karst outlets.

In this work, these approaches are deepened and coupled:

1. Discharge has been systematically added to the hysteresis curves, hence providing hydrodynamical information, necessary for the understanding of transport properties.
2. Turbidity analyses were compared to classical major ions analyses and included in PCA. PCA was performed for data collected at the karst outlet and also for three different sites (swallow hole, spring and well) during three rain events with different intensities. This comparison appeared to be decisive in understanding the behavior of the system with respect to particulate/dissolved mass transfer.
3. The two previous approaches are coupled and compared, which constitutes the innovative aspect of this study of karst aquifer vulnerability.

Study site and methods

Geomorphological and hydrogeological settings

The karst system studied is located in the Pays de Caux (Haute-Normandie, France) on the north bank of the Seine River, about 40 km from the Seine estuary (Fig. 1). From a morphological point of view, the Pays de Caux is characterized by chalk plateaus covered with clay-with-flints owing to chalk weathering (Laignel et al. 1999, 2002a,b). These clay layers are themselves covered with Quaternary silts. The clay-with-flints constitutes a fairly impervious layer that covers the chalk. Swallow holes locally penetrates the chalk through the above-mentioned impervious layer, resulting in a strong connection of the surface with the aquifer. Plateaus are situated on the sides of the lower Seine Valley, which is filled by Holocene alluvial deposits.

The karst system has been widely studied and its boundaries (geographical limits, hydraulic connections between swallow hole, spring and well) have become quite well known (Massei 2001; Massei et al. 2002a,b, 2003; Dussart-Baptista 2003; Dussart-Baptista et al. 2003a,b). The main

Fig. 3 Residence time distribution for four dye tracer tests. Spring discharge remained fairly constant and no rainfall occurred during each test (reprinted from Massei et al. (2003), with permission from Elsevier)

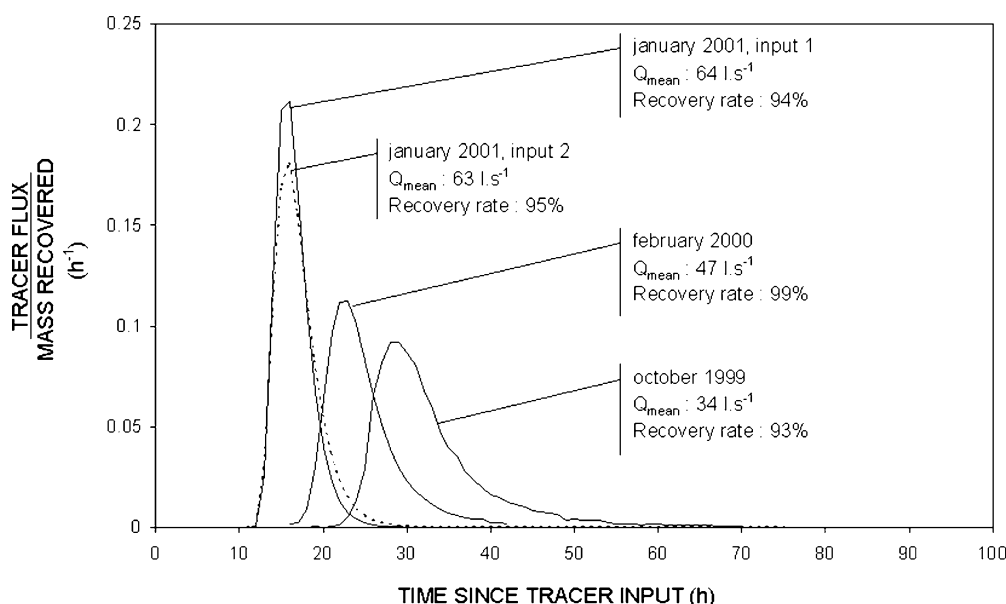


Table 1 Measured data and calculated parameters from dye tracer test (reprinted from Massei et al. (2003), with permission from Elsevier)

Period of the tracer test	October 1999	February 2000	January 2001 (1)	January 2001 (2)
Mean spring discharge (l.s^{-1})	34	47	64	63
Mean transit time t_m (h)	32.6	23.6	16.5	17.0
Mean apparent transfer velocity (m.h^{-1})	67.5	93.2	133.3	129.4
Volume of main conduit (m^3)	3.996×10^3	3.970×10^3	3.801×10^3	3.885×10^3
Tracer recovery rate (%)	93	99	94	95
Variance of the normalized breakthrough curves	0.59	0.59	0.49	0.44
Dispersivity (m)	19.7	18.9	12.7	12.9

karst system features are a swallow hole (or sinkhole), a spring, and a well. The swallow hole is the point of infiltration of Bébec Creek on the plateau, and drains a small watershed of about 10 km^2 . Virtually 100% of land use in the watershed consists of agriculture (wheat and cornfields with spreading of farmyard manure and chemical fertilizers, dairy herds, etc.). Soils on the plateau, consisting of silts approximately 10 m thick, are highly susceptible to crusting, compaction, and erosion, particularly during autumn and winter sowing. Bébec Creek discharge is variable, from 3 l.s^{-1} in dry summer periods to more than 500 l.s^{-1} after major winter storms. During these periods, turbidity in Bébec Creek can reach more than 1,000 NTU (nephelometric turbidity units).

The spring is located at the base of the plateau at a place named 'Le Hannetot'. The Hannetot spring is a barrier spring and originates from the permeable formation of the chalk karst aquifer. It is an overflow in this part of the aquifer, at the contact between chalk and the fine semi-permeable alluvial deposits of the Seine Valley (Fig. 2).

Several tracer tests were realized by Massei (2001), each one being performed during periods of no rainfall, either in dry or wet seasons. They are represented in Fig. 3 as residence time distributions. Massei et al. (2003) analyzed these tracer tests and their results are presented in Table 1. These results show that this system presents typical karstic characteristics, with significant apparent transfer velocities. The recovery rates of the tracer are high. The unimodal shape of the breakthrough curves and the high apparent transfer velocities allows one to consider the system as a main conduit, accounting for the major part of the surface stream introduced in the swallow hole (Massei et al. 2003). After storms, the turbidity of the water discharging from the spring can exceed 600 NTU. In the past, the Hannetot spring was a source of water supply, but drinking water is now obtained from a well drilled 130 m away in the alluvial plain. The well is cased through the overlying alluvium and screened in the chalk.

Materials

Data from the three sites (swallow hole, spring and well) were collected continuously at 15-min intervals and samples were collected during responses to rain events. YSI 6820 multi-parameter water quality sondes were used in the field, each comprising one turbidity probe, one electrical conductivity probe, and one pressure sensor. The datasondes were installed at the three points of the karst system (swallow hole, spring, and well). At the swallow

hole, the datasonde was dipped directly into the creek; at the spring, the sonde was immersed into a small pool where karst water flows out. The third sonde was immersed into groundwater in the well. Each datasonde was connected to an Isco 6700 automatic sampler, which allowed both recording of all the measured parameters and water sample collection.

An Isco 674 rain gauge is sited in the watershed to record the rain events. Discharge was determined in Bébec Creek at the entrance to the swallow hole and at the Hannetot spring to allow the calculation of tracer fluxes and particulates, using an Isco 4150 Doppler flow logger to perform flow measurements every 15 min. Each datasonde, installed at the three points of the karst system (swallow hole, spring and well), was connected to an Isco 6700 automatic sampler, which allows the recording of all the measured parameters.

Major elements analyzes (SiO_2 as dissolved silica, Mg^{2+} , Ca^{2+} , HCO_3^- , Na^+ , Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , K^+ , PO_4^{3-} , NH_4^+ , Fe as total dissolved iron) were performed on the samples collected at the three sites by the automatic samplers. Samples collected were filtered through pre-

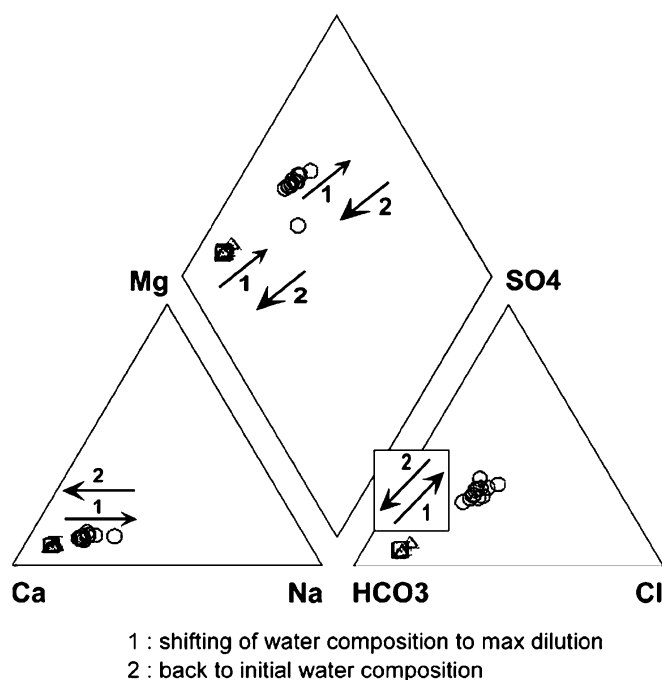


Fig. 4 Piper diagram illustrating the chemical facies of infiltrating and discharging waters; Bébec Creek (empty circle), spring (empty triangle), well (empty square). Reprinted from Massei et al. (2002b), with permission from Elsevier

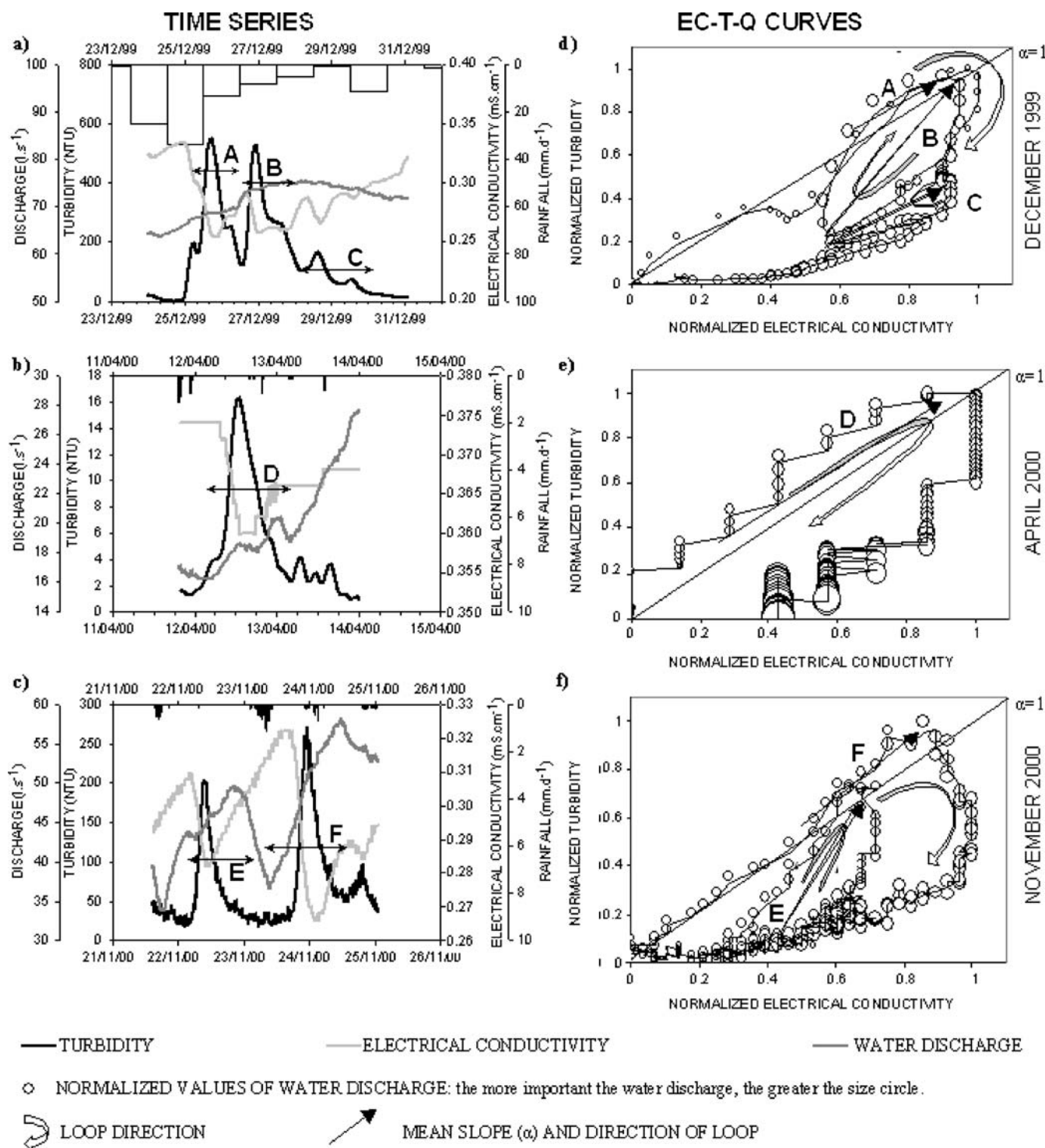


Fig. 5 Raw data recorded at the Hannetot spring (a–c) and normalized EC–T–Q curves (d–f) during December 1999 (a, d), April 2000 (b, e) and November 2000 (c, f) rain events; *A* first single hydrological event of December 1999; *B* second single hydrological event of December 1999; *C* third single hydrological event of December 1999; *D* single hydrological event of April

2000; *E* first single hydrological event of November 2000 and *F* second single hydrological event of November 2000; in normalized EC–T–Q curves, water discharge values are represented by circle size: the more important the water discharge, the greater the circle's size; mean slope is α , which allows for identification of deposition ($\alpha < 1$), direct transfer ($\alpha = 1$) and resuspension ($\alpha > 1$) of sediment

weighed Millipore filters (0.45- μm pore size), and the resulting concentrations analyzed by acid-base titrimetry (total dissolved solids (TDS), HCO_3^-), atomic absorption spectrometry (SiO_2 , Fe, Ca^{2+} , Na^+ , NH_4^+ , K^+ , Mg^{2+}) and

ion chromatography (Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-}). Hydrochemistry demonstrates that the waters of the spring are really close in character to those of the well bore, that is, typical calcium bicarbonate facies. Yet, at peak dis-

Table 2 Means and standard deviations of physico–chemical variables measured at the three points (swallow hole, spring, well) of the system during three rain events (December 1999, April 2000, November 2000) For PCA, unavailable EC data are replaced by the mean EC value for the site considered. *NA* data not available

Variable	Unit	December 1999			April 2000			November 2000		
		Swallow hole	Spring	Well	Swallow hole	Spring	Well	Swallow hole	Spring	Well
SiO ₂	mg.l ⁻¹	5.7±2.5	5.8±0.9	7.9±0.6	11.4±1	8.3±0.2	8.2±0.2	7.1±2.4	7.5±3	8.9±2.7
Mg ²⁺		2.6±0.7	3.9±0.6	5.5±0.1	3.5±0.1	5.3±0.1	5.7±0.1	2.6±0.5	4.1±0.2	5.5±0.1
Ca ²⁺		27.9±9.8	75.5±8.6	93.3±4.9	44.7±2.2	89.4±6.5	90.1±5	25.3±6.8	75.1±4.2	97.7±1.1
K ⁺		5.2±1	4.4±0.6	2.8±0.1	2.5±0.5	2.6±0.1	2.7±0.1	5.6±0.3	4.2±0.2	2.7±0.1
Na ⁺		7.8±2	9.1±1.7	10.6±0.2	12.8±0.6	12.5±0.3	12.7±0.3	7.2±1.3	9.2±0.5	10.4±0.3
Fe		0.4±0.4	0±0	0±0	0±0	0±0	0±0	0±0	0±0	0±0
NH ₄ ⁺		0.2±0.2	0.1±0	0.1±0	0±0.1	0±0	0.5±0.1	0.1±0	0.1±0	0.1±0
NO ₃ ⁻		10.4±3	18.2±2.3	20.5±0.6	12±0.5	25.6±0.7	22.9±0.4	9.5±2.1	20.8±1.1	25.1±0.6
NO ₂ ⁻		0.2±0.2	0±0.1	0.1±0.1	0±0	0±0	0±0	0±0	0±0	0±0
HCO ₃ ⁻		54.5±16.7	198.3±18.8	253.7±14.5	105.6±6.1	255.8±10.4	259.5±13.2	54.4±12.2	197.1±8	264.9±2.4
PO ₄ ³⁻		0.3±0.1	0.2±0.1	0.1±0.1	0.1±0	0±0	0±0	0.8±0.2	0.8±0.2	0.6±0.2
SO ₄ ²⁻		25.9±6.4	11.7±4.7	15.1±0.5	28.9±1.2	16.3±0.6	15.5±0.3	19.6±6.1	8.4±2.9	15.4±0.4
Cl ⁻		17.5±4.9	19±3.3	21.1±0.6	21.5±0.8	21.2±0.2	21.6±0.2	15.8±3	18.5±1.3	21.5±0.4
TDS		163±45	346±41	431±20	243±11	440±13	445±7	148±30	346±18	453±4
Turbidity	NTU	698.3±547.5	211.7±190.2	4.3±2.5	20.5±9.5	5.5±4.8	0.4±0.04	42.5±46.9	27±37.7	1.9±0.5
Q	l.s ⁻¹	146.3±93.8	69.5±4.3	6.2±5.9	18.1±2	17.8±1.3	5.6±5.9	105.9±78.5	49.5±5.1	7.9±5.2
EC	µS.cm ⁻¹	137±32	286±29	NA	NA	368±6	558±0	127±27	291±13	543±2
Ph		7.5±0.1	8.2±0.1	8.1±0.1	7.7±0.3	7.9±0.1	7.6±0.1	7.3±0.2	7.8±0.1	8.2±0.1

charge, spring water facies shift towards the Bébec Creek water facies due to increasing dilution (Fig. 4).

Description of flood events

Three rain events were sampled (Fig. 5): (1) 23–31 December 1999 (Fig. 5a), cumulative rainfall of 105 mm; (2) 11–12 April 2000 (Fig. 5b), characterized by two successive phases of rainfall of weak intensity (3.6 mm in 105 min, then 1.5 mm in 45 min); (3) 23 November 2000 (Fig. 5c; 10.3 mm in 405 min). The samples were collected before, during and after the peaks of turbidity observed during the event. The December flood is exceptional in terms of duration and rainfall amount. The April event arises at the end of the recharge period after 1 month without rain. The November event is the first rainfall after the low water flow season. It can be considered as intermediate between the December event and the April event. Table 2 shows the mean values and the standard deviation of the variables according to their site and date. Table 2 illustrates that waters of the spring and well are identified by high values in pH, EC, TDS, Mg, Ca, HCO₃ and NO₃, and swallow hole water is identified by high values in SiO₂, K, PO₄ and turbidity. Standard deviation is linked to the rain event: the more intense the rain event, the higher the standard deviation. Moreover, standard deviation of the spring is less than that of the well (Table 2).

Data analysis

Comparison of EC, turbidity and discharge at the spring by means of normalized EC–*T*–*Q* curves

Many authors (Williams 1989; Goodwin et al. 2003; Morehead et al. 2003; Seeger et al. 2004) showed that it

was possible to characterize the transport properties of a river by studying the relationships between the sediment concentration and the flow during the rain events. Williams (1989), in studying the relationship between the sediment concentration and discharge for river floods, established five classes of relationships between sediment concentration and discharge describing the five possible scenarios of transport of the dissolved and particulate solids. In karst hydrology, the transport of particles is a complex process implying direct transfer, deposition and release phenomena (Massei 2001; Massei et al. 2002a,b, 2003; Dussart-Baptista 2003; Dussart-Baptista et al. 2003a,b; Valdes et al. 2005, 2006). Hence, at the flood scale, the observed turbidity would have two potential origins: (1) an allochthonous origin corresponding to the direct transfer of particulate materials from the inlet to the outlet of the karstic system, and (2) a resuspended origin, which is related to resuspension of intrakarstic sediment previously deposited within the karstic network. Valdes et al. (2005, 2006) adopted the method of Williams to karst hydrogeology using *T*–EC relationships, where *T* is the turbidity (representing the suspended solids concentration) and EC is the electrical conductivity. The analysis of *T*–EC relationships results in improved understanding of dissolved and suspended solids transport in response to rain events by highlighting the hydrosedimentary processes: direct transport, resuspension of intrakarstic sediments, or deposition of suspended matter. In karst hydrology, many authors (Bakalowicz 1979; Plagnes 1997; Mahler and Lynch 1999; Mahler et al. 1999; Reynaud et al. 1999; Massei et al. 2002a,b, 2003; Alessandro Grasso et al. 2003; Birk et al. 2004) studied the relationships between electrical conductivity (EC), turbidity (*T*) and water discharge (*Q*) for investigating the transport properties of dissolved and particulate matter in relation with hydrodynamics. In this study, the EC–*T*–*Q* relationships concern the spring only

and were explored using normalized variables. The normalization is necessary (1) to compare the different graphs to each other (i.e., different floods), (2) to compare two different quantities (turbidity in NTU and EC in $\mu\text{S}\cdot\text{cm}^{-1}$), the purpose of these graphs being the comparison of their respective variations, (3) to determine at a glance the slope of the trend (equal to 1 or not, which means synchronous occurrence of turbidity and EC or not). The variable normalization has been realized by using the minimum (min) and maximum (max) values during the studied event. Equations (1), (2) and (3) allow normalization of turbidity, electrical conductivity, and water discharge, respectively.

$$T_{\text{normalized}} = \frac{(T - T_{\min})}{T_{\max} - T_{\min}} \quad (1)$$

$$\text{EC}_{\text{normalized}} = \frac{(\text{EC} - \text{EC}_{\max})}{(\text{EC}_{\min} - \text{EC}_{\max})} \quad (2)$$

$$Q_{\text{normalized}} = \frac{(Q - Q_{\min})}{(Q_{\max} - Q_{\min})} \quad (3)$$

The most significant relation is the relation between T and EC since it allows for comparison of the transport properties of the dissolved and particulate elements and identification of the surface water output at the karst spring. So, EC was plotted against T . Normalized EC values are represented on the x-axis and normalized turbidity values are represented on the y-axis. To represent normalized Q values, the circle size was chosen, i.e., the more important the water discharge, the greater the circle size (Fig. 6).

The study and comparison of the EC– T – Q curves were made by the observation of the different slopes (α) to identify the transport properties, according to Williams (1989) and Valdes et al. (2005, 2006). Three types of relationship have been defined according to slope (α) and Q -values (Fig. 6):

Class I. If $\alpha=1$, normalized turbidity increases and normalized EC decreases at the same rate. The single value curve corresponds to a fully synchronous transfer of both particulate and dissolved matter, referred to as “direct transfer” throughout the paper (Fig. 6a,d).

Class II. If $\alpha>1$, the increase in normalized turbidity occurs before the decrease in normalized EC, this clockwise loop corresponds to the intra-karstic sediments resuspension (Fig. 6b,e).

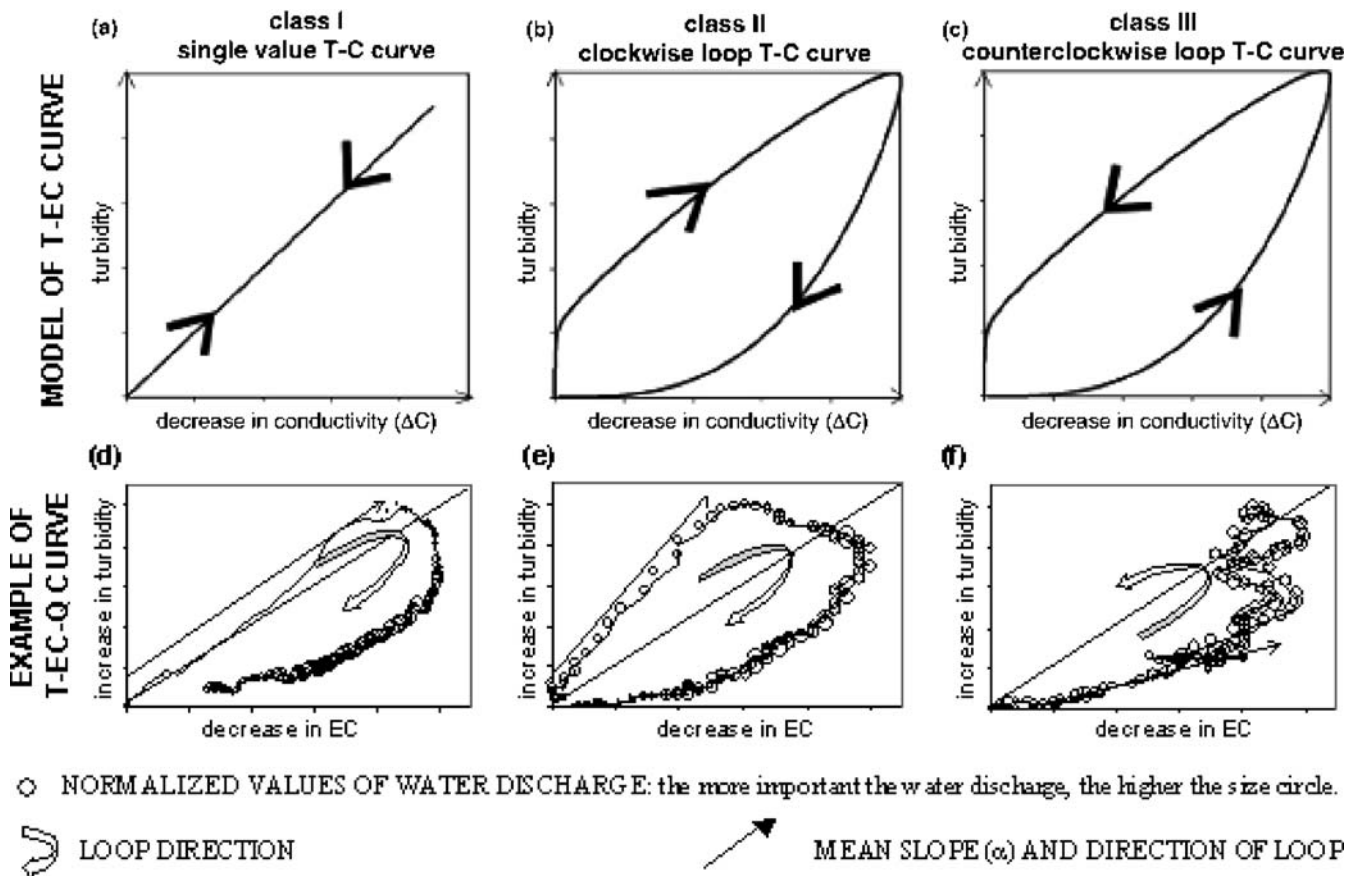


Fig. 6 Models of T -EC curve (a–c, according to Valdes et al. 2006) and examples of normalized EC– T – Q curve (d–f); class I single value curve (a, d); class II clockwise loop (b, e); class III counterclockwise loop (c, f)

Class III. If $\alpha < 1$, this means a normalized turbidity increase after an normalized EC decrease and this counter-clockwise loop puts in evidence suspended matter deposition within kart aquifer (Fig. 6c,f).

Multivariate analysis

Principal component analysis (PCA) is a multivariate statistical technique used for data reduction and for deciphering patterns within large sets of data (Ashley and Lloyd 1978; Jolliffe 1986; Wold et al. 1987). It has proved useful as an aid in the interpretation of hydrogeological data (Bakalowicz 1994; Aruga et al. 1995; Johannesson et al. 1996; Ben Othman et al. 1997; Join et al. 1997; Reisenhofer et al. 1998; Helena et al. 1999, 2000; Stetzenbach et al. 1999, 2001; Vidal et al. 2000; Motelay-Massei et al. 2003). The specific purpose of PCA is to investigate the linear relationships between many variables for large datasets. It allows calculation of principal components that define the degree of correlation between all variables. Only those that correspond to the highest percentage of variance explaining the variability of the correlation matrix are retained (generally 3 or 4).

The principle of PCA can be described in more detail, as follows:

1. As a preliminary step, the raw analytical data are standardized to avoid misclassifications due to the different order of magnitude and range of variation of the analytical parameters. Samples showing correlation coefficients $r > 0.7$ are considered to be strongly correlated, whereas $r > 0.5$ – 0.7 shows moderate correlation at a significance level (p) of 0.05 (Adams et al. 2001).
2. The PCA technique starts with the covariance matrix describing the dispersion of the original variables (measured parameters). Diagonalization of the correlation matrix transforms the original p -correlated variables into p -uncorrelated (orthogonal) variables called principal components (PCs), which are weighted linear combinations of the original variables. There are as many PCs as original variables. However, the PCs retained for interpretation are those which provide information on the most meaningful parameters describing the whole dataset according to data reduction with minimal loss of information (Vega et al. 1998; Helena et al. 1999, 2000; Adams et al. 2001).
3. Correlation of PCs and original variables is given by loadings, and individual transformed observations are called scores (Vega et al. 1998).

A principal component analysis (PCA) was performed using three sampling sites (Bébec Creek swallow hole, the Hannetot spring, and the well) during three rain events (December 1999, April 2000, November 2000). A total of 31 samples were taken at the swallow hole: 12 during December 1999 (1B1–1B12), 9 during April 2000 (2B1–2B9), 10 during November 2000 (3B1–3B10). Thirty-five

Table 3 Correlation matrix of principal component analysis. Correlation coefficients close to 1 or -1 show, respectively, a strong correlation or anti-correlation between variables

	pH	SiO ₂	Mg ²⁺	Ca ²⁺	K ⁺	Na ⁺	Fe	NH ₄ ⁺	NO ₃ ⁻	NO ₂ ⁻	HCO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Turbidity	EC	Q
pH	1																
SiO ₂	0.132	1															
Mg ²⁺	0.637	0.32	1														
Ca ²⁺	0.762	0.198	0.949	1													
K ⁺	-0.531	-0.517	-0.798	-0.711	1												
Na ⁺	0.342	0.566	0.691	0.558	-0.846	1											
Fe	-0.335	-0.454	-0.512	-0.479	0.398	-0.477	1										
NH	-0.37	-0.223	-0.07	-0.154	0.214	-0.114	0.295	1									
NO ₃ ⁻	0.663	0.213	0.922	0.954	-0.67	0.557	-0.47	-0.179	1								
NO ₂ ⁻	-0.134	-0.352	-0.295	-0.283	0.268	-0.32	0.476	0.203	-0.33	1							
HCO ₃ ⁻	0.724	0.192	0.95	0.991	-0.716	0.564	-0.453	-0.12	0.954	-0.274	1						
PO ₄ ³⁻	-0.104	0.113	-0.295	-0.196	0.441	-0.558	-0.035	-0.2	-0.132	-0.117	-0.208	1					
SO ₄ ²⁻	-0.302	0.293	-0.273	-0.481	-0.039	0.247	0.115	0.05	-0.455	0.105	-0.509	-0.337	1				
Cl ⁻	0.514	0.52	0.726	0.608	-0.72	0.848	-0.564	-0.159	0.6	-0.235	0.571	-0.419	0.313	1			
Turbidity	-0.304	-0.47	-0.56	-0.503	0.475	-0.511	0.805	0.254	-0.493	0.603	-0.489	-0.046	0.12	-0.508	1		
EC	0.55	0.338	0.865	0.829	-0.758	0.63	-0.376	0.075	0.813	-0.31	0.84	-0.18	-0.249	0.609	-0.447	1	
Q	-0.544	-0.45	-0.771	-0.696	0.75	-0.741	0.738	0.222	-0.665	0.371	-0.676	0.275	-0.003	-0.772	0.727	-0.665	1

Table 4 Eigenvalues, percentage of variance explained and cumulative variance of principal components (PCs)

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10	PC11	PC12	PC13	PC14	PC15	PC16	PC17
Eigenvalues	8.784	2.359	1.979	1.073	0.768	0.61	0.405	0.263	0.235	0.168	0.113	0.102	0.064	0.039	0.026	0.009	0.004
% variance explained	51.7	13.9	11.6	6.3	4.5	3.6	2.4	1.5	1.4	1	0.7	0.6	0.4	0.2	0.2	0.1	0
% cumulative variance	51.7	65.5	77.2	83.5	88	91.6	94	95.5	96.9	97.9	98.6	99.2	99.5	99.8	99.9	100	100

samples were taken at the Hannetot spring: 10 during December 1999 (1S1–1S10), 10 during April 2000 (2S1–2S10), 15 during November 2000 (3S1–3S15). Finally, 31 samples were taken at the well: 9 during December 1999 (1F1–1F9), 8 during April 2000 (2F1–2F8), 14 during November 2000 (3F1–3F14). The number located after the letter (e.g., 3F1 or 3F6) corresponds to the sampling chronology during a rain event at a site of karst system.

The final PCA comprises 97 samples with 17 normalized variables (SiO_2 , Mg^{2+} , Ca^{2+} , HCO_3^- , Na^+ , Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , K^+ , NO_4^{3-} , NH_4^+ , Fe, pH, EC, T , Q). The matrix correlation (Table 3) gives the correlation between variables. The first two principal components explain 65.6% of the total variance: PC1 explains 51.7% and PC2 explains 13.9% (Table 4).

In the variable space (Fig. 7), the best-described variables are close to the circle in the first factorial plane (PC1–PC2), which expressed 66% of the total variance. PC1 is related to EC, HCO_3^- , Ca^{2+} , Mg^{2+} , pH and NO_3^- in the positive part, opposed to Q , turbidity, Fe, K^+ , and at a lower level, NO_2^- , PO_4^{3-} in the negative part. PC1 can be interpreted as the water origin: the storm-derived water in the agricultural watershed in the negative part of PC1 which defined cluster C, and the groundwater of the chalk aquifer in the positive part of PC1 which defined cluster B. PC2 related to SO_4^{2-} , Na^+ , Cl^- , SiO_2 , which illustrated the Bébec Creek water defined by cluster A (Fig. 7).

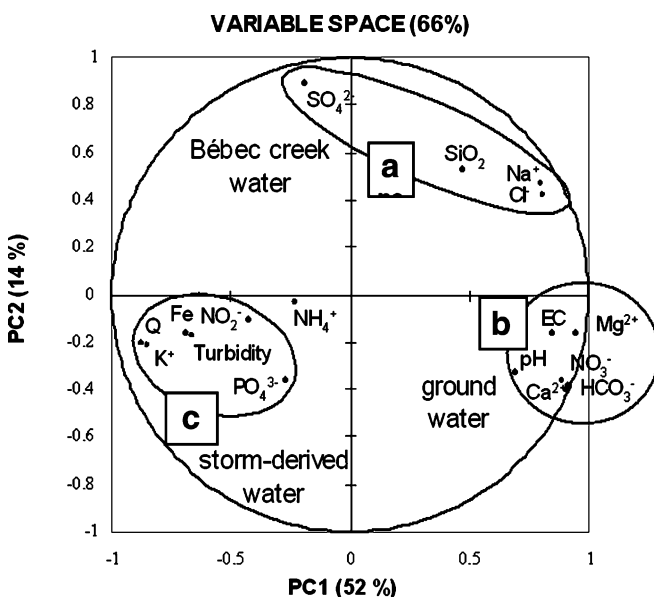


Fig. 7 PCA results in variable space; A variables characterizing Bébec Creek water during dry period; B variables characterizing groundwater; C variables characterizing storm-derived water streaming on the watershed and infiltrating at the swallow hole

In the sample space (Fig. 8), eight clusters were identified by ellipses, which have been drawn manually to group samples of the same location and rain event. Clusters 1B, 2B and 3B gather the Bébec Creek water samples respectively for the December 1999 (1B1–1B12), the April 2000 (2B1–2B9), and the November 2000 (3B1–3B10) rain events. Cluster 2S–2F gathers the Hannetot spring water (2S1–2S10) and the well water (2F1–2F8) samples for the April 2000 rain event. Clusters 1S and 3S bring together the Hannetot spring water samples respectively for the December 1999 (1S1–1S10) and the November 2000 (3S1–3S10) storm events. Clusters 1F and 3F linked the well water samples respectively for the December 1999 (1F1–1F9) and the November 2000 (3F1–3F14) storm events.

Turbidity dynamics

The December 1999 rain event generated three turbidity peaks (Fig. 5a). They are represented by three loops in the EC– T – Q curves (Fig. 5d). The first loop (A) is close to the single-valued line and the EC– T relation has a slope of 1. The synchronous behavior of turbidity and EC illustrates the direct transfer between the swallow hole and the spring. The second loop (B) is a clockwise loop with a EC– T relationship of slope > 1. It occurs when the turbidity peak arrives at the spring before the anti-correlated EC peak. This puts in evidence the resuspension of intrakarstic sediments by pressure transfer since this loop occurs during an increase of water discharge, as can be seen on Fig. 5a and d, on which the circles represent discharge, their size being proportional to discharge value. The third loop (C) is a single-valued line and the EC– T relation has a slope < 1. It is always a direct transfer because the turbidity and EC peaks are simultaneous. However, the turbidity peak is relatively shorter than the EC peak. The numerical value of these EC– T ratios decreases systematically as one moves along the rising limb of the EC peak (Williams 1989; Valdes et al. 2005, 2006).

The April 2000 rain event is a single hydrologic event of weak intensity after 1 month without rainfall (Fig. 5b). It shows a clockwise loop for EC– T – Q relations graph (Fig. 5e), in which two parts can be distinguished. The first part corresponds to a single-valued line with a slope = 1, which illustrates a direct transfer. The second part shows a higher and quick turbidity decrease before the EC increase, which illustrates a suspended matter deposition in the karstic network.

The November 2000 rain event is a complex two-peak hydrologic event of higher intensity (Fig. 5c). In the EC– T – Q relation graph (Fig. 5f), it shows a clockwise loop in

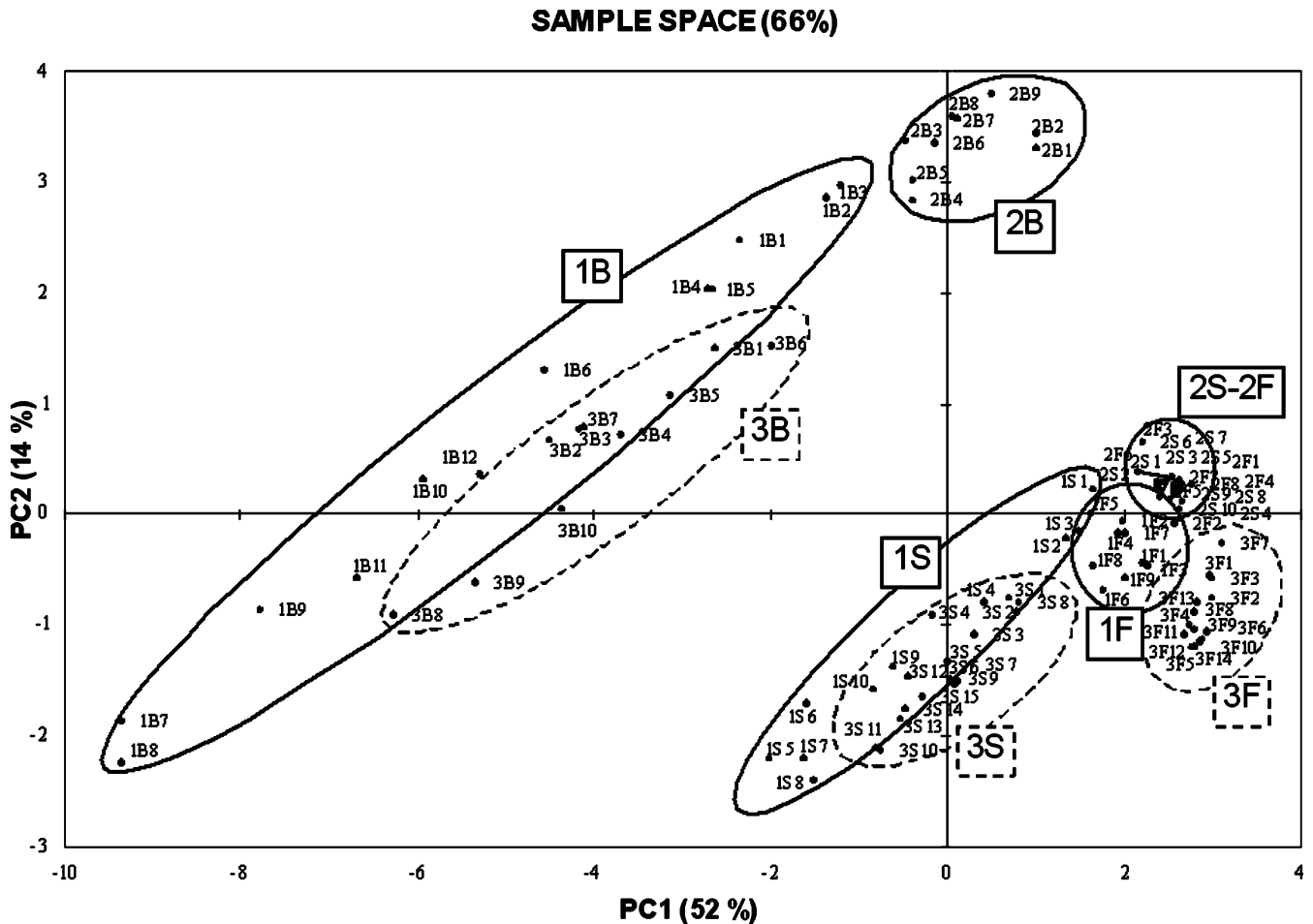


Fig. 8 PCA results in sample space; *ellipses* group samples of the same location and rain event: 1B1–1B12 samples of December 1999 rain event at the swallow hole; 2B1–2B9 samples of April 2000 rain event at the swallow hole; 3B1–3B10 samples of November 2000 rain event at the swallow hole; 1S1–1S10 samples of December 1999 rain event at the spring; 2S1–2S10 samples of April 2000 rain event at the spring; 3S1–3S15 samples of

November 2000 rain event at the spring; 1F1–1F9 samples of December 1999 rain event at the well; 2F1–2F8 samples of April 2000 rain event at the well; 3F1–3F14 samples of November 2000 rain event at the well. The number located after each letter indicates the sampling chronology during a rain event at a given site in the system

a first time (E), which confirms the resuspension of intrakarstic sediments. In a second time (F), it shows the same evolution of the April 2000 rain event: a single-valued line with a slope of 1 and a higher water discharge, which illustrates a direct transfer. Then a higher and quick turbidity decrease before an EC increase confirms the suspended matter deposition in the karstic network during the decrease of the water discharge.

Characterization of the observed water types

In Fig. 9, the ellipse 2S-2F demonstrate that the waters of the spring are really close to those of the well, that is, groundwater type. Yet, the ellipses 1S (samples of December 1999 rain event at the spring) and 3S (samples of November 1999 rain event at the spring) show that spring water facies shifts towards the storm-derived water facies, as can be seen in the Piper diagram (Fig. 4). Clusters 1B, 3B, 1S and 3S show the same hydrochemical

facies evolution (Fig. 9). At the beginning of each flood, the hydrochemical facies at the swallow hole is close to the Bébec Creek steady-state water, defined by cluster A in Fig. 7, and the hydrochemical facies at the spring is close to the groundwater, defined by cluster B in Fig. 7. Then both the swallow hole and spring hydrochemical facies move towards storm-derived water, defined by cluster C, and finally move back to their initial state. This corresponds respectively to the increasing stage, first and second maxima and falling stage of each turbid flood. Clearly, this karst aquifer does not permit any homogenization of waters, owing to the fast transit of waters to the Hannetot spring. This illustrates the spring water contamination by the storm-derived water infiltrated at the swallow hole during rain events, and demonstrates that the importance of the mix of spring water and Bébec Creek water is a function of the rain intensity. The more intense the rain events, the more contaminated are the Bébec Creek waters and spring waters, leading to a greater dispersion of cluster 1S compared to cluster 3S (Fig. 9).

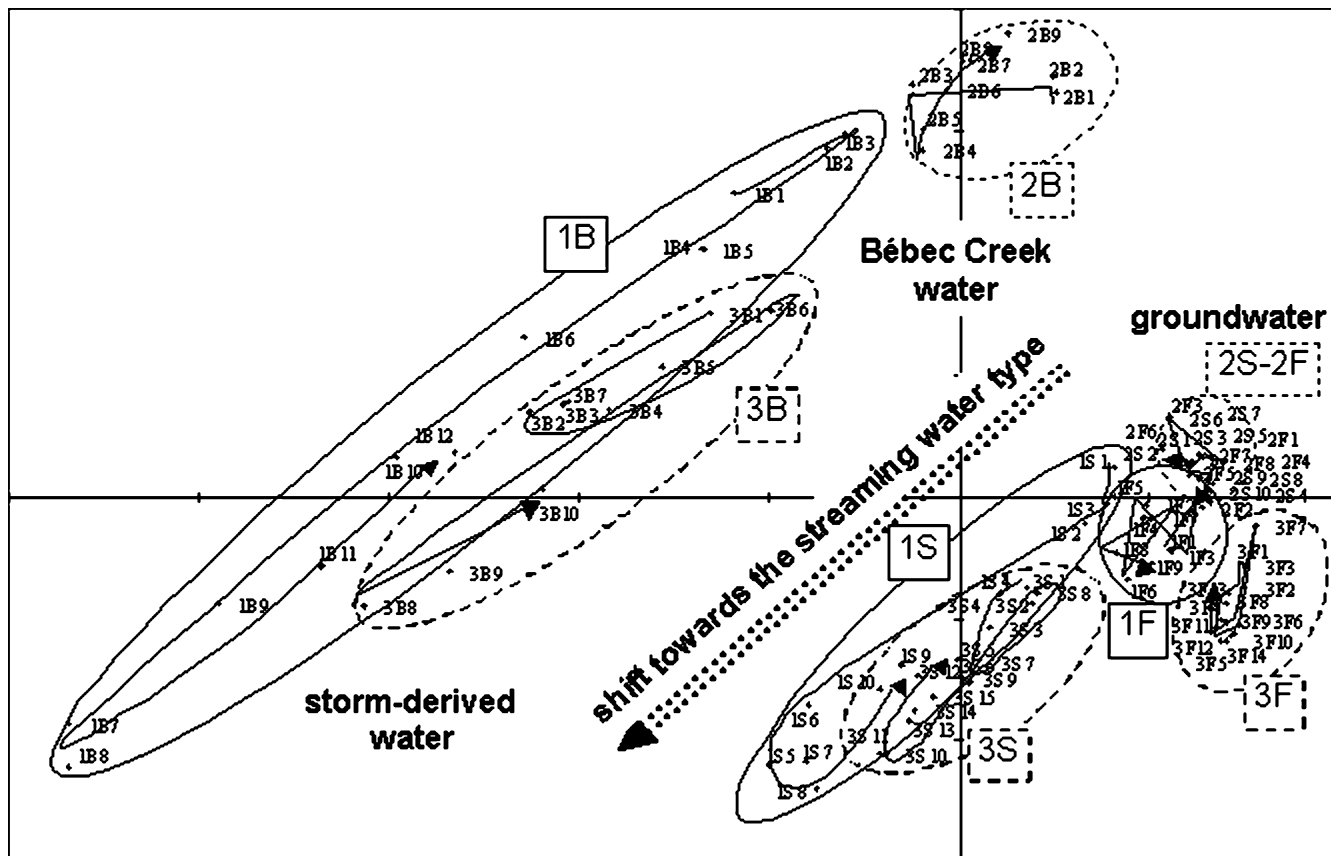


Fig. 9 Schematic results of PCA illustrating the temporal evolution of water geochemistry during the rain event at the swallow hole, spring, and well; *solid-line arrows* represent the sampling chronology during the rain events studied; the *dotted-line arrow* illustrates the shift of Bébec Creek water and groundwater towards the storm-derived water pole; *ellipses* group samples of the same location and rain event: 1B1–1B12 samples of December 1999 rain event at the swallow hole; 2B1–2B9 samples of April 2000 rain event at the swallow hole; 3B1–3B10 samples of November 2000

rain event at the swallow hole; 1S1–1S10 samples of December 1999 rain event at the spring; 2S1–2S10 samples of April 2000 rain event at the spring; 3S1–3S15 samples of November 2000 rain event at the spring; 1F1–1F9 samples of December 1999 rain event at the well; 2F1–2F8 samples of April 2000 rain event at the well; 3F1–3F14 samples of November 2000 rain event at the well. The number located after each letter indicates the sampling chronology during a rain event at a given site in the system

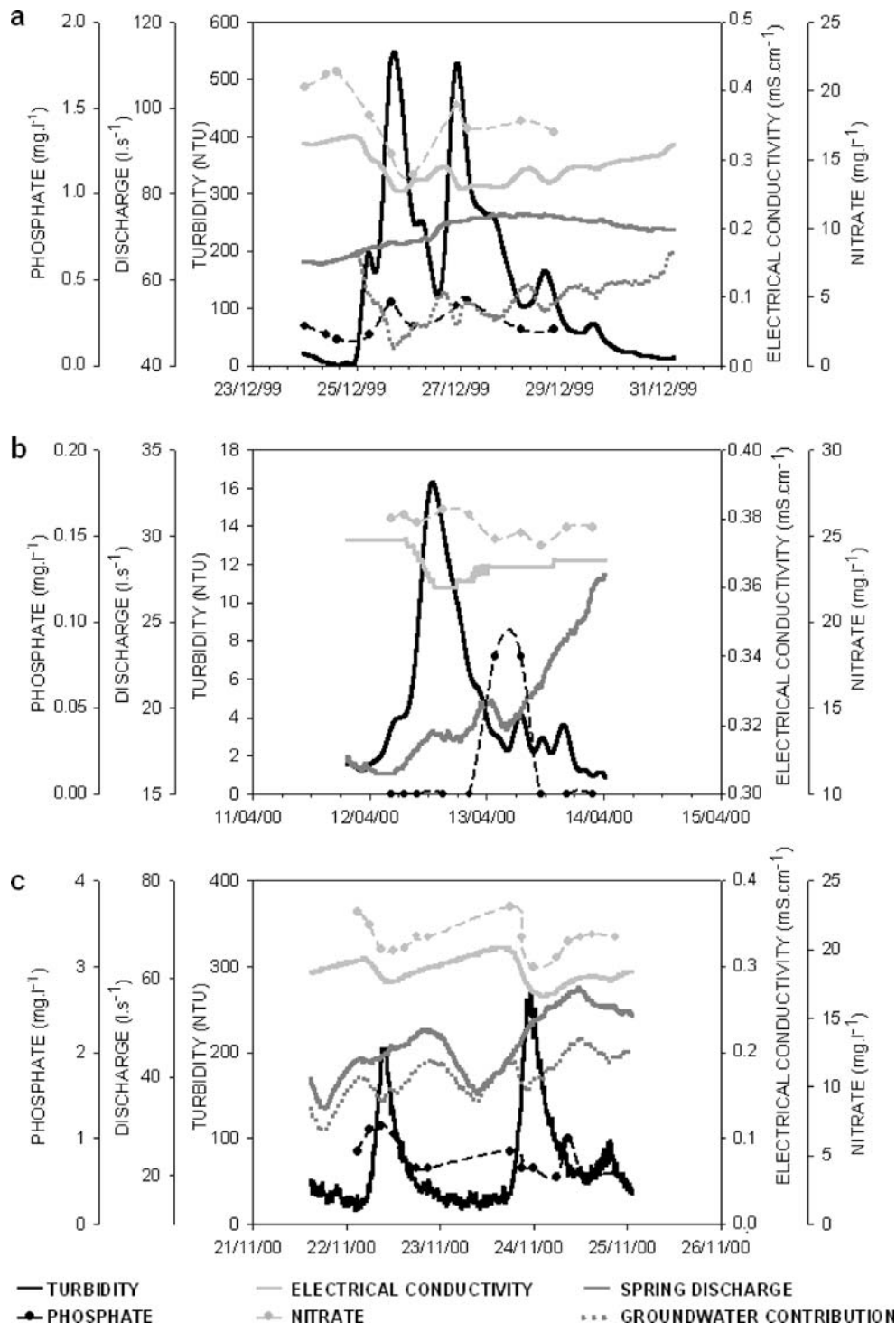
During the April event, selected for its weak amplitude, the hydrochemical facies remain remarkably stable. The waters of Bébec Creek are only a little diluted with surface waters, and the hydrochemical water-type of the chalk aquifer prevails at the spring; the hydrochemical facies of the samples at the spring and the well are fairly similar, that is calcium-bicarbonate (Fig. 8). So, groundwater geochemistry is dominated by hydrogencarbonate and calcium, the species that have the highest concentrations (Table 2). Storm-derived water originating from the surface (i.e. introduced at the swallow hole) presents low HCO_3^- and Ca concentrations and high turbidity and phosphate concentrations (Table 2). As a consequence, the arrival of storm-derived water at the spring induces (1) a decrease in HCO_3^-/Ca concentrations (and thus a decrease in EC), since those species, initially present in the chalk aquifer, are being diluted by surface water (Fig. 10), and (2) an increase in turbidity and phosphate concentrations present in surface waters which are streaming in the watershed. The correlation between NO_3^- and HCO_3^- and Ca (Table 2) shows that the same

process holds for nitrate, which is diluted by the arrival of surface water at the spring (Fig. 10). Consequently, nitrate is initially present in the chalk aquifer and contributes to the background geochemistry of the aquifer. Figure 11 highlights the very similar behavior of nitrate and HCO_3^-/Ca , which underline the common origin of these species. Figure 12 shows the strong positive correlation between nitrate concentration and percentage of groundwater contribution at the spring and demonstrates that nitrate originates from groundwater. Decreases in nitrate concentrations in spring during high rainfall conditions are related to the amount of mixing with storm-derived water, which contains low nitrate concentrations and elevated concentrations of phosphate.

Behavior and vulnerability of the karst aquifer

The Hannetot karst system is characterized by rapid vertical/horizontal flows (runoff, a rapid process in which storm-derived water reaches the spring directly through a swallow

Fig. 10 Physico-chemical output at the spring during the three rain events (*a* December 1999, *b* April 2000, *c* November 2000)



hole), which are identified by high turbidity and high phosphate concentration. Hence, turbidity and phosphate represent a point-source contamination of Hannetot spring water originating from the infiltration of storm-derived water at the swallow hole. On the other hand, nitrate corresponds to a diffuse source of contamination of Hannetot spring water. At the peak discharge, groundwater at the spring is diluted by the arrival of storm-derived water infiltrated at the

swallow hole (Fig. 10). Sample dispersivity, represented by the size of ellipses in PCA, is linked to the dilution rate of groundwater by storm-derived water: the more important the dilution, the larger the ellipse size (Fig. 9).

According to Massei et al. (2003), the high contrast in EC between groundwater and storm-derived water allows use of this parameter as a good indicator of surface water arrival at the spring in such a small system, which has

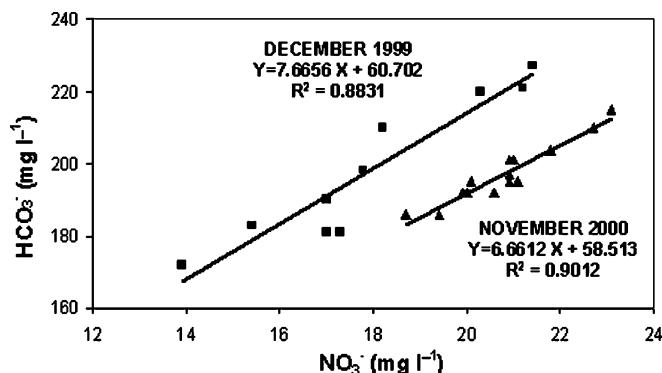


Fig. 11 Linear regression between nitrate and bicarbonate at the spring during December 1999 (filled square) and November 2000 (open triangle) rain events

high reactivity and rapid response time (less than 1 day). In these conditions, EC can be used as a conservative natural tracer of surface water and is representative of mixing between surface water and groundwater. In Massei et al. (2003), the variations at the spring of the EC were used successfully for spring hydrograph separation with a simple two-component mixing model. So, according to the method developed by Massei et al. (2003), EC were used to quantify the contribution of storm-derived water to total spring discharge. At the spring, the instantaneous discharge measured every 15 min is given by:

$$Q_S = Q_{Karst} + Q_{ES} \quad (4)$$

Also, the instantaneous flux of dissolved ionic species (measured indirectly by means of the EC every 15 min) is:

$$Q_S EC_S = Q_{Aq} EC_{Aq} + Q_{Stw} EC_{SH} \quad (5)$$

Where Q_S is the total spring discharge, Q_{Aq} the karstic component of spring discharge, Q_{Stw} the surface component of the spring discharge (storm-derived water flux contribution to total spring discharge), EC_S the recorded specific electrical conductivity at the spring (25°C–

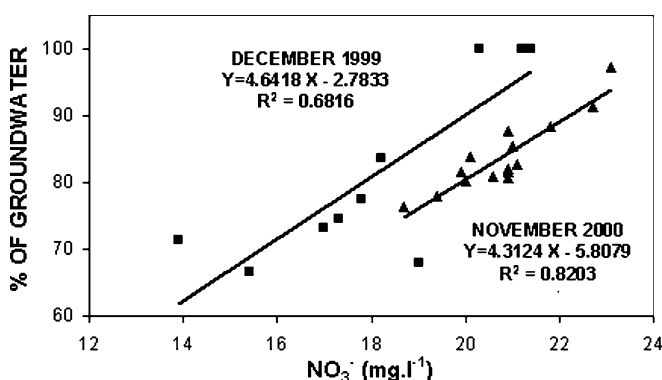


Fig. 12 Linear regression between nitrate and percentage of groundwater contribution at the spring during December 1999 (filled square) and November 2000 (open triangle) rain events

compensated electrical conductivity), EC_{SH} the recorded specific electrical conductivity (25°C–compensated) of surface water entering the Bébec swallow hole, for which variations are related to runoff, and EC_{Aq} (constant) the electrical conductivity at the spring during dry periods. Solving Eqs. (4) and (5) gives:

$$Q_{Aq} = Q_S \frac{(EC_S - EC_{SH})}{(EC_{Aq} - EC_{SH})}$$

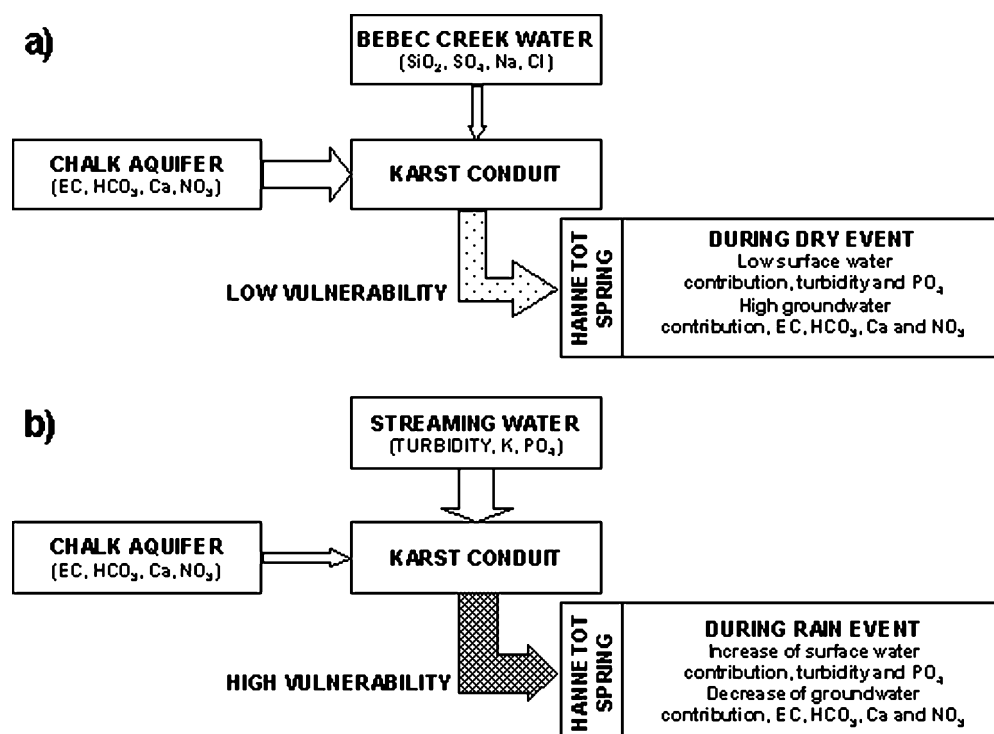
$$Q_{Stw} = Q_S \frac{(EC_S - EC_{Aq})}{(EC_{SH} - EC_{Aq})}$$

Table 5 shows the results of groundwater contribution at the spring obtained during December 1999 and November 2000 rain events, according to Massei et al. (2003). Peaks A and F, which are direct transfer peaks according to the EC– T – Q curve (Fig. 6), are composed of 64 and 75% groundwater and 36 and 25% surface water, respectively. Peaks B and E, which are resuspension peaks according to the EC– T – Q curve (Fig. 6), are composed of 68 and 80% groundwater and 32 and 20% surface water, respectively. The same method used at the well shows a contribution equal to 10% surface water for the December 1999 and November 2000 rain events. The study of EC– T – Q relations showed that the peaks A, C, D, and F come from the direct transfer of surface water peaks infiltrated at the swallow hole. The water contributions to the spring, calculated according to Massei et al. (2003), give 36 and 25% surface water for the peaks A and F (peak D: data not available). These contributions of surface water generate reductions in EC and increase in PO_4^{3-} and turbidity in more or less significant proportions. For the peaks B and E the surface water contribution calculated according to Massei et al. (2003) is respectively 32 and 20%. However, that corresponds only to one increase of 10% of the surface water contribution to the spring compared to the base level. The study of EC– T – Q relations showed that these peaks come from the resuspension of intrakarstic sediments. This phenomenon comes from the pressure transfer, which allows the increase of velocity inside the karst conduit. The decrease of EC during the peak B is less significant than that during the peak E in spite of the same surface water contribution. Moreover, during peak B the nitrate concentration increases, whereas during peak E it decreases, like EC, with the surface water contribution. In December 1999, the groundwater flow was naturally

Table 5 Contribution of groundwater to the spring calculated according to Massei et al. (2003)

Rain event	Peak	Contribution of groundwater
December 1999	Peak A (direct transfer)	64%
	Peak B (resuspension)	68%
November 2000	Peak E (resuspension)	80%
	Peak F (direct transfer)	75%

Fig. 13 Conceptual scheme of the karst aquifer vulnerability during dry events (a) and rain events (b); the size of arrows represent the different origins of water and their contribution



significant (from 45 to 60 l.s⁻¹). The peak B of resuspension occurs during groundwater rising (to more than 50 l.s⁻¹). Thus, the resuspension of intrakarstic sediments during the peak B comes from a pressure transfer via groundwater rising. It explains the increase in nitrate and the weak reduction in EC.

The conceptual scheme (Fig. 13) explains the vulnerability of the Hanne Tot karst aquifer. The follow-up of EC, *T* and *Q*, coupled with the calculation of the groundwater contribution to the spring and with the space and time evolution of water geochemistry, make it possible to distinguish two types of contamination: (1) a point-source of contamination by water with high turbidity and phosphate concentration originating from the infiltration of storm-derived water in the swallow hole, and (2) a diffuse source of contamination of the chalk aquifer by nitrate that originates from the leaching of soils by slowly infiltrating surface water recharging the chalk aquifer (Igbal and Krothe 1995; Nebbache et al. 2001). Hanne Tot spring water is the result of a mixture between groundwater and storm-derived water. Groundwater contribution depends on the rain-event intensity. When the latter becomes important, storm-derived water fills up the karst conduit and prevents groundwater from entering the karst conduit (Fig. 13).

Conclusion

The turbidity dynamics could be identified and compared thanks to normalized EC–*T*–*Q* curves that allowed the identification of different phases of transport: direct transport, deposition of suspended particulate matter and

intrakarstic sediments resuspension by pressure transfer. The variable amounts and respective contributions of these two types of dynamics could be assessed for the three investigated flood events. These respective contributions depend on the rain-event intensity, which determines the quantity (water discharge) and the quality (EC, turbidity, hydrochemistry) of the spring waters. Storm-derived water contribution at the Hanne Tot spring can reach 36%, which makes Hanne Tot spring waters strongly vulnerable to storm-derived contamination such as, for instance, turbidity and phosphate. A high background concentration of nitrate not related with the karst behavior has also been observed at the spring, which provides evidence that nitrate contamination is a diffuse source of contamination of the chalk groundwater, unlike point source contamination (turbidity, PO₄³⁻) related to karst features.

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