Mudry, J., Charmoille, A., Robbe, N., Bertrand, C., Batiot, C., Emblanch, C. and Mettetal, J. P. 2002. Use of hydrogeochemistry to display a present recharge of confined karst aquifers. Case study of the Doubs valley, Jura mountains, eastern France. In: Carrasco, F., Durán, J. J. y Andreo, B. (Eds.) *Karst and Environment*. 123-129

Use of hydrogeochemistry to display a present recharge of confined karst aquifers. Case study of the Doubs valley, Jura mountains, eastern France

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RESUMEN

Después del siglo diecinueve, se han realizado perforaciones en las calizas jurásicas del valle del Doubs para el suministro de agua a industrias (fábricas de papel) y abastecimiento urbano. Para determinar la tasa relativa de recarga de los acuíferos kársticos confinados, se han determinado diferentes trazadores de tiempo de residencia largo (^{3}H, ^{13}C, rMg/rCa,) o corto (COD, nitratos) en las aguas de los sondeos. Al mismo tiempo, se han muestreado las salidas naturales de los acuíferos kársticos no confinados, para evaluar la influencia de la diferencia en el tiempo de residencia dentro de las calizas. Existe un grupo de puntos poco profundos, no confinados, de flujo rápido, con un contenido de tritio del presente, valores negativos de ^{13}C, baja relación rMg/rCa, elevados contenidos en COD y de nitratos y un grupo de puntos correspondientes al acuífero profundo y confinado, de flujo lento, con bajo contenido en tritio, agua enriquecida en ^{13}C, elevada relación rMg/rCa y bajos contenidos en COD y nitratos. La posición de las diferentes perforaciones en los graficos que combinan estos trazadores informa sobre la capacidad de recarga del acuífero del valle del Doubs. Varias perforaciones aparecen muy cerca del grupo de puntos poco profundos, lo cual indica que captan niveles acuíferos fácilmente recargables y vulnerables a contaminantes antrópicos. Asimismo, se detecta un grupo de sondeos cuyas muestras presentan características de paleoaguas. En este caso el agua está bien protegida de la superficie, no se puede asegurar que exista una recarga y los procesos de reducción pueden empeorar la calidad de agua, incorporando metales pesados en la disolución.

Palabras clave: hidrogeoquímica, isotópos, karst, recarga, tiempo de residencia

ABSTRACT

As early as the nineteenth century, boreholes have been drilled in the Jurassic limestones of the Doubs valley for industrial (paper mills) and drinking water supplies. In order to determine the relative recharge rate of these confined karst aquifers, we combined different long (^{3}H, ^{13}C, rMg/rCa,) and short (DOC, nitrates) residence time tracers. In the same limestone series, the natural outlets of unconfined karst aquifers have been sampled simultaneously, in order to evaluate the influence of the difference in residence time within the limestones. So we expected a shallow and unconfined cluster of fast flow, with a present tritium content, a negative carbon-13, a low rMg/rCa, a high DOC and a high nitrate contents, and a deep and confined slow flow cluster, with a low tritium content, an enriched carbon-13 ratio, a high rMg/rCa, a low DOC and a low nitrate contents. The position of the different boreholes in the scattergrams which combine these residence-time tracers gives information about the recharge ability of the aquifer. Several confined boreholes appear very close to the shallow cluster, meaning that these aquifers are easily recharged and are vulnerable to anthropogenic contaminants. On the contrary, a trend, with characteristics of old water can be observed. For this category of water, well-protected from the surface, we cannot be sure that a present recharge exists, and reduction processes can worsen the water quality, bringing heavy metals in solution.

Key words: hydrogeochemistry, isotopes, karst, recharge, residence time

1. INTRODUCTION

The Doubs valley upstream Besançon is situated in the NW ridge of the Jura (fig. 1). This folded area includes Jurassic series made of limestones (Dogger, Malm) or marls (Liassic, Oxfordian). The Oxfordian marls can overburden the Dogger limestones.

As early as the nineteenth century, boreholes have been drilled in the Jurassic limestones of the Doubs valley for industrial (paper mills) and drinking water supplies. These boreholes generally have good productivities, despite the fact that the limestones are covered by marl series. The objective of this research is to evaluate and to compare the recharge conditions for these deep aqui-

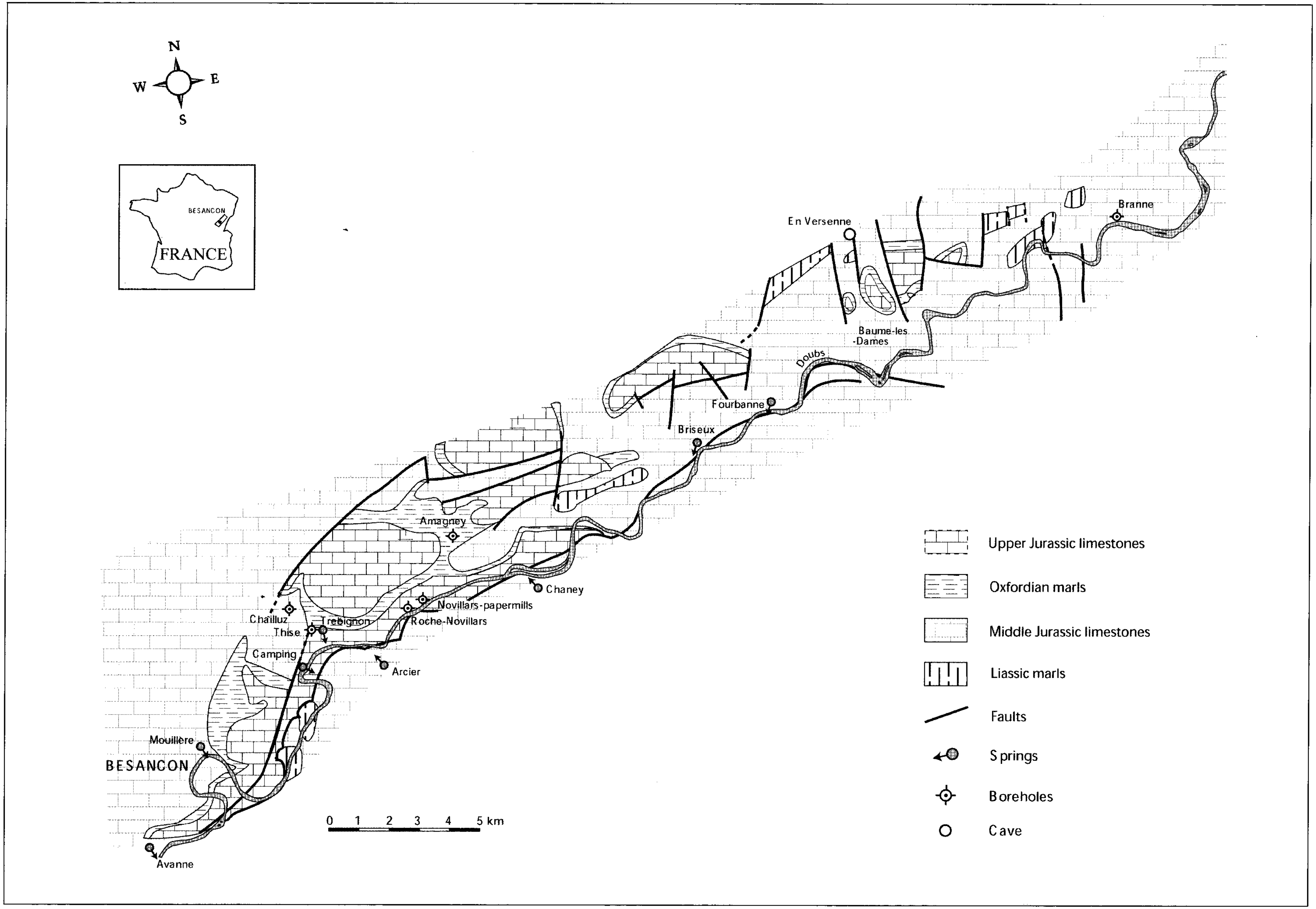

Figure 1. Doubs valley karst area: geological sketch map

fers, using the physical, chemical and isotopical content of the borehole waters. In the same limestone series, springs are the outlets of unconfined karst aquifers. In order to evaluate the effect of long residence times within the limestones, the hydrogeochemistry of boreholes is compared to that of springs.

The main goals of the research are:

- to determine boreholes with a long residence time water
- to evaluate gas - water - rock interactions
- to assess the vulnerability of the aquifer to diffuse pollution

2. MATERIALS AND METHODS

2.1. Sampling and analyses

The physical, chemical and isotopical content of water has been determined during instant samplings.

In the field, temperature, pH, Redox and electrical conductivity are measured, during the pumping of the borehole.

Several flasks are filled with the sampled water:

- one, made of polyethylene, for the volumetric measurement of alcalinity,
- one, made of polyethylene, acidified, for major cation measurement by Atomic Absorption Spectrometry (Perkin-Elmer 1100B)
- one, made of polyethylene, for major anion measurement by High Pressure Ionic Chromatography (Dionex, DX 100)
- one, made of polyethylene, acidified, for heavy metal measurement by High Pressure Ionic Chromatography (Dionex, DX 500)
- one, made of polyethylene, for Tritium measurement by Liquid Scintillation Counter.
- one, made of smoked glass, with mercuric chloride added (to kill bacteria), for Dissolved Organic Carbon measurement, by Element Analysis (O.I. Analytical model 700)
- two, made of smoked glass, for 18-Oxygen and 13-Carbon measurement (Finnigan Mat – Delta S)

2.2. Long transits

Three, among the analysed tracers, can be considered as long residence time indicators:

- Tritium. As its present yearly level in rainfall is nearly constant, a low content means a radioactive decrease and then the existence of non-present waters. We expect relatively high values for springs (unconfined conditions), and low for deep aquifers, slowly and not easily recharged;
- ^{13}Carbon. A stœchiometric origin of Carbon of hydrogenocarbonate in water, half from the soil atmosphere (≈ - 22 ‰) and half from the solid carbonate of the aquifer (≈ 0 ‰) would give a ≈ - 11 ‰ ratio. Such a ratio definitely signifies a recently infiltrated water, with no timewise interaction between water and reservoir, nor without any later CO_2 dissolution from the soil atmosphere (Emblanch, 1997; Emblanch *et al.*, 1998a; Batiot *et al.*, 2001). We expect enriched values (versus - 11 ‰) in a water-rock isotopic exchange (which requires time to complete), and impoverished values for a lasting contact with the shallow carbon reservoir (unconfined conditions).
- rMg/rCa. Due to the incongruent dissolution of dolomite, this ratio increases versus time (Mudry, 1987; Emblanch *et al.*, 1999). Then, in the same layers, we expect a high ratio for long-residence time waters, and a low one for rapidly recharged ground waters.

These three tracers are supposed to validate what we expect, and then to enable a distinction, within the confined aquifers, between those that receive a visible yearly recharge and those which mix these steady recharges within a wide reservoir.

2.3. Short transits

In order to display the impact of quick infiltration components, two specific tracers have been used:

- Dissolved Organic Carbon, that is acquired within the soil, during seepage episodes (Emblanch, 1997; Emblanch *et al.*, 1998b, 2001). This tracer is non-conservative: the humic acids mineralize over time and slow infiltration water has a low content versus quick infiltration.
- Nitrate, originating also from the soil (lixiviation of natural organic matter or dissolution of fertilizers). The absence or low contents of nitrates can mean 'old' water or strong reducing conditions within the aquifer.

2.4. Extreme expected behaviours

Considering the aptness of this reasoning, we can expect two extreme cases:

- spring waters, open to the soil atmosphere (oxygen and carbon gas), with short-residence time waters and nitrate inputs due to the agricultural activities, would constitute a cluster characterised by a high tritium content, a very negative $\delta^{13}C$, a low rMg/rCa ratio, a high DOC and a high nitrate content.
- boreholes extracting confined water, closed to the soil atmosphere (anoxic and not recharged in carbon dioxide), with long residence-time waters. This cluster

will be characterised by a low tritium content, a weakly being negative $\delta^{13}C$, a high rMg/rCa ratio, a low DOC and a low nitrate content.

3 - RESULTS (instant samplings of 2000 and 2001)

3.1. Residence times

Several scattergrams enable to display the relative situation of the different harnessing boreholes. Fig. 2A shows a well-defined spring cluster, and a relative situation of the boreholes versus this shallow and quick cluster.

The scattergram of rMg/rCa vs. tritium displays two different relationships: at the bottom of the graph; a first group, constituted of springs, has a low ratio and a low tritium content. At the top, the boreholes fit another relationship which is roughly parallel to the previous one. Two springs show an intermediate position in the graph. The borehole relationship opposes Amagney to the other boreholes.

Fig. 2B displays two different logics: for boreholes, the less negative are the ^{13}C values, the less tritium content they have. For the springs, despide a huge dispersion, the logic is that negative values are associated to low tritium contents.

3.2 Influence of present infiltration

Plotting nitrate *vs.* rMg / rCa (fig. 3A) displays water points whose ratio is higher than 0.1 and nitrate lower

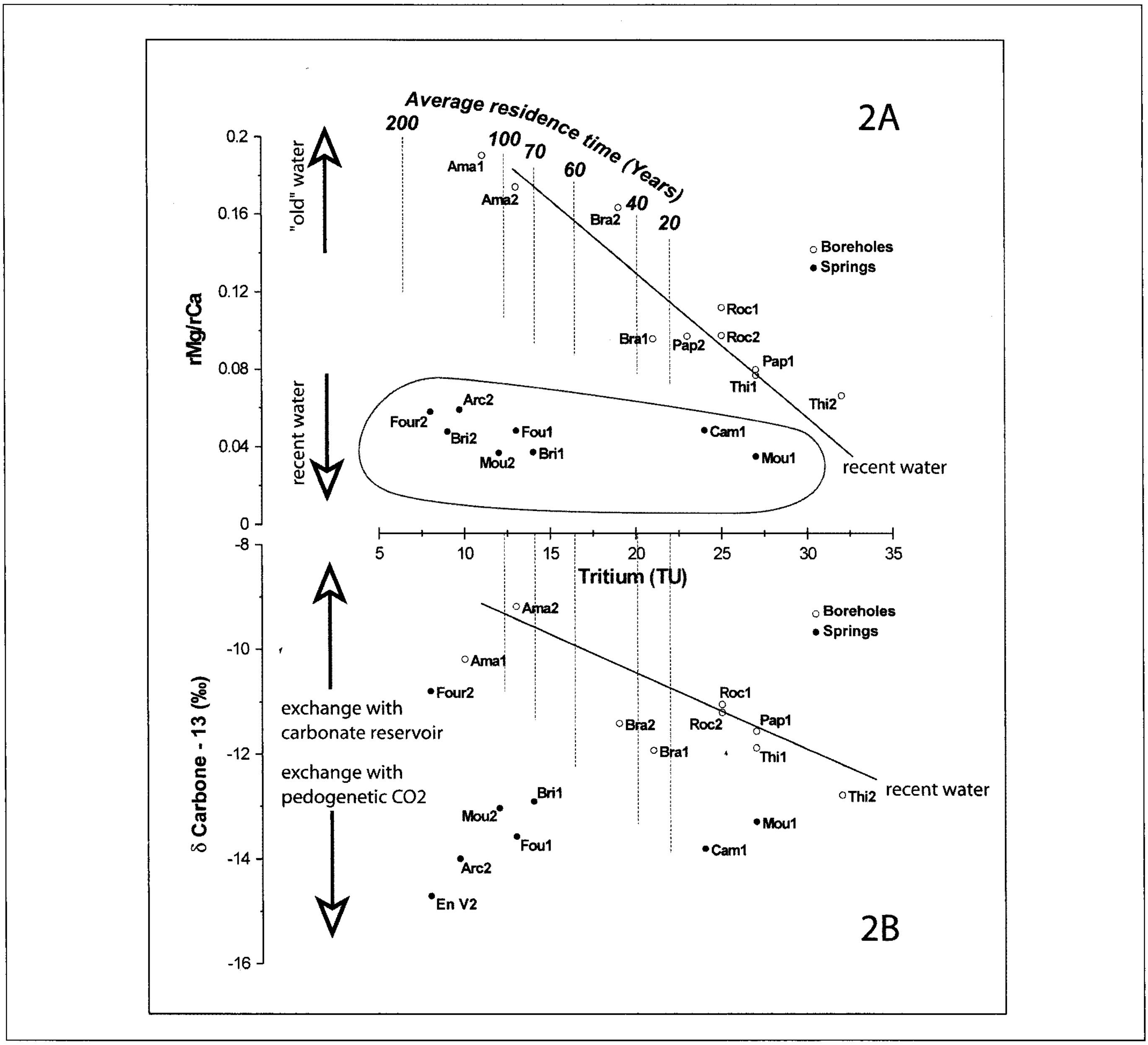

Figure 2. Doubs valley karst area. A: rMg/rCa *vs.* tritium, B: ^{13}C *vs.* tritium

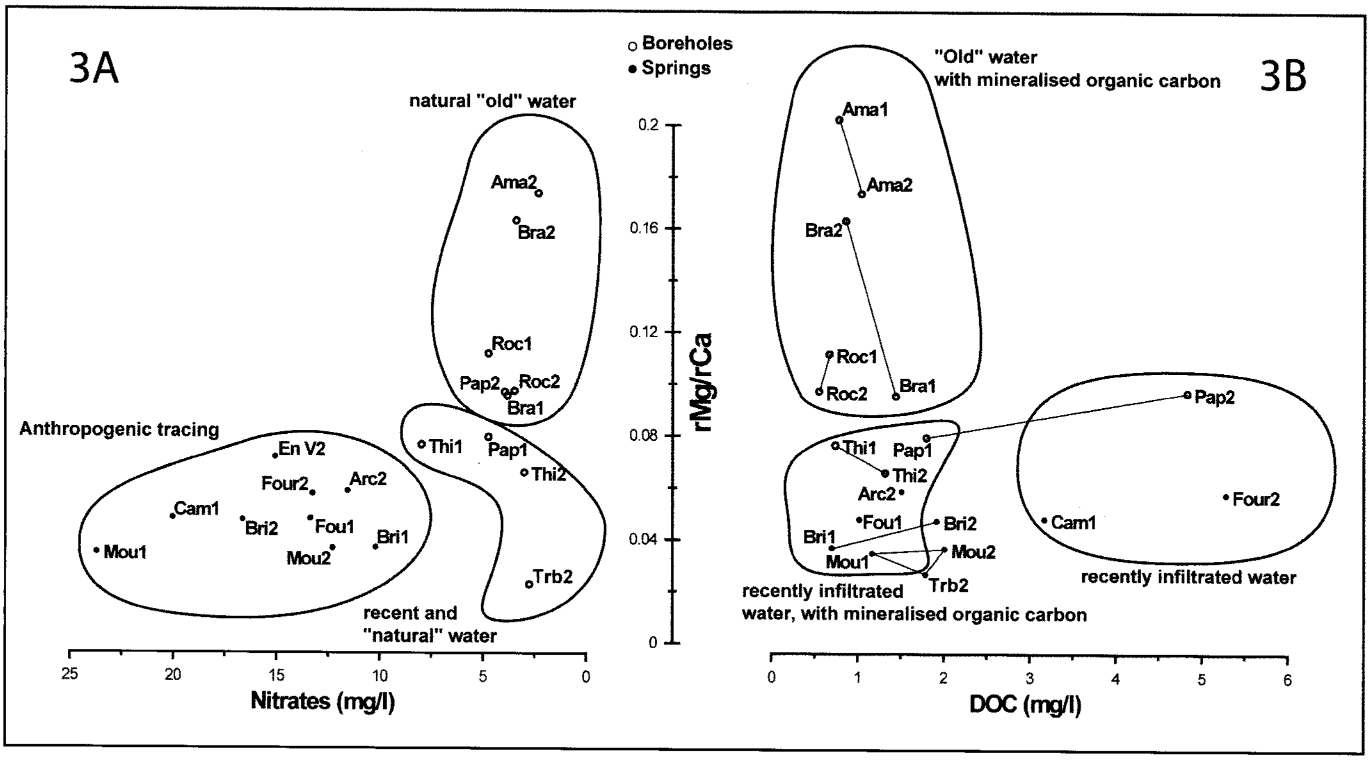

Figure 3. Doubs valley karst area. A: rMg/rCa *vs.* Nitrates B: rMg/rCa vs DOC

than 5 mg/l. These 'old' waters are not affected by a current infiltration. On the contrary, several spring waters have a low ratio, and nitrate contents higher than 10 mg/l. It means that a part of their anthropogenic nitrate is tracing them.

Plotting DOC *vs.* rMg / rCa (Fig. 3B) displays water points whose ratio is higher than 0.1 and DOC lower than 1.5 mg/l. This 'old' water had enough time to get its OC mineralised. Conversely, few points have a high DOC content, which attests a very short infiltration time. In the flow of most of the springs and boreholes, infiltration has enough time to get its organic matter mineralised.

4. DISCUSSION

4.1 Mixing model

Using a simple perfect mixing model of equal recharges, the tritium output can be estimated:

$$O_n = \sum_{p=0}^{p=\infty} \alpha * (1-\alpha)^p * \lambda^p * I_{(n-p)}$$

where

O_n is the output of the year n

α is the recharge coefficient. $\alpha = (2 - \tau) / (2 * \tau)$;

τ is the residence time;

λ is the radioactive decay coefficient;

p is the rank of the recharge

$I_{(n-p)}$ is the input signal of the year (n-p)

The theoretical output curve is an asymetric bell curve, which induces an indetermination for the 10 - 20 UT range.

The combination of tritium measurements with rMg/rCa ratios (fig. 2A) enables to raise the indecision: the 'spring' cluster outflows a water younger than 10 years, whereas the 'borehole' cluster outflows water that can be more than 10 years of age.

In addition, ^{13}C *vs.* tritium enables to separate two different behaviours: an exchange with the carbonate matrix (little negative) and a dissolution of pedogenetic CO_2 (very negative).

So we can distinguish, among the boreholes, Amagney which samples 'old' confined water (100 yr) with a ^{13}C enrichment within the carbonate reservoir, and the other boreholes which sample more recent water, more or less open to the pedogenetic CO_2. Roughly calibrating the ratios on the computed output tritium contents, it appears that Amagney's water is about 90-150 years old, while Branne extracts water that is 20 to 50 years old. The other boreholes extract more recent water, characterized by a moderate CO_2 input from the soil, and a rMg/rCa ratio which is higher than that of the springs draining the same layers.

Type	Point	N°	Residence Time rMg/rCa	Residence time ^{13}C	NO^3	DOC	Residence time	Influence of infiltration	Vulnerability
spring	Arcier	2	Low	Low	Medium	Low	Low	Medium	High
spring	Mouillère	1	Low	Low	Medium	Low	Low	Medium	High
spring	Mouillère	2	Low	Low	High	Medium	Low	High	Very high
temp.spr.	Trébignon	2	Low	-	Low	Medium	Low	Medium	High
spring	Camping	1	Low	Low	Low	High	Low	High	Very high
borehole	Thise	1	Medium	Medium	Medium	Low	Medium	Medium	High
borehole	Thise	2	Low	Low	Low	Low	Low	Low	Medium
borehole	Roche-Novillars	1	Medium	Medium	Low	Low	Medium	Low	Low
borehole	Roche-Novillars	2	Medium	Medium	Low	Low	Medium	Low	Low
borehole	Paper mill	1	Medium	Medium	Low	Medium	Medium	Medium	High
borehole	Paper mill	2	Medium	-	Low	High	Medium	High	High
borehole	Amagney	1	High	High	Low	Low	High	Low	Very low
borehole	Amagney	2	High	High	Low	Low	High	Low	Very low
spring	Briseux	1	Low	Low	Low	Medium	Low	Medium	High
spring	Briseux	2	Low	-	High	Medium	Low	High	Very high
cave	En Versenne	2	-	-	Medium	-	-	-	-
spring	Fourbanne	1	Low	Low	Medium	Low	Low	Medium	High
spring	Fourbanne	2	Low	Medium	Medium	High	Low	High	Very high
borehole	Branne	1	Medium	Medium	Low	Low	Medium	Low	Medium
borehole	Branne	2	High	Medium	Low	Low	High	Low	Very low

Table 1. Vulnerability of the water points

4.2. Estimation of vulnerability

With these reactions, we can classify (table 1) the different aquifers according to their behaviour:

- their absolute (tritium) or relative (^{13}C, rMg/rCa) mean residence time enables to classify the size of the reservoir;
- their reaction to infiltration (NO_3^- and DOC) enables to distinguish their buffering capacity versus recharge.

Combined, these two descriptors can be used as a validation tool for a vulnerability estimation. So, most of the spring samples appear as highly vulnerable, and part of the borehole samples appear lowly vulnerable, while others look more vulnerable.

5. CONCLUSION

This comparison of the chemical and isotopical behaviours of springs and boreholes which are draining the same Jurassic layers appears as a successful means of appreciation of a current recharge of these aquifers, as well as their global vulnerability.

Acknowledgments

We thank Mrs Sophie Maraux for the improvement of the translation into English, and Bartolome Andreo for the "resumen".

REFERENCES

Batiot, C., Emblanch, C. and Blavoux, B., (2001) Caractérisation du fonctionnement des systèmes karstiques par la variabilité des teneurs en COT à leur exutoire. Expérimentation sur différents aquifères du Sud - Est de la France. 7th Conference on Limestone Hydrology and Fissured Media, Besançon 20-22 sep. 2001, J. Mudry and F. Zwahlen (Eds.), *Sciences & Techniques de l'Environnement,* Mém. H. S. n° 13 : 27-30, 4 fig., 1 tabl.

Emblanch, C. (1997) *Les équilibres chimiques et isotopiques du carbone dans les aquifères karstiques: étude en région méditerranéenne de montagne.* Thèse de doctorat de l'Université d'Avignon, 197 p.

Emblanch, C, Blavoux, B., Puig, J. M. and Couren, M. (1998a) Le marquage de la zone non saturée du karst à l'aide du carbone 13. *C. R. Acad. Sci. Paris,* Série II a, tome 326, n° 5 mars 1998, p 327-332.

Emblanch, C., Blavoux, B., Puig, J. M. and Mudry, J. (1998b) Dissolved organic carbon of infiltration within the autogenic karst hydrosystem. *Geophysical Research Letters,* vol 25, n°. 9, p 1459-1462.

Emblanch, C., Puig, J.M., Zuppi, G.M., Mudry, J. and Blavoux, B. (1999) Comportement particulier lors des montées de crues dans les aquifères karstiques, mise en évidence d'une double fracturation et/ou de circulation profonde: exemple de la Fontaine de Vaucluse. *Eclogae Geologicae Helvetiae,* 92/2: 251-257, Birkhäuser Verlag, Basel.

Emblanch, C., Batiot, C., Mudry, J., Blavoux, B. and Puig, J.M. (2001) Utilisation du carbone organique dissous pour mettre en évidence une infiltration rapide en début de crue: cas d'un petit aquifère karstique. 7th Conference on Limestone Hydrology and Fissured Media, Besançon 20-22 sep. 2001, J. Mudry & F. Zwahlen (Eds.), *Sciences & Techniques de l'Environnement,* Mém. H. S. n° 13 : 141-144, 2 fig., 1 tabl.

Mudry, J. (1987) Apport du tracage physico-chimique naturel à la connaissance hydrocinématique des aquifères carbonatés. Thèse Sciences Naturelles, Uni. Besançon, 378 p.