Contribution of time tracers (Mg^{2+}, TOC, $\delta^{13}C_{TDIC}$, NO_3^-) to understand the role of the unsaturated zone: A case study-Karst aquifers in the Doubs valley, eastern France

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Contribution of time tracers (Mg^{2+}, TOC, $\delta^{13}C_{TDIC}$, NO_3^-) to understand the role of the unsaturated zone: A case study—Karst aquifers in the Doubs valley, eastern France

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[1] Time tracers (NO_3^-, TOC, $\delta^{13}C_{TDIC}$, Mg^{2+}) have been used to define the hydrodynamic behavior of a karst system: high values in NO_3^- and TOC reflect rapid infiltration and consequently a short residence time within the aquifer, whereas enriched $\delta^{13}C_{TDIC}$ and high Mg^{2+} are expected for "old water". 9 Springs and 5 boreholes have been sampled during three field campaigns in the Doubs valley karst aquifer: low water, flood and recession periods. A clear differentiation can be highlighted between boreholes, characterized by a long residence time, and springs that show a rapid infiltration. Considering only the springs values, it appears that TOC and $\delta^{13}C_{TDIC}$ contents can easily be correlated to the sampling period. We show then the contribution of the unsaturated zone to the discharge during the low-water period, and the existence of reserves that seem badly connected to the drainage network, and that contribute poorly to the minimal flow. *INDEX TERMS:* 1040 Geochemistry: Isotopic composition/chemistry; 1829 Hydrology: Groundwater hydrology; 1875 Hydrology: Unsaturated zone; 1803 Hydrology: Anthropogenic effects. **Citation:** Celle-Jeanton, H., C. Emblanch, J. Mudry, and A. Charmoille, Contribution of time tracers (Mg^{2+}, TOC, $\delta^{13}C_{TDIC}$, NO_3^-) to understand the role of the unsaturated zone: A case study—Karst aquifers in the Doubs valley, eastern France, *Geophys. Res. Lett.*, *30*(6), 1322, doi:10.1029/2002GL016781, 2003.

1. Introduction

[2] The vadose or unsaturated zone in a karst system typically consists of a soil layer, an epikarst and a transition zone (unsaturated zone s.s.), between the epikarst and the saturated zone, that could be several hundred meters thick. In the soil layer, water infiltrating through the soil matrix gets typical chemical and isotopic signatures by mineral and/or soil CO_2 gas dissolution [*Albéric and Lepiller*, 1998]. The new rain water is able to recharge the aquifer rapidly, possibly through fractures or surface swallets, and mobilizes older, deeper water out of the aquifer that was residing in smaller fractures and pores. This older water is at or near the equilibrium with limestone carbonates, but the new water is not. Many approaches were then used to evaluate the mixing between the two types of water: oxygen-18 [*Lakey and Krothe*, 1996; *Vallejos et al.*, 1997; *Marc et al.*, 2001], carbon-13 [*Emblanch et al.*, 1998a], Mg^{2+} [*Wels et al.*, 1991; *Blavoux et al.*, 1992] and Total Organic Carbon (TOC) [*Emblanch et al.*, 1998b]. In this study, we have used a combination of these chemical and isotopic tracers to reduce the uncertainties experienced while using a single tracer. We focused on TOC, major ions, $\delta^{13}C_{TDIC}$ (Total Dissolved Inorganic Carbon), pCO_2 measurements on springs and boreholes to understand the complexity of the Doubs valley aquifers [*Abdelgader et al.*, 1996; *Mudry et al.*, 2002]: a definition of the water origin and a determination of the rough mixing ratio of pre-existing water and rapid infiltration will be given.

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2. Site and Analytical Method

[3] The plateau of Besançon (Jura, Eastern France) spreads between the wide valley of the Ognon to the North and the enclosed valley of the Doubs to the South. The 200 m thick aquifer is composed of Bajocian and Bathonian limestones, that are unconfined on their greater part and become overburdened by Oxfordian marls towards the Doubs Valley. This aquifer has a great importance, as it is used for industrial purposes (paper mills) and drinking water supplies.

[4] 9 springs and 5 boreholes have been sampled during three field campaigns that cover the main hydrological events: low water (June 2000), flood (November 2000) and recession (May 2001) periods. They were analysed for cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), anions (Cl^-, SO_4^{2-}, NO_3^-), $\delta^{13}C_{TDIC}$ and TOC. Field parameters (pH, electric conductance, and HCO_3^-) were measured immediately after the sampling. Major elements were analysed at the Geosciences Department of the University of Franche-Comté at Besançon, analysis of carbon-13 and TOC were processed at the Hydrogeology Department of Avignon.

3. Results

[5] A principal component analysis (PCA) was carried out to summarise the relations between chemical variables (Figure 1). The 2 principal axis of PCA explain 74% of the sampling variance. Axis 1 (47%) is mainly determined by SO_4^{2-}, NO_3^-, Cl^-, Na^+ and electric conductance is the anthropogenic factor. SO_4^{2-} could also be due to a contact with marls. Axis 2 (27%) is determined by TOC and Mg^{2+} and represents the residence time factor. In factor plan 1–2, 3 groups of water can be distinguished. Boreholes have the highest Mg^{2+} contents, which suggests a long residence time within the aquifer, according to the slow dissolution kinetics of dolomite. Conversely, springs, which are resurgent cave streams, closely associated with surface runoff through sinkholes, have the highest content in TOC. The

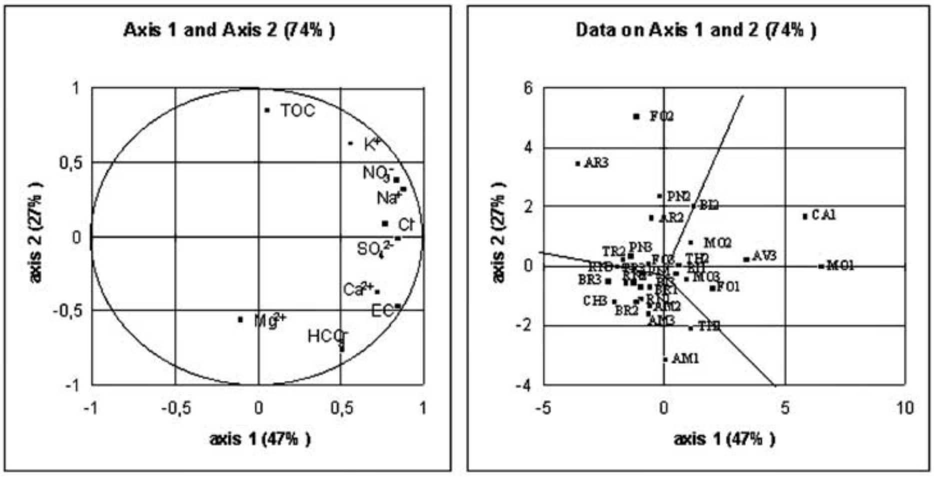

Figure 1. Principal Component Analysis (29 measurements).

third group is characterised by the springs that emerge in agglomerations undergoing human pollution.

[6] To confirm this preliminary result, all the data was plotted on a NO_3^- *versus* Mg^{2+} diagram (Figure 2). These two ions are good tracers of both residence time and pollution: (1) as ground waters flow through the same limestones, and according to the incongruent dissolution of dolomite, the increase of Mg^{2+} [*Blavoux et al.*, 1992] corresponds to the increase of the residence time within the limestones (which have a low Mg^{2+} content); (2) NO_3^-, that comes from the lixiviation and mineralisation of the natural organic matter of the soil or from the dissolution of fertilizers, which characterises rapid infiltration. These two tracers highlight the difference between two groups. The springs are characterised by a low Mg^{2+} content (below 4.5 mg/l) and by variable values of NO_3^- ranging from 1.14 mg/l to 23.7 mg/l. The maximum values are attributed to Camping (CA) and Mouillère (MO), located in polluted areas. The boreholes have a low NO_3^- content and show variable Mg^{2+} values that increase from Thise (TH) to Amagney (AM) and Branne (BR) with the transit time in the aquifer. The highest Mg^{2+} values are those of Amagney (AM) and Branne (BR); these are the deepest boreholes of the sector (110 m), characterised by the longest residence time. As opposed, Thise (TH) is located in the shallowest part of the aquifer (piezometric level of −3 m) and then appears to be closer to the contents of the springs (4.72 mg/l and 6.85 mg/l).

[7] The water sampled from the springs, except Fourbanne (FO2) and Camping (CA1) (5.28 mg/l and 3.17 mg/l respectively) reveals a content of TOC ranging from 0.66 to 2 mg/l. These values have the same order of magnitude as typical groundwater that contains less than 2 mg/l [*Drever and Stillings*, 1997] and Southeastern France karst systems [*Emblanch et al.*, 1998b] with values ranging from 0.5 mg/l to 2 mg/l. Figure 3 displays variations of TOC versus $\delta^{13}C_{TDIC}$ for the three campaigns. The right-hand inset indicates that boreholes are usually enriched in $\delta^{13}C_{TDIC}$ and depleted in TOC compared to springs. Considering the classical $\delta^{13}C_{TDIC}$ ratio from carbonate (0 ± 3‰), from atmospheric CO_2 (−8‰) [*Butcher et al.*, 1992] and from biogenic CO_2 (−22‰) [*Fleyfel and Bakalowicz*, 1980; *Dever*, 1985; *Eichinger*, 1987; *Merlot et al.*, 1996], enriched values in $\delta^{13}C_{TDIC}$ are expected for "old water" whereas infiltration has a depleted value. According to *Drever and Stillings* [1997], TOC in groundwater is usually derived from the organic layer in soils. Heterotrophic bacteria, present in the unsaturated zone, aerobically degrade TOC to produce CO_2. Then, high values in TOC reflect a rapid infiltration and consequently a short residence time within the aquifer [*Batiot et al.*, 2003]. Considering only the spring values, it appears that TOC and $\delta^{13}C_{TDIC}$ contents can easily be correlated to the sampling period. The low flow stage (BI1, FO1, MO1) is characterised by average TOC values, the most depleted $\delta^{13}C_{TDIC}$ (Figure 3) values and the highest Mg^{2+} values (Figure 2). The Camping spring (CA) has a high TOC content, compared to the other springs, due to its location in a polluted area. During the flood period (BI2, FO2, MO2), a $\delta^{13}C_{TDIC}$ and TOC enrichment and an Mg^{2+} impoverishment can be observed. The recession period (BI3, FO3, MO3) leads to a decrease of the TOC and Mg^{2+} contents and an enrichment in $\delta^{13}C_{TDIC}$ for all the

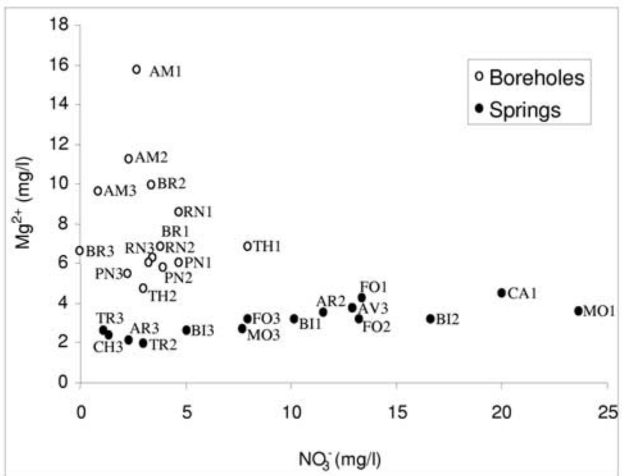

Figure 2. Mg^{2+} (mg/l) versus NO_3^- (mg/l).

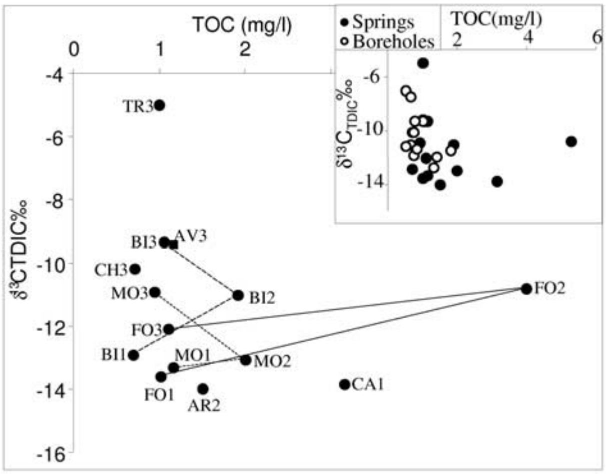

Figure 3. TOC (mg/l) versus $\delta^{13}C_{TDIC}$ (‰) for the springs of the Doubs valley aquifer. On the right-hand inset, both springs and boreholes values are plotted.

springs (TR: Trébignon, AV: Avanne, CH: Chaney, MO: Mouillère, BI: Briseux, FO: Fourbanne).

4. Discussion

[8] PCA and Mg^{2+} *versus* NO_3^- diagrams have shown that the springs are mainly characterised by recent infiltrations whereas boreholes have a longer residence time. We then consider that boreholes catch ''old'' water whereas springs are characterised by a rapid infiltration (high anthropogenic components and low Mg^{2+}). Mg^{2+}, TOC and $\delta^{13}C_{TDIC}$ values over time should give some information on old *versus* new water entering the system during three stages : low flow, flood and recession periods. The low stage flow has the longest residence time according to the Mg^{2+} (Figure 2) and TOC (Figure 3) values. The $^{13}C_{TDIC}$ (Figure 3) and TOC values, relatively high (ranging from 0.67 to 3.17 mg/l), suggest an origin from the unsaturated zone, where the system is open to the soil CO_2. The flood period shows a decrease of the residence time (increase of TOC and lowering of Mg^{2+}) due to the rapid infiltration of new water. A tiny enrichment in $\delta^{13}C_{TDIC}$, compared to the low stage flow, could have three origins: (1) a participation of the saturated zone, where groundwater is closed off from the source of soil CO_2; (2) CO_2 a degassing due to the two-phase turbulent flow (this hypothesis cannot explain TOC and Mg^{2+} variations); (3) an infiltration of surface waters, characterised by $\delta^{13}C_{TDIC}$ from atmospheric CO_2. This latter hypothesis only explains the variations observed at the outlet of the Fourbanne cave stream (FO). The recession stage reveals an absence of rapid infiltration, according to the decrease in TOC and the average values in Mg^{2+} (similar to the autumn ones). As in the previous stage, the $\delta^{13}C_{TDIC}$ enrichment should reflect an increase in the participation of the transmissive part of the saturated zone.

[9] The phenomenon observed during the low stage flow shows a significant contribution of the unsaturated zone to the discharge during the low-water period in this system. The water seems to have a long residence time through the unsaturated zone, as the content in Mg^{2+} ranges from 3.15 mg/l to 4.45 mg/l. *Emblanch et al.* [2003] found values for the unsaturated zone waters of the Ventoux karst systems from 3 to 5 mg/l. Ratios Mg/Ca measured on the Ventoux karst system range between 0.06 and 0.11. For the Doubs karst system, we found values range between 0.008 and 0.025. In first estimate, we should expect a maximum value of 5mg/l in the unsaturated zone. This leads to the conclusion that the summer campaign (low flow) corresponds to waters that have circulated in the unsaturated zone ($\delta^{13}C_{TDIC}$, TOC) where they acquired their Mg^{2+} content. According to the values found in boreholes with an Mg^{2+} increase when the residence time increases, we assume that reserves could be found but seem badly connected to the drainage network, and contribute poorly to the minimal flow.

5. Conclusion

[10] By using time tracers (TOC, NO_3^-, $\delta^{13}C_{TDIC}$, Mg^{2+}), we have shown that the Doubs valley karst aquifer is a complex system, composed of an unsaturated zone that is badly connected with the saturated zone. The latter is characterised by two types of fractures, related respectively to transmissive and storage functions.

[11] The behaviour of the system could be summarized as follows: during the flood period, rainwater infiltrates through the soil (very negative $\delta^{13}C_{TDIC}$), enriched in water-soluble organic matter (high TOC content) and provokes a high pressure transfer within the aquifer that connects the saturated zone (two types of fractures providing the transmissive and capacitive functions). This mixing between pre-existent water and recent infiltration leads to an enrichment in $\delta^{13}C_{TDIC}$. During the recession period (springtime), the stock of water-soluble organic matter decreases and then the waters have a lower content in TOC. The pressure excess homogenises between the conduits and the fissures in the saturated zone. The unique flow participation is then linked to the mixing of recent infiltrations with stored waters ($\delta^{13}C_{TDIC}$ enriched). During the depletion period, the saturated zone is poorly connected and the minimal flow can be roughly attributed to the unsaturated zone.

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