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Dissolved organic carbon of infiltration within the autogenic karst hydrosystem

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Abstract. This work aims at using the Dissolved Organic Carbon (DOC) as a tracer of infiltration in karstic aquifers with only diffuse recharge. Regular measurements of DOC have been carried out in three karstic systems located in South-eastern France during an hydrogeological cycle. Considering that the DOC is mainly located in the soil, it might be used as a tracer of the infiltration. The behavior of the tracer considerably varies between the high and low flow periods.

The low concentrations of DOC occur when the flow is mainly due to a long residence time of the water in the saturated zone, whereas the concentration of DOC increases with the contribution of recent waters during the flood period. So the DOC can be used as a tracer of the infiltration. A comparison between the magnesium and the DOC allows to demonstrate the ability of using the DOC as a tracer of the water residence time.

Introduction

Dissolved Organic Carbon (DOC) has previously been used, as a tracer in karst, only in particular cases when its high content is both a pollution indicator and a potential source of CO₂ due to its mineralization (JAMES, 1981 ; ALBERIC & LEPILLER 1996).

The purpose of this work is to characterize the variation range of DOC and to study its potential as a natural tracer in karst aquifers of the lowly anthropized Mediterranean zone.

In this aim, three aquifers of the Vaucluse experimental area have been surveyed. The DOC content of the three outlets is studied, according to hydrodynamic conditions. Further more, we have compared the DOC to several natural tracers which are commonly used, especially magnesium. The latter is known as a good tracer of residence time in these systems where the limestone Mg²⁺ content is low and rather regionally constant.

Sites and Method

Three karst systems of the Vaucluse experimental area (Southeastern France) have been surveyed during 8 months. This period includes a recession period and a proceeding of flood period. The sampling has been done weekly in low-water periods and daily in flood ones.

The three systems are different by their size and their elevation range. The Fontaine de Vaucluse is one of the largest European karst aquifers, with its 1130 km² and its yearly average discharge of 20 m³/s; the average elevation of its catchment area is 870 m (BLAVOUX *et al.*, 1992).

Millet spring displays the particularity of being a perched system inside the catchment area of Fontaine de Vaucluse. This small system (2 km²) outflows at a height of 1000 m. Its average discharge is 30 l/s (EMBLANCH *et al.*, 1997).

Notre-Dame des Anges system is situated at the north-east limit of the Fontaine de Vaucluse one, its surface is 20 km², its discharge 120 l/s and its average altitude 700 m (Lastennet *et al.*, 1995).

In the three cases, the aquifer is made of recifal limestone free from organic matter (MASSE, 1968, 1972). So we can consider the soil as the unique source of organic carbon in this case. For DOC analysis, we used in Avignon a Bioritech TOC 700 analyzer, whose principle is elimination of total dissolved mineral carbon by acid attack and analysis of transformed DOC into CO₂ by hot oxydising. Accuracy of this measurement is 0,05 mg/l. Magnesium, used as a tracer of residence time, with a 0,1 mg/l accuracy.

Results

In a first step, this work deals with DOC and its relationships with hydrodynamic conditions. Figure 1 displays seasonal variation of discharge and DOC for the three monitored systems. It immediately appears that variations have the same order of magnitude, with lower contents of about 0,5 mg/l in dry periods and higher ones which are close to 2 mg/l during flood periods. Despite the low contents in DOC compared to Total Dissolved Carbon (TDC 65 mg/l), its variation range offers a good possibility of interpretation.

All the DOC obtained values are exactly situated in the classical range of groundwaters (SIGG *et al.*, 1992 ; BEYNEN *et al.*, 1997 ; MULLER et SEILLER, 1997). The low content values are observed during low stage flow, the high contents during floods.

A lag is visible between discharge variations (pressure transfer) and DOC variations (transit). The lag time is variable according to the studied system. This variation can be explained by the own inertia of each system. This inertia depends mainly on the volume of water to push out before the arrival of recent water at the spring.

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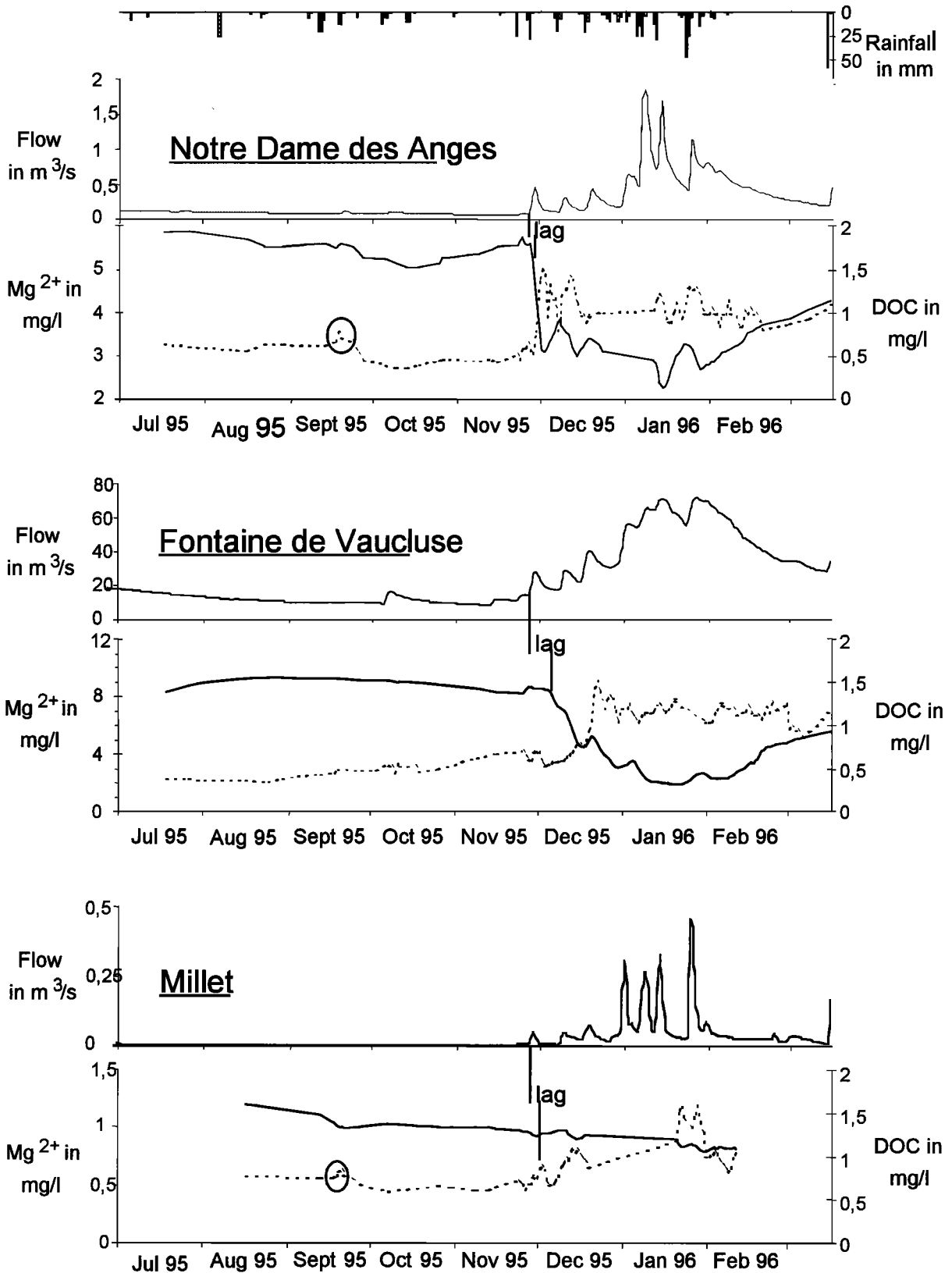


Figure 1 : Comparison of variations in DOC and Mg²⁺ with a 3 days moving average.

Discussion

Figure 1 clearly displays significant differences between low water figures of different springs. The contents of Millet range from 0,6 to 0,7 mg/l, those of Notre-Dame des Anges are about 0,5 mg/l while those of Fontaine de Vaucluse are about 0,4 mg/l. Natural tracing using magnesium and tritium demonstrates that the mean residence time of water in the Fontaine de Vaucluse is longer than in Notre-Dame des Anges, which is itself longer than in Millet spring (BLAVOUX *et al.*, 1991 ;EMBLANCH, 1997).

It appears during depletion periods that the more residence time is increasing, the more mineralization of DOC into mineral carbon is consequent, which promotes DOC as a valuable potential tracer of residence time.

As a consequence, outflows of water highly mineralized in DOC must reveal outflows of infiltration water, with a short residence time within the aquifer because the DOC acquired during infiltration had not time enough to mineralize. Residual contents which are observed even in long residence time waters can be explained by the fact that a part of organic matter can hardly be mineralized and so remains within the system, even during low water periods.

On 19th September 1995, we can observe simultaneously significant DOC peaks at Notre-Dame des Anges and Millet. These peaks are associated to discharge variations which are hardly measurable. The fact of finding this peak on two different systems and not on the third one enables us to affirm that it was not an operating error, but a reality.

It corresponds to an arrival, at the outlet, of infiltration water originating from summer rainfalls. The fact that the Fontaine de Vaucluse system does not display any response can be simply explained by a more important inertia. The DOC is in this case the only tracer whose variations are significant of an arrival of recent water at the outlet of the system. All the major elements which were analyzed, even if they all display oscillations at this period, have no significant variations.

During flood period, DOC is also an accurate tracer. At Notre-Dame des Anges, LASTENNET *et al.* (1995 ;1997) showed a noticeable transit of quick infiltration water which is characterized by dilution. This quick infiltration is appearing very clearly during the flood increasing of the 11/27/1995, when an important and sudden peak of DOC is observed.

During the depletion period, DOC can indicate hydrodynamical modifications with no significant variation of the discharge. Is it the same during flood periods ? In February, 1996, while the Fontaine de Vaucluse shows a depletion phase which is apparently not disturbed, the DOC indicates a recent water transit within the system. Heterogeneity and complexity of flows within karst aquifers are thus clearly displayed. Even during recessions, plenty of infiltration waters can outflow.

Ability of Tracing Residence Time

A simple study of DOC and discharge already enabled to demonstrate the high sensitiveness of this tracer as a tracer of infiltration and heterogeneity of water flows in the karst aquifers. Comparing it with Mg^{2+} can confirm the possibility of using DOC as a tracer of residence time.

On figure 1, we can see DOC and Mg^{2+} variations with weekly samplings during low-water periods and daily ones in flood periods, on which was calculated a moving average on three

points. So it will be necessary to interpret separately these two periods when the calculation is not comparable.

On the three systems, it exists a very clear opposition between Mg^{2+} and DOC variations. This reverse symmetry shows that DOC can be used as a tracer of residence time. Moreover, considering the respective variation ranges of both tracers, we can, in the studied aquifers, estimate that the rate of mineralisation of DOC is close to that of acquiring Mg^{2+} . For Millet spring, we notice the same opposition between both elements, in spite of the low variation of Mg^{2+} .

In systems such as Millet, where variations of magnesium and other classical tracers of residence time like silica are hardly interpretable, DOC appears as a very worthy tracer for monitoring evolutions of residence time.

Conclusion

This high sensitiveness of DOC has been demonstrated for tracing infiltration waters flows at the outlets of karst systems without allogenic concentrated recharge. So, during low waters, it was possible to display hydrodynamical modifications, which were unmeasurable in discharge.

A significant result of this study is the possibility of using DOC as a tracer of residence time in the type of the studied system, even when other usual tracers of residence time are not usable.

Without any knowledge about nature and contents of DOC in infiltration water, this tracer do not enable us a quantitative monitoring of the evolution of the average residence time in the aquifer. It allows a qualitative monitoring, even where we cannot do it with usual tracers.

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