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Use of Total Organic Carbon (TOC) as tracer of diffuse infiltration in a dolomitic karstic system: The Nerja Cave (Andalusia, southern Spain)

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[1] Recent studies in several karstic systems in France have highlighted that Total Organic Carbon (TOC) was a relevant parameter in order to characterise the behaviour of aquifers, to differentiate the water types that participate in karstic flow (fast infiltration, unsaturated zone, saturated zone) and to evaluate their vulnerability. This study on TOC dynamics at the experimental site of the Nerja Cave has been performed to test the potential of this tracer in a particular climatic (Mediterranean climate), lithologic (dolomitic marbles) and hydrodynamic (diffuse flow behaviour) context. TOC evolution, compared to those of classical tracers used in hydrogeology, permits the understanding of the hydrodynamical behaviour of the unsaturated zone of this dolomitic aquifer, whose response to precipitation is slower than that commonly obtained in karstic aquifers of calcareous nature. *INDEX TERMS:* 1010 Geochemistry: Chemical evolution; 1055 Geochemistry: Organic geochemistry; 1832 Hydrology: Groundwater transport 1875 Hydrology: Unsaturated zone. **Citation:** Batiot, C., C. Liñán, B. Andreo, C. Emblanch, F. Carrasco, and B. Blavoux, Use of Total Organic Carbon (TOC) as tracer of diffuse infiltration in a dolomitic karstic system: The Nerja Cave (Andalusia, southern Spain), *Geophys. Res. Lett.*, *30*(22), 2179, doi:10.1029/2003GL018546, 2003.

1. Introduction

[2] In the case of aquifers made of organic matter free carbonates, all the TOC results from organic matter decomposition by bacterial activity in the soil, so it is an interesting tracer of fast infiltration [*Albéric and Lepiller*, 1998; *Emblanch et al.*, 1998]. In calcareous karstic systems, where the magnesium distribution is homogeneous, Mg^{2+} is a good indicator of the water residence time because of its low dissolution kinetics. Recent research on the experimental site of Vaucluse (south-eastern France) highlighted the complementary nature of these two tracers and their relevance in the study of water transit in the aquifer [*Emblanch et al.*, 1998; *Batiot et al.*, 2003]. Indeed, during flood events, the arrival of recent water at the spring is evidenced by an increase of TOC values and a decrease of magnesium. On the other hand, during low flow conditions, the dis- charge of long residence time water is characterised by an increase in magnesium and a depletion in TOC. Then, the use of these two parameters permits the characterisation of the different water types that participate in karstic flow. Moreover, *Batiot et al.* [2003] showed that TOC is the most relevant tracer of the fast infiltration compared to others classical tracers such as Ca^{2+}, NO_3^-, Mg^{2+} or ^{18}O.

[3] The aim of this work is to know the potential and the sensitivity of TOC as a tracer of the infiltration in the pilot site of Nerja Cave where water infiltrates slowly in the epikarst under climatic (Mediterranean climate), lithological (dolomitic marbles) and hydrodynamic conditions (diffuse flow behaviour) different to those of the south-eastern France aquifers. Since 1991, extensive research about environmental parameters, physical and chemical character- istics of the water have been carried out, both inside and outside the cave [*Carrasco et al.*, 1995, 1999; *Liñán et al.*, 1999; *Andreo et al.*, 2002]. Therefore, the cave is an interesting site to study the behaviour of TOC with respect to other commonly used tracers (i.e., major ions or isotopes).

2. Site and Methods

[4] The Nerja Cave, located in Andalusia (southern Spain), in the province of Málaga, about 5 km east of the coastal town of Nerja, is one of the most visited natural sites in Andalusia, South Spain [*Carrasco et al.*, 1999]. The cave extends almost horizontally between limits of 123 and 191 m a.s.l. and occupies a volume of about 300,000 m³. The climate outside the cave is typically Mediterranean, with a wet season from October to February and a long dry season specially marked during summer. The mean annual values are 490 mm for rainfall and 17.3°C for temperature.

[5] From the geological viewpoint the Nerja Cave is situated in southern border of Sierra Almijara, within the Alpujarride Complex of the Betic Cordillera, and it is developed within dolomite marbles of middle Triassic age. The marbles are permeable due to fracturing and karstifi- cation and, thus, constitute a carbonate aquifer. As a result of the Plio-Quaternary tectonic activity which affected this area, the cave is currently located in the unsaturated zone of the aquifer, above the piezometric level. The thickness of the unsaturated zone above the cave is highly variable, from 4 to 90 m. Except for gardens near the entrance, there is only low developed plant (shrubland species) or soil cov- erage above the cave. Rainfall and irrigation water from the gardens infiltrates through fissures and fractures of the marble to drip through the cave roof [*Liñán et al.*, 1999; *Andreo et al.*, 2002]. After several years of hydrochemical monitoring, a representative drip water point was selected within the cave, located in the Cataclysm Chamber, where

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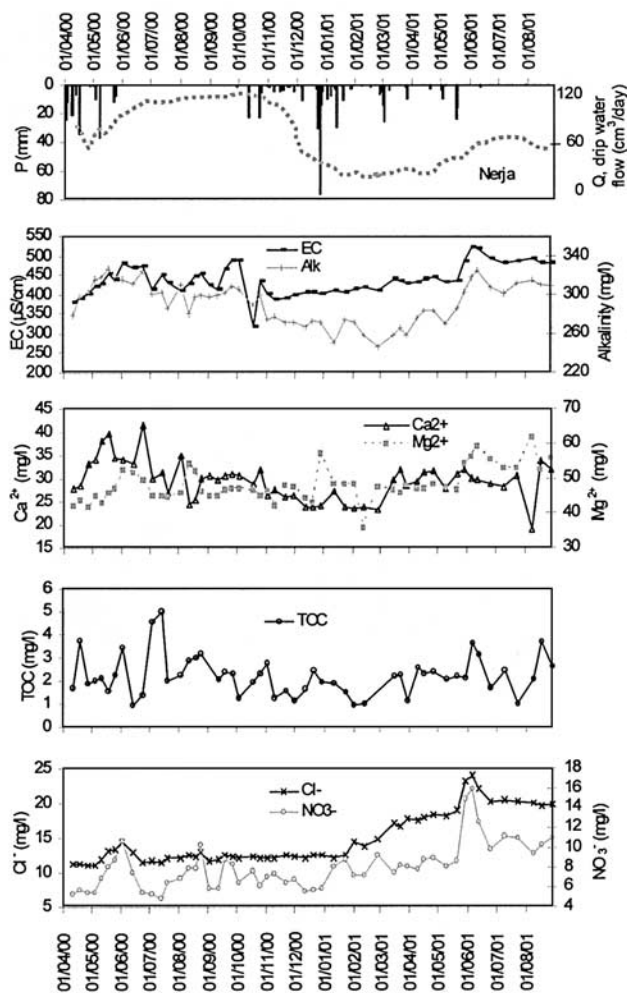[4]Laboratoire d'Hydrogéologie, Université d'Avignon, Avignon, France.

Figure 1. Temporal evolution of discharge (Q) electrical conductivity (EC), alkalinity (Alk), Ca^{2+}, Mg^{2+}, TOC, Cl^- and NO_3^-. Rainfall at Nerja.

there is no infiltration of irrigation water. During 17 months (from April 2000 to August 2001), the chemical composition of the drip water has been monitored with approximately weekly periodicity. The following parameters were measured in situ : electrical conductivity (EC), pH and temperature of water. Major ions were analysed in the laboratory of the Nerja Cave Institute. The analyses of TOC were performed in the University of Avignon using samples previously treated with $HgCl_2$.

3. Results

[6] Drip flow within the cave is very low. Under average rainfall conditions, total drip flow within the cave may be around $10-100$ m^3/year [*Andreo et al.*, 2002]. At the drip water point located in the Cataclysm Chamber, the mean drip flow is 89 cm^3/day [*Liñán et al.*, 1999]. On a multi-annual scale, the hydrograph of this point shows a wave-shape with maximum values during the summer months and minimum during the winter. Due to technical problems the discharge was not recorded during the study period and, thus, the outflow displayed in Figure 1 has been estimated by means of the correlation obtained with the earlier series

of rainfall-drip flow data. The absolute values of flow obtained could be not accurate but the general trend is absolutely in agreement with the results obtained since 1995 [*Liñán et al.*, 1999; *Andreo et al.*, 2002]. According to these researchers, there is a seasonal lag of several months from when the water enters the aquifer until it appears inside the cave. The unsaturated zone over the cave is made of medium and coarse-grained dolomite marbles, karstified and highly fractured, although they are partly plugged by carbonate precipitation or clays. This geological setting involves a very slow infiltration of rainfall water through the marbles to drip through the cave roof. The mean water residence time varies from 2 months after exceptionnal rain events, to 8 months under dry climatic conditions; so it depends on rainfall quantity but also on the volume of water stored in the unsaturated zone over the cave. These estimations of residence time have been made by comparing chemical (Cl^-, K^+) and isotopical (^{18}O) signals of the rainfall and drip water [*Liñán et al.*, 1999; *Andreo et al.*, 2002]. The drip water collected within the cave is of Ca-Mg-HCO_3 type and its average electrical conductivity is 437 μS/cm (Table 1). Several workers have shown, according to the chemical and isotopic compositions of rainfall and drip water, that the drip water is of apparent meteoric origin [*Carrasco et al.*, 1995; *Caballero et al.*, 1996; *Liñán et al.*, 1999]. Drip water is normally supersaturated in calcite throughout the year, and so calcium carbonate is deposited (Table 1). The mean pCO_2 is 0.18%, largely higher than that of the atmosphere (0.035%), and is higher in summer than in winter [*Carrasco et al.*, 1999]. The chemical composition of drip water is mainly determined by its alkalinity, Ca^{2+} and Mg^{2+} content which are controled by the pCO_2, but also by Cl^- and K^+ content (Figure 1 and Table 1). The pCO_2 determines the rate of saturation of drip water in calcite and dolomite and, consequently, the formation and growth of speleothems. In annual terms, electrical conductivity increases during the summer, when the water is most alkaline and had the highest Ca^{2+} and Mg^{2+} contents; moreover, during this period the water had higher pCO_2 values and was less supersaturated in calcite. Then, electrical conductivity falls progressively from autumn onwards, coinciding with the temporal evolution of drip water flow, and shows minimal values during the winter, when the precipitation of calcite is higher because the drip water is more supersaturated [*Andreo et al.*, 2002].

[7] TOC values are between 1 to 5 mg/l, with a mean value of 2.2 mg/l (Table 1). These contents are higher than those measured in several karstic systems from France, not influenced by anthropogenic pollution, where average values are often near 1 mg/l [*Batiot et al.*, 2003]. At the springs of Vaucluse, TOC content varies as a function of the discharge. For example, Fontaine de Vaucluse is characterised by a pressure transfer 24 to 72 hours after a sufficient rainfall event, and fast infiltration occurs. However, in the case of the unsaturated zone of the Nerja Cave, transfer and transport times are very slow. Concentrations and discharge increase in summer whereas the recharge period occurs during winter. This highlights the lag of several months between periods when rainfall infiltrates the soil and the hydrodynamic and hydrochemical response in the drip water point in the Cave (Figure 1).

Table 1. Statistical summary of the chemical data recorded in drip water from April 2000 to August 2001

	EC (μS/cm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na$^+$ (mg/l)	K$^+$ (mg/l)	Alk (mg/l)	Cl$^-$ (mg/l)	SO$_4^{2-}$ (mg/l)	NO$_3^-$ (mg/l)	SiO$_2$ (mg/l)	pCO$_2$ (%)	SI$_D$	SI$_c$	TOC (mg/l)
Max	521	41.4	61.7	9.7	1.5	326.5	24.0	12.5	12.9	5.7	0.60	2.68	1.00	5.00
Min	317	19.2	35.9	6.9	0.0	246.0	11.0	8.2	4.9	4.0	0.05	0.82	−0.06	0.95
Mean	437	29.5	48.1	7.8	0.9	292.0	14.6	9.3	8.0	4.6	0.18	1.98	0.66	2.23
V(%)	8.8	14.5	10.1	7.9	32.3	7.1	24.9	11.1	28.9	8.6	76.70	24.00	39.00	39.45

Number of samples: 53, m: arithmetic mean, v: coefficient of variation, EC: electrical conductivity, Alk: alkalinity, SI$_d$ and SI$_c$: saturation index in dolomite/calcite.

[8] The following tracers, TOC, Mg^{2+}, Ca^{2+}, Cl$^-$ and NO$_3^-$ show approximately the same annual evolution, although their source differs: on one hand, TOC, NO$_3^-$ and Cl$^-$ come from the infiltration of the rainfall in the system (atmospheric and/or pedogenic origin) and, on another hand, Ca^{2+} and Mg^{2+} have an internal origin since they come from the dissolution of the dolomitic marbles. Nevertheless, the temporal variation of TOC concentration is large and irregular compared to that of chloride concentration, which proves that TOC is a more sensitive tracer to infiltration than chloride.

4. Discussion

[9] The high concentration of TOC in drip water in Nerja Cave is due to the elevated content of organic matter in the soils that are poorly developed on the marbles of the study area [*ICONA*, 1986]. The shrubland species that cover Sierra Almijara grow and flower mainly during spring, while the vegetative activity decreases during summer (dry period) and it is minimum in winter [*Navarro and Cabezudo*, 1998]. During summer, as an adaptation mechanism to drought stress, leaf fall occurs, which are degraded, producing organic matter that is stored in the soil and then transported into the aquifer by the infiltration of rainwater. For this reason the soil water shows high TOC values at the base of the soil (142.6 mg/l average value, Table 2).

[10] The concentration of TOC in drip water is also higher with significant variations, up to 4 mg/l (Table 1), and a measurement accuracy of 0.05 mg/l. TOC displays similar evolution to other tracers of the infiltration, as NO$_3^-$ and Cl$^-$. The highest values of TOC (Figure 1) are recorded in summer because water at the drip point derives from rainwater that entered the aquifer after the previous dry season, transporting carbon from the soil when it has the highest content in organic matter from the degradation of the plants and then entering the aquifer in the recharge period of autumn-winter. Minimal TOC contents are

recorded during winter, due to the mineralization of TOC and to the arrival of infiltrated rainwater at the drip point in winter-spring, after the degraded organic matter has been washed-out into the aquifer by the previous period of recharge.

[11] The differences observed for major ion concentrations of drip water comes from variations in evaporation in the epikarst (particularly for chloride content) and, from differences in the solution-precipitation of carbonate minerals. During the dry period, the highest values of temperature are recorded, the mineralization of waters stored in the epikarst increases progressively due to evaporation (Figure 1) and by solution of the dolomitic marbles, although the high pCO$_2$ proves the low positive saturation index for calcite (SI$_c$) and, consequently its precipitation is quite limited, the opposite to what occurs in winter period [*Liñán et al.*, 1999; *Andreo et al.*, 2002]. Thus, at the end of the dry period, water stored in the unsaturated zone is characterised by high contents of Mg^{2+}, Ca^{2+}, Cl$^-$ and K$^+$.

[12] Therefore, elevated Mg^{2+} values recorded in the drip point correspond to an increase of water with a relatively long residence-time in contact with the dolomitic marbles of the unsaturated zone. As the increase of Mg^{2+} content is linked with concentrations of TOC and NO$_3^-$ in drip water, it suggests that rainwater infiltrated in the autumn-winter period (after the dry period) is progressively concentrated at a similar rate for both NO$_3^-$ and TOC contents. This can be explained by the hydrodynamic behaviour of the unsaturated zone in Nerja Cave system, which involves piston flow as deduced by comparison of isotopical and chemical data, between rain and drip waters [*Liñán et al.*, 1999; *Andreo et al.*, 2002]. Thus, the first rainfall infiltrated in autumn, with highest TOC content because the soil is particularly rich in organic matter (Table 2), is pushed towards existing water (with lower TOC content) stored in the unsaturated zone. In addition, some mixing occurs between these two water types, progressively increasing rainwater infiltrated after the dry period (in autumn-winter period), and consequently increasing the TOC contents in the solution. The same

Table 2. TOC Input and Output Signals (IS and OS) for the systems of the Nerja Cave and Vaucluse

Nerja TOC IS (mg/l) [1]		Vaucluse TOC IS (mg/l) [2]		MRT (months) [3]		Mean TOC OS (mg/l)		% of TOC mineralised	
				Nerja	*Vaucluse*	*Nerja*	*Vaucluse*	*Nerja*	*Vaucluse*
21/11/02	179.0	Min	10						
25/11/02	123.0								
11/12/02	133.7	Max	30						
16/12/02	134.7								
Mean (n = 4)	**142.6**	Mean (n = 18)	**18**	3−6	3−6	2−3	0.5−1	**98−99**	**94−97**

(1) Water sampled under a poorly developed lithosol above the dolomite marbles of the cave; (2) Values obtained under 3 representative soils of Vaucluse, developed above limestone, under mediterranean to mountain Mediterranean vegetation; (3) MRT: Mean Residence Time.

phenomenon can explain the high values of NO_3^- detected in dripwater during summer period.

[13] The elevated TOC concentrations in infiltration water explain the difference observed between those measured at the sampling points of Nerja cave and those of Vaucluse karst systems for a comparable water residence times. Table 2 shows that the percentages of TOC mineralised in these aquifers are very similar and the differences observed are only due to different input signals in TOC. Mineralisation kinetics of TOC are similar in spite of the climatic, lithologic and hydrodynamic differences. So, this demonstrates the sensitivity of TOC as tracer of the infiltration process, whatever the type of karst aquifer is studied. Even in karst systems such as Nerja Cave, the TOC is a good tracer, better than the measured discharge, because normally there is not a rapid discharge response to rainfall events and, TOC content displays a good variability which permits the characterization of infiltration.

[14] Therefore, as observed in the systems of Vaucluse, TOC is a relevant tracer of infiltration in Nerja Cave system. Nevertheless, there is a fundamental difference concerning its relationship with the other residence time tracers. Indeed, in the case of the experimental site of Vaucluse, TOC and Mg^{2+} shows an opposite evolution, whereas they display similar trends at the Nerja Cave. This can be explained by the particular behaviour of this system and its climatic, lithologic and hydrodynamic context, which demonstrate that Mg^{2+} varies in a different way compared to classical interpretations.

5. Conclusions

[15] TOC is a sensitive tracer of infiltration, even in the case of a system such as the Nerja Cave, which is made up of dolomitic marbles and where the mean residence time varies from 2 to 8 months because no fast infiltration exists. In this context, tracers of the infiltration such as (TOC, NO_3^- and Cl^-) display similar trends to those which indicate residence time in contact with the dolomitic marbles which comprise the aquifer (i.e., Mg^{2+}). This phenomenon can be explained by the important role of evaporation, and dissolution processes in the unsaturated zone of the dolomitic system with diffuse flow behaviour and a long water residence time.

[16] Mineralisation kinetics of TOC are similar in Vaucluse and Nerja systems although their climatic, lithologic and hydrodynamic contexts, as well as the TOC inputs, are strongly different. Therefore, TOC appears a relevant tool to study the infiltration processes in different types of karstic environments.

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