



Characterisation of dissolved organic matter in karst spring waters using intrinsic fluorescence: Relationship with infiltration processes

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ABSTRACT

From analysis of spectrophotometric properties of dissolved organic matter (OM) and the hydrochemical responses of some karst springs under different hydrologic conditions, an assessment of the origin and transfer pathway of OM present in karst spring waters, from soil and epikarst toward the spring, has been conducted for three karst aquifers in southern Spain: Alta Cadena, Sierra de Enmedio and Los Tajos. Intrinsic fluorescence (excitation–emission matrices or EEMs), together with major water chemistry (electrical conductivity, temperature, alkalinity, Cl^- , Mg^{+2}) and P_{CO_2} along with natural hydrochemical tracers (TOC and NO_3^-), have been monitored in 19 springs which drain the three karst aquifers examined in this study. The spring water EEM spectra indicate that fulvic acid-like substances, produced in the soil as a consequence of the decomposition of OM, are the dominant fluorophores, although some of the OM appears to originate from *in situ* microbiological activity but could be indicative of contamination present in recharge waters from livestock. During each recharge event, TOC and NO_3^- concentrations increased and variations in fluorescence intensities of peaks attributed to fulvic acid-like compounds were observed. In areas with minimal soil development, spatial and temporal variations in the fluorescence intensity of fulvic acid-like substances and other fluorophores derived from microbiological activity, together with other hydrochemical parameters, provide insights into the hydrogeological functioning of karst aquifers and the infiltration velocity of water from soil and facilitate assessment of contamination vulnerability in these aquifers.

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1. Introduction

Fluorescence spectroscopy is one of the main tools in current use for the characterisation of organic matter (OM) found in natural waters. It is a rapid, selective technique based on the simultaneous scanning of emission and excitation wavelengths to generate emission–excitation matrices (EEMs). The most common fluorophores, traditionally identified in the EEMs of non-contaminated natural waters, are attributed to humic and fulvic acids, and correspond to specific spectral features (Senesi et al., 1991; Coble, 1996; Baker and Genty, 1999; Parlanti et al., 2000; Hudson et al., 2008), including A peaks ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ 220–260/400–450 nm) and C peaks ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ 300–350/400–460 nm), together with signatures that represent protein-like OM with peaks similar to those of the fluorescent amino acids tryptophan, represented by T peaks ($T_1 = \lambda_{\text{ex}}/\lambda_{\text{em}}$ 270–295/330–380 nm and $T_2 = \lambda_{\text{ex}}/\lambda_{\text{em}}$ 210–240/330–380 nm) and tyrosine, represented by B peaks ($\lambda_{\text{ex}}/\lambda_{\text{em}}$ 210–230/305–320 nm). Humic and fulvic acid-like fluorescent OM is produced by the incomplete decomposition of OM in soil, while the substances in the protein-like

group are present due to microbiological activity occurring within the system (autochthonous matter) or transport of biological material into the system (allochthonous matter).

Numerous studies have made use of intrinsic fluorescence to characterise the OM present in marine and continental waters (Coble et al., 1990; Senesi et al., 1991; De Souza Sierra et al., 1994; Coble, 1996; Mobed et al., 1996). Using insights from these studies, it is now possible to assess the origin and nature of the OM in aquatic systems (Patel-Sorrentino et al., 2002; Cammack et al., 2004), to determine the relationship between dissolved OM and fluorescence (Cumberland and Baker, 2007), and between the fluorescence and certain geochemical and ecological parameters (light absorption, Biochemical Oxygen Demand, etc.) related to water quality in rivers and lakes (Baker et al., 2008; Hudson et al., 2008). Other authors have focused on the potential use of intrinsic OM fluorescence as a natural tracer of groundwater flow in aquifers by comparing the fluorescence with other natural tracers (Baker and Lamont-Black, 2001; Lapworth et al., 2008), or as an indicator of the interaction between surface water and groundwater (Lapworth et al., 2009).

Studies of carbonate aquifers, especially karst aquifers, have focused on the fluorescent properties of the OM present in infiltration water of caves (Baker and Genty, 1999; Cruz et al., 2005; Ban et al., 2008; Hartland et al., 2010). This has revealed the potential use of the dissolved organic

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carbon and fluorescence as temporal and spatial tracers (Baker et al., 1997; Baker and Genty, 1999; Birdwell and Engel, 2009), the influence of climatic variations (seasonal and annual) on the presence and concentration of fluorophores in speleothem drip water (Cruz et al., 2005), and the effects of temperature, dilution and filtration on the fluorescence properties of OM present in this water (Hartland et al., 2010). The latter study shows the influence of pH on fluorescence intensities of A and C peaks in groundwater, in the same way that Patel-Sorrentino et al. (2002) and Spencer et al. (2007) have reported for surface waters.

Blondel (2008) and Blondel et al. (2010) used fluorescence as a spatial and temporal tracer of the water flowing through the matrix of the unsaturated zone in a karst system. To do so, they analysed the fluorophores present in water samples taken from different zones of the Vaucluse system (soil, epikarst and unsaturated zone) and from their fluorescence data determined values of the humification index (HIX) (Zsolnay et al., 1999), which is based on the scattering of the 254 nm excitation spectrum of A peak and emission range between 300 and 480 nm. This enabled quantification of the reduction in size of the molecules that generate fluorescence and to relate this to the transit time of the water through the unsaturated zone. Birdwell and Engel (2010) characterised the OM dissolved in cave and spring waters, many of which are karstic, using fluorescence and UV absorbance spectroscopy. Results obtained revealed a strong presence of fluorescence signals associated with T and B peaks, whose source was the result of *in situ* microbiological activity, and had fluorescence intensities that were generally greater than those of the humic and fulvic acid-like peaks (A and C).

Despite these advances, fluorescence spectroscopy has not been widely applied to the characterization of OM in spring waters that drain karst aquifers. The hydrogeological characteristics presented by this type of medium indicate that OM fluorescence may be a very useful tool for examining karst aquifer systems. Aquifer recharge may be diffuse or concentrated, and may be derived from the outcrops of karst rocks (autochthonous recharge) or from beyond them (allochthonous recharge) via karst sinkholes. They present a high degree of heterogeneity, flow velocities may be high and, moreover, there is usually a strong hydrogeological connection between the exokarst features and the groundwater drainage to the discharge points (White, 1988; Bakalowicz, 1995, 2005; Ford and Williams, 2007). From its initial production within the soil until it reaches the spring, OM is subject to the effects produced upon it by hydrogeochemical processes within the aquifer (flow velocity, transport, sedimentation, calco-carbonic equilibrium, etc.) all of which are the consequence of the above-mentioned hydrogeologic characteristics. Moreover, the potential for contamination is prevalent, with sources including agriculture or livestock farming above recharge areas or near springs. All these factors can influence OM fluorescence properties in the relevant waters (Batiot, 2002; Blondel, 2008).

For all these reasons, utilisation of fluorescence spectroscopy together with other natural tracers (total organic carbon and NO_3^-), may help us understand the processes of infiltration and hydraulic flows into aquifer systems and facilitate characterization of the hydrogeologic functioning of karst aquifers (Mudarra and Andreo, 2010). These aspects are fundamental to understanding the contamination vulnerability for this type of aquifer and may be useful when defining spring protection areas.

The aim of the present study is to characterize the OM present in waters collected from several karst springs using fluorescence spectroscopy in order to analyse the relationships between intrinsic fluorescence and some important hydrochemical variables that can be used to describe the hydrogeological functioning of karst aquifers. To this end, water samples obtained from 19 springs located in southern Spain (Fig. 1) have been collected during 11 months for analysis. These springs present different hydrogeological responses to precipitation events and correspond to the main drainage points from three important carbonate aquifers (Fig. 1): Alta Cadena, Sierra de Enmedio and Los Tajos.

2. Site description

Alta Cadena, Sierra de Enmedio and Los Tajos are situated in southern Spain, 30 km NE of the city of Malaga (Fig. 1). The relief is rugged, mainly aligned west-east, with altitudes ranging from 500 to 1640 m above sea level. The climate in the zone is mild Mediterranean. Rainfall is mainly in the autumn, winter and spring, and is associated with humid winds from the Atlantic. The historic mean annual precipitation is 650 mm (Mudarra and Andreo, 2007) although the value recorded during the study period (April 2008 - March 2009) was 980 mm (data from rain gauge station situated at 1130 m a.s.l., Fig. 1). The historic mean temperature in the region is 16 °C (Mudarra and Andreo, 2007). Both precipitation and temperature vary depending on the altitude and on the north or south orientation of the slopes.

From a hydrogeologic point of view, Alta Cadena, Sierra de Enmedio and Los Tajos aquifers are comprised of Jurassic limestones and dolomites, fractured and karstified, occupying a surface area of 70 km², 20 km² and 8 km², respectively. The geological structure of the study area is characterized by the existence of folds, from which overthrusts have developed with vergence toward S-SE. Around the aquifers and overthrusting they, are outcrops of Flysch-type clays and sandstones (Fig. 1). The entire structural body has been affected by more recent fractures, which originates the different karst systems studied in present work. The hydrogeological characteristics of these aquifers have been described in previous works (Mudarra and Andreo 2010, 2011; Mudarra et al., *in press*). Recharge takes place through the direct infiltration of rainwater, while most of the discharge occurs through springs situated on the borders of the carbonate outcrops (at the northern edge of Alta Cadena and at the southern edge of Los Tajos and Sierra de Enmedio). The location of the springs sampled in the present study is shown in Fig. 1 and the outflow altitude is shown in Table 1. Some of these springs constitute the main supply points of drinking water for nearby urbanised areas such as it is the case of the followings springs: Villanueva del Rosario (PS-2), Pita (PS-3), Higuera (PS-6), 100 Caños (PS-8), Batán (PS-10) and Auta (PS-12)

Surface karstification is not homogeneous in the study area. At higher altitudes, karstification is more strongly developed, mainly on the surface of limestone outcrops. In these zones, epikarst is made up of karrenfields, dolines and uvalas. There are also some karst swallow holes in Alta Cadena which become operational during heavy rainfall (Fig. 1). In fact, a multi-tracer test was done in the Alta Cadena range in winter of 2009. The results showed that water infiltrated through swallow holes (see location in Fig. 1) arrived only at PS-2 spring with average velocity of 200 m/hour (Mudarra et al., 2010). This demonstrated a partitioning of the carbonate outcrops in different aquifer systems according to geological structure and also a high degree of development of karstification in depth.

Most of the uplands have no soil cover and only locally, in endorreic zones and where slopes are shallow, is it possible to find an edaphic layer (10–15 cm maximum). As a consequence, vegetation is scant and of a Mediterranean type, found mainly in areas where there is such cover. In the study area, there are few potential sources of water contamination; there is only scattered livestock farming activity over the carbonate outcrops, and this is concentrated in areas of shallow slopes or that are slightly endorreic, and also in the surrounding of some of the springs. This livestock activity may generate some contamination, particularly NO_3^- enrichment of the water drained by the springs. In any case, contamination sources are widely scattered and the aquifers remain in near pristine condition.

3. Materials and methodology

During the period of record (May 2008–March 2009), the springs were affected by different hydrological conditions (recharge, recession, depletion). The results obtained are representative of high and low water conditions in the aquifers. The normal sampling period was weekly,

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