Science of the Total Environment 569–570 (2016) 700–715

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Influence of regional hydrogeological systems at a local scale: Analyzing the coupled effects of hydrochemistry and biological activity in a Fe and CO_2 rich spring

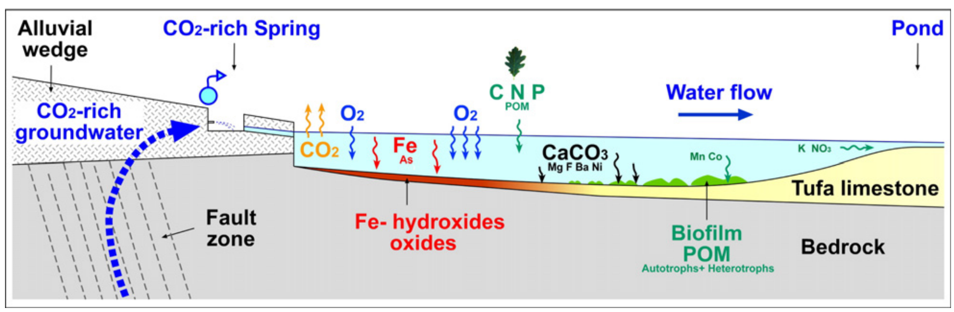
A. Menció [a,*], H. Guasch [b], D. Soler [a], A. Canelles [a], M. Zamorano [a], D. Brusi [a]

[a] Grup de Geologia Aplicada i Ambiental (GAiA), Department of Environmental Sciences, University of Girona, Faculty of Sciences, Campus de Montilivi, 17071 Girona, Spain
[b] Grup de Recerca en Ecosistemes Continentals (GRECO), Institute of Aquatic Ecology, University of Girona, Faculty of Sciences, Campus de Montilivi, 17071 Girona, Spain

HIGHLIGHTS

- Electrical resistivity tomography detected CO_2 rich groundwater.
- High Fe concentrations inhibits both algal growth and $CaCO_3$ precipitation.
- Tufa precipitation doesn't coincide with the highest growth of algae.
- Physicochemical and biological processes may improve groundwater quality from regional systems.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 March 2016
Received in revised form 22 June 2016
Accepted 22 June 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Fe and CO_2 rich spring
Diatoms
Electrical resistivity tomography
Hydrochemical modeling
Regional hydrogeological systems
Tufa limestone

ABSTRACT

A multidisciplinary approach was used in this study to determine the origin of a Fe and CO_2 rich spring, an extreme freshwater system and to evaluate the coupled effects of hydrochemistry and biological activity at a local scale. An electrical resistivity tomography survey was conducted to delineate the geological context in which water emerges from a Plio-Quaternary supracrustal fault zone, and a bulk resistivity decrease was detected when CO_2 rich groundwater occurred. Nine water samples, together with eight biofilm samples, and three sediment samples were taken along the spring canal for their analysis. Major ions, nutrients, and metals were analysed in water samples. Sediment analyses determined the main solid phases precipitated (mainly as $CaCO_3$ and $Fe(OH)_3(a)$). Biofilm analyses permitted to obtain biovolume per cell measures, total biovolume values, diatom density, chlorophyll *a* concentrations, and the Margalef Index values. Inverse modeling and batch reaction models were used to determine the physicochemical processes affecting the spring water, obtaining the total amount of $CaCO_3$/L formed; the Fe and Mn compounds, which mainly precipitated as $Fe(OH)_3(a)$ and $Mn(OH)_2$; as well as the total CO_2 released to the atmosphere. Analyzing these results together with the patterns of variation of hydrochemical and biological parameters, different interactions were observed: a) the effects of Fe inhibition in travertine formation, even though when the highest CO_2 release was occurring; b) the fate and effects of chemicals limiting and/or inhibiting algal growth (mainly Fe, As and phosphate); c) the lack of coincidence between algal growth and tufa limestone precipitation; d) the relationship between some divalent metals (Mn and Co) and biotic activity.

* Corresponding author.
E-mail addresses: anna.mencio@udg.edu (A. Menció), helena.guasch@udg.edu (H. Guasch).

http://dx.doi.org/10.1016/j.scitotenv.2016.06.185

1. Introduction

Springs with Na-HCO_3 facies, some with CO_2 rich waters, have been usually described as characteristic of long transit time hydrogeological systems (Nordstrom et al., 1989; Catwright et al., 2000; Vilanova, 2004; Chae et al., 2006; Carrillo-Rivera et al., 2007; Folch et al., 2011). Choi et al. (2009) analysed CO_2-rich groundwaters in South Korea, and observed that Na-HCO_3 waters were influenced by a deep CO_2-rich environment, showing longer transit times than groundwaters with Ca-Na-HCO_3 and Ca-HCO_3 characteristics; Chae et al. (2006) also observed that Na-HCO_3 types of water were characteristic of deep groundwater, but in this case, these facies were also linked with thermal waters; Koh et al. (2008) observed that CO_2 rich thermal waters showed significantly higher TDS, and also Fe, Na, K, Ca, Mg, SiO_2, and Sr contents than alkaline thermal waters, and their hydrochemical evolution were distinct depending on the extent of CO_2 gas influx at depth. Another study conducted by Wexsteen et al. (1988), analysed the existence of different types of cold CO_2-rich springs in the Swiss Alps, linked to local groundwater fluxes. In this case, all these springs were affected by CO_2 of crustal origin, which enhanced the interaction with silicate rocks, showing springs with Na-HCO_3-Cl and Na-Mg-HCO_3-SO_4 facies in igneous materials, with positive correlations between Na, HCO_3, Mg, SO_4, and Fe, among others ions. Cerón et al. (2000) studied CO_2 rich waters in sedimentary environments and observed that endogenous CO_2 was also responsible for exceptionally high values of bicarbonate and also higher concentrations of ions, such as Ca, Mg and SO_4. Although Na-HCO_3 facies have been attributed to longer transit times in most of the previous studies, the presence of endogenous CO_2 enhanced the interactions with rocks, being thus responsible for higher salinities.

Therefore, in intraplate extensional regions, mantellic emanation of CO_2 along faults leads to rapid and massive release of metals such as Fe and As from sediments and rocks, followed by their incorporation to groundwater systems. In these systems strong hydrochemical changes often take place (Agnelli et al., 2016; Piqué et al., 2010). In recent years, abundant research has developed on the effects that gas leakages from CO_2 sequestration sites and natural analogues have on groundwater quality (e.g. Apps et al., 2010; Keating et al., 2010; Little and Jackson, 2010; Harvey et al., 2012). Electrical resistivity tomography (ERT) has been used as a suitable tool for diagnostic monitoring at natural analogue degassing sites (Schütze et al., 2013), and it has been successfully applied in the shallow characterization of sites related to extensional faults (e.g. Zarroca et al., 2012; Prado-Pérez et al., 2014; Sandig et al., 2014; Agnelli et al., 2016).

From a management point of view, regional groundwater systems may be of great importance since they can suppose an additional source of groundwater in arid and semiarid environments (Menció et al., 2010; Folch et al., 2011; Mas-Pla et al., 2013a). However, springs linked to these regional groundwater systems, with CO_2 rich waters, may present high concentrations of heavy metals (such as Fe), even higher than the values defined by the WHO (World Health Organization) (2011) as guideline values for drinking water.

These type of springs have a great ecological and geological value as extreme freshwater systems because their unusual chemical composition, unique microbiota and contribution to biomineralization and formation of solid phases. From an ecological point of view, springs are small field laboratories that provide the opportunity of investigating the response of microbial communities (biofilms), along marked chemical gradients that are created when groundwater comes into contact with the oxidizing atmosphere (Wellborn et al., 1996). Moreover, understanding mechanisms of assembly and succession of modern day biofilms provides clues regarding past environmental conditions that led the formation of solid phases. Biofilms can be observed in real-time and monitored over spatial scales to elucidate mechanisms of formation under various geochemical and hydrological conditions (Beam et al., 2016).

Some studies have analysed the effect of one of these metals, Fe, among other hydrochemical parameters, on biofilms growth. Their results indicate that high Fe conditions commonly found in Fe-springs may limit nutrient availability and cause stress on the algal communities, with significant effects in diatoms size and also in their distribution (Noiri et al., 2005; Tsuda et al., 2005; Koh et al., 2008; Shakeri et al., 2008; Morin et al., 2008; Guasch et al., 2009). Although Fe is essential for all living organisms because it is a constituent of important macromolecules, excess free Fe is a potential detrimental because of its propensity to react with O_2 and to generate harmful free radicals by the Fenton reaction. Fe toxicity can occur when the anti-oxidative capacity of cell is overwhelmed at high Fe concentrations (Cassin et al., 2009; Neves et al., 2009; Ravet et al., 2009; Guasch et al., 2009). Consequently, the hydrochemical characteristics of CO_2 rich springs may cause a significant influence on biofilms, but, simultaneously, the hydrochemical characteristics of these springs may be affected by the biological activity providing a great opportunity to demonstrate the existence of strong interlinks between microbial activity and chemical conditions in environmental gradients. This is the case of travertine and tufa formation, which may be influenced by biological activity. According to Pentecost (2005), carbonate precipitation can result from biological processes, such as photosynthesis, nitrate uptake, bacterial sulphate reduction, methanogenesis, etc. and plant and microbial surfaces may also provide calcium carbonate nucleation or particle trapping on their surfaces.

The Can Verdaguer spring is located in the north-western boundary of the Selva basin (NE Spain), which is linked to the fault network that created this tectonic graben (Fig. 1). In this area, CO_2-rich springs related to extensional faults have been identified, some of them also associated to thermal waters (París and Albert, 1976; Vehí, 2001; Vilanova, 2004; Piqué et al., 2010). The Can Verdaguer spring shows a Na-HCO_3 facies with high CO_2 and Fe contents, characteristics associated to regional groundwater flow systems in this area (Folch et al., 2011).

Although the local effects of surface groundwater fluxes in streams, and groundwater dependent ecosystems, have already been evaluated (for example, Menció et al., 2010; Menció et al., 2014), the local effects of these regional Fe and CO_2 rich waters have not been studied yet.

Therefore, the aim of this study is to go into detail about the origin of this spring and to evaluate the coupled effects of hydrochemistry and biological activity once this kind of regional groundwater fluxes reach the surface. Accordingly, a multidisciplinary approach has been conducted to analyze the local effects of these regional groundwater systems: 1) an hydrochemical model of spring water evolution through the canal has been built; 2) similarities among variables concerning their longitudinal patterns of variation have been used to describe the sequence of biogeochemical processes throughout the canal; and 3) an electrical resistivity tomography (ERT) survey has been conducted to detect the possible pathways followed by CO_2-rich groundwater released from a fault zone.

2. Geological and hydrogeological setting

The Can Verdaguer spring is located above the trace of Llorà fault (Fig. 1), one of the NW-SE trending, NE dipping normal faults that control the half-graben structure of the Transverse Ranges and the Selva basin in the northeasternmost corner of the Iberian Peninsula. The Llorà fault has a surface cartographic length close to 30 km, although it probably extends for at least 15 km more to the SE across the Selva basin. The fault dip-slip increases from 800 m in the NW to 1700 m in the SE. The upthrown wall hosts a Paleozoic igneous and metamorphic basement and its Paleogene sedimentary cover. On the downthrown block, Paleogene sedimentary formations tilted towards the fault plane crop out in the NW segment, while Upper Pliocene to Quaternary alluvial deposits fill the Selva basin to the SE (Saula et al., 1994). The Llorà fault has associated low to moderate instrumental seismicity