Science of the Total Environment 551–552 (2016) 186–196

Contents lists available at ScienceDirect

Science of the Total Environment

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

Monitoring priority substances, other organic contaminants and heavy metals in a volcanic aquifer from different sources and hydrological processes

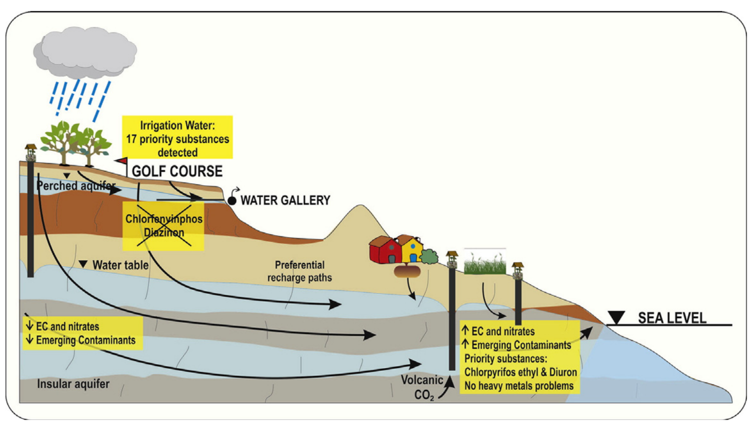
Esmeralda Estevez [a,c], María del Carmen Cabrera [a,b,*], Juan Ramón Fernández-Vera [c], Antonio Molina-Díaz [d], José Robles-Molina [d], María del Pino Palacios-Díaz [e]

[a] Dpt. Física (GEOVOL), Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Canary Islands, Spain
[b] IMDEA Water Institute, Alcalá de Henares, Madrid, Spain
[c] Agrifood and Phytopathological Laboratory (Cabildo de Gran Canaria), 35413 Arucas, Canary Islands, Spain
[d] Analytical Chemistry Research Group, Department of Physical and Analytical Chemistry, University of Jaen, 23071 Jaen, Spain
[e] Dpt. de Patología Animal, Producción Animal, Bromatología y Tecnología de los Alimentos (GEOVOL), Universidad de Las Palmas de Gran Canaria, 35413 Arucas, Canary Islands, Spain

HIGHLIGHTS

- A relationship between contaminant presence and hydrogeochemistry has been demonstrated.
- No priority substance exceeded EU limits but 17 were detected in reclaimed water.
- Seven pesticides exceeded the threshold concentration for groundwater (2006/108/EC).
- Priority substances chlorpyrifos ethyl and diuron must be monitored in groundwater.
- Hydrochemically variable wells are recommended in pollution monitoring.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form 26 January 2016
Accepted 26 January 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Reclaimed water
Organic contaminants
Heavy metals
Groundwater

ABSTRACT

Irrigation with reclaimed water (R) is necessary to guarantee the sustainability of semi-arid areas. Results obtained during a two years monitoring network (2009–2011) in Gran Canaria are presented, including the analysis of chemical parameters, N and S isotopes, priority substances (2008/105/EC, 2013/39/EU), other organic contaminants and heavy metals in groundwater and R used to irrigate a golf course. The aims of this work are to evaluate the contamination in a volcanic aquifer, relate the presence of organic contaminants and heavy metals with the hydrogeochemistry and identify pollution sources in the area. No priority substance exceeded the EU thresholds for surface water, although seventeen were detected in R. The most frequent compounds were hexachlorobenzene, chlorpyrifos ethyl, fluorene, phenanthrene and pyrene. These compounds were detected at low concentration, except chlorpyrifos. Chlorpyrifos ethyl, terbuthylazine, diuron, terbutryn, procymidone, atrazine and propazine exceeded the European threshold concentration for pesticides in groundwater (100 ng L^{-1}). Therefore, the priority substances chlorpyrifos ethyl and diuron must be included in monitoring studies. The priority pesticides chlorfenvinphos and diazinon were always detected in R but rarely in groundwater. Besides, the

* Corresponding author at: Dpt. Física (GEOVOL), Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Canary Islands, Spain.
E-mail addresses: eestevez@proyinves.ulpgc.es (E. Estevez), mcarmen.cabrera@ulpgc.es (M.C. Cabrera), jrfernandezv@grancanaria.com (J.R. Fernández-Vera), amolina@ujaen.es (A. Molina-Díaz), jroblesmol@gmail.com (J. Robles-Molina), mp.palaciosdiaz@ulpgc.es (M.P. Palacios-Díaz).

http://dx.doi.org/10.1016/j.scitotenv.2016.01.177
0048-9697/

Chlorpyrifos ethyl
Diuron

existence of contaminants not related to the current R irrigation has been identified. Absence of environmental problems related to heavy metals can be expected. The relationship among contaminant presence, hydrogeochemistry, including the stable isotopic prints of $\delta^{18}O$, $\delta^{15}N$ and $\delta^{34}S$ and preferential recharge paths has been described. The coastal well shows high values of EC, nitrate, a variable chemistry, and 50% of organic contaminants detected above 100 ng L^{-1}. The well located in the recharge area presents a stable hydrochemistry, the lowest value of $\delta^{15}N$ and the lowest contaminants occurrence. The area is an example of a complex volcanic media with several sources of contaminants such as leakages from septic tanks and sewerage, agriculture practices, irrigation with reclaimed water or urban runoff.

1. Introduction

The importance of groundwater in semi-arid regions is widely acknowledged in the literature. In Spain, groundwater meets about one-fifth of the total water demand and is used to irrigate over one-third of the total irrigated land (De Stefano et al., 2015). Alternatives such as reclaimed water reuse contribute to mitigate the shortage of fresh water. Non-conventional water resources offer a guaranteed supply and constitutes an important source of irrigation in semi-arid zones (Kinney et al., 2006), but the possible impact to the environment must be controlled (Fatta-Kassinos et al., 2011; Vo et al., 2014; Assouline et al., 2015). In Gran Canaria, groundwater is used to meet the greater part of the agricultural demand and much of the potable supply demand in the middle and upper parts of the Island, with more than 1300 groundwater horizontal and vertical groundwater works in a total surface of 1.560 km^2 (CIAGC, 1999, 2015). Reclaimed water currently represents 8% of water resources in the island (Palacios et al., 2008) and it has been used for irrigation over more than thirty years (Marrero and Palacios, 1996). In 2002, the effluent quality of the Wastewater Treatment Plant of Las Palmas de Gran Canaria was improved by installing a desalination and disinfection system for the secondary effluent.

Nowadays, only nitrate contents (threshold value of 50 mg L^{-1}) and pesticides (100 ng L^{-1}) are compounds regulated for groundwater by the European Commission (EU Directive, 2006). For surface water, 45 organic contaminants and heavy metals are included in the list of European priority substances (EU Directives, 2008, 2013), which requires the setting of environmental quality standards (EQS). However, other source of concern related to groundwater quality is the presence of the unregulated pollutants such as emerging contaminants and transformation products, other organic contaminants and heavy metals. Emerging contaminants can be defined as chemicals not commonly monitored, but has the potential to enter the environment and cause suspected ecological and human health effects are causing growing concern. It is no necessary for these contaminants to persist in the environment to cause negative effects since their high transformation/removal rates can be compensated by their continuous introduction into the environment (Daughton and Ternes, 1999; Daughton, 2004; Kümmerer, 2004). This group includes pharmaceuticals, industrial chemicals, pesticides and its degradation products. The recent widespread and increasing detection of emerging contaminants in European groundwater has been described by a range of authors (Jurado et al., 2012; Lapworth et al., 2012; Loos et al., 2010; Meffe and de Bustamante, 2014; Postigo and Barcelo, 2015; Stuart et al., 2012). The main sources of emerging organic compounds in groundwater are related to wastewater effluents or reuse, septic tanks, livestock activities and leakages in sewerage (Balderacchi et al., 2013; Kurwadkar and Venkataraman, 2013; Lapworth et al., 2012).

As most of these sources can be identified by the presence of high nitrate concentration in the aquifer, isotopic composition ($\delta^{15}N$-NO_3) of dissolved nitrate (Létolle, 1980; Mongelli et al., 2013) can be used to identify the possible nitrate origin, especially useful in areas with a very mixed pattern of human activities or for islands or near-coastal areas where other inorganic co-indicators can be compromised by seawater impact (Heaton et al., 2012). They can come from the use of synthetic nitrogen fertilizers (Chae et al., 2009; Choi et al., 2011) and wastewaters and manure (Benkovitz et al., 1996; Choi et al., 2007). Sulfate in groundwater can also be indicators of groundwater pollution. This ion is often present at relatively high concentration in some anthropogenic sources (domestic, livestock, agricultural and industrial wastes) (Berner et al., 2002; Hosono et al., 2011; Hosono et al., 2007; Moncaster et al., 2000; Otero et al., 2008; Van Donkelaar et al., 1995). Dual sulfur and oxygen isotope ratios of dissolved sulfate ($\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4) can also help to distinguish different origins (Bottrell et al., 2008; Dogramaci et al., 2001; Tuttle et al., 2009), although its application is not clear due to the isotopic processes than can occur during the sulfur cycle (Mook, 2001).

Apart from industrial sources and wastewaters, there are a variety of possible sources of PAHs in the environment, including atmospheric deposition, traffic, oil spills and urban runoff (Metcalfe et al., 2011). Atmospheric PAHs that escape photolysis and radical oxidative degradation in the air are accumulated at land surfaces through dry and wet deposition. Once deposited, PAHs tend to accumulate in soil or to become roof and street dust in the urban environment for a long period of time (Ockenden et al., 2003). In addition, surface soil and street dust PAHs will go back to the atmosphere by wind action and volatilization (Manoli et al., 2002). Moreover, street dust and surface soil contained PAHs are carried into the drainage network by storm runoff and are eventually transported to aquatic environments (Boonyatumanond et al., 2006).

The main processes controlling organic contaminants during migration through the soil, unsaturated zone and aquifer are sorption, ion exchange, and microbial degradation or transformation (Blackwell et al., 2007; Drillia et al., 2005; Lapworth et al., 2012; Löffler et al., 2005; Wells, 2006). In volcanic areas, the presence of preferential paths in the unsaturated zone can favor rapid recharge, so contaminants can reach the aquifer in relative short times.

In Gran Canaria, 70% of water is pumped from volcanic formations with ages from Miocene to Pleistocene. These formations have a non-negligible primary porosity accorded by the conglomeratic levels, sediments, and cooling cracks or fissures. The poor exploitation of more permeable formations (alluvium, Miocene–Pliocene detritics and Holocene Basalts) is due to their low representation and because they are above the saturated zone (SPA-15, 1975; Custodio, 2003).

The presence of organic contaminants has been previously described in irrigation water used in a golf course and in groundwater of Gran Canaria (Estévez et al., 2012), since July 2009 to May 2010. The most frequent compounds were caffeine, nicotine, chlorpyrifos ethyl, fluorene, phenanthrene and pyrene. Concentrations were below 50 ng L^{-1}, although some pharmaceuticals and the pesticide chlorpyrifos ethyl were occasionally detected at higher concentrations.

The aims of this study were to evaluate the contamination in a volcanic aquifer and to determine whether the presence of some organic contaminants, heavy metals and nitrate could be related to potential sources or hydrochemical setting in the Las Goteras aquifer in Gran Canaria using monitoring data collected over a two-year period.

2. Material and methods

2.1. Study site

The Bandama Golf Course is located in the NE of the Gran Canaria Island in the central part of the Las Goteras basin, 450 m high (Fig. 1).