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# Screening of emerging contaminants and priority substances (2008/105/EC) in reclaimed water for irrigation and groundwater in a volcanic aquifer (Gran Canaria, Canary Islands, Spain)

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#### ABSTRACT

In semiarid regions, reclaimed water can be an important source of emerging pollutants in groundwater. In Gran Canaria Island, reclaimed water irrigation has been practiced for over thirty years and currently represents 8% of water resources. The aim of this study was to monitor contaminants of emerging concern and priority substances (2008/105/EC) in a volcanic aquifer in the NE of Gran Canaria where the Bandama Golf Course has been sprinkled with reclaimed water since 1976. Reclaimed water and groundwater were monitoring quarterly from July 2009 to May 2010. Only 43% of the 183 pollutants analysed were detected: 42 pharmaceuticals, 20 pesticides, 12 polyaromatic hydrocarbons, 2 volatile organic compounds and 2 flame retardants. The most frequent compounds were caffeine, nicotine, chlorpyrifos ethyl, fluorene, phenanthrene and pyrene. Concentrations were always below 50 ng  $L^{-1}$ , although some pharmaceuticals and one pesticide, cholrpyrifos ethyl, were occasionally detected at higher concentrations. This priority substance for surface water exceeded the maximum threshold (0.1  $\mu g L^{-1}$ ) for pesticide concentration in groundwater (2006/ 118/EC). Sorption and degradation processes in soil account for more compounds being detected in reclaimed water than in groundwater, and that some contaminants were always detected in reclaimed water, but never in groundwater (flufenamic acid, propyphenazone, terbutryn and diazinon). Furthermore, erythromycin was always detected in reclaimed water (exceeding occasionally  $0.1 \mu g L^{-1}$ ), and was detected only once in groundwater. In contrast, some compounds (phenylephrine, nifuroxazide and miconazole) never detected in reclaimed water, were always detected in groundwater. This fact and the same concentration range detected for the groups, regardless of the water origin, indicated alternative contaminant sources (septic tanks, agricultural practices and sewerage breaks). The widespread detection of high adsorption potential compounds, and the independence of concentration with origin and depths, indicates the existence of preferential flows phenomena as potential contamination route in volcanic fractured materials.

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#### 1. Introduction

In recent years, the improvement of analytical methods has led to the discovery of emerging contaminants in the environment. This results in increased interest and has become one of the priority research areas of major organisations (World Health Organization, the Agency for Environmental Protection, the European Commission). Emerging contaminants are defined as chemicals whose presence in the environment has recently been detected, and their ecological and health effects are causing growing concern. They include pharmaceuticals, personal care products, pesticides and disinfectants, among others. 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, 2004; Daughton and Ternes, 1999; Petrović et al., 2003; Sedlak et al., 2000). More ecotoxicological data and contribution of risk are required for most of these compounds, or for combinations of them, to allow predictions of ecological and human health effects (Fent et al., 2006; Jjemba, 2008).

Only 33 of those compounds have been included in the list of priority substances in surface water (DIR 2008/105 EC), while the threshold values for total and individual pesticides (0.5 and 0.1  $\mu$ g L<sup>-1</sup> respectively) and their metabolites and degradation products have been established in the Daughter Groundwater Directive (2006/118/EC) for the European Union Water Framework Directive (2000/60/EC).

Recently, Lapworth et al. (2012) reviewed existing occurrence data in groundwater for a range of emerging organic contaminants

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from main sources and pathways: wastewater effluents, septic tanks, hospital effluents, livestock activities, subsurface storage of household and industrial waste, and groundwater-surface water exchange. In Wastewater Treatment Plants (WWTP), removal of emerging compounds in sludge is a dominant process for hydrophobic compounds, whereas persistent hydrophilic compounds are present mainly in effluents. If these compounds, their metabolites and transformation products are not eliminated during sewage treatment, they may enter the aquatic environment. This fact depends on reclaimed water quality, soil and subsurface environment characteristics such as mineralogy and organic matter content (Blackwell et al., 2007; Drillia et al., 2005; Löffler et al., 2005; Tolls, 2001), transport phenomena and contaminant physicochemical properties (Sedlak and Pinkston, 2001; Wells, 2006). The main processes controlling emerging organic contaminants during migration through soil, unsaturated zone and aquifer are sorption mainly to organic matter and clay minerals, ion exchange, and microbial degradation or transformations. Indeed, contaminant properties, the transit time through unsaturated zone and groundwater residence time, redox conditions and total loading will prove important in determining presence and persistence in groundwater.

Many studies have investigated the fate of these organic micropollutants in groundwater following infiltration of wastewaters (sewage and industrial), artificial recharge and contaminated surface water sources, as well as septic tanks leakage (Lapworth et al., 2012). However, further research is required to determine the reclaimed water irrigation impact on the extent of migration of micropollutants through soil and unsaturated zone and their potential to leach to groundwater. This research is especially necessary in semiarid zones, where reclaimed water is an important source of irrigation water, and where the introduction of emerging compounds into the environment via irrigation is a highly relevant exposure route (Chefetz et al., 2008; Kinney et al., 2006; Stumpe and Marschner, 2007). In Gran Canaria, reusing treated wastewater for irrigation has been a practice used for more than thirty years given the scarce water resources on the island (Marrero and Palacios, 1996). For this reason, the Bandama Golf Course has been selected to characterise the emerging contaminant contents in the area and the processes involved. It has been irrigated with reclaimed water since 1976 and a considerable amount of data, including irrigation water quantity and quality, is available.

The aim of this study was to survey the occurrence of emerging contaminants and priority substances (2008/105/EC) in reclaimed water used for golf course irrigation and in aquifer in the study area (NE of Gran Canaria, Spain).

#### 2. Material and methods

#### 2.1. Location and description of the study area

The Bandama Golf Course is located in the NE of the Gran Canaria Island in the central part of the Las Goteras basin, between 400 m and 500 m high. The Las Goteras basin is included in the N4 zone of the Gran Canaria Water Administration Plan (CIAGC (Consejo Insular de Aguas de Gran Canaria), 1999), which is represented in Fig. 1. Average precipitation in the area is 300 mm per year, the average annual temperature is 19 °C, and minimum humidity in winter and maximum humidity in summer are 78% and 85%, respectively. Since 1976, the Bandama Golf Course has been irrigated with reclaimed water from the Las Palmas de Gran Canaria Wastewater Treatment Plant, where tertiary treatment has consisted in desalination and disinfection since 2002 (Estévez et al., 2010).

The study area is next to the quaternary Bandama volcanic complex, and includes a volcanic caldera (Fig. 1). Fresh basaltic and basanitic lavas and pyroclastic materials (2000 years old) outcrop in the area (Hansen and Moreno, 2008). These materials overlie fractured basanitic lava flows and landslide breccias, which cover Miocene phonolites. Interbedded alluvial conglomerates outcrop inside the Bandama Caldera (Fig. S1). The Gran Canaria hydrogeological structure can be sketched as a unique groundwater body recharged by rainfall infiltration that discharges into the sea or some discharging points into springs and ravines. The island has a low permeability "core" (dike sets, intrusive bodies and thermally metamorphosed rocks) with successive covers of younger, more permeable materials where groundwater flow concentrates (Custodio, 2003; SPA-15, 1975). Previous hydrogeological studies in the area (Cabrera et al., 2009) have shown that the groundwater flows from summits to coast (Fig. 1) follow a preferential flow line through the Las Goteras ravine. The groundwater table head is located 250 m below the Bandama Golf Course and a groundwater flow from the golf course to the ravine has been identified (Fig. 1). The aquifer system in the study area is exploited by shaft wells of 2.5-3 m in diameter

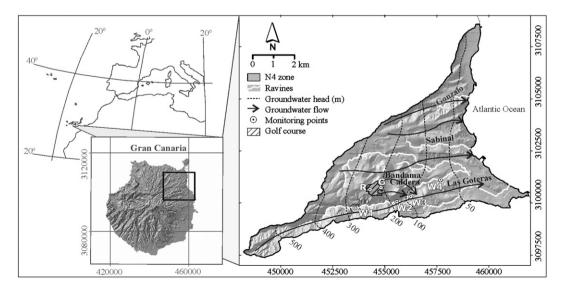


Fig. 1. Study area location, monitoring points (reclaimed water: R, large diameter shaft wells: W1–W4 and the El Culatón water gallery: G) and piezometric map for January 2009 (Cabrera et al., 2009, modified).

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