

## TEMPORAL EVOLUTION OF EMERGING CONTAMINANTS, PRIORITY SUBSTANCES AND HEAVY METALS MOST FREQUENTLY DETECTED IN RECLAIMED WATER AND GROUNDWATER IN A VOLCANIC AQUIFER

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### EXTENDED ABSTRACT

The presence of emerging contaminants has been previously described in reclaimed water and groundwater of Gran Canaria (Spain). Despite of the environmental risk associated to irrigation with reclaimed water (R), this practice is necessary considering sustainability of the hydrological cycle in semiarid zones, especially regarding agricultural activity.

The aim of this study was: i) to analyse the evolution during two years of contaminants of emerging concern, priority substances (2008/105/EC) and heavy metals in reclaimed water (R) and in a volcanic aquifer in the NE of Gran Canaria where a golf course has been irrigated with R since 1976 and ii) to relate this presence with physicochemical water properties and hydrogeological media.

Reclaimed water and groundwater (GW) were monitoring quarterly from July 2009 to September 2011. Sorption and degradation processes in soil account for more compounds being detected in R. Diazinon and chlorfenvinphos were detected always in R and terbutylazine, terbutryn and diuron at 90% of frequency. Considering all the samples, the most frequent compounds were chlorpyrifos ethyl, fluorene, phenanthrene and pyrene. Although their concentrations were frequently below 50 ngL<sup>-1</sup>, some contaminants, were occasionally detected at higher concentrations. Chlorpyrifos ethyl and diuron are priority substances detected frequently and at high concentrations so they must be included in monitoring studies. Geology and location seem to be related to the emerging compounds presence due to occasional contamination events (not related to R irrigation) and therefore not to an existence of a dangerous diffuse contamination level. Thus, it is preferable to select wells with less stable chemical water quality, in order to monitor the risk of emerging compounds presence. Considering the relationship between contaminant presence, chemical water quality, seasonal variation, hydrogeological characteristics and wells location we can conclude that chlorpyrifos ethyl and diuron were the most dangerous priority substances in terms of GW quality so they must be included in all of the monitoring studies, at least in Canary Islands.

**Keywords:** emerging contaminants, priority substances, heavy metals, reclaimed water, groundwater, irrigation, volcanic zone.

## 1. INTRODUCTION

Reclaimed water reuse offers a guaranteed supply and contributes to mitigate the shortage of natural water resources, especially, in semiarid zones, where reclaimed water constitutes an important source of irrigation water (Kumar *et al.*, 2005; Kinney *et al.*, 2006). In Gran Canaria (Spain), this practice has been used for more than thirty years (Marrero and Palacios, 1996), and reclaimed water currently represents 8% of water resources (Palacios *et al.*, 2008). Nowadays, advances in treatment processes result in acceptable reclaimed water qualities. In the study area, effluent quality has been improved due to the installation of new infrastructures, highlighting a desalination system of the secondary effluent since 2002. Aquifers integrate recharge water (natural or from irrigation returns) from different times, especially in semiarid zones and if groundwater table head is deep.

The main sources of emerging organic compounds in groundwater are related to wastewater effluents or reuse, septic tanks, livestock activities and hospital effluents (Lapworth *et al.*, 2012). The main processes controlling emerging contaminants during migration through the soil, unsaturated zone and aquifer are sorption mainly to organic matter and clay minerals, ion exchange, and microbial degradation or transformations. Indeed, the contaminant properties as well as transit time through the unsaturated zone and groundwater residence time, redox conditions and total loading will be important in determining presence and persistence in groundwater. In volcanic materials, the presence of preferential paths in the unsaturated zone can favour a rapid recharge, so emergent contaminants can reach the aquifer in relative short times.

The presence of emerging contaminants has been previously identified and described in reclaimed water used for irrigate a golf course and in groundwater of the NE of Gran Canaria (Estévez *et al.*, 2012). This study monitors 183 contaminants of emerging concern and priority substances (2008/105/EC) since July 2009 to May 2010. The most frequent compounds were caffeine, nicotine (stimulants), chlorpyrifos ethyl (organophosphate insecticide), fluorene, phenanthrene and pyrene (PAHs). Concentrations were always below 50 ngL<sup>-1</sup>, although some pharmaceuticals and one pesticide, chlorpyrifos ethyl, were occasionally detected at higher concentrations. This paper points to more entry routes apart from reclaimed water irrigation: agricultural practices, septic tanks leaks and sewerage breaks, and mentions the importance of adsorption, degradation and preferential flows phenomena. However, temporal variations of the contaminants concentration had not been observed and a longer sampling period was recommended.

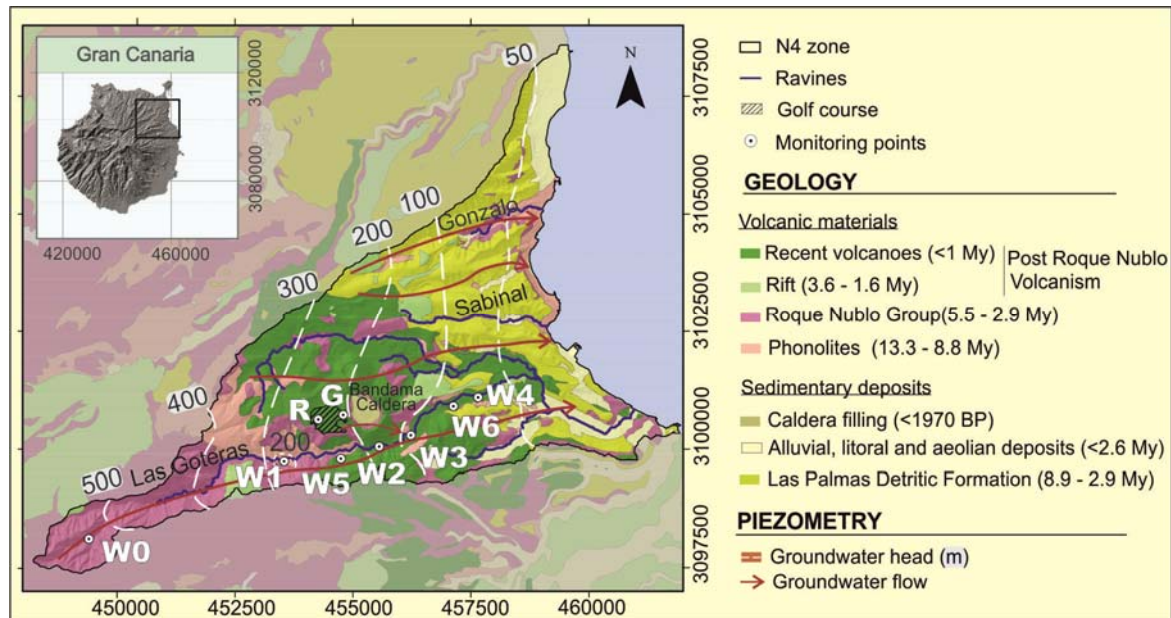
One of the aims of our study was to analyse the temporal evolution 36 contaminants of the total detected by Estévez *et al.* (2012), also including the results of an extended period until September 2011 and the results of 20 compounds non detected in the first study. A secondary objective was to relate their presence with chemical water properties and hydrogeological conditions. Results of analyses of heavy metals in the whole period are also presented.

## 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 Góteras basin, between 400 m and 500 m high. The Las Góteras basin is included in the N4 zone of the Gran Canaria Water Administration Plan (CIAGC, 1999),

which is represented in Figure 1. Average precipitation in the area is 300 mm per year, the average annual temperature is 19°C, and the range of humidity is from 78% to 85%. Since 1976, the Bandama Golf Course has been irrigated with reclaimed water from the Wastewater Treatment Plant of Las Palmas de Gran Canaria, where tertiary treatment installed since 2002, consisted in desalination and disinfection (Estevez *et al.*, 2010).



**Figure 1.** Location and geology of the study area (modified from Balcells *et al.*, 1990), situation of the main ravines, the Bandama Caldera, the golf course and monitoring points (reclaimed water: R, wells: W0-W6 and the El Culatón water gallery) and piezometry for January 2009 (Cabrera *et al.*, 2009, modified).

The study area is next to the quaternary Bandama volcanic complex, and includes a volcanic caldera. Fresh basaltic and basanitic lavas and pyroclastic materials (2,000 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. 1). The island has a low permeability “core” 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 follow a preferential flow line through the Las Góteras ravine and that there is a groundwater flow from the golf course to the ravine. The groundwater table head is located 250 m below the Bandama Golf Course. The aquifer system in the study area is exploited by shaft wells of 2.5-3 m in diameter (“canarian” wells) and 15-300 m depths. These irrigating wells, described in Table 1, exploit mainly the fractured Miocene phonolites with equivalent continuous yields lower than 1 Ls<sup>-1</sup> per day. Cabrera *et al.* (2010) demonstrated that groundwater salinity increases from summit to shore and that hydrogeochemistry changes from sodium bicarbonate (occasionally with an endogenous gas supply) to chloride sodium bicarbonate in the middle area and to sodium chloride on the coastal fringe. Also, nitrate contents increase from summit to shore (up to 180 mgL<sup>-1</sup>), exceeding normative thresholds (Directive 91/676 EEC) so it is designed as a vulnerable zone by the Regional Canary Islands Government. The mentioned study concluded that the water from the El Culatón water gallery: G (Figure 1 and Table 1), about 40 m long and located 60 m below the golf course, drains a perched aquifer with a constant flow rate of 0.05 Ls<sup>-1</sup> and receives water from different sources, including golf course leachates. The water gallery

hydrogeochemistry differs slightly from the groundwater sampled in the wells located at the bottom of the Las Goteras ravine (Cabrera *et al.*, 2009).

**Table 1.** Description of groundwater sampling stations (1: Depth (m), 2: Bottom elevation (m), 3: Exploited Formation, 4: Hydrochemical groundwater type) and chemical parameters of the monitoring network points presenting mean (x) and standard deviation (sd).

	W0		W1		W2		W3		W4		W5		W6		G		R	
	x	sd	x	sd	x	sd	x	sd	x	sd	x	sd	x	sd	x	sd	x	sd
1	208		133		32		158		34		70		96		40**			
2	504		168		183		27		76		205		57		430			
3	Roque Nublo		Phonolites		Recent Basalts		Recent Basalts - Phonolites		Phonolites		Phonolites		Recent Basalts - Phonolites		Roque Nublo Slipped breccia			
4	HCO <sub>3</sub> -Na		Cl-HCO <sub>3</sub> -Na		Cl-Na		HCO <sub>3</sub> -Na		Cl-Na		Cl-SO <sub>4</sub> -Na		Cl-Na		Cl-Na			
pH	7.8b	0.3	7.6b	0.2	7.9b	0.3	6.6a	0.2	7.7b	0.2	8.0b	0.2	7.7b	0.0	7.7b	0.2	7.7b	0.2
EC	0.5a	0.0	1.6b	0.1	2.4c	0.1	3.0d	0.2	3.5e	0.2	1.6b	0.2	3.0d	0.1	1.7b	0.1	0.4a	0.1
NO <sub>3</sub> <sup>-</sup>	7.2a	2.5	38.6b	4.3	117.0d	5.8	64.6c	18.3	185.0e	12.0	76.2c	13.5	133.0d	1.4	59.3c	7.9	8.1a	3.1
Na <sup>+</sup>	50a	1.0	200bc	2.9	252cd	22.4	590f	57.7	468e	33.5	183b	10.1	436e	24.7	304d	5.7	49a	28.2
K <sup>+</sup>	10.3bc	0.5	13.1c	0.7	17.8d	1.3	37.8f	4.4	41.9g	2.5	12.3c	1.0	33.0e	1.4	7.6ab	0.7	3.8a	1.8
Ca <sup>2+</sup>	22.8b	0.5	51.9cd	5.0	99.3e	11.5	39.4c	6.8	107.7e	7.2	56.6d	8.0	62.0d	5.7	8.0a	0.4	11.6ab	1.6
Mg <sup>2+</sup>	15.7ab	0.5	43.8c	5.2	76.5d	9.6	23.8b	4.5	88.6e	7.0	51.4c	7.1	76.0d	5.7	9.4a	0.6	8.7a	1.8
Cl <sup>-</sup>	31.3a	2.9	236.6b	7.0	412.0e	54.5	324.1c	18.6	676.5e	65.8	224.9b	17.0	624.0e	32.5	328.9c	10.3	58.4a	27.5
SO <sub>4</sub> <sup>2-</sup>	7.9a	1.9	155.2b	9.6	232.1c	24.5	371.0d	45.7	335.5d	14.7	233.6c	29.5	251.5c	6.4	130.0b	4.1	17.2a	6.9
HCO <sub>3</sub> <sup>-</sup>	246bc	14	310cd	14	275cd	15	839e	127	346d	21	181ab	11	303cd	29	132a	12	93a	19
SiO <sub>2</sub>	89.5d	0.6	66.4c	1.3	40.2b	2.5	67.3c	4.4	48.8b	2.0	69.1c	5.0	72.0c	4.2	64.8c	4.2	28.3a	5.7
P	0.09a	0.0	0.09a	0.1	0.24bc	0.1	0.12ab	0.1	0.11ab	0.1	0.10a	0.1	0.25c	0.1	0.42d	0.0	0.13abc	0.1
B	0.06a	0.0	0.23ab	0.0	0.46ab	0.1	1.07b	0.1	0.83ab	0.1	0.18a	0.0	0.56ab	0.0	0.53ab	0.0	0.34ab	0.2
Fe	0.00a	0.0	0.00a	0.0	0.00a	0.0	0.00a	0.0	0.00a	0.0	0.01a	0.0	0.00a	0.0	0.00a	0.0	0.09b	0.1
Mn	0.01a	0.0	0.00a	0.0	0.03a	0.1	0.32b	0.1	0.01a	0.0	0.01a	0.0	0.00a	0.0	0.00a	0.0	0.02a	0.0

W represents the 3 m-diameter wells, G: water gallery and R: reclaimed irrigation water. Electric conductivity (EC).

\*: Data with the same letter are not significantly different at 0.05.

\*\*: Length of the water gallery. Depth from the golf course to the water gallery: 60m

## 2.2. Monitoring network

In the monitoring network carried out until September 2011 were sampled the golf course irrigation water (R), the El Culatón water gallery (G) and the same wells considered in Estévez *et al.* (2012): W1, W2, W3 and W4, adding a control well located at the highest altitude and two wells: W5 (nearer the golf course) - W6 (between W3 and W4).

Samples were taken in amber glass bottles with Teflon caps (1L) to analyse organic compounds and in PE-LD bottles (250 ml and 500 ml) to analyse heavy metals and chemical parameters respectively. All samples were immediately stored in an insulated container chilled with ice packs to be dispatched by express delivery to the laboratory. All the samples were taken on the same date and were dispatched within 48h. Irrigation water was sampled directly from a water outlet located in a fairway of the golf course, water gallery samples were taken from a pipe discharging directly from it, and well samples were taken after pumping a minimum of 15 minutes.

This paper presents the results of the occurrence of 65 emerging contaminants and priority substances (2008/105/EC) in nine quarterly campaigns conducted from July 2009 to September 2011. Only R and G were sampled in all the dates. In the rest of the monitoring points the number of available data is: 4 (W0), 6 (W1), 8 (W2), 7 (W3 and W4), 3 (W5) and 2 (W6).

## 2.3. Methods of analysis

The analysis of organic compounds and heavy metals was conducted by the Laboratory of Analytical Chemistry at the University of Jaén by using two different analytical methods (Table 2). The sample pre-treatment applied for the isolation and pre-concentration of non-polar and semi-polar volatile compounds was a liquid-liquid extraction (LLE) with n-hexane (Robles-Molina *et al.*, 2010), followed by gas chromatography coupled with mass spectrometry analysis (GC-MS). The instrument used was a CP-3800 gas chromatograph coupled with a 300-MS triple quadrupole mass spectrometer (Varian Inc. Walnut Creek, California, USA). This methodology was satisfactorily validated and obtained good recovery rates, as well as the RDS (%) for most compounds. The methods' limits of detection, together with the rest of validation parameters for those compounds found in the samples were presented in Estévez *et al.* (2012). Heavy metals were determined by mass spectrometer with inductively coupled plasma (ICP-MS, Agilent Technologies 7500 Series) after vacuum filtration of the samples.

The rest of the chemical parameters were determined in the Laboratory of the Council of Gran Canaria (Laboratorio Agroalimentario y Fitopatológico Laboratorio del Cabildo de Gran Canaria): pH and EC; cations, SiO<sub>2</sub>, P and B by ICP coupled by Optical emission spectrophotometer (OES) and anions by ionic chromatography except carbonates and bicarbonates (Potentiometric Determination).

**Table 2.** Analytical methods employed in this work together with the detected and non-detected compounds which were classified into the following groups: pesticides, Polycyclic Aromatic Hydrocarbons (PAH), pharmaceuticals and heavy metals.

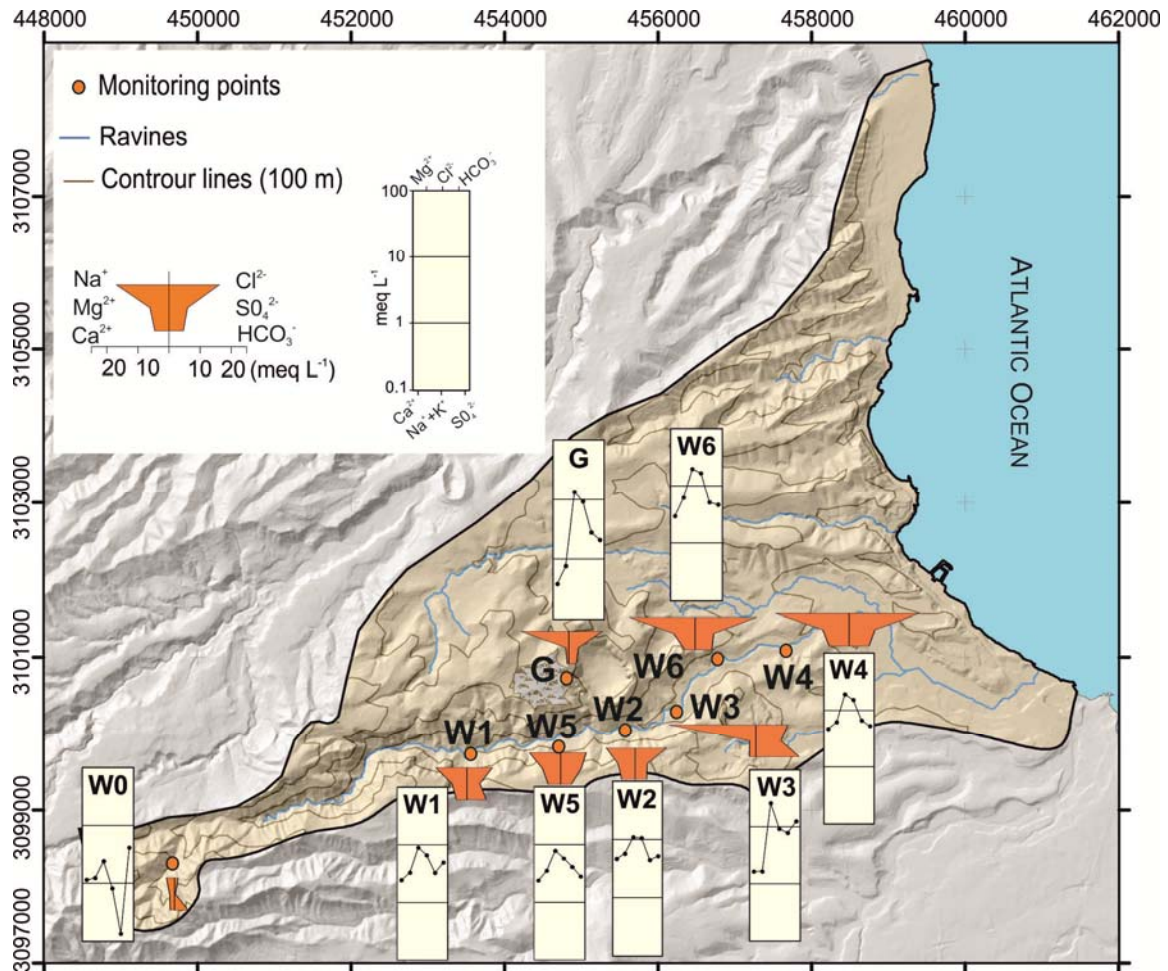
GC-MS method		
Pre-treatment	Extraction method	Analytical Method
<ul style="list-style-type: none"> <li>No filtration</li> <li>pH adjustment (3-4)</li> </ul>	<ul style="list-style-type: none"> <li>Liquid-Liquid Extraction (LLE)</li> <li>Solvent: n-Hexane</li> </ul>	<ul style="list-style-type: none"> <li>Gas Chromatography coupled to Triple Quadrupole Mass Spectrometry (GC-TQMS). Operation mode: MRM.</li> <li>Column: Varian FactorFour VF-5-ms (30m x 0.25mm i.d. x 0.25 µm)</li> </ul>
GC-MS: non detected compounds		GC-MS: detected compounds
<p><u>Pesticides:</u> <i>alachlor</i>, ametryn, aldrin, atrazine desethyl, deltamethrin, dieldrin, endosulfan sulphate, ethion, endrin, heptachlor, isodrin, iprodione, parathion, parathion methyl, trifluralin, <math>\alpha</math>-HCH, <math>\beta</math>-endosulfan, <math>\beta</math>-HCH, <math>\delta</math>-HCH.</p>		<p><u>Pesticides:</u> 4,4'-DDE, 4,4'-DDT, <i>atrazine</i>, <i>chlorfenvinphos</i>, chlorotoluron, <i>chlorpyrifos ethyl</i>, diazinon, <i>diuron</i>, <i>hexachlorobutadiene</i>, <i>hexachlorobenzene</i>, <i>isoproturon</i>, metoxychlor, oxyfluorfen, parathion ethyl, <i>pentachlorobenzene</i>, procymidone, propazine, <i>simazine</i>, terbutylazine, terbutryn*, <math>\alpha</math>-cypermethrin, <math>\alpha</math>-endosulfan, <math>\gamma</math>-HCH.</p> <p><u>Pharmaceuticals:</u> acetaminophen, antipyrine.</p> <p><u>PAH:</u> acenaphtylene, <i>anthracene</i>, <i>benzo(a)anthracene</i>, <i>benzo(a)pyrene</i>, <i>benzo(b)fluoranthene</i>, <i>benzo(g,h,i)perylene</i>, <i>benzo(k)fluoranthene</i>, chrysene, dibenzo(a,h)anthracene, fluorene, <i>indene(1,2,3-cd)pyrene</i>, phenanthrene, pyrene.</p>
ICP-MS method		
Pre-treatment	Analytical Method	
<ul style="list-style-type: none"> <li>Vacuum Filtration</li> </ul>	<ul style="list-style-type: none"> <li>Mass spectrometer with inductively coupled plasma. Babington nebulizer, spray chamber double refrigerated (2 ° C) of Peltier quartz and Agilent I-AS autosampler.</li> <li>RF power: 1500 W, plasma gas flow of 15 Lmin<sup>-1</sup>; nebulizer gas flow: 1 Lm<sup>-1</sup>; auxiliary gas flow: 0.9 min<sup>-1</sup>; suction velocity of the sample: 0.25mLmin<sup>-1</sup>.</li> </ul>	
ICP-MS: non detected compounds		ICP-MS: detected compounds
<u>Heavy metals:</u> Hg, Sn, Pt and Pd		<u>Heavy metals:</u> Cd, Cu , Ni, Pb, Zn and Tl.

Priority substances (2008/105/EC) are in *course*.

### 3. RESULTS

#### 3.1. Hydrogeochemical characterization.

Figure 2 presents Schoeller-Berkaloff and Stiff diagrams obtained with the last analytical results (September 2011). As it was described by Cabrera *et al.* (2010) GW quality remains constant over time, since similar diagrams had been depicted.



**Figure 2.** Schoeller-Berkaloff and Stiff diagrams for the groundwater monitoring points obtained for September 2011.

As it was expected, W0 represents sodium bicarbonate low mineralized groundwater, similar than the water recharge in this area. This groundwater coincides significantly in terms of most of the chemical parameters with R (Table 1), except with higher contents for K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, SiO<sub>2</sub> and Fe, resulting from the volcanic rocks hydrolysis. W3 water is sodium bicarbonated with significantly larger content of Na<sup>+</sup>. Its low pH and high content of HCO<sub>3</sub><sup>-</sup> indicates that groundwater is been enriching by endogenous CO<sub>2</sub> gas contributions. It coincides just with the well that exploits the aquifer more deeply.

The water pumped from W4 is significantly different from the rest of the wells in many of the chemical parameters (EC, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) except of SiO<sub>2</sub> (Table 1). W4 represents groundwater near the discharge area (the coast), where groundwater quality is the result of the progressive mineralization through the groundwater flow



direction, the influence of saline recharge water due to aridity in coastal areas and anthropogenic activities.

The chlorided sodic water from the water gallery presents a deficit of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and  $\text{HCO}_3^-$ , an excess of  $\text{NO}_3^-$  and the highest P content detected. This fact would be related with preferential flow phenomena. Comparing with R, G is more concentrated and seems to receive also alternative water sources.

### 3.1. Priority substances and Contaminants of Emerging Concern

Table 3 shows the frequency, mean and maximum concentration for the monitoring network results. In the previous study (Estévez *et al.*, 2012) the pesticides and PAH presenting a 100% of frequency were: chlorpyrifos ethyl, fluorene, phenanthrene and pyrene. However, once the period of time was extended and the monitoring points were increased, the frequency of chlorpyrifos ethyl detection decreased to 80% (Table 3). The concentration of this priority substance (2008/105/CE) is in a range of  $10 \text{ ngL}^{-1}$  (below the  $30 \text{ ngL}^{-1}$  AA-EQS), although 20% of samples were over this value, exceeding in the 5% of the results the European threshold limit in groundwater ( $100 \text{ ngL}^{-1}$ ) (2006/118/CE). These exceeding values were always detected in summer, although in summer 2010 it was only detected in three samples and below  $10 \text{ ngL}^{-1}$  (Figure 3). The widespread presence of this chlorinated organophosphate insecticide, acaricide and nematicide is related to its broad spectrum and use in agricultural practices, golf courses, cattle and urban media. The continued use of this pesticide poses a risk to farmworkers and their families therefore the EPA is seeking to end agricultural use of chlorpyrifos. Although its soil persistence may depend on the formulation, rate of application, soil type, climate and other conditions (Roberts *et al.*, 1999) chlorpyrifos is stable in soils with reported half-lives ranging between 7 and 120 days (Christensen *et al.*, 2009). As chlorpyrifos does not partition easily from soil to water its presence in runoff water is likely a result of soil-bound from eroding soil, rather than from dissolved chlorpyrifos (EPA, 1999). The high frequency and concentration of this adsorbable compound detected in the Las Goteras aquifer are consistent with the preferential flow transport described in volcanic aquifers. In this sense, the highest values obtained in groundwater coincided with higher EC or nitrate contents. Hence, its presence in high concentrations seems to correspond to occasional contamination events (not related to RW irrigation) and not to an existence of a dangerous diffuse contamination level. On April 15, 2009, EPA included chlorpyrifos ethyl in the initial list of chemicals to be screened for their potential effects on the endocrine system (EPA, 2009), which aims to cover all pesticide chemicals, as well as substances that may occur in sources of drinking water to which a substantial population may be exposed. Nowadays, EPA is reviewing test order responses and making available the status or test order responses (EPA, 2013).

As occurred in our previous study, fluorene, phenanthrene and pyrene (PAH compounds) were detected with frequencies of 100%. These compounds are included in the list of the 30 most frequently detected compounds reported in the UK Environmental Agency Groundwater Micropollutant Database (Stuart *et al.*, 2012). The range concentration of fluorene is less than  $7 \text{ ngL}^{-1}$ . Phenanthrene and pyrene (Figure 4) concentration were always below  $25 \text{ ngL}^{-1}$  in GW, except for the anomalous maximum values described in Estevez *et al.*, (2012) (close to  $60 \text{ ngL}^{-1}$ ). Non seasonal variation was observed (Figure 4) for those PAHs.

**Table 3.** Concentration ( $\mu\text{gL}^{-1}$ : heavy metals,  $\text{ngL}^{-1}$ : rest of substances) and frequency of detection per sample (irrigation water: R, water gallery: G and wells: W0- W6), for those compounds detected at least once in the whole period (July 2009 – September 2011). N°: Compound Number ordered by group (pesticides: 1-23, PAH: 24-36, heavy metals: 37-42 and pharmaceuticals: 43-44) and by frequency of detection, X: mean concentration, Max: maximum concentration, nt: total number of analysis, nd: number of detections, %T: total frequency (GW and R), %R: reclaimed water frequency and %GW: groundwater frequency.

N°	R		G		W0		W1		W2		W3		W4		W5		W6		Frequency		
	X	Max	X	Max	X	Max	X	Max	X	Max	X	Max	X	Max	X	Max	X	Max	% T	% R	%GW
	nt = 9		nt = 9		nt = 4		nt = 6		nt = 8		nt = 7		nt = 7		nt = 3		nt = 2				
1	5.9	27.2	4.2	9.3	1.3	2.9	2.3	4.1	2.4	9.9	5.3	13.4	3.1	6.8	2.4	4.4	3.6	5.6			
nd/nt	6/9		6/9		4/4		5/6		8/8		6/7		6/7		3/3		2/2		83.3	66.7	86.7
2*	6.8	18.1	10	39	3.3	5.3	62	223	52	294	7.7	28.2	51	262	3	6.3	5.2				
nd/nt	6/9		7/9		3/4		5/6		6/8		7/7		6/7		3/3		1/2		79.6	66.7	82.2
3*	9.8	42.3	2.8	4.6	2.6		9.3	13.8	8	25	4.8	7.6	131	624	3	3.7					
nd/nt	8/9		5/9		1/4		4/6		5/8		4/7		5/7		2/3				61.1	88.9	55.6
4*	6.2	18	1.7	2.8	1		3.8	8.1	2.8	6.3	2	2.6	68	195	0.5						
nd/nt	8/9		3/9		1/4		5/6		6/8		4/7		3/7		1/3				55.6	88.9	48.9
5	1.8	3.2	2.7	7.6	1.6	2.4	4.5	11.7	2.3	3.4	2.4	7.3	1.3	1.5	0.9	1.6	3.2				
nd/nt	5/9		4/9		3/4		3/6		5/8		4/7		3/7		2/3		1/2		53.7	55.6	53.3
6	12	36.1	1.8				0.7	1.3	0.9		0.9		0.8								
nd/nt	9/9		1/9				2/6		4/8		3/7		2/7						38.9	100	26.7
7*	4.1	11.3	1.6		1		2.9	4	5.5		1.7	3.9	126	250							
nd/nt	8/9		1/9		1/4		2/6		1/8		3/7		2/7						33.3	88.9	22.2
8*	0.4		0.7	0.8	1.9		14	34.5	14	36			164	325							
nd/nt	1/9		2/9		1/4		3/6		3/8				2/7						22.2	11.1	24.4
9* x	35	191											101								
nd/nt	9/9												1/7						18.5	100	2.2
10*	1.3		2.5				9.1	13.8	4	6.7	2.8	4.3	242	484							
nd/nt	1/9		1/9				2/6		2/8		1/7		2/7						18.5	11.1	20
11*	2.2		0.2				2.5	4.4	2.8		1.6	2.3	109	217							
nd/nt	1/9		1/9				2/6		1/8		2/7		2/7						16.7	11.1	17.8
12	0.4		1.2	1.7			1.6		0.4	0.5	0.3	0.4	0.3		1.0						
nd/nt	1/9		2/9				1/6		2/8		2/7		1/7		1/3				14.8	11.1	15.6
13			0.8				1.3	2.1	2.8		2.8		6.4	11							
nd/nt			1/9				2/6		1/8		1/7		2/7						13	0	15.6
14	0.4		1.2		0.5		5.1														
nd/nt	1/9		1/9		1/4		1/6												9.3	11.1	8.9
15	8	14.7			1.5		1.8														
nd/nt	2/9				2/4														7.4	22.2	4.4
16			0.1								0.2						0.5				
nd/nt			1/9								1/7						1/2		5.6	0	6.7
17			6.5		9		8				42										
nd/nt			1/9		1/4		1/6				1/7								5.6	0	6.7
18			0.2				0.2		1.5												
nd/nt			1/9				1/6		1/8										5.6	0	6.7
19	3	3																			
nd/nt	2/9																		3.7	22.2	0
20							0.3		0.8												
nd/nt							1/6		1/8										3.7	0	4.4
21	20																				
nd/nt	1/9																		1.9	11.1	0
22									0.9												
nd/nt									1/8										1.9	0	2.2
23							12														
nd/nt							1/6												1.9	0	2.2
24	8.1	60	1.2	3.1	1	2.2	1.3	3.2	1.9	6.5	1.7	5.6	1.4	2.1	0.7	1.4	1.6	1.8			
nd/nt	9/9		9/9		4/4		6/6		8		7/7		7/7		3/3		2/2		100	100	100
25	6	18.7	5.7	18	6.4	14			13	57	6.9	18.9	5.8	9.8	2.7	5.8	9.4	13			
nd/nt	9/9		9/9		4/4				8/8		7/7		7/7		3/3		2/2		100	100	100



26 nd/n <sub>t</sub>	4.9 9/9	17.6	3.9 9/9	8.9	4.4 4/4	6.7	4.5 6/6	6.9			9.4 7/7	23	2.5 3/3	5	7.1 2/2	11			100	100	100
27 nd/n <sub>t</sub>	1 2/9	1.6	0.5 3/9	0.6	0.4 1/4		0.5 1/6		0.4 3/8	0.7	0.5 3/7	0.8	0.4 2/7		0.4 1/2			27.8	22.2	28.9	
28 nd/n <sub>t</sub>	2.3 3/9	6.2	2.7 4/9	9.3	0.5 1/4		0.9 2/6	1.2	4.8 3/8	12	11 2/7	21.4	8.5 2/7					25.9	11.1	28.9	
29 nd/n <sub>t</sub>	0.2 5/9	0.2	0.3 2/9	0.4			0.3 1/6		0.4 2/8	0.4	0.2 3/7	0.4	0.2 2/7					24.1	33.3	22.2	
30 nd/n <sub>t</sub>	0.3 2/9	0.3	0.3 2/9	0.4			0.3 2/6	0.4	0.4 3/8	0.8	0.5 2/7	0.7	0.2 2/7					24.1	22.2	24.4	
31 nd/n <sub>t</sub>	0.7 3/9	1.2	0.7 2/9	0.9			0.5 2/6	0.6	0.6 2/8	0.6	1.2 2/7	1.8	1.3 1/7					22.2	33.3	20	
32 nd/n <sub>t</sub>	0.3 1/9		0.4 2/9	0.5			0.8 1/6		1.2 2/8	1.4	0.4 2/7	0.6	0.4 1/7					16.7	11.1	17.8	
33 nd/n <sub>t</sub>	0.2 1/9		0.3 2/9	0.4			0.6 1/6		1.1 2/8	1.2	0.3 2/7	0.4	0.4 1/7					16.7	11.1	17.8	
34 nd/n <sub>t</sub>	0.8 2/9	0.9	0.3 2/9	0.4			0.3 2/6	0.4			0.3 2/7	0.4						14.8	22.2	13.3	
35* nd/n <sub>t</sub>	7.7 1/9		14 1/9						0.5 1/8			105	0.5 1/3					9.3	11.1	8.9	
36 nd/n <sub>t</sub>			0.3 1/9		18 1/4				0.5 1/8									5.6	11.1	4.4	
37* nd/n <sub>t</sub>	425 9/9	811	351 9/9	1022	280 3/4	396	381 6/6	1006	292 7/8	532	362 7/7	563	377 7/7	610	216 3/3	353	282 2/2	317	98.1	100	97.8
38* <sup>x</sup> nd/n <sub>t</sub>	347 9/9	1732	5.6 8/9	24	2.2 3/4	3.7	29 6/6	140	8.6 6/8	34	3.8 7/7	6.9	5.4 6/7	18	1.2 2/3	2	4.3 2/2	4.7	81.5	100	77.8
39 nd/n <sub>t</sub>	10 7/9	24.7	4.4 9/9	15	4.5 2/4	5.6	4.9 6/6	12.6			15 7/7	35.3	10 7/7	19	2.5 3/3	3.3	6.9 2/2	11	81.5	77.8	82.2
40 nd/n <sub>t</sub>	0.2 4/9	0.4	0.2 4/9	0.4			0.2 4/6	0.5	0.2 4/8	0.3			0.2 3/7	0.4	0.1 1/3			37	44.4	35.6	
41 nd/n <sub>t</sub>	0.3 3/9	0.6	0 5/9	0.1	0.1 1/4		0.1 1/6				0.7 5/7		0.4 1/7		2.7 1/3			16.7	33.3	13.3	
42 nd/n <sub>t</sub>	0.05 1/9		0.007 1/9						0.007 1/8		1.1 1/7			0.9 1/3		0.007 2/2		13	11.1	13.3	
43 nd/n <sub>t</sub>	51 5/9	92																9.3	55.6	0	
44 <sup>x</sup> nd/n <sub>t</sub>	1832 1/9				35 1/4													3.7	11.1	2.2	

\*: Compounds detected at least once in the groundwater (G or W0 - W6) at a concentration higher than 0.1 µg/L<sup>-1</sup>.

<sup>x</sup>: detected at least once in the reclaimed water (R) at a concentration higher than 0.1 µg/L<sup>-1</sup>.

**N°** = Compound Number ordered by group (Pesticides: 1- 23, PAH: , Pharmaceuticals: and heavy metals: ) and frequency of detection.

**PESTICIDES:**

1: hexachlorobenzene, 2\*: chlorpyrifos ethyl, 3\*: terbuthylazine, 4\*: diuron, 5: oxyfluorfen, 6: chlorfenvinphos, 7\*: terbutryn, 8\*: procymidone, 9\*<sup>x</sup>: diazinon, 10\*: atrazine, 11\*: propazine, 12: pentachlorobenzene, 13: simazine, 14: chlorotoluron, 15: γ-HCH, 16: 4,4'-DDT, 17: α-endosulfan, 18: 4,4'-DDE, 19: isoproturon, 20: hexachlorobutadiene, 21: α-cypermethrin, 22: metoxychlor, 23: parathion ethyl.

**PAH:**

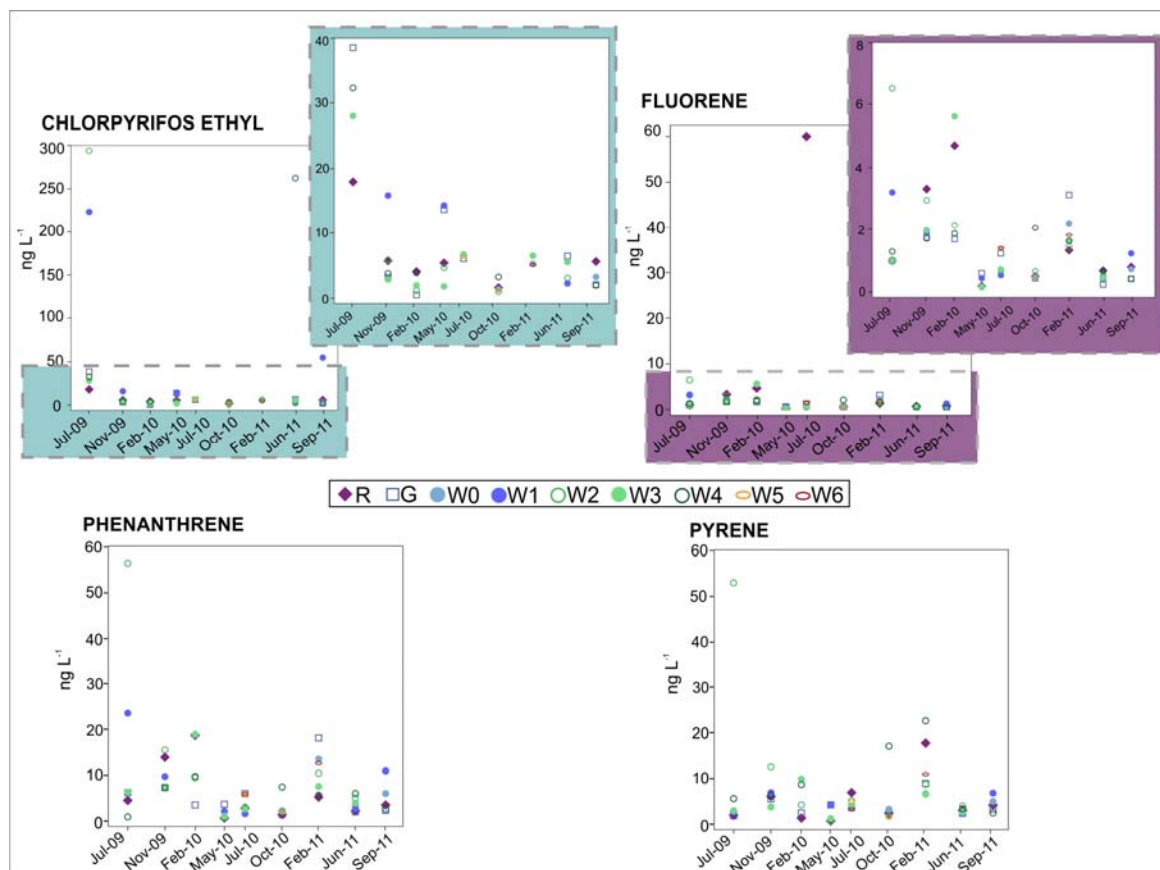
24: fluorene, 25: phenanthrene, 26: pyrene, 27: acenaphthylene, 28: chrysene, 29: benzo(b)fluoranthene, 30: benzo(a)anthracene, 31: benzo(ghi)perylene, 32: indene(1,2,3-cd)pyrene, 33: dibenzo(a,h)anthracene, 34: benzo(k)fluoranthene, 35\*: anthracene, 36: benzo(a)pyrene.

**HEAVY METALS:**

37\*: Zn, 38<sup>x</sup>: Cu, 39: Ni, 40: Cd, 41: Pb and 42: Tl.

**PHARMACEUTICALS:**

43: antipyrine, 44<sup>x</sup>: acetaminophen.



**Figure 4.** Temporal evolution of chlorpyrifos ethyl, fluorene, phenanthrene and pyrene, per sample (irrigation water: R, water gallery: G and wells: W0- W6) and monitoring sampling date.

Among the most frequently detected pesticides, hexachlorobenzene (83%) concentration remained quite constant in the whole period (less than  $10 \text{ ng L}^{-1}$ ), except for the d highest values, already mentioned in the first year study ( $0.03 \mu\text{g L}^{-1}$  in R at 67% and  $0.013 \mu\text{g L}^{-1}$  in GW at 87%). This priority substance is included in the second list of chemicals to be screened for their potential effects on the endocrine system (EPA, 2010).

The pesticides diazinon and chlorfenvinphos were always detected in R, reaching respectively a maximum of 200 and  $40 \text{ ng L}^{-1}$  (below the threshold value). Terbutylazine, terbutryn and diuron were presented at 90% of frequency in R and at 50% in GW (except terbutryn at 20%). Oxyfluorfen was detected at the same frequency both in R and GW (50%).

Chlorfenvinphos was detected at 20% in GW but always below  $2 \text{ ng L}^{-1}$ . Diazinon, always presented in R but never in GW in the previous study (until 2010), was detected once (June 2011) in W4 and at a high concentration ( $100 \text{ ng L}^{-1}$ ). This anomalous value coincides (same well and date), with high concentrations of diuron, terbutryn, chlorpyrifos and terbutylazine: 200, 250, 270 and  $600 \text{ ng L}^{-1}$  respectively, in which mean concentrations are usually below  $20 \text{ ng L}^{-1}$ . Atrazine and propazine (P) also exceeded the threshold limit in the same well and date, and the anthracene's (PAH) concentration was below the limit but in a noticeable level. Therefore a relation between the pesticide occurrence and GW chemical quality is observed. As above-mentioned, W4 presents a significantly variable chemistry comparing to the rest of the wells. There were also measured anomalous high values of EC and nitrate content ( $210 \text{ ng L}^{-1}$ ) and the

mentioned pesticides in the same date (June 2011). In this sense, it is preferable to select less stable wells in terms of chemical water quality (which use to be an available information), to monitor the risk of emerging compounds presence.

The heavy metals most frequently detected were Zn, Ni and Cu. Zn and Ni were always detected in R and at more than 80% of frequency in GW. Cd, Ni and Pb (heavy metals included in the list 2008/105/EC) did not exceed the threshold concentration for surface waters and Hg was never detected.

## **5. CONCLUSIONS**

After a considerable period of sampling, 20 of the total substances from the EU list of priority substances in surface waters (been analysed 25 of them) were detected in GW and RW respectively.

Eleven pesticides and six PAH included in the list of priority substances were detected in R, although always one orders of magnitude below threshold values. Our results let us to conclude that R presents a good quality. Therefore, R is properly treated before irrigation and it is not a noticeable source of GW contamination. Thus, R is perfectly useful as an alternative water resource for irrigation without implying any environmental risk.

Regarding GW, chlorpyrifos ethyl was frequently detected (82%) and exceeded the threshold limit in three different locations (W1, W2 and W4). Its presence in high concentrations seems to correspond to occasional contamination events (not. Atrazine and propazine (Pesticides) also exceeded the threshold limit but only once (July 2011, W4). In the same well and date, the (PAH) concentration of anthracene was in a noticeable level. Other 10 P and 6 PAH included in the priority list of substances were detected in GW, although always one orders of magnitude below the legislated value.

Only 4 of the list of priority substances were detected above the EU threshold, being 2 of them in the same well and date (atrazine and anthracene). Chlorpyrifos ethyl and diuron were the most dangerous priority substances in terms of GW quality so they must be included in all of the monitoring studies, at least in Canary Islands and probably in the rest of the volcanic subtropical archipelagos. Fluorene, phenanthrene and pyrene are the PAH substances most frequently detected (most of the pharmaceutical compounds are not included in this study), but they do not imply a high environmental impact.

From the total wells analysed, there is one of them (W4) in which 50% of the total compounds detected above the EU limit are localized. This coastal well also presents significant differences among sampling dates in various chemistry parameters and high values of leachable parameters (EC and nitrates) coincided with the highest values of emerging compounds. Thus, geology and location seem to be related with contamination events and therefore with the emerging compounds presence. In fact, the "control well" W0 (upstream the ravine) presented more stable chemical quality parameters and the lowest contaminants occurrence. Thus, it is preferable to select less stable wells in terms of chemical water quality, (which use to be an available information) to monitor the risk of emerging compounds presence. These wells are probably also related with preferential flow phenomena that occurs in fractured rocks.

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