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

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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
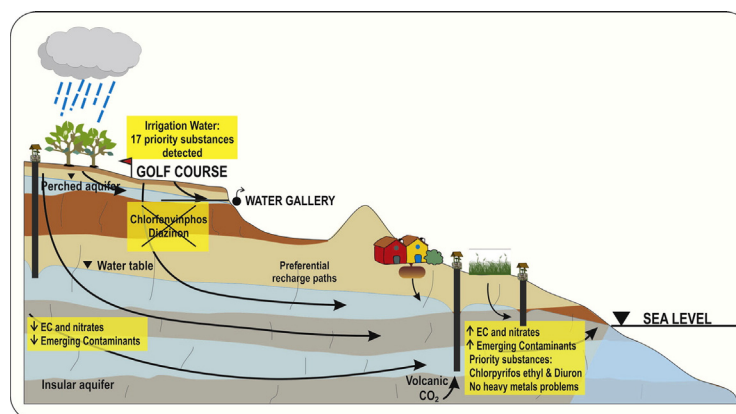
ABSTRACT

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

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).
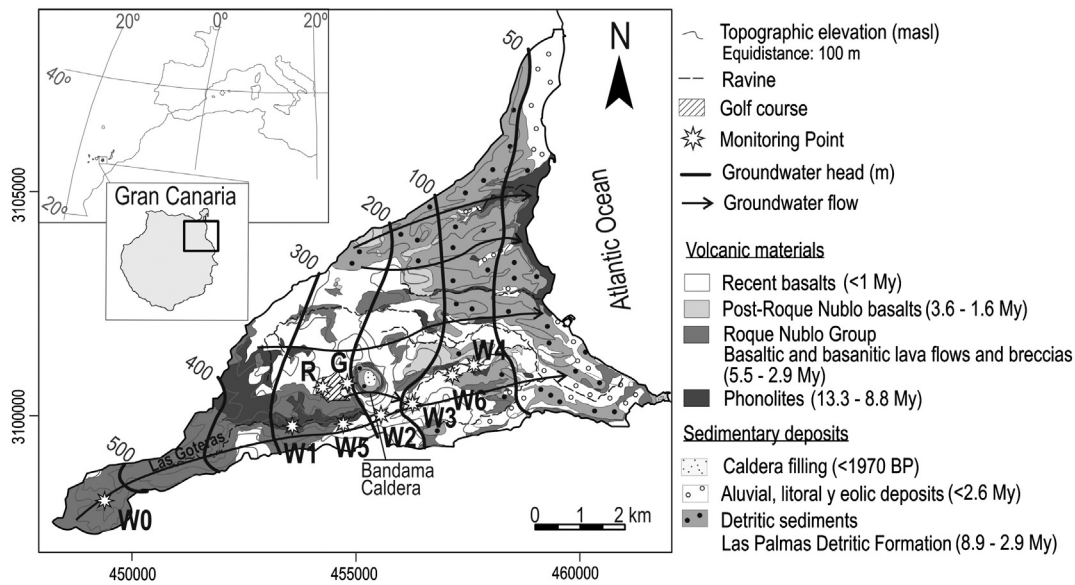
Fig. 1. Location and geology of the study area (modified from Balcells et al., 1990), situation of the main ravines, the Bandama Caldera, the golf course and piezometry for January 2009 (modified from Cabrera et al., 2009). Monitoring points correspond to reclaimed water: R; wells: W0–W6 and the El Culatón water gallery: G.

Average precipitation is 300 mm per year, average annual temperature is 19 °C, and humidity in the range of 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 (Estévez et al., 2010).

Fresh basaltic and basanitic lavas and pyroclastic materials (2000 years old) outcrop in the area (Hansen and Moreno, 2008) which includes the volcanic Bandama Caldera. These materials overlie fractured basanitic lava flows and landslide materials (Roque Nublo Group), which cover Miocene phonolites (Fig. 1). The island can be considered a unique groundwater body, recharged by rainfall infiltration and discharging by springs into gullies and into the sea along the coast, depending on lithological changes (Custodio, 2003; SPA-15, 1975). Previous studies in the study area (Cabrera et al., 2009) have shown that groundwater flows from the summit to the coast and from the golf course to the ravine, as reflected in Fig. 1. Groundwater table head is located 250 m below the golf course and more than 100 m below the Caldera bottom. The aquifer system is exploited by shaft wells (3 m diameter and 15–300 m depth). In the area, irrigation water for arable crops, vineyards and citrus come from the local aquifer, but reclaimed water is also used. A wide range of agrochemicals is used due to the variety of crops.

2.2. Monitoring network

The monitoring network included the golf course reclaimed irrigation water (R), the El Culatón water gallery (G), the same wells (W1–W4) considered in Estévez et al. (2012) and three added wells: W0 (control well located at the highest altitude), W5 (nearer the golf course) and W6 (between W3 and W4). Its location is shown in Fig. 1.

Table 1 shows the main hydrogeological and hydrogeochemical characteristics of the selected wells for sampling, which exploit mainly the fractured Miocene phonolites with equivalent continuous yields lower than 1 L s^{-1} per day. The wells exploit the aquifer at different depths, as indicated by the bottom elevation. These values express the altitude where groundwater is pumped, normally corresponding with the well bottom. Groundwater salinity increases from summit to shore and groundwater facies are sodium bicarbonate (occasionally with an endogenous gas supply) to sodium chloride-bicarbonate in the middle area and to sodium chloride on the coastal fringe (Cabrera et al., 2009). Nitrate contents increase from summit to shore (up to

180 mgL^{-1}). The mentioned study concluded that the El Culatón water gallery (G in Fig. 1 and Table 1), located 60 m below the golf course, drains a perched aquifer. It receives water from different sources, including golf course leachates, as its hydrogeochemistry differs from the wells sampled at the bottom of the ravine (Cabrera et al., 2009; Estévez et al., 2013).

The sampling was carried out quarterly from July 2009 to September 2011. Therefore, during nine campaigns 65 analysis for organic contaminants and heavy metals (HM), including some priority substances (2008/105/EC and 2013/39/EU) were performed. R and G were sampled in all the dates. In the rest of the monitoring points the number of samples was: 4 (W0), 6 (W1), 8 (W2), 7 (W3 and W4), 3 (W5) and 2 (W6).

Samples were taken in amber glass bottles with Teflon caps to analyze organic compounds and in PE-LD bottles to analyze HM and chemical parameters. All samples were stored in an insulated container chilled with ice packs, and were dispatched within 48 h to the laboratory. Irrigation water was sampled directly from a water outlet, water gallery samples were taken from a pipe, and well samples were taken after pumping a minimum of 15 min.

2.3. Analytical methods

Table 2 shows a brief description of the applied methodologies. These methods have validated for wastewater and the recovery rates, RSD (%) and limits of quantitation were presented in Estévez et al. (2012). Results obtained guarantee the QA/QC of the analyses.

The remaining chemical and physicochemical parameters were determined in the "Laboratorio Agroalimentario y Fitopatológico del Cabildo de Gran Canaria": pH and EC were determined using electrometric methods, Na, K, Ca, Mg, SiO$_2$, P and B were determined by ICP coupled by optical emission spectrometry and anions by ion chromatography, except carbonate and bicarbonate which were determined potentiometrically.

Isotopic determination of δ^{15}N and δ^{18}O from the dissolved nitrate were made in the Centres Científics iTècnics of the Universidad de Barcelona (CCiT-UB). Dissolved nitrate were concentrated using anion-exchange columns Bio Rad® AG 1-X8 (Cl−) 100–200 mesh resins after extracting the SO$_4^{2-}$, and PO$_4^{3-}$ by precipitation with BaCl$_2$·2H$_2$O and filtration. The dissolved NO$_3$ was then eluted with HCl and converted to AgNO$_3$ by adding Ag$_2$O, after which the AgNO$_3$ solution was freeze-dried to purify the AgNO$_3$ for analysis with a Carlo Erba

Table 1

Description of sampling stations, including reclaimed irrigation water (R), water gallery (G) and wells (W0–W6). BE: bottom elevation (m), EF: exploited formation, HF: hydrochemical facies, n: number of samples and chemical parameters of the monitoring network points, x: mean values, sd: standard deviation, EC: electric conductivity (mS cm^{-1}). Depth in m and concentrations in mg L^{-1} —: under limits of detection, being LOD: 0.05, 0.005, 0.01 and 0.005 mg L^{-1} for P, B, Fe and Mn respectively.

	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
Depth	208		133		32		158		34		70		96		40[a]			
BE	504		168		183		27		76		205		57		430			
EF	Roque Nublo		Phonolites		Recent basalts		Recent basalts — phonolites		Phonolites		Phonolites		Recent basalts — phonolites		Roque Nublo landslide deposits			
HF	Na–HCO$_3$		Na–Cl–HCO$_3$		Na–Cl		Na–HCO$_3$		Na–Cl–Na		Cl–SO$_4$		Na–Cl		Na–Cl			
n	4		6		8		7		7		3		2		9		9	
pH	7.8	0.3	7.6	0.2	7.9	0.3	6.6	0.2	7.7	0.2	8.0	0.2	7.7	0.0	7.7	0.2	7.7	0.2
EC	0.5	0.0	1.6	0.1	2.4	0.1	3.0	0.2	3.5	0.2	1.6	0.2	3.0	0.1	1.7	0.1	0.4	0.1
NO$_3^-$	7.2	2.5	38.6	4.3	117.0	5.8	64.6	18.3	185.0	12.0	76.2	13.5	133.0	1.4	59.3	7.9	8.1	3.1
Na$^+$	50	1.0	200	2.9	252	22.4	590	57.7	468	33.5	183	10.1	436	24.7	304	5.7	49	28.2
K$^+$	10.3	0.5	13.1	0.7	17.8	1.3	37.8	4.4	41.9	2.5	12.3	1.0	33.0	1.4	7.6	0.7	3.8	1.8
Ca^{2+}	22.8	0.5	51.9	5.0	99.3	11.5	39.4	6.8	107.7	7.2	56.6	8.0	62.0	5.7	8.0	0.4	11.6	1.6
Mg^{2+}	15.7	0.5	43.8	5.2	76.5	9.6	23.8	4.5	88.6	7.0	51.4	7.1	76.0	5.7	9.4	0.6	8.7	1.8
Cl$^-$	31.3	2.9	236.6	7.0	412.0	54.5	324.1	18.6	676.5	65.8	224.9	17.0	624.0	32.5	328.9	10.3	58.4	27.5
SO$_4^{2-}$	7.9	1.9	155.2	9.6	232.1	24.5	371.0	45.7	335.5	14.7	233.6	29.5	251.5	6.4	130.0	4.1	17.2	6.9
HCO$_3^-$	246	14	310	14	275	15	839	127	346	21	181	11	303	29	132	12	93	19
SiO$_2$	89.5	0.6	66.4	1.3	40.2	2.5	67.3	4.4	48.8	2.0	69.1	5.0	72.0	4.2	64.8	4.2	28.3	5.7
P	0.09	0.0	0.09	0.1	0.24	0.1	0.12	0.1	0.11	0.1	0.10	0.1	0.25	0.1	0.42	0.0	0.13	0.1
B	0.06	0.0	0.23	0.0	0.46	0.1	1.07	0.1	0.83	0.1	0.18	0.0	0.56	0.0	0.53	0.0	0.34	0.2
Fe	—	—	—	—	—	—	—	—	—	—	0.01	0.0	—	—	—	—	0.09	0.1
Mn	0.01	0.0	—	—	0.03	0.1	0.32	0.1	0.01	0.0	0.01	0.0	—	—	—	—	0.02	0.0

[a] Length of the water gallery. Depth from the golf course to the water gallery: 60 m.

elemental analyzer (EA) Coupled in the continuous flow to a Finnigan Delta CIRMS. δ^{18}O was analyzed in duplicate with a ThermoQuest high temperature conversion analyzer (TC/EA) unit with a Finnigan Matt Delta C IRMS. Precision ($\equiv 1\sigma$) was of ± 0.6‰ for δ^{15}N and ± 0.7‰ for δ^{18}O.

Isotopic determination of δ^{34}S and δ^{18}O from the dissolved sulfate were made in the Stable Isotope Laboratory of the University of Salamanca, by precipitation of BaSO$_4$ after dissolution of HCL 2.5 N, following by addition of 5% (weight/volume percent) BaCl$_2$. Sulfur isotopic ratios were measured on SO$_2$ obtained by combustion off-line, which was analyzed on a dedicated dual-inlet VG ISOGAS SIRA series II mass spectrometer. The δ^{18}O values were determined on CO gas obtained by pyrolysing the BaSO$_4$ prepared using an EuroVector elemental analyzer, coupled in-line to an ISOPROME (Micromass) continuous flow mass spectrometer. Precision ($\equiv 1\sigma$) was of ± 0.2‰ for δ^{34}S and δ^{18}O. During the sampling, insufficient quantity of precipitate was obtained in well W0, due to its low mineralization, so these data are not available.

3. Results and discussion

3.1. Hydrogeochemical characterization

The groundwater hydrogeochemistry is shown in Fig. 2. Isonitrate contour lines (mg L^{-1}) have been drawn from a field sampling including more than 20 wells in all the area carried out in 2009 (Cabrera et al., 2009). Schoeller–Berkaloff and Stiff diagrams reflects the data obtained from the September 2011 results. The comparison between the chemical data over the time shows that groundwater quality remains constant over time (Cabrera et al., 2009; Estévez et al., 2013).

As it was expected, groundwater salinity increases to the coast. W0 pumps sodium bicarbonate low mineralized groundwater, similar to recharge water in this area. This groundwater coincides significantly in terms of most of the chemical parameters with R (Table 1), except for the higher contents for K$^+$, HCO$_3^-$, SiO$_2$ and Fe., that come from the volcanic rocks silicates hydrolysis (Custodio, 2003).

Groundwater from W4 and W6 are of sodium-chloride type with high levels of nitrate (Table 1 and Fig. 2). They are located near the discharge area, where groundwater quality is the result of the progressive mineralization through the flow direction, the influence of saline recharge water due to aridity in coastal areas and anthropogenic activities. Similar conditions have been described for the Western aquifer of Gran Canaria, where a numerical model has confirmed a complex hydrogeogical and hydrogeochemical behavior of an aquifer in a valley with intensive agriculture with semiarid climate conditions (Cruz-Fuentes et al., 2014). W3 is of sodium bicarbonate type, with significantly larger content of Na$^+$, low pH and high content of HCO$_3^-$ indicating that in this point the aquifer is enriched with endogenous CO$_2$ gas contributions, as this well exploits the aquifer more deeply. This

Table 2

Analytical methods employed in this work for organic compounds (gas chromatography–mass spectrometry) and heavy metals (inductive coupled plasma-mass spectrometry).

GC–MS method

Pre-treatment	Extraction method	Analytical method
• No filtration	• Liquid–Liquid extraction (LLE)	• Gas chromatography coupled to triple quadrupole mass spectrometry (GC–TQMS). Operation mode: MRM.
• pH adjustment (3–4)	• Solvent: n-Hexane	• Column: Varian FactorFour VF-5-ms (30 m × 0.25 mm i.d. × 0.25 μm)

ICP-MS method

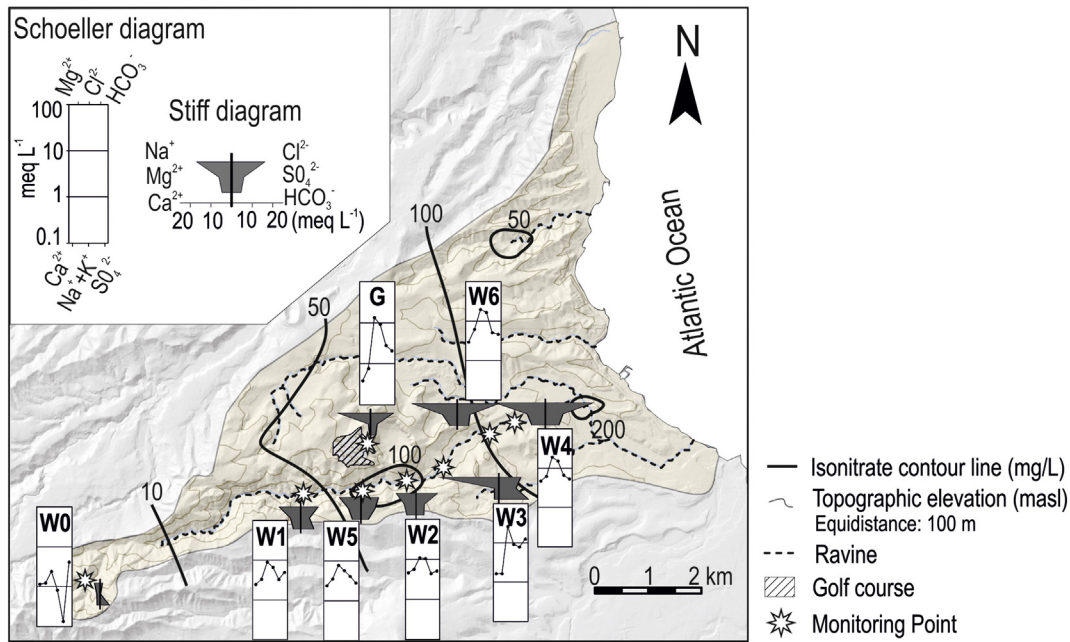| Pre-treatment		Analytical Method
		• Mass spectrometer with inductively coupled plasma. Babington nebulizer, spray chamber double refrigerated (2 °C) of Peltier quartz and Agilent I-AS autosampler.
• Vacuum filtration		• RF power: 1500 W, plasma gas flow of 15 L min^{-1}; nebulizer gas flow: 1 L m^{-1}; auxiliary gas flow: 0.9 min^{-1}; suction velocity of the sample: 0.25 mL min^{-1}.

Fig. 2. Groundwater hydrogeochemistry of the study area reflected by isonitrate contour lines (mg L^{-1}) for 2009 groundwater analysis and Schoeller–Berkaloff and Stiff diagrams for the groundwater monitoring points obtained for September 2011.

phenomena is common in wells located in some areas of the Island, normally where Holocene basalts outcrop. Nowadays, surficial manifestations are not visible, but aragonite travertine deposits precipitated from carbonated springs before insular watertable drawdown have been identified in the north of the Island (Rodriguez-Berriguete et al., 2012). G corresponds to the perched aquifer and is of sodium chloride type, with a deficit of Ca^{+2}, Mg^{+2} and HCO_3^-, an excess of NO_3^- and the highest P content detected. Comparing with R, G is more concentrated and seems to receive also alternative water sources, including the golf course leachates.

The stable isotopes results are shown in Table 3.

Irrigation water (R) $\delta^{15}N$ value (22.7‰) clearly indicates the organic origin of nitrate (Mook, 2001; Curt et al., 2004), as expected due to its origin. The well located in the summit of the area (W0) presents the lowest value and must be representative of the aquifer baseline due its low nitrate concentration, unaffected by agricultural contamination. $\delta^{15}N$ (‰) vs. $\delta^{18}O$ (‰) in dissolved nitrate (Fig. 3A) reflects that groundwater represents a mixing between the natural aquifer contents (W0) and the organic origin (R), with variable $\delta^{18}O$ (‰) contents due to its different possible origins: air oxygen, denitrification processes and volcanic CO_2 contribution. Inorganic fertilizers can be discarded as an origin, attending to the Kendall diagram (Fig. 3A), but they are used in the area, so some mixing processes can be expected. The mixing
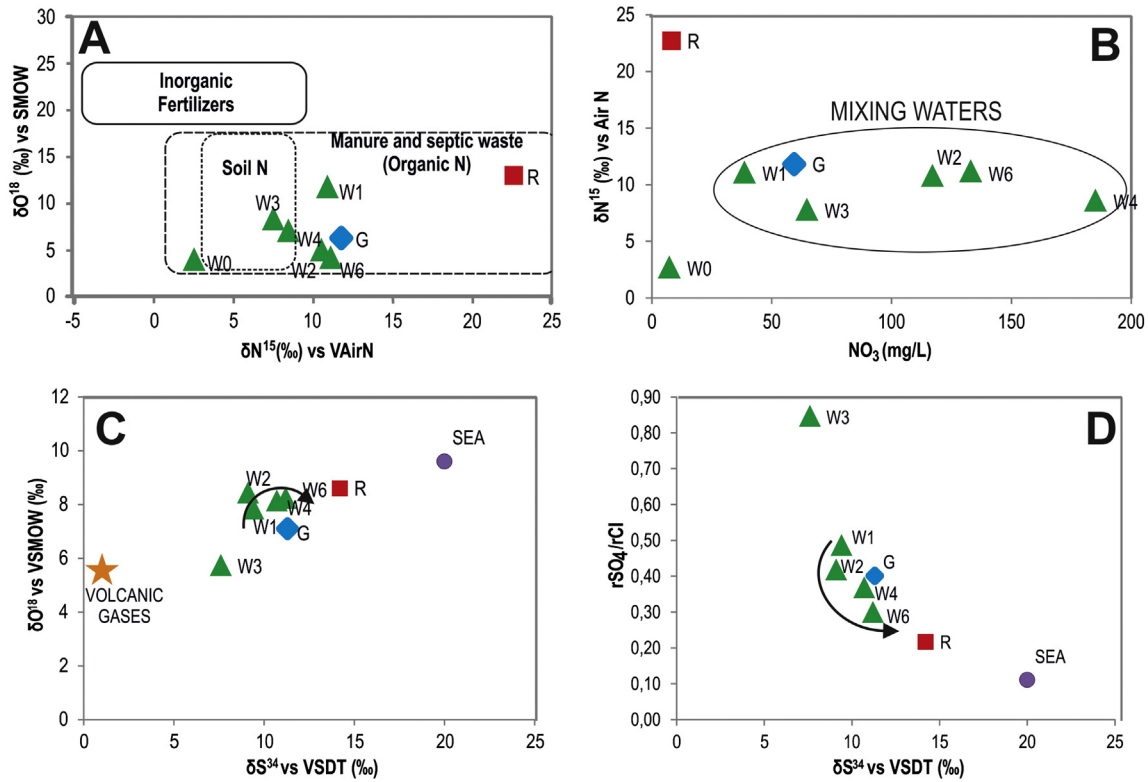
between the $\delta^{15}N$ print in groundwater is reflected also in Fig. 3B, independently from the nitrate contents. The $\delta^{34}S$ determinations show a high influence of a marine origin for R (Fig. 3C and D), assuming +20‰ as the actual marine value (Pearson and Rightmire, 1980). It can be explained attending to its primary origin: sea water desalinated for population supply before been treated to become reclaimed water. All the wells show also the marine influence, increased by proximity to the coast, as indicated in the Figures, excepting W3. The endogenous contribution of volcanic gases is clearly confirmed for this well in Fig. 3D, with $\delta^{34}S$ values close to those determined by Albert-Beltrán et al. (1990) in gases from water galleries in Tenerife Island.

3.2. Priority substances, other organic pollutants and heavy metals

After a considerable period of sampling, 20 substances from the list of priority substances in surface water of the European Community were detected (Table 4). Eight pesticides (P) and six polyaromatic hydrocarbons (PAH) included in this list were detected in R, although always one order of magnitude below EQS values.

Fig. 4 shows concentration ranges of the compounds detected with a frequency higher than 15% in GW and in R, respectively. The compounds are sorted by group: P, PAH and HM, and from higher to lower total frequency. The priority substances are highlighted. Simazine (priority substance) and alpha endosulfan (an organochlorine pesticide banned since 2007 in Spain), are not represented in the figure as they were detected at a total frequency lower than 15%. Although they were detected in GW, they were never detected in R.

In general, the most frequent compounds were: hexachlorobenzene and chlorpyrifos ethyl, fluorene, phenanthrene and pyrene, and Zinc, Copper and Nickel. Concentrations of organic compounds were almost always below 50 ng L^{-1}, although some pesticides were occasionally detected at higher concentrations in GW, even exceeding the European threshold value (2006/118/EC) for pesticides in groundwater (100 ng L^{-1}). Any priority substance exceeded the maximum available concentration (MAC) environmental quality standard (EQS) for surface water (2008/105/EC). However, some priority substances in surface water were detected in R close to EQS: the isomer "γ" of hexachlorocyclohexane (detected at 0.015 mg L^{-1}, being EQS of the parent compound and priority hazardous substance maximum for "other surface

Table 3
Stable isotopes composition of $\delta^{15}N_{AIRN}$ and $\delta^{18}O_{VSMOW}$ for dissolved nitrate and $\delta^{34}S_{VCDT}$ and $\delta^{18}O_{VSMOW}$ for dissolved sulfates (‰) for irrigation water and groundwater from the study area.

SAMPLE	Dissolved NO$_3$		Dissolved SO$_4$	
	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{15}N_{air\ N}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{34}S_{VCDT}$ (‰)
R	12.8	22.7	8.6	14.2
G	6.1	11.8	7.1	11.3
W0	3.5	2.6		
W1	11.3	11	7.8	9.4
W2	4.3	10.7	8.4	9.1
W3	7.9	7.7	5.7	7.6
W4	6.6	8.5	8.1	10.7
W6	3.9	11.1	8.2	11.2

Fig. 3. Nitrate and sulfate groundwater and irrigation water isotopic composition plots. Location of the groundwater sampling points are shown in Fig. 1. A) Pattern of typical ranges of $\delta^{18}O$ and $\delta^{15}N$ for different nitrate sources and values measured in the study area pointing to a mixing process in the aquifer. B) $\delta^{15}N$ versus nitrate concentration in groundwater. C) $\delta^{18}O$ versus $\delta^{34}S$ plot and D) $\delta^{34}S$ versus rSO_4/rCl ratios (r = meq L^{-1}). In C and D plots isotopic composition of Canarian volcanic gases (Albert-Beltrán et al., 1990) and the sea mean composition (Pearson and Rightmire, 1980) are shown.

waters" of 0.02 mg L^{-1} according to 2013/39/EU) and hexachlorobenzene (HCB) (0.03 in R and 0.013 mg L^{-1} in GW, with maximum EQS for "other surface waters "of 0.05 mg L^{-1} in 2013/39/EU).
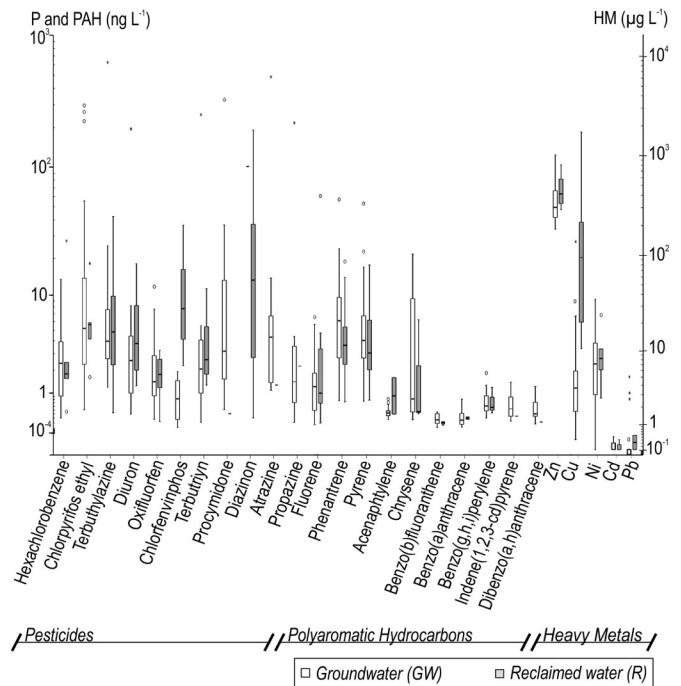
3.2.1. Pesticides

In R and GW, seven pesticides occasionally exceeded 100 ng L^{-1} (2006/118/EC): chlorpyrifos ethyl, terbuthylazine, diuron, terbutryn

Table 4
Detected and non-detected heavy metals and organic compounds which were classified into the following groups: pesticides – polycyclic aromatic hydrocarbons (PAH) – pharmaceuticals.

Non detected organic compounds	Detected organic compounds
Pesticides: *alachlor*, ametryn, *aldrin*, atrazine desethyl, deltamethrin, *dieldrin*, endosulfan sulfate, ethion, *endrin*, heptachlor, *isodrin*, iprodione, parathion, parathion methyl, trifluralin, α-HCH, β-endosulfan, β-HCH, δ-HCH	Pesticides: 4,4′-DDE, 4,4′-DDT, *atrazine*, *chlorfenvinphos*, chlorotoluron, *chlorpyrifos ethyl*, diazinon, *diuron*, *hexachlorobutadiene*, *hexachlorobenzene*, *isoproturon*, metoxychlor, oxyfluorfen, parathion ethyl, *pentachlorobenzene*, procymidone, propazine, *simazine*, terbuthylazine, terbutryn, α -cypermethrin, α-endosulfan, γ-HCH.
	PAH: acenaphtylene, *anthracene*, *benzo(a)anthracene*, *benzo(a)pyrene*, *benzo(b)fluoranthene*, *benzo(g,h,i)perylene*, *benzo(k)fluoranthene*, chrysene, dibenzo(a,h)anthracene, fluorene, *indene(1,2,3-cd)pyrene*, phenanthrene, pyrene.
	Pharmaceuticals: acetaminophen, antipyrine.
Non detected heavy metals	Detected heavy metals
Hg, Sn, Pt and Pd	*Cd*, Cu, *Ni*, *Pb*, Zn and Tl

Priority substances in surface water (2008/105/EC and 2013/39/EU) are in *italics*.

Fig. 4. Boxplot diagrams of the compounds detected with a total frequency greater than 15%, in groundwater (GW, white) and reclaimed water (R, gray). The left scale corresponds to the concentration of pesticides (P) and polycyclic aromatic hydrocarbons (PAH) and the right scale corresponds to the concentration of heavy metals (MP). The frequency detection (%) per compound is indicated below each one in the following order: total of the samples–GW samples–R samples. The compounds are sorted by frequency.

(detected with frequencies >50%), procymidone, atrazine and propazine (detected with frequencies >20%). Chlorpyrifos ethyl was presented at 80% of frequency, its concentration is in a range of 10 ng L^{-1}, and the 5% of the results exceeds the European threshold standard in groundwater, with an extreme concentration of 294 ng L^{-1} (Table 5). Terbuthylazine, diuron and terbutryn (90% of frequency in R and at 50% in GW, except terbutryn at 20%) were in a range of 10 ng L^{-1}, but reaching extreme values of 624, 195 and 250 ng L^{-1}, respectively (Table 5). Procymidone, atrazine and propazine were presented at a 20% of frequency, bellow 10 ngL^{-1}, but reaching extreme values of 325, 484 and 217 ng L^{-1}, respectively (Table 5).

Hexachlorobenzene (HCB), chlorpyrifos ethyl and diuron were priority pesticides detected in a frequency higher than 50% (Table 5). HCB was detected at a frequency of 83%. Its concentration remains quite constant (less than 10 ng L^{-1}) over the whole period, even considering the highest values (27 ng L^{-1} in R and 13 ng L^{-1} in GW) already mentioned in a previous study carried out during one year (Estévez et al., 2012).

Oxyfluorfen was detected at the same frequency both in R and GW (50%) but in low concentrations. The priority pesticides chlorfenvinphos and diazinon, although detected in a total frequency less than 50%, were always detected in R, reaching a maximum of 36 and 191 ng L^{-1}, (Table 5) (below their EQS, 2008/105/EC although above 30 ng L^{-1}, 2013/39/EU). Diazinon was detected in a total frequency less than 50%, although it was also always detected in R, reaching a maximum of 191 ng L^{-1} (Table 5). Chlorfenvinphos was also detected in GW (at a frequency of 20%) but always below 2 ng L^{-1}. Diazinon, always presented in R was detected once (June 2011) in the most contaminated well W4 and at a high concentration (101 ngL^{-1}) (Table 5). This anomalous value coincides (same well and date), with high concentrations of chlorpyrifos ethyl, terbuthylazine, diuron, and terbutryn (Table 5) 294, 624, 195 and 250 ng L^{-1} respectively, in which mean concentrations are usually below 20 ng L^{-1}. Atrazine and propazine (P) also exceeded the threshold limit in the same well and date.

Therefore there is a relation between the pesticide occurrence and groundwater chemical quality, although it should be noted that soil characteristics and water management are also shown as critical factors to explain the occurrence of a contaminant (Estévez et al., 2010, 2012). As above-mentioned, W4 presents a significantly variable chemistry (Table 1) comparing to the rest of the wells. There were also measured anomalous high values of EC and nitrate content (210 ng L^{-1}) and the mentioned pesticides in the same date (June 2011).

Temporal evolution of most frequent detected P: HCB, chlorpyrifos ethyl and diuron, per sampling point (R, G and W0–W6) is presented in Fig. 5. As observed, similar concentrations of HCB were detected in all of the monitoring points, tending to increase in February. The ubiquitous presence of HCB is consistent with Kumar et al. (2013), who state that once HCB enters the environment, it degrades very slowly (half-life of 3–6 years in soil 5–11 years and ground water), so it is extremely persistent, being considered as a member of POPs (persistent organic pol. HCB is one of the priority hazardous substances designated in Directive 2013/39/EU (with an EQS for "other surface waters" of 50 ng L^{-1}) due to its high toxicity and persistency. It is included in the second list of chemicals to be inspected for their potential effects on the endocrine system (EPA, 2010). Besides its origin from industry, HCB has been related with the use of pesticides in past times, atmospheric deposition or diesel particulates from the traffic along the roads (Bailey, 2001; Kumar et al., 2013). Every of the mentioned sources can be found in this area, so it is difficult to determine the HCB provenance.

Chlorpyrifos ethyl is widely used in the area. It presented its maximum values in summer, although in summer 2010 it was only detected in three samples and bellow 10 ng L^{-1} (Fig. 5).The widespread presence of this chlorinated organophosphate insecticide, acaricide and nematicide (sold in Spain by 42 commercial products), is related to its broad spectrum and use in agricultural practices, golf courses, veterinary, cattle and urban media. As pest presence is related by many factors, it is

difficult to determine what the cause of Chlorpyrifos ethyl lowest detection in 2010 summer samples was. Although its soil persistence may depend on the formulation, rate of application, soil type, climate and other conditions (Roberts and Hutson, 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 R irrigation) and not to an existence of a dangerous diffuse contamination level. EPA included chlorpyrifos ethyl in the initial list of chemicals to be screened for their potential effects on the endocrine system (EPA, 2009). Nowadays, EPA is reviewing test order responses and making available the status (EPA, 2013).

No seasonal pattern was observed in diuron concentration, as it remained constant. This result is coincident with obtained by Lapworth et al. (2005) who concluded that no systematic temporal trends were observed throughout their survey in a chalk aquifer. Diuron is a broad-spectrum residual herbicide used by a diverse range of industries and sold in Spain by 13 commercial products.

As pointed out by Lapworth et al. (2005) groundwater pesticide composition was shown to vary greatly both between and within sample sites, highlighting the complex nature of pesticide transport and degradation within the soil and aquifer. In spite of this, in our study, the highest pesticide values obtained in groundwater coincided with higher EC and/or nitrate contents. This can be explained because it is a discharge area with long residence times in the phonolitic aquifer and to the salinity of the natural and irrigation returns recharge due to aridity in the coastal area. The aquifer integrates also nitrate coming from septic tanks, irrigation return flows and sewage systems leakages, which are also sources of organic contaminants.

3.2.2. Polyaromatic hydrocarbons

As occurred in our previous study, fluorene, phenanthrene and pyrene 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 ng L^{-1}, detecting the highest concentration value (60 ng L^{-1}) in R in July, 2010 (Table 5). Phenanthrene and pyrene concentrations were always below 25 ng L^{-1} in GW, except for the anomalous high values described in Estévez et al. (2012) (Fig. 5). Non seasonal variation was observed for those PAH (Fig. 5). The GW data with the highest PAH values were sampled in the same well (W2, Table 5) and date (Jul 09), although pyrene and anthracene were detected at highest concentration in W4. Acenaphtylene and chrysene were detected at a frequency higher than 25%. The rest of priority PAH detected in a frequency range of 25 to 15% presented lower concentration than the already mentioned PAH (Fig. 5). Therefore, fluorene, phenanthrene and pyrene are the PAH substances most frequently detected, but they do not imply a high environmental impact due to the low detected concentration. This is consistent with the lack of industry in the area. The minimal occurrence of this compounds can be related to the no significant traffic and the atmospheric deposition in the zone (Metcalfe et al., 2011).

3.2.3. Heavy metals

The HM most frequently detected were Zn, Cu (the highest concentration in R), and Ni (in W3, Table 5). Zn and Ni were always detected in R, and at more than 80% of frequency in GW. Cd (detected only during the first year of sampling), Ni and Pb never exceed the EQS for surface waters (2008/105/EC and 2013/39/EU). Hg was never detected. As

Table 5
Mean (X) and maximum (Max) concentration (ng L^{-1}: organic substances; µg L^{-1}: heavy metals) and frequency of detection per sample (R: irrigation water, G: water gallery and W0- W6: wells:), for those compounds detected at least once in the whole period (July 2009–September 2011), sorted by group (pesticides, PAH, heavy metals and pharmaceuticals) and by frequency of detection in % (T: total of the samples, R: reclaimed water and GW: groundwater). nt: Total analysis per monitoring point. Bold letters correspond to maximum concentration detected per compound in all the samples.

Monitoring points (nt): R = 9, G = 9, W0 = 4, W1 = 6, W2 = 8, W3 = 7, W4 = 7, W5 = 3, W6 = 2.

	R X	R Max	G X	G Max	W0 X	W0 Max	W1 X	W1 Max	W2 X	W2 Max	W3 X	W3 Max	W4 X	W4 Max	W5 X	W5 Max	W6 X	W6 Max	Freq T	Freq R	Freq GW
Hexachlorobenzene	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		83.3	66.7	86.7
Chlorpyrifos ethyl	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	79.6	66.7	82.2
Terbuthylazine	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			61.1	88.9	55.6
Diuron	6.2	18	1.7	2.8		1	3.8	8.1	2.8	6.3	2	2.6	68	**195**	0.5				55.6	88.9	48.9
Oxyfluorfen	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	53.7	55.6	53.3
Chlorfenvinphos	12	**36.1**		1.8			0.7	1.3		0.9		0.8							38.9	100	26.7
Terbutryn	4.1	11.3		1.6		1	2.9	4		5.5	1.7	3.9	126	**250**					33.3	88.9	22.2
Procymidone		0.4	0.7	0.8		1.9	14	34.5	14	36			164	**325**					22.2	11.1	24.4
Diazinon	35	**191**												101					18.5	100	2.2
Atrazine		1.3		2.5			9.1	13.8	4	6.7	2.8	4.3	242	**484**					18.5	11.1	20
Propazine		2.2		0.2			2.5	4.4		2.8	1.6	2.3	109	217					16.7	11.1	17.8
Pentachlorobenzene		0.4	1.2	**1.7**						1.6	0.4	0.5	0.3	0.4		1.0			14.8	11.1	15.6
Simazine				0.8			1.3	2.1		2.8		2.8	6.4	**11**					13	0	15.6
Chlorotoluron		0.4		1.2		0.5		**5.1**											9.3	11.1	8.9
γ-HCH	8	**14.7**						1.5		1.8									7.4	22.2	4.4
4,4′-DDT,				0.1								0.2						**0.5**	5.6	0	6.7
α-Endosulfan				6.5		9				8				42					5.6	0	6.7
4,4′-DDE				0.2						0.2		**1.5**							5.6	0	6.7
Isoproturon	3	**3**																	3.7	22.2	0
Hexachlorobutadiene										0.3		**0.8**							3.7	0	4.4
α-Cypermethrin		**20**																	1.9	11.1	0
Metoxychlor												0.9							1.9	0	2.2
Parathion ethyl																			1.9	0	2.2
Fluorene	8.1	**60**	1.2	3.1	1	2.2	1.3	**12**	1.9	6.5	1.7	5.6	1.4	2.1	0.7	1.4	1.6	1.8	100	100	100
Phenanthrene	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	100	100	100
Pyrene	4.9	17.6	3.9	8.9	4.4	6.7	4.5	6.9					9.4	**23**	2.5	5	7.1	11	100	100	100
Acenaphtylene	1	**1.6**	0.5	0.6		0.4		0.5	0.4	0.7	0.5	0.5	0.4	0.5				0.4	27.8	22.2	28.9
Chrysene	2.3	6.2	2.7	9.3		0.5	0.9	1.2	4.8	12	11	**21.4**	8.5	17					25.9	11.1	28.9
Benzo(b)fluoranthene	0.2	0.2	0.3	**0.4**						0.3	0.4	**0.4**	0.2	**0.4**	0.2	0.3			24.1	33.3	22.2
Benzo(a)anthracene	0.3	0.3	0.3	0.4			0.3	0.4	0.4	**0.8**	0.5	0.7	0.2	0.2					24.1	22.2	24.4
Benzo(ghi)perylene	0.7	1.2	0.7	0.9			0.5	0.6	0.6	0.6	1.2	**1.8**		1.3					22.2	33.3	20
Indene(1,2,3-cd)pyrene			0.3	0.4		0.5				0.8	1.2	**1.4**	0.4	0.6		0.4			16.7	11.1	17.8
Dibenzo(a,h)anthracene			0.2	0.3		0.4				0.6	1.1	**1.2**	0.3	0.4		0.4			16.7	11.1	17.8
Benzo(k)fluoranthene	0.8	**0.9**	0.3	0.4				0.3		0.4			0.3	0.4					14.8	22.2	13.3
Anthracene		7.7		14								0.5		**105**		0.5			9.3	11.1	8.9
Benzo(a)pyrene				0.3		**18**				0.5		0.5							5.6	11.1	4.4
Zn	425	811	351	**1022**	280	396	381	1006	292	532	362	563	377	610	216	353	282	317	98.1	100	97.8
Cu	347	**1732**	5.6	24	2.2	3.7	29	140	8.6	34	3.8	6.9	5.4	18	1.2	2	4.3	4,7	81.5	100	77.8
Ni	10	24.7	4.4	15	4.5	5.6	4.9	12.6			15	**35.3**	10	19	2.5	3.3	6.9	11	81.5	77.8	82.2
Cd	0.2	0.4	0.2	0.4					0.2	**0.5**	0.2	0.3	0.2	0.4		0.1			37	44.4	35.6
Pb	0.3	0.6	0	0.1		0.1				0.1				**0.7**		2.7			16.7	33.3	13.3
Tl		0.05		0.007						0.007				**1.1**		0.9		0.007	13	11.1	13.3
Antipyrine	51	**92**																	9.3	55.6	0
Acetaminophen		**1832**				35													3.7	11.1	2.2
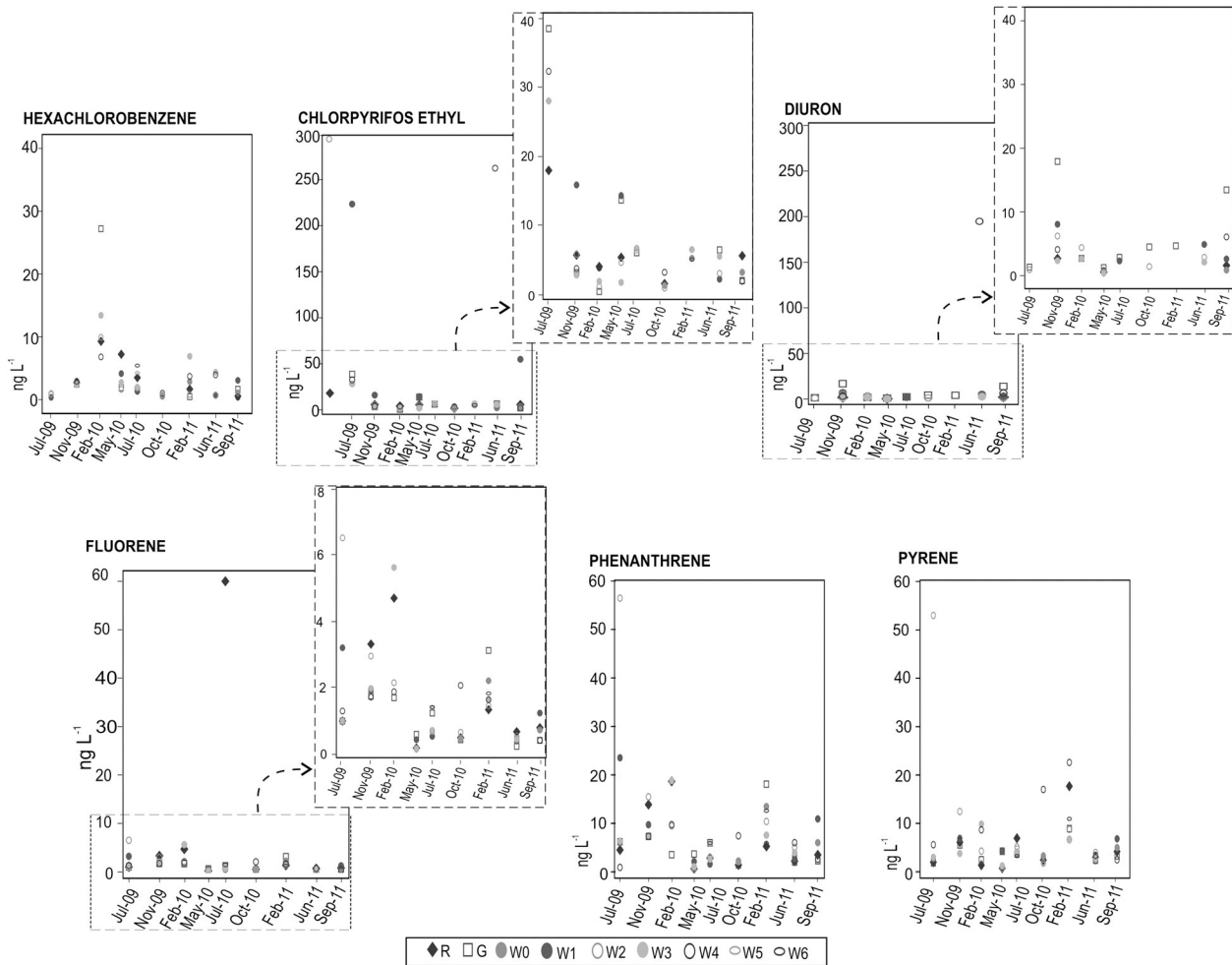
Fig. 5. Temporal evolution of the organic contaminants most frequently detected (hexachlorobenzene, chlorpyrifos ethyl, diuron, fluorene, phenanthrene and pyrene), per sample (irrigation water: R, water gallery: G and wells: W0–W6) and monitoring sampling date.

mentioned for P, W4 was the well having the highest concentration relating to the most of HM (Table 5). Absence of environmental problems related to the presence of HM can be expected, but some contamination in GW can come from the pipes and tubes of the wells and the water gallery installations, as indicated in Vasallo et al. (1974). This fact is consistent with the land use including a mixture of residential, arable farmland and shrubs (there is no industrial land use in the area).

3.2.4. Pharmaceuticals

Two pharmaceuticals (PH), antipyrine and acetaminophen, were determined more frequently in R (56% and 11%) than in GW (0% and 2%), presenting occasionally high concentrations (Table 5). Antipyrine is an analgesic used to relieve ear pain which mainly is used along with antibiotics to treat an ear infection. Although not frequently detected, acetaminophen (also denominated paracetamol) is widely used as analgesic and antipyretic.

4. Conclusions

The most frequent compounds detected in R and GW are: the pesticides hexachlorobenzene and chlorpyrifos ethyl; the PAH fluorene, phenanthrene and pyrene; and the HM Zinc, Copper and Nickel. Although seventeen priority substances were detected in R, none priority substance exceeded the EU limits for surface water (2008/115/EC), except chlorfenvinphos, pesticide detected just above 30 ng L^{-1} (2013/36/EU).

Chlorpyrifos ethyl, terbuthylazine, diuron terbutryn, procymidone, atrazine and propazine exceeded the threshold concentration for groundwater (2006/108/EC). The priority pesticides chlorfenvinphos and diazinon were always detected in R but rarely occurred in GW, suggesting an adequate degradation through the unsaturated zone. Fluorene, phenanthrene and pyrene were detected always, but it does not imply a high environmental impact due to their low concentration. The absence of environmental problems related to the presence of HM can be expected as there is no industrial land use in the area. Antipyrine and acetaminophen analgesics, although widely used, were not frequently detected. Therefore, chlorpyrifos ethyl and diuron are the most dangerous substances in terms of GW quality, so they must be included in monitoring studies, at least in many of the volcanic subtropical archipelagos.

There is a relationship between the contaminants' occurrence and GW hydrochemistry, including the stable isotopic prints of δ^{15}N and δ^{18}O in dissolved nitrate and δ^{34}S and δ^{18}O in dissolved sulfates. The well situated in the recharge area (W0) presented a stable hydrochemistry and the lowest contaminants occurrence. The wells located in the coastal area (W4 and W6) presents a significantly variable chemistry, and anomalous high values of EC, nitrate content and contaminants (50% of the total compounds detected above the EU limit). Thus, hydrogeology and location are related to contamination events and therefore to the emerging compounds presence. Therefore, to monitor the risk of emerging compounds presence it is preferable to select less

stable wells in terms of chemical water quality. These wells are probably related to preferential flow phenomenon that occurs in fractured rocks.

No seasonal pattern of the presence of the contaminants in the aquifer has been observed; probably because in semiarid zones there are no pronounced rainfall and runoff periods, irrigation water management has no high variations among periods, nor low temperatures that can limit the biological activity. Furthermore, the existence of occasional contamination events (not only related to R irrigation) suggests considering extended monitoring periods to detect anomalous concentrations.

As a general conclusion, it can be noted that the relationship between the quality and quantity of irrigation water and the presence of contaminants in groundwater is not simple, given the long transit time through a considerable vadose zone. In addition it is influenced by many parameters, including widespread diffuse contamination, many different input sources to irrigation water, the wide variety of individual pollutants, and soil degradation processes. All these factors make it difficult to track, trace and define a definite pattern of behavior. Furthermore, there are local additional factors of the study area that make the process more complex. They are the characteristics of the geology of the unsaturated zone, the long use of reclaimed water for irrigation in Gran Canaria, the climatic particularities, the management of irrigation and the existence of isolated population centers not connected to the sewer network. Despite these difficulties, we have demonstrated the ubiquity of organic contaminants with great interest due to their potential adverse effects on public health and the environment in a complex media. Furthermore, our work can help to corroborate the typical hydrogeological contamination processes in volcanic regions (fissures in the unsaturated zone), to be taken into account when managing and controlling the quality of the aquifer by the Water Administration. In this sense, monitoring studies to determine the presence of organic contaminants in the aquifers is recommended, complemented with hydrogeochemical and isotopic studies. It can improve the risk assessment and the evaluation of possible sources of contamination.

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