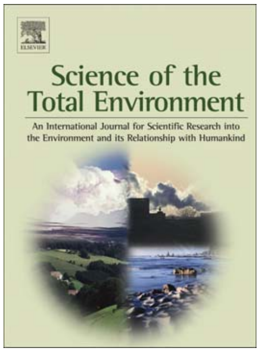

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SCREENING OF EMERGING CONTAMINANTS AND PRIORITY SUBSTANCES (2008/105/EC) IN RECLAIMED WATER FOR IRRIGATION AND GROUNDWATER IN A VOLCANIC AQUIFER (GRAN CANARIA, CANARY ISLANDS, SPAIN)

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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 µg 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 µg 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.

Keywords: emerging contaminants, priority substances, reclaimed water, groundwater, irrigation, soil, volcanic zone, chlorpyrifos ethyl.

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 µg L^{-1} 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 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 of this, 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, 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 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 (Estevez et al., 2010).

The study area is next to the quaternary Bandama volcanic complex, and includes a volcanic caldera (Figure 1). 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. 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 (Figure 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 ("canarian" wells), dug by hand or with explosives to reach depths in the 15-300 m range. These irrigating wells exploit mainly the fractured Miocene phonolites with equivalent continuous yields lower than 1 Ls^{-1} per day (Table 1). Groundwater salinity increases from summit to shore. Groundwater hydrochemistry changes from sodium bicarbonate (occasionally with an endogenous gas supply) at the top to chloride sodium bicarbonate in the middle area and to sodium chloride on the coastal fringe. Nitrate contents increase from summit to shore (up to 180 mg L^{-1}), exceeding normative thresholds (Directive 91/676 EEC). This scenario has led to the Regional Canary Islands Government designating a section of the area as a vulnerable zone.

The above-mentioned study concluded that the water from the El Culatón water gallery (G in Figure 2), about 40 m long and located 60 m below the golf course, drains a perched aquifer that receives water from different sources, including golf course leachates. The El Culatón water gallery is located on the west escarpment of the Bandama Caldera and lies above the island water table elevation, in a slipped fractured volcanic breccia, with a constant flow rate of 0.05 Ls^{-1}. This perched aquifer presents a stable chemical sodium chloride composition with excesses of Na (300 mg L^{-1}) and nitrates contents (50 mg L^{-1}). 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).

2.2. Monitoring network

In 2009, a monitoring network was designed to sample the golf course irrigation water (R) and groundwater (GW) from five sampling points: four active wells (W1, W2, W3 and W4) located in the influence area of the irrigated golf course and the El Culatón water gallery (G) situated 60 m below the golf course (Figure 1 and Table 1). Samples were taken in amber glass bottles with Teflon caps (1L) and 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 pumping wells samples were taken after waiting a minimum of 15 minutes, to obtain representative samples from the aquifer.

This paper presents the results of the occurrence of 183 emerging contaminants and priority substances (2008/105/EC) in four quarterly campaigns conducted in: July 2009 (MS1), November 2009 (MS2), February 2010 (MS3) and May 2010 (MS4). Monitoring points W1 and W4 were not sampled in MS3 and MS4, respectively.

2.3. Methods of analysis

The analysis of the samples was conducted by the Laboratory of Analytical Chemistry at the University of Jaén by using two different analytical methods (Table 2) depending on the physicochemical characteristics of the pollutants. 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. The instrument used was a CP-3800 gas chromatograph coupled with a 300-MS triple quadrupole mass spectrometer (Varian Inc. Walnut Creek, California, USA). On the other hand, a solid phase extraction (SPE) procedure with MeOH, similar to that described by Gros et al. (2006), was performed for the isolation and pre-concentration of polar and semi-polar compounds, followed by liquid chromatography coupled with mass spectrometry analysis. For this purpose, a high-performance liquid chromatograph (Agilent series 1200, Agilent Technologies, Santa Clara, California) connected to a time-of-flight mass spectrometer (Agilent 6220 accurate mass TOF, Agilent Technologies, Santa Clara, California) was employed.

Both methodologies were 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, are provided in Table S1 as Supplementary Information.

3. Results and discussion

Table 2 presents the target compounds, either detected or not, at least once in the reclaimed water (R) or the groundwater (G and W1-W4) samples, which were classified into five groups: Pharmaceuticals and Drugs of Abuse (PH), Pesticides (P), Polyaromatic Hydrocarbons (PAH), Volatile Organic Compounds (VOC) and Flame Retardants (FR). The results confirm the widespread occurrence of emerging contaminants and priority substances in both R and GW. Of the 183 substances analysed, 78 were detected at less once (42 PH, 20 P, 12 PAH, 2 VOC and 2 FR), representing 43% of the total analysed.

Figure 2 presents the concentration range per group of compounds detected at each sampling point. One preliminary consideration was that all the groups were present in reclaimed water, thus confirming that they persist or are metabolised during depuration and desalination treatments. More compounds were detected in the R than in the GW samples (67 vs. 55), including 40 and 23 PH, respectively, which is probably a response to sorption and degradation processes in soil. Furthermore, some contaminants were always detected in R, but never in GW: flufenamic acid, propyphenazone, terbutryn and diazinon (at a maximum of 0.8 μg L^{-1}, 0.03μg L^{-1}, 0.01 μg L^{-1} and 0.025 μg L^{-1}, respectively). However, pesticide occurrence was lower in the R than in the GW samples (14 and 16, respectively), suggesting an alternative source in groundwater for some of these substances such as agricultural practices. Besides the grass species growing on the golf course, vineyards, citrus fruits and vegetables, have been cultivated in the study area over the last decades. Thus, due to the diversity of the cultivated species, a large amount of different pesticides could be detected in GW.

On the other hand, septic tanks are a usual practice in the area where old houses were built previously to the sewerage system. Nowadays, the lower part of the ravine is stated as being "deficient in sewerage" in the last Water Plan draft (CIAGC, 2009). Thus, introduction of PH into the aquifer seems to be produced not only by irrigation using reclaimed water, but also by septic tanks and sporadic pulses produced by breaks or leaks in sewers.

In all the detected compounds, the concentration range was below 50 ng L^{-1}, although PH and P concentrations were occasionally higher. As PH are used at low concentrations, higher P concentrations are expected to be detected than PH ones. Nevertheless, PH were detected at higher concentrations than P in both water sources, and the concentration range tendency per chemical groups for all the monitoring points was: PH > P > PAH-VOC. Thus, regardless of the water origin, average concentrations were respectively about 10 ng L^{-1}, 5 ng $L^{-1}$and 1 ng L^{-1} in PH, P, and PAH-VOC. In contrast, FR was the most variable group, ranging from 10 ng L^{-1} (R and W3) to 1 ng L^{-1} (G and W4). Attenuation of emerging contaminants concentration could be expected to be correlated with sampling depth in homogeneous media. Nevertheless, no relation between the depth of the sampling points (Table 1) and a high PH concentration was observed (Figure 2): only one PH exceeding 0.1 μg L^{-1} was detected in the shallowest wells (W2 and W4), while two PH exceeded 0.1 μg L^{-1} in the W1 samples and three PH in G and W3 (the deepest well). These facts could be attributed to the preferential flows phenomena, which are dominant in fractured volcanic materials (Custodio, 2004). It has been described as an important process in the hydrogeological behaviour of Miocene fractured phonolites in the ravine of Telde, located in the south adjacent ravine (Cabrera and Custodio, 2004). These materials are the main exploited formation by the wells located in the Las Goteras ravine. The geological characteristics of the slipped breccias, where the El Culatón water gallery is dug, also indicate the existence of preferential paths through the fractures.

Figure 3 represents the concentration range of the groups of compounds on the different monitoring sampling dates (MS1-MS4) for each sampling point (R, G, W1-4), with a higher scale for pharmaceuticals and pesticides than for PAH, VOC and FR. The presence of emerging compounds and their concentration detected in the aquifer did not seem to depend on temporal variations. In order to improve these results, longer sampling periods must be considered.

Figure 4 depicts frequency of detection, expressed as the number of dates on which compounds were detected simultaneously at all the sampling points (black columns) divided by the total sampling dates and sorted by classes of substances. Moreover, those compounds which were always detected in R, but never in groundwater (grey columns), and those detected at all the sampling points of GW (G, W1-W4), but never in the R (empty columns), are represented. The values represented for each compound correspond to the maximum concentration (ng L^{-1}) detected in GW (triangles) and R (circles). Caffeine and nicotine (stimulants), chlorpyrifos ethyl (organophosphate insecticide), fluorene, phenanthrene and pyrene (PAH) were always detected in all the samples. Hexachlorobenzene and terbuthylazine (pesticides) were detected at all the sampling points (R and GW) at a frequency of 75% (3 monitoring sampling dates), while benzalkonium chloride (antiseptic), theophylline (bronchodilator) and theobromine (caffeine metabolite), diuron, oxyfluorfen (herbicides) and five PAH were present at all the sampling points at a frequency of 50% (2 monitoring sampling dates). Codeine (Drug of Abuse) and chlorfenvinphos (organophosphate insecticide), pentachlorobenzene (pesticide), two PAH (benzo (K) fluoranthene and Indene (1,2,3-cd) pyrene) and triethyl phosphate (FR) were detected only once at all the sampling points. Table 3 shows the most frequent compounds detected simultaneously in GW and R, and provides some statistical concentration data as well as typical uses.

Caffeine and nicotine have been reported to be two of the most abundant individual compounds detected in groundwater in other European countries (Loos et al., 2010; Stuart et al., 2012; Teijon et al., 2010) given their abundant use and inefficient removal. However, environmental caffeine concentrations in subtropical regions have been rarely reported. Knee et al. (2010) obtained 88 ng L^{-1} as a maximum caffeine concentration sampled in springs and pumped from wells installed on the beach face of Hanalei

Bay (Hawaii), while the maximum GW value detected in our study was 45 ng L^{-1}. Besides, this maximum GW concentration detected in our study was lower than 189 , 140 and 505 ng L^{-1}, as indicated in the aforementioned European groundwater studies, respectively (Loos et al., 2010; Stuart et al., 2012; Teijon et al., 2010) or than 110 ng L^{-1} as reported by Lapworth et al. (2012), including international studies. However, the GW mean caffeine concentration (11.4 ng L^{-1}) was comparable to the value of 13 ng L^{-1} reported by Loos et al. (2010). Studies in a German karst system (Hillebrand et al., 2012), seawater and freshwater in the United States (Peeler et al., 2006; Siegener and Chen, 2002), Europe (Buerge et al., 2003; Weigel et al., 2004) and Australia (Chen et al., 2002) have linked caffeine concentrations in ground and surface waters to wastewater contamination, and have suggested that caffeine can be used as a wastewater tracer. However in aquifers with long residence times, most caffeine and paraxanthine are degraded before reaching the groundwater head. Thus, Seiler et al. (1999) suggested that the usefulness of caffeine as a tracer might be limited because it is not conservative. Therefore, the widespread occurrence and detected concentrations of caffeine and its metabolites (theophilline and teobromine) in the aquifer system of the Las Goteras basin should indicate preferential entry routes through fractured unsaturated zone.

The GW nicotine mean content presented in Table 3 (37 ngL^{-1}) is less than that for the groundwater samples (63 ngL^{-1}) measured by Teijon et al. (2010), but the maximum concentration is similar (115 ngL^{-1} and 144 ngL^{-1}, respectively), but lower than 8.07 ng L^{-1} mentioned by Stuart et al. (2012), which was obtained during the UK Environment Agency monitoring from 1992 to 2009. Regarding water origin, R nicotine mean content presented in Table 3 (7.7 ng L^{-1}), is lower than that detected in GW (37.0 ng L^{-1}). In contrast, Lapworth et al. (2012) mentioned that there was a GW downgradient from the source of contamination due to the high potential for dilution and attenuation for the total loading of emerging organic contaminants to groundwater. This fact could indicate the aforementioned existence of alternative sources of contamination in the Las Goteras basin, even when considering the improvement in R quality due to the tertiary treatment installed in 2002.

Fluorene, phenanthrene and pyrene (PAH compounds) were also detected in our study 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). GW maximum concentrations were 6.5, 56.5 and 52.6 ng L^{-1}, respectively (Table 3).

Herbicides diuron and terbuthylazine were detected at the maximum concentration of 8.1 and 24.9 ng

L^{-1}, respectively (Table 3), while these compounds in other groundwater screenings (Loos et al., 2010; Teijon et al., 2010) presented higher maximums (279 ng L^{-1} and 716 ng L^{-1}, respectively). In contrast, the average values for diuron (2.8 versus 3 ng L^{-1}) and terbuthylazine (7.3 versus 7.3 ng L^{-1}) were similar in our study and in that of Loos et al., 2010. The other compounds detected at a relatively high frequency (hexachlorobenzene, benzalkonium chloride, teophylline and oxyfluorfen) have not been reported at similar frequencies in other European studies.

It is important to point out that some of the contaminants detected in all the R samples were never detected in the GW ones (Figure 4): flufenamic acid (maximum of 0.8 μg L^{-1}), propyphenazone (another analgesic which never exceeded 0.03 μg L^{-1}), terbutryn and diazinon (pesticides presented at low concentrations, below 0.01 and 0.025 μg L^{-1}, respectively). This result is consistent with the properties of these substances. Regarding pesticides, terbutryn is easily adsorbed in soils with a high organic or clay content, so it does not leach in agricultural soils (Mesiter, 1994). Furthermore, Eisler et al. (1986) mentioned that diazinon (whose average degradation time in soil is from 2-4 weeks) can remain biologically available for six months under low temperature and humidity conditions, but seldom migrates below topsoil (1.3 cm).

In contrast, phenylephrine (Drug of Abuse), nifuroxazide (antibiotic) and miconazole (antifungal) were never detected in R, but were found at all the GW sampling points (although nifuroxazide and miconazole were found on only one date) (Figure 4). This result indicates the occurrence of other sources of contamination linked to septic tanks or sporadic discharges produced by breaks in sewerage.

In legislation terms, chlorpyrifos ethyl is an organophosphorus insecticide included in the list of priority substances in surface water (2008/105/EC) which exceeded the European groundwater quality standard threshold for pesticides (100 ng L^{-1}, 2006/118/EC) in two samples (W1 and W2 in July 2009). In contrast, some authors (Hernandez et al., 1998; Liang et al., 2011; Roy et al., 2001) have suggested that chlorpyrifos should be considered an improbable leacher given its high affinity adsorption. Other authors (Teijon et al., 2010) have also detected this pesticide frequently (85%) in groundwater, but at a maximum concentration below 20.78 ng L^{-1} in the Llobregat Delta aquifer, where reclaimed water was injected directly instead of being used for irrigation purposes. The high frequency and concentration of this absorbable compound detected in the Las Goteras aquifer (Figure 4 and Table 3) are consistent with the above-mentioned preferential flow transport.

Table 4 offers the statistical data of the priority substances (List of priority substances in surface water, 2008/105/EC) investigated in R or GW. The compounds in R with a concentration closer to the threshold limit include: γ-hexachlorohexane, detected at 0.015 µg L^{-1} (not detected in GW), while the maximum threshold concentration for "other surface waters" was 0.02 ng L^{-1}, hexachlorobenzene was detected at 0.03 µg L^{-1} (0.013 µg L^{-1} in GW), and the maximum threshold concentration for "other surface waters" was 0.01 µg L^{-1}. No specific legislation has been established for emerging contaminants in groundwater, except for individual pesticides, their metabolites and degradation products (< 0.1 µg L^{-1}) (2006/118/EC).

Those compounds, detected at least once at levels above 100 ng L^{-1} (the European groundwater quality standard threshold for pesticides, 2006/118/EC) are marked in Table 2 respectively by ^{X} and * for the R and GW samples (Figure S2). Benzalkonium chloride and theobromine exceeded this concentration in both types of water sampled. Chlorpyrifos ethyl, nicotine and nifuroxacide exceeded 100 ng L^{-1} in GW, while teophylline, flufenamic acid and erythromycin exceeded this concentration only in R. Erythromycin was always detected in R (twice at a high concentration: 194 ng L^{-1} in July and 745 ng L^{-1} in November), and was also found once in the well W1 (43 ng L^{-1}), where 20% of the groundwater was pumped by the well owner for house water supplies. This wide-spectrum macrolide antibiotic is used to treat several types of infections in humans and animals (respiratory tract infections, skin infections, acute pelvic inflammatory disease, erythrasma, etc.), and is considered one of the most commonly reported antibiotics (Lapworth, 2012). One important concern is that the widespread presence of antibiotics may induce resistance in bacterial strains and, in turn, could result in untreatable diseases (Hirsh et al., 1999; Solomons, 1978). In agreement, Kumar et al. (2005) demonstrated that most of the antibiotics found in surface waters were detected only in minute quantities, except for erythromycin and some sulpha drugs, because most antibiotics are strongly adsorbed in soils and are not readily degraded. Regarding Drugs of Abuse, apart from the aforementioned (caffeine, codeine, nicotine and phenylephrine), benzoylecgonine, EDDP, ephedrine, methadone and morphine were detected at least once in R and at concentrations lower than 6 ngL^{-1}.

4. Conclusions

The obtained results confirm the widespread occurrence of 46% of the 183 emerging contaminants and priority substances analysed in reclaimed water (R) and groundwater (GW) sampled quarterly during one year (July 2009-September 2010) in the study area. Caffeine and nicotine (stimulants), chlorpyrifos ethyl (organophosphate insecticide), fluorene, phenanthrene and pyrene (PAH) were always detected in all the samples.

The concentration range in all the detected compounds was below 50 ng L^{-1}, although occasionally the PH and P concentrations were higher. The average concentrations per chemical groups remained constant for all the sampling points, regardless of the water origin: PH (10 ng L^{-1}) > P(5 ng L^{-1}) > PAH(1 ng L^{-1})-VOC(1 ng L^{-1}). This fact, along with the absence of some contaminants in R, which were present at all the GW sampling points (phenylephrine, nifuroxazide and miconazole), indicate alternative contamination sources besides golf course irrigation, such as agricultural practices, septic tanks and sewerage breaks.

The same concentration range regardless of the sample origin and the depth of the sampling points and the widespread occurrence and the detected concentrations of caffeine, its metabolites and chlorpyrifos ethyl (a pesticide that twice exceeds the European groundwater threshold, 2006/118/EC), could be attributed to the preferential flows phenomena, which is as an important process in the hydrogeological behaviour of main exploited formations (fractured Miocene phonolites and slipped breccias).

Two priority substances concentrations came closer to those included in the Environmental Quality Standards of the surface water list (2008/105/EC): γ-hexachlorohexane (0.015 ng L^{-1} in R, but not detected in GW) and hexachlorobenzene (0.03 ng L^{-1} and 0.013 ng L^{-1} in R and GW, respectively). Some chemicals other than pesticides that exceeded the 2006/118/EC limit for pesticides in groundwater were: benzalkonium chloride, nicotine and nifuroxacide in GW; benzalkonium chloride, teophylline, flufenamic acid and erythromycin in R.

Erythromycin, a wide-spectrum antibiotic, was always detected in R (exceeding 0.1 μg L^{-1} on 2 occasions), but was detected only once in W1. Therefore, we must take into account the possibility of developing resistant strains of the bacteria that cause these compounds being ineffective for the purpose for which they were designed.

The presence of emerging compounds and their concentrations detected in the aquifer did not seem to depend on temporal variations; therefore a longer sampling period must be considered. Knowledge of the chemicals detected in this study will help identify the specific contaminants targeted for monitoring and future research, such as potential health effects, source or actions to control their presence or treatment.

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FIGURE CAPTIONS

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).

Fig. 2. Concentration range detected at each sampling point of these groups of compounds: Pharmaceuticals (PH), Pesticides (P), Polycyclic Aromatic Hydrocarbons (PAH), Volatile Organic Compounds (VOC) and Flame Retardants (FR).

Fig. 3. Concentration range detected at each sampling point (reclaimed water: R, wells: W1-W4 and the El Culatón water gallery: G) of each group of compounds on the monitoring sampling dates (MS). The scale is higher for Pharmaceuticals and Pesticides than it is for Polycyclic Aromatic Hydrocarbons (PAH), Volatile Organic Compounds (VOC) and Flame Retardants (FR).

Fig. 4. Frequency of detection of compounds according to water quality (reclaimed water: R, groundwater: G-W, and both) and to the group of compounds (Pharmaceuticals, Pesticides, Polycyclic Aromatic Hydrocarbons: PAH and Flame Retardants: FR), and maximum concentration detected in R (X) or GW (circles). Frequency is expressed as a number of dates on which compounds were detected simultaneously at all the sampling points (black columns) for a specific date divided by the total sampling dates, compounds which were always detected in R, but never in G-W (grey columns) and those compounds detected at all the sampling points of groundwater (G, W1-W4), but never in R (empty columns). *Indicates the most frequent compounds always detected in both water qualities.

Table 1

Chemical, hydrogeological characteristics and use of pumped water of the monitoring network groundwater points.

Sampling stations	**Depth (m)**	**Bottom elevation (m)**	**Exploited geological Fm.**	**Hydrochemical groundwater type**	**EC (μS cm^{-1})**	**NO_3^- (mg L^{-1})**	**Use**
W1	133	168	Phonolites	$Cl-HCO_3$_Na	1500-1700	34	Irrigation (80%)- water supply (20%)
W2	31.5	182.5	Recent Basalts	Cl-Na	2300-2600	121	Irrigation (100%)
W3	158	27	Phonolites	HCO_3_Na	2800-3100	76	Irrigation (100%)
W4	34	76	Phonolites	Cl-Na	3300-3600	180	Irrigation (100%)
G	Length(*): 40m	430	Slipped breccia	Cl-Na	1600-1900	50	Irrigation (100%)

W represents the 3 m-diameter wells and G means the water gallery. Electric conductivity (EC) and nitrate contents are referred to the as the 2009 samples.

*: Depth from the golf course to the water gallery: 60m

Table 2

Analytical methods employed in this work together with the detected and non-detected compounds which were classified into the following groups: Pharmaceuticals and Drugs of Abuse (PH), Pesticides (P), Polycyclic Aromatic Hydrocarbons (PAH), Volatile Organic Compounds (VOC), Flame Retardants (FR).

<table>
<tr><td colspan="3">GC-MS method</td></tr>
<tr><td>Pre-treatment
• No filtration
• pH adjustment (3-4)</td><td>Extraction method
• Liquid-Liquid Extraction (LLE)
• Solvent: n-Hexane</td><td>Analytical Method
• Gas Chromatography coupled to Triple Quadrupole Mass Spectrometry (GC-TQMS). Operation mode: MRM.
• Column: Varian FactorFour VF-5-ms (30m x 0.25mm i.d. x 0.25 µm)</td></tr>
<tr><td colspan="2">GC-MS: non detected compounds</td><td>GC-MS: detected compounds</td></tr>
<tr><td colspan="2">Pesticides: alachlor, ametryn, aldrin, atrazine desethyl, chlorotoluron, deltamethrin, dieldrin, endosulfan sulphate, ethion, endrin, heptachlor, isodrin, iprodione, parathion, parathion methyl, trifluralin, α-HCH, β-endosulfan, β-HCH, δ-HCH.
PAH: anthracene
VOC and FR: 1,2,3-TCB</td><td>Pesticides: 4,4’-DDE, 4,4’-DDT, chlorfenvinphos, chlorpyrifos ethyl*, diazinon, diuron, hexachlorobutadiene, hexachlorobenzene, metoxychlor, oxyfluorfen, pentachlorobenzene, α-endosulfan, γ-HCH.
PAH: acenaphtylene, 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.
VOC and FR: 1,2,4-TCB, 1,3,5-TCB</td></tr>
<tr><td colspan="3">LC-MS method</td></tr>
<tr><td>Pre-treatment
• Vacuum Filtration
• No pH adjustment</td><td>Extraction method
• Solid Phase Extraction (SPE)
• Solvent: MeOH
• Oasis HLB cartridge (200mg, 6 mL)</td><td>Analytical Method
• Liquid Chromatography coupled to Time of Flight Mass Spectrometry (LC-TOFMS). Operation mode: Fullscan.
• Column: Zorbax XDB C18 (4.6 mm × 100 mm and 1.8 µm)</td></tr>
<tr><td colspan="2">LC-MS: non detected compounds</td><td>LC-MS: detected compounds</td></tr>
<tr><td colspan="2">Pharmaceuticals and Drugs of Abuse: 11-nor-9-carboxy-THC, 3-methylxanthine, 4-AA, acetylmorphine, amphetamine, atropine, bendroflumethiazide, benzothiazol, cannabidiol, carbadox, cefotaxime, chlorotetracycline, clembuterol, cloxacillin, cocaine, demeclocycline, dicloxacillin, digoxigenin, digoxin, doxycyclyne, enalapril, enoxacin, enrofloxacin, ethylamphetamine, ethylmorphine, famotidine, fenofibrate, flumequine, heroin, hydroflumethiazide, indomethacine, josamycin, ketamine, leucomalachite green, lomefloxacin, malachite green, MDA, MDEA, MDMA, meclofenamic acid, methamphetamine, metformin, metronidazole, mevastatin, minocycline, naproxen, norfloxacin, oxolinic acid, oxytetracicline, phenacetin, phenylbuthazone, pindolol, pipemidic acid, pravastatin, ranitidine, roxithromycin, salbutamol, sarafloxacin, spiramycin I, sulfachloropyridazine, sulfadiazine, sulfamerazine, sulfanilamide, sulfathiazole, tetracycline, timolol, tylosine, warfarin, δ-9-THC.
Pesticides: ethoxyquin, thiabendazole, tributyltin chloride, N-nitrosodiethylamine, N-nitrosodimethylamine, N-nitrosodi-n-dibutylamine, N-nitrosomethylethylamine, N-nitrosomorpholine, N-nitroso-n-diphenylamine, N-nitrosopiperidine, N-nitrosopyrrolidine.</td><td>Pharmaceuticals and Drugs of Abuse: acetaminophen, antipyrine, atenolol, benzalkonium chloride*^{x}, benzoylecgonine, bezafibrate, caffeine, carbamazepine, cimetidine, cis-diltiazem, clarithromycin, codeine, danofloxacin, diphenhydramine, EDDP, ephedrine, erythromycin^{x}, estrone, flufenamic acid^{x}, gemfibrozil, ibuprofen, ketoprofen, lincomycin, mebendazole, mefenamic acid, methadone, miconazole, morphine, nicotine*, nifuroxazide*, ofloxacin, oxacillin, phenylephrine, propranolol, propyphenazone, sulfadimethoxin, sulfamethizole, sulfamethoxazole, sulfapyridine, theobromine*^{x}, theophylline^{x}, trimethoprim.
Pesticides: atrazine, isoproturon, procymidone, propazine, simazine, terbuthylazine, terbutryn.
VOC and FR: TBP, TEP.</td></tr>
</table>

*: detected at least once in the groundwater (G or W1-W4) at a concentraction higher than 0.1 µg L^{-1}, x: detected at least once in the reclaimed water (R) at a concentraction higher than 0.1 µg L^{-1}

Table 3

Most frequent compounds detected simultaneously in GW (groundwater) and R (reclaimed water), statistical concentration data, use and Chemical Abstract Service Registry Number.

Compound	**Frequency (%)**	**GW (ng L^{-1})**			**R (ng L^{-1})**			**Typical use**	**CASRN**
		Maximum	**Median**	**Media**	**Maximum**	**Median**	**Media**		
Caffeine	100	44.9	6.0	11.4	27.2	11.5	13.0	Non-prescription stimulant (coffee, tea, caffeinated soft drinks)	58-08-2
Nicotine	100	115.5	20.0	37.0	12.6	7.5	7.7	Non-prescription stimulant (tobacco ingredient), insecticide	54-11-5
Chlorpyrifos ethyl	100	294.0	5.3	38.4	18.1	5.6	8.4	Organophosphorus insecticide	39475-55-3
Fluorene	100	6.5	1.7	2.0	4.7	2.2	2.3	PAH used to make dyes, plastics, and pesticides	86-73-7
Phenanthrene	100	56.5	7.4	10.6	18.7	9.3	9.5	PAH used to make dyes, plastics and pesticides, explosives and drugs	85-01-8
Pyrene	100	52.6	4.3	7.6	6.1	1.7	2.6	PAH used to make dyes, plastics, and pesticides	129-00-0
Hexachlorobenzene	75	13.4	2.8	4.9	27.2	2.4	10.5	Fungicide	118-74 -1
Terbuthylazine	75	24.9	3.9	7.3	42.3	10.5	17.5	Herbicide	5915-41-3
Benzalkonium chloride	50	197.5	8.4	33.5	119.4	17.1	38.5	Antiseptic and spermicide	8001-54-5
Theophylline	50	35.2	22.2	19.9	138.5	3.2	36.4	Bronchodilator, Metabolite of caffeine	58-55-9
Theobromine	50	252.5	28.0	49.0	695.0	34.8	243.9	Vasodilator, diuretic, and heart stimulant, Metabolite of caffeine	83-67-0
Diuron	50	8.1	2.5	2.8	18.0	2.1	5.8	Herbicide	330-54-1
Oxyfluorfen	50	11.7	1.5	3.1	2.6	1.8	1.5	Herbicide	42874-03-3

Table 4

Maximum concentration of the priority substances detected in reclaimed water (R) and groundwater (G and W1-W4) and Maximum Allowable Concentration (MAC) described in the Environmental Quality Standards (EQS) listed in Directive 2008/105/EC.

Compound	Group	GW ($\mu g\ L^{-1}$)	R ($\mu g\ L^{-1}$)	MAC-EQS ($\mu g\ L^{-1}$)	
		Maximum	Maximum	Inland surface waters	Other surface waters
Alachlor	P	N.d.	N.d.	0.7	0.7
Atrazine	P	0.001	0.001	2	2
Chlorfenvinphos	P	0.002	0.036	0.3	0.3
Chlorpyrifos ethyl	P	0.294	0.018	0.1	0.1
Diuron	P	0.008	0.018	1.8	1.8
Hexachlorobenzene	P	0.013	**0.027**	0.05	**0.05**
Hexachlorobutadiene	P	0.001	N.d.	0.6	0.6
Isoproturon	P	N.d.	0.003	1	1
Pentachlorobenzene	P	0.002	0.0004	not applicable	not applicable
Simazine	P	0.003	N.d.	4	4
Tributyltin chloride	P	N.d.	N.d.	0.0015	0.0015
α-Endosulfan	P	0.042	N.d.	0.01	0.004
β-Endosulfan	P	N.d.	N.d.	0.01	0.004
α- Hexachlorocyclohexane	P	N.d.	N.d.	0.04	0.02
β- Hexachlorocyclohexane	P	N.d.	N.d.	0.04	0.02
δ- Hexachlorocyclohexane	P	N.d.	N.d.	0.04	0.02
γ- Hexachlorocyclohexane	P	N.d.	**0.015**	0.04	**0.02**
Anthracene	PAH	N.d.	N.d.	0.4	0.4
Benzo(a)pyrene	PAH	0.0004	N.d.	0.1	0.1
Benzo(b)fluoranthene	PAH	0.0004	0.0002	not applicable	not applicable
Benzo(g,h,i)perylene	PAH	0.002	0.001	not applicable	not applicable
Benzo(k)fluoranthene	PAH	0.001	0.0004	not applicable	not applicable
Indeno(1,2,3-cd)pyrene	PAH	0.001	0.0003	not applicable	not applicable
1,2,3 TCB	VOC	N.d.	N.d.	not applicable	not applicable
1,2,4 TCB	VOC	0.001	0.001	not applicable	not applicable
1,3,5 TCB	VOC	0.0003	N.d.	not applicable	not applicable

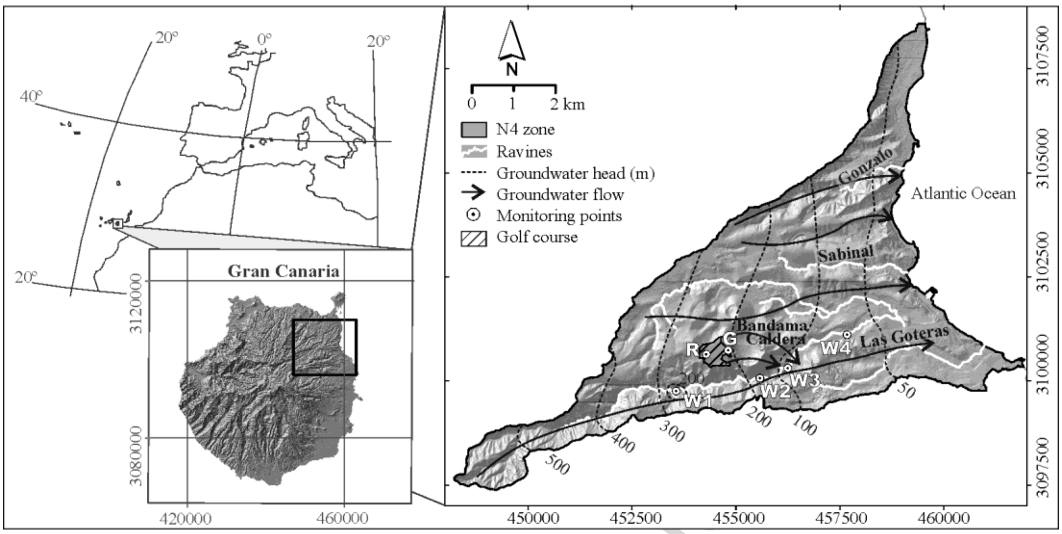
20°
0°
20°
40°
20°
Gran Canaria
3120000
3080000
420000
460000
N
0 1 2 km
N4 zone
Ravines
Groundwater head (m)
Groundwater flow
Monitoring points
Golf course
Atlantic Ocean
Gonzalo
Sabinal
Bandama Caldera
Las Goteras
R
G
W1
W2
W3
W4
500
400
300
200
100
50
3107500
3105000
3102500
3100000
3097500
450000
452500
455000
457500
460000

Fig. 1

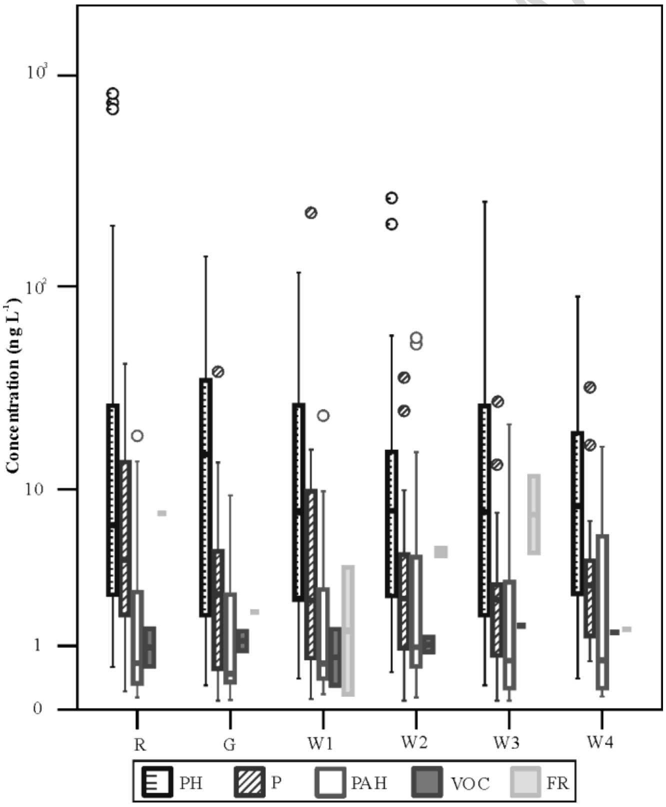
10^3
10^2
10
1
0
Concentration (ng L^{-1})
R
G
W1
W2
W3
W4
PH
P
PAH
VOC
FR

Fig. 2

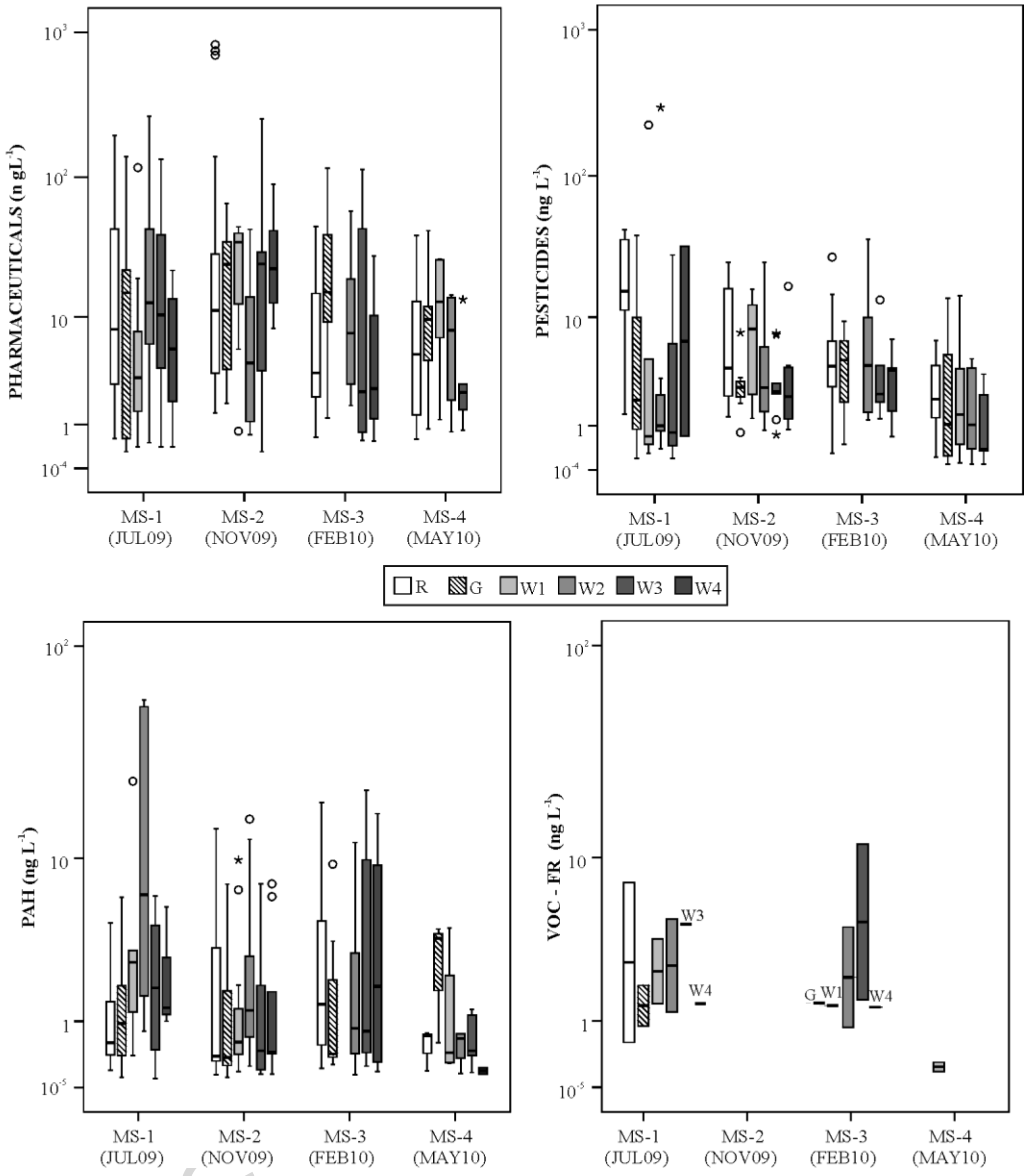
PHARMACEUTICALS (ng L-1)
PESTICIDES (ng L-1)
PAH (ng L-1)
VOC - FR (ng L-1)
10³
10²
10
1
10⁻⁴
10⁻⁵
MS-1 (JUL09)
MS-2 (NOV09)
MS-3 (FEB10)
MS-4 (MAY10)
R
G
W1
W2
W3
W4

Fig. 3

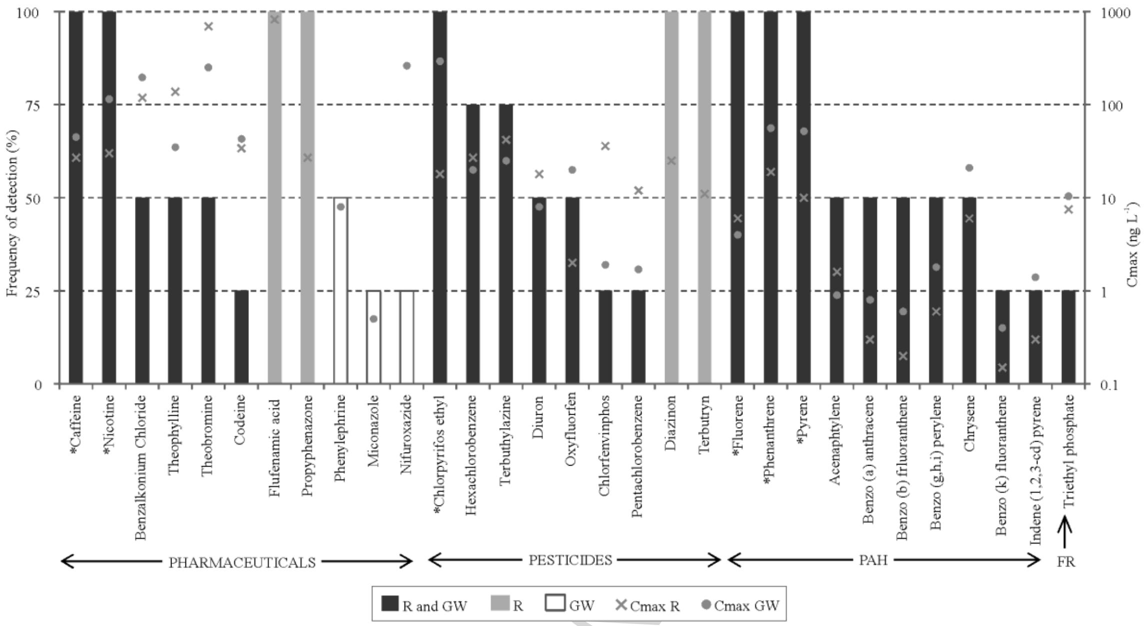
Frequency of detection (%)
100
75
50
25
0
Cmax (ng L-1)
1000
100
10
1
0.1
*Caffeine
*Nicotine
Benzalkonium Chloride
Theophylline
Theobromine
Codeine
Flufenamic acid
Propyphenazone
Phenylephrine
Miconazole
Nifuroxazide
*Chlorpyrifos ethyl
Hexachlorobenzene
Terbuthylazine
Diuron
Oxyfluorfen
Chlorfenvinphos
Pentachlorobenzene
Diazinon
Terbutryn
*Fluorene
*Phenanthrene
*Pyrene
Acenaphtylene
Benzo (a) anthracene
Benzo (b) fluoranthene
Benzo (g,h,i) perylene
Chrysene
Benzo (k) fluoranthene
Indene (1,2,3-cd) pyrene
Triethyl phosphate
PHARMACEUTICALS
PESTICIDES
PAH
FR
R and GW
R
GW
Cmax R
Cmax GW

Fig. 4

HIGHLIGHTS

Emerging contaminants in groundwater and reclaimed water used for irrigation since 1976 were investigated.

During one year, 46% of the 183 contaminants were always found to be lower than 50 ngL^{-1}, except some pharmaceuticals and cholrpyrifos ethyl.

The most frequent compounds were caffeine, nicotine, chlorpyrifos ethyl, fluorene, phenanthrene and pyrene.

Soil acts as an additional treatment by reducing the compounds detected in groundwater and by eliminating some contaminants, which were always detected in reclaimed water, but never in groundwater.

There are alternative contaminant sources which account for the absence of compounds in reclaimed water, which were always detected in groundwater.